Water Quality Characterization of Three Central Lake Erie Tributaries:

Big Otter, Catfish, and Kettle Creeks

(2007-2009)

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Executive Summary

The nearshore area of Lake Erie is the interface between land and lake. It is a dynamic area that is heavily influenced by natural processes such as wind and wave action, drainage from tributaries and point source discharges. This is also an area which supports many human and natural uses: cottage development and associated recreation, beaches, and drinking water intakes and therefore, the quality of the nearshore waters important to those that use this area of the lake.

Discharge from a single tributary can have localized effects on the water quality and ecology of the nearshore and impact public uses. However, given the dynamic nature of the nearshore area, it is very difficult to fully characterize and understand the state of the nearshore area. The objective of this study is to investigate and characterize water quality, specifically nutrients; in the discharge of three small tributaries discharging to the central basin of Lake Erie through field based monitoring across seasons and environmental conditions. This information will then be used in a subsequent study to evaluate tributary plumes and their effect on nearshore water quality using river and lake hydrological models.

Water quality monitoring results from three tributaries draining to the central basin of Lake Erie: Big Otter Creek; Catfish Creek; and Kettle Creek is summarized and presented. Sampling sites were selected close to the mouth of each tributary so that water quality best describes tributary water quality. Samples were collected across seasons to best characterize the range of flows in each tributary. Samples were analyzed for a suite of water quality parameters, including total phosphorus, total suspended sediments, total nitrates and chloride between 2007 and 2009.

The landscape on Lake Erie's northern shore in southern Ontario reflects both the geology and European colonization of the region in the 19th century (AquaResource Inc., 2009; (Lake Erie Source Protection Region Technical Team 2008; Lake Erie Source Protection Region Technical Team 2008; Lake Erie Source Protection Region Technical Team 2008). Geological features created during glaciation combined with a long growing season make this region favorable for agricultural production. As a result, many stream networks in the region drain watersheds with greater than 70% of the land in agricultural production (Lake Erie Source Protection Region Technical Team 2008).

Indicators of climate conditions (flow, temperature, and precipitation) during the sample period (2007-2009), showed that 2007 as one of the driest years on record while 2008 and 2009 were amongst the wettest when compared to the long term records for each of the watersheds. As a result, the water quality datasets for each of the watersheds cover the range in climate conditions observed within the last 25 years.

The water quality datasets collected between 2007 and 2009 characterized melt conditions, non event spring and summer flows, and summer storm events but not winter low flows and fall conditions. As such, interpretation of the datasets is limited to these conditions.

Water quality data was described seasonally with descriptive statistics and with box and whisker plots. A seasonal comparison was run on each dataset and correlations were investigated seasonally and in the full dataset for selected pairs of parameters. Non-parametric statistics were used as the distribution of the data was often not homogeneous.

Water quality in each tributary varied with season while different trends were observed in each tributary. Higher levels of turbidity, total phosphorus and suspended sediment concentrations were observed during winter seasons in all three tributaries. In contrast, relatively higher alkalinity, conductivity and dissolved inorganic carbon concentrations were observed during the summer in all three tributaries. The seasonal trends in phosphate and total nitrate in Kettle Creek were distinctly different from those observed in Big Otter Creek and Catfish Creek.

A general linear regression model was applied to a subset of water quality parameters and the corresponding sampled flow. For this analysis the datasets were *ln* transformed to equalize the variance and allow parametric test to be applied. Results from this analysis showed a strong relationship between water quality and sampled flow.

The linear regressions produced equations which were used to estimate the loading of nutrients from each watershed monthly and annually based on hourly flow measurements. For total nitrate, phosphate, and total phosphorus, the largest loads resulted from melt events occurring during the winter and spring months. The load estimates during the wet years were greater than twice the amount of the loads estimated for the dry years. To facilitate the comparison of loads between tributaries, each load was corrected for watershed area, (e.g. export coefficient) and for the weight of water, (expressed in ppm and corresponds with the average concentrations expressed in mg/L). These ratios showed that the type of year, either wet or dry, affected the export coefficients but had less effect on the ratio between the solute load and the amount of water. Using these comparisons for all tested parameters, the watersheds were more similar than expected with overlap occurring in the standard errors of the mass ratios for all parameters, except chloride which was higher in Kettle Creek.

The regression equations were used to calculate predicted concentrations for select water quality parameters and compare them with the observed concentrations. The difference between the predicted and the observed concentrations was less than 20% of the observed concentrations for some parameters such as total nitrate and chloride. However, it was almost double the observed concentration for other parameters such as phosphate and total ammonia. When the difference between the observed and predicted concentrations was plotted in time series relative to the hydrograph, the deviation of the predicted concentrations tended to correspond with hydrologic events such as storm or snowmelt events.

The sampled snowmelt and summer storm events which tended to have large differences between the observed and predicted concentrations were plotted with the predicted hourly loads and the observed hourly loads relative to the event hydrograph. Comparisons show that the observed hourly loads fell within the error range for the predicted hourly loads during melt events. However, the observed loading just prior to the rise in the storm hydrograph and the end of the event hydrograph were often higher that predicted for summer storm events.

Introduction

It has long been recognized that the management of lentic and coastal waters must be done on a catchment scale as point and non-point source loading to the river systems is transmitted to the receiver, often producing ecologically significant effects (Staver and Brinsfield 2001; Alexander, Smith et al. 2008). Load estimating of parameters of concern (i.e. phosphorus) is a common approach which has been successfully used to look at nutrient budgets for the receiver, and to set water quality goals to improve the condition of the receiver (Dolan 1993; Winter, Dillon et al. 2002). This approach has been applied as a monitoring tool to Lake Erie which has been degraded and the focus of rehabilitation efforts since the 1970's (Dolan and McGunagle 2005). However, it does not necessarily address issues in the lake which occur at the smaller scale as a result of small discharges with localized effects such as beach fouling and closures or nuisance algae growth.

Discharges from a single tributary can have localized effects on the associated shoreline and nearshore without necessarily affecting the condition of the entire lake. Because the nearshore of a lake has public importance for recreation (i.e. beaches) and as a source of drinking water, understanding variation in an individual tributary discharge and how the discharge interacts with the lake environment is important for effective management of the watershed and lake resources.

Water movement in the nearshore of a large lake is influenced predominantly by larger lake currents and wind driven wave actions (Rao and Schwab 2007). The fate of an individual tributary discharge once it enters the lake is subject to the lake conditions which determine how the tributary discharge will be mixed and transported within the nearshore. Therefore, the movement of water within the lake is required to understand the local effects of tributary discharges on the water quality in the nearshore. Within the Great Lakes basin, studies to understand the effects of tributary plumes on nearshore water quality have relied on modeling approaches to incorporate variability in the lake environment into the study designs. As a result of this, the fate of individual tributary plumes and associated changes in water quality such as temperature or *E. coli* concentrations have been shown (He, Rao et al. 2006; Nevers, Whitman et al. 2007; Nevers and Whitman 2008).

In addition to variability in the lake environment, the tributary discharge is subject to variation in both quality and quantity in response to environmental and watershed conditions (Dillon and Kirchner 1975; Detenbeck, Brady et al. 2005). Because the quality and quantity of tributary discharges are a reflection of the larger climatic system and natural and anthropogenic landscape from which they are generated (Dodds and Oakes 2008), it is necessary to have a good understanding of how the watershed functions to understand variation in the quality and quantity of discharge (Green, Nieber et al. 2007).

In 2007, a monitoring study commenced in partnership with the Ontario Ministry of the Environment (MOE), Grand River Conservation Authority, Kettle Creek Conservation Authority, Catfish Creek Conservation Authority and Long Point Region Conservation Authority to monitor the quality and quantity of three tributaries draining to the central basin of Lake Erie. At the same time, the MOE collected samples along the nearshore region of Lake Erie in the vicinity of these three tributaries. The objective of this study was to characterize tributary water quality and quantity and to understand their influence on the nearshore region of Lake Erie. This report focuses on characterizing stream water quality and quantity while a subsequent in-lake hydrodynamic assessment of the tributary plumes was completed by MOE. Specific objectives of this report are:

- To summarize the quality of waters discharged from three small tributaries draining to the north shore of Lake Erie's central basin (Big Otter Creek, Catfish Creek, and Kettle Creek) in the context of the characteristics of each watershed;
- To determine how water quality varies seasonally in these three small tributaries;
- To identify water quality parameters which behave similarly across the full datasets and if these trends are similar across seasons;
- To evaluate relationships between stream flow and water quality;
- To estimate and characterize variation in nutrient loads discharged from each watershed; and
- To provide insight into natural and anthropogenic factors within each of the watersheds influencing the quality and quantity of tributary discharges through contrasting watersheds.

Big Otter Creek

Watershed Characterization

Big Otter Creek drains 712 km^2 on the north shore of Lake Erie in southwestern Ontario. It is located on the western side of a surficial sand deposit laid down during glaciation know as the Norfolk Sand Plain. As a result, sandy soils occur in the lower reaches of the watershed along the Lake Erie shoreline and up the eastern border of the watershed representing approximately half the watershed (52%; Table 1). The remainder of the watershed drains diamictonic tills (37%; Table 1) in the form of moraines (St. Thomas, Tillsonburg, and Norwich) and till plains (AquaResource Inc. 2009). The moraines in the northwestern portion of the watershed represent the highest points of elevation (~ 300 m above sea level) being approximately 150 m higher than the river mouth (Lake Erie Source Protection Region Technical Team 2008).

Table 1: The percent of soil types occurring in the Big Otter Creek watershed.

Surficial Geology Category	Distribution (%)
Clay	5
Silt	4
Diamicton (Till)	38
Gravel	<1.0
Fill	<1.0
Organic Deposits	<1.0
Paleozoic Bedrock	0
Sand	52

Agriculture covers a substantial percentage of the land base in southern Ontario and this is no exception in the Big Otter Creek watershed as 74% of the landscape is under agricultural production (Table 2). The presence of the Norfolk Sand Plain influences the agricultural character of the watershed as the drainage capacity of the soils makes the area suitable for the production of cash crops such as tobacco, ginseng, and vegetables (Lake Erie Source Protection Region Technical Team 2008). These crops also have high water requirements and producers of these crops rely on irrigation systems more strongly than producers in other regions of Ontario as indicated by an increased density of Permits to Take Water in the Norfolk Sand Plain (AquaResource Inc. 2009). Other crops produced in the Big Otter Creek watershed are corn, soy, and grains and are produced mostly in the western and central regions of the watershed (Lake Erie Source Protection Region Technical Team 2008).

Urban development is limited in the watershed, with the highest population densities in the municipality of Tillsbough located in the central portion of the watershed. One municipal wastewater facility serves this municipality and two other small facilities can be found in the headwaters of the watershed and at the river mouth serving much smaller communities (Lake Erie Source Protection Region Technical Team 2008).

Table 2: The percent of different land use categories occurring in the Big Otter Creek watershed.

Land use Category	Land Cover Distribution (%)
Treed land	14
Wetland	7
Urban	5
Extraction	<1.0
Agriculture	74

Temporal trends in stream flow within the lower portion of Big Otter Creek reveal a high contribution of surface run-off during snowmelt periods but a stable base flow suggesting sufficient ground water discharge in the system (Lake Erie Source Protection Region Technical Team 2008). Annually, the contributions of surface run-off and ground water discharge to stream flows are approximately equal across the watershed with select sub-basins showing a relatively higher ground water component compared to the run-off component (AquaResource Inc. 2009). Two flow regulation structures operate to reduce peak flows and increase base flows in the Big Otter Creek watershed. The first, Norwich Dam, is located on a tributary to Big Otter Creek in the headwaters of a watershed. The second is located in the upper reaches of the watershed on the main stem of Big Otter Creek at Otterville, Ontario.

Methods

Water quality monitoring of the Big Otter Creek discharge began in 2007 at a site near the mouth but upstream of any influence of Lake Erie. In 2007, water quality samples were collected biweekly May through October in correspondence with nearshore sampling. During nearshore sampling, water samples were also collected from various locations between the intensively sampled site and the river mouth to ensure that the intensively sampled site was representative of conditions in the river discharge (see Appendix A) for a comparison of water quality above and below the intensive sampling sites in Big Otter Creek, Catfish Creek and Kettle Creek). In 2008, more intensive sampling was started to characterize spring melt conditions and summer rain events. The intensive sampling continued throughout the 2008 and 2009 seasons with increased focus on characterization of the observed range in environmental conditions, including peak and low flows across seasons. Sampling programs in 2008 and 2009 included both grab samples and the employment of ISCO samplers to characterize individual storm events.

Water samples were sent to the Ministry of the Environment (MOE) Laboratory in Etobicoke, Ontario and analyzed for a suite of physical, chemical, and biological water quality parameters (Table 3). Laboratory procedures are outlined in the Laboratory Information Management System (LIMS) (LIMS Project Team 1994; Todd 2006).

Table 3: List of water quality variables analyzed in water samples collected in Big Otter Creek between 2007 and 2009.

Water Quality Variable Category	Water Quality Variable
Nutrients	Dissolved Nutrients: ammonia, nitrite, nitrate, phosphate, silicate Total Nutrients: total phosphorus, Kjeldahl nitrogen Dissolved Carbon: dissolved inorganic carbon, dissolved organic carbon
Solids	Suspended Solids
Major Ions	Chloride
Routine Chemistry	pH, alkalinity, conductivity
Routine Physical	Temperature, turbidity
Bacterial	*E. coli*
Productivity	Chlorophyll[1]

[1] Chlorophyll analysis was limited to those samples collected through the river survey by boat in 2007.

Hourly flow data for each watershed was collected as part of the Water Survey of Canada hydrological monitoring network (see www.wsc.gc.ca for more information). Because flow gauges were located at different points from the sampling locations, the sampled flow at the monitoring site was modeled from this record (see Appendix B for the methods used to model flow at the sampling sites).

Data Analysis

Sample period

The sample period (2007-2009) was characterized relative to long term trends in flow and climate data from the Water Survey of Canada and the Environment Canada climate databases. The flow gauge used for this assessment was located near Carlton, Ontario at Big Otter Creek (02GC026). The air temperature was taken from the climate station at the Shand Dam in Fergus, Ontario within the Grand River watershed (see http://climate.weatheroffice.ec.gc.ca for more information).

Sample program

Because water quality monitoring data cannot be used to describe environmental conditions which are not represented in the dataset (i.e. winter under ice conditions), a good understanding of the composition of the dataset is necessary to define the limitations of interpretation. The representation of environmental conditions which occurred between 2007 and 2009 were evaluated in the water quality dataset through three methods:

1) the frequency of samples collected across months and years;
2) the sampled flow was plotted relative to the observed hydrograph between 2007 and 2009; and
3) the percent of flow sampled across seasons was calculated.

Note that most water quality parameters were analyzed within each sample; however, *E. coli* measurements were taken in fewer samples due to extended sample holding times.

Seasonal water quality summary

Water quality data was summarized by season with box and whisker plots (Figure 1) and descriptive statistics. Because few of the ISCO samples effectively captured the full event, these samples were included with the grab samples for analysis. The following descriptive statistics were also used to characterize the dataset: sample size; mean; median; range; and dataset skewness. Skewness in the dataset was assessed relative to two times the standard error of skewness (the square root of 6 divided by sample size; Appendix C).

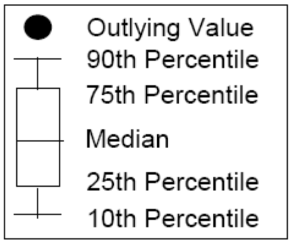

Figure 1. Box and whisker plot showing the 90th, 75th, median, 25th and 10th percentile distribution of the datasets. Black dots are data points beyond the 90th and 10th percentiles.

Tributary water quality was evaluated as concentrations, instantaneous loading rates (g/sec) and the proportion of the total nutrient pool to evaluate the change in dissolved versus particulate fractions. Seasonal comparisons were performed using a non-parametric Kruskal Wallis group test (Appendix C).

Table 4: Equations for all transformations and calculations performed on the water quality dataset

Parameter	Equation
loading rates:	
- mg/L → g/sec	[sampled flow (m^3/sec)]x [concentrations (mg/L)]
- CFU/100ml →CFU/sec	[sampled flow (m^3/sec)]x [concentrations (CFU/100ml)x10^4]
Total Nitrogen	Total Nitrate (mg/L) + Kjeldahl Nitrogen (mg/L)
Organic Nitrogen	Kjeldahl Nitrogen (mg/L) – total ammonia (mg/L)
Residual Phosphorus	Total phosphorus (mg/L) – phosphate (mg/L)
Nutrient Proportions	100 x [nutrient species (mg/L)/ total nutrient (mg/L)]

Correlations between parameters

Correlations between select parameter concentrations were assessed graphically and with a Spearman non-parametric correlation coefficient for each season and across the full dataset. The correlations investigated were: chloride vs. total nitrate, chloride vs. phosphate, suspended solids vs. turbidity, suspended solids vs. *E. coli*, suspended solids vs. total nitrogen, suspended solids vs. organic nitrogen, suspended solids vs. total phosphorus, suspended solids vs. residual phosphorus, and suspended solids vs. phosphate.

Load estimates

Parameters of concern to the nearshore (nutrients, sediments, and *E. coli*) were analyzed for relationships with sampled flows using *ln* transformed observed loading rates and the *ln* transformed sampled flows for samples collected between 2007 and 2009 from the intensive sampling site (see Appendix D: Regression plots for parameter loading rates vs. flows). The linear regression was assessed in SPSS v.14. The standard error for each constant in the equation was calculated and presented.

Monthly and annual load estimates for total nitrate, total phosphorus, and phosphate were calculated from the hourly flow record with the linear regression equation between January 2007 and September 2009.

The calculation of export coefficients is one method often used to correct load estimates from watershed areas allowing comparisons and contrasts between watersheds or drainage areas to occur. Export coefficients are calculated by dividing the total load by the drainage area producing a load per unit area. Unfortunately the numbers generated from the calculation can vary between years and across seasons due to variation in hydrological conditions between years. Considering the limitations of the approach, an alternative correction of load estimates was performed to allow comparison between watersheds. Given the importance of stream flow on the load estimates, the total load estimated was divided by the water load for the same period producing a ratio for each period and watershed. This ratio was expressed in parts per million and is equivalent to a concentration. These ratios were also determined for the standard error of the load estimate providing an error estimate on the ratio. The calculation of hourly water weight was determined from the flow data based on the following conversions:

$$1\ \text{m}^3/\text{sec} = 1000\ \text{L/sec} = 360{,}000\ \text{kg/hr}$$

From the linear regression equations, predicted concentrations were calculated. The difference between the observed concentrations and the predicted concentrations were plotted in time series relative to the hydrograph to see when stream flow did not predict water quality. Storm events showed the greatest deviation from predicted concentrations and three individual events sampled over the event period were identified. As a result, a time series plot of the storm events, the estimated hourly loads, and the observed loading rates was created.

Results

Sample Period

Environmental conditions during the sample period covered the range of conditions observed in the long term records. Annual average stream flows in 2007 fell at or below the 5th percentile of the long term record while in 2008 and 2009 approached the 95th percentile (Figure 2). To understand the general climatic conditions in 2007 to 2009, other climatic data such as precipitation and annual average temperature for the study period were compared to the long term average. Precipitation and air temperature data from the Shand Dam, near Fergus was used as a sentinel site for comparison purposes although this location is not located near the study area. Precipitation records indicate that while 2008 fell into the upper quartile of the distribution, 2007 was near the bottom quartile. Further, both 2007 and 2008 were among the higher quartiles and generally experienced warmer conditions when compared to the long term dataset (Figure 3).

The distribution of monthly average flows across years reflects the trends observed in the annual records (Figure 4). Average flows in 2007 most often fell within the lowest quartile of the distribution, while 2008 and 2009 fell into the upper most quartile of the distribution. In particular, peak summer flows during the later years were amongst the highest on record. Similarly, precipitation was particularly low during the summer months of 2007 relative to the long term distribution, and 2008 and 2009 which typically fell within the upper half of the sample distribution (Figure 3**Error! Reference source not found.**). Monthly average temperature showed elevated temperatures occurring during the summer and fall relative to the long term average (Figure 3). Temperatures were often lower during the summer months of 2008 and 2009.

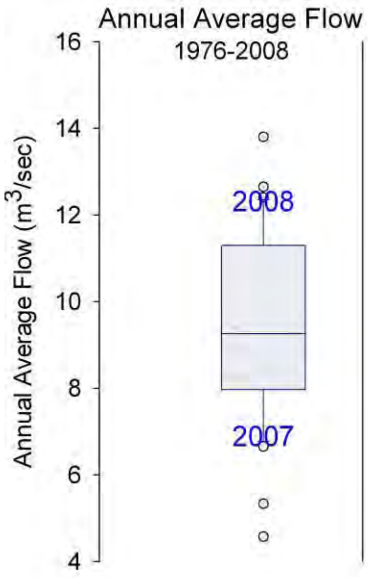

Figure 2: The annual average flows (m^3/sec) at the Carlton Gauge in the Big Otter Creek watershed in 2007-2008 relative to annual averages from 1976-2008.

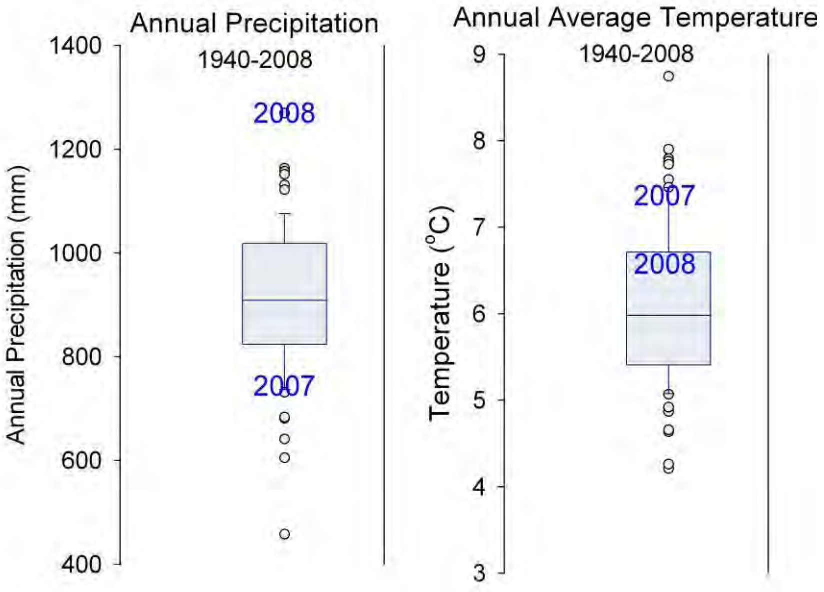

Figure 3. The annual precipitation (mm) (left) and temperature (right) at the Shand Dam in Fergus, Ontario in the Grand River watershed in 2007-2008 relative to annual totals from 1940-2008.

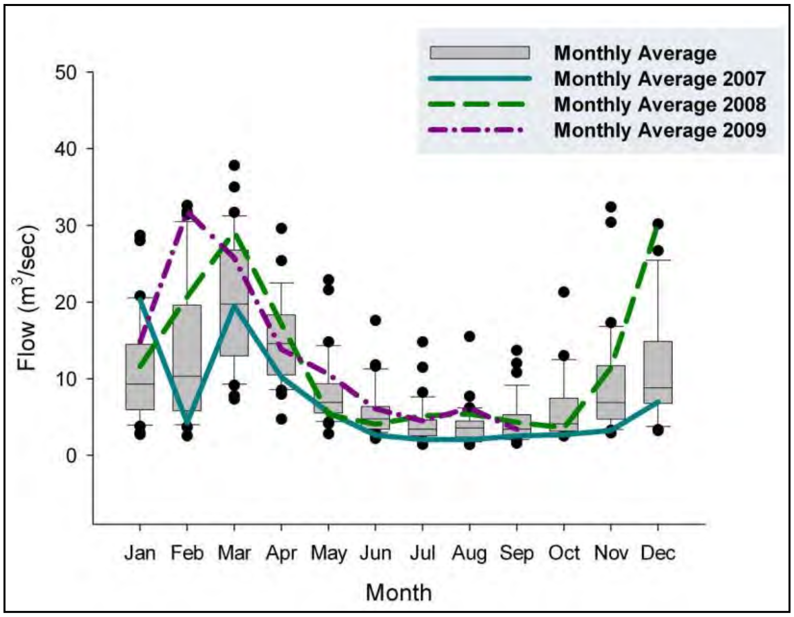

Figure 4: The monthly average flows (m^3/sec) at the Carlton Gauge in the Big Otter Creek watershed in 2007-2009 relative to monthly averages from 1976-2009

Sample Program

The water quality dataset for Big Otter Creek is made up of samples collected during the late winter, spring, and summer months in 2007, 2008 and 2009; however, most of the data in the dataset are from 2009 (Figure 5).

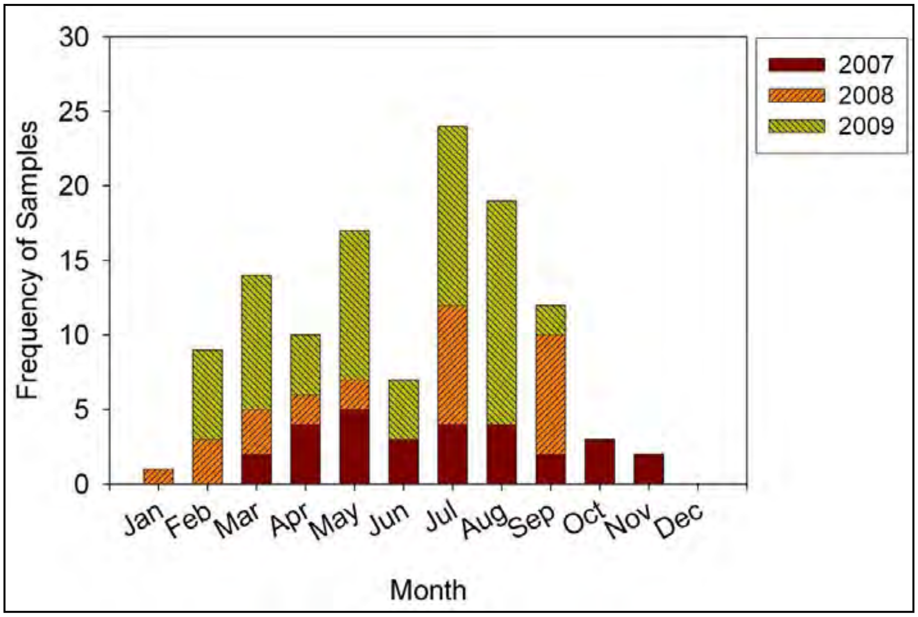

Figure 5: The monthly frequency of water quality samples collected at the mouth of Big Otter Creek by year between 2007 and 2009.

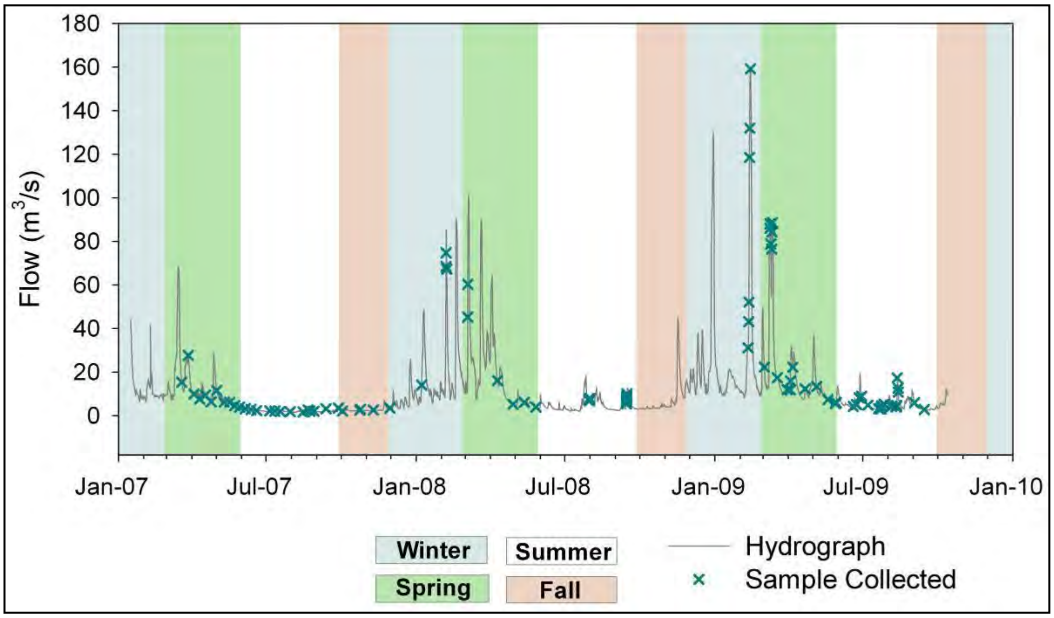

Figure 6: The stream flows (m^3/sec) sampled for water quality at the mouth of Big Otter Creek relative to the hydrograph with the seasons identified (winter, spring, summer, fall) between 2007 and 2009.

Melt events were well sampled in Big Otter Creek with peak flows being sampled in winter and spring months in 2009 (Figure 6). High summer flows were also well characterized by sampling. Conditions which were not well represented were winter low flow and fall high flow conditions. These observations are reflected by the percent of the flow range sampled across seasons which shows good characterization of the range in flow from winter through summer but not during the fall (Table 5;Figure 7). The range of sampled temperatures is shown in Figure 8.

Table 5: The percent of flow sampled at the mouth of Big Otter Creek per season (winter, spring, summer, fall) in 2007, 2008, and 2009.

Year	Season			
	Winter (Dec - Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
2007	n/a	37%	72%	28%
2008	67%	57%	28%	n/a
2009	84%	98%	85%	n/a
Total	91%	86%	86%	n/a

Water Quality Summary

For turbidity, suspended solids, total phosphorus, residual phosphorus, and phosphate concentrations, observations were distinctly higher and more variable during the winter (e.g. Figure 9; Figure 10). The spring and summer observations were lower but had elevated outliers to the dataset, and the fall datasets showed very little variation and values were low. This seasonal pattern seemed to follow that observed in the sampled flows with the exception that the values of the outliers in the summer and spring were higher relative to winter observations for the parameters and not in the flow record. The proportion of phosphorus forms did not appear to vary seasonally with the proportion of residual phosphorus being consistent at approximately.

For total nitrogen, total ammonia, and organic nitrogen, concentrations were higher during the winter, lower during the spring and summer, and low and stable during the fall (e.g. Figure 11). However, the size of the difference in the winter dataset relative to the spring and summer was less distinctive than observed in the previously described group of water quality parameters.

Alkalinity, conductivity, and dissolved organic carbon concentrations showed seasonal trends which were opposite to those observed in the sampled flows, turbidity, suspended solids, and phosphorus (e.g. Figure 12). The observations during the winter were most variable but were distinctly lower than the spring and summer observations. Outliers to the spring and summer datasets tended also to be lower approaching winter observations. Seasonal trends in silicate concentrations show an increasing pattern from winter through fall but the distinctiveness of the winter dataset from the other seasons as observed for alkalinity, conductivity, and dissolved organic carbon concentrations was not observed.

Seasonal trends were not very distinctive in the chloride, *E. coli*, dissolved organic carbon, total nitrate, and nitrite datasets (e.g. Figure 13). Differences in patterns of variation between seasons could be observed and slight increasing or decreasing trends in the median values were also observed. However, relative to the trends observed in the other water quality parameters, these trends are weak.

Seasonal trends in the proportion of the different nitrogen forms were observed (Figure 14). The proportion of organic nitrogen and total ammonia decreased (approximately 35 to 15% and 5 to 1 %, respectively) from the winter through the fall dataset while the corresponding proportion of total nitrate increased (approximately 65 to 85%). The proportion of phosphate (as estimated by soluble reactive phosphorus) remained consistent in all seasons (about 20 percent) (Figure 15).

When all concentration measurements were converted to loading rates, seasonal trends reflected those observed in the sampled flows with the exception of outliers to the spring loading dataset which were often some of the highest observations.

Box and whisker plots for all routine water chemistry parameters sampled in Big Otter Creek are in Appendix E.

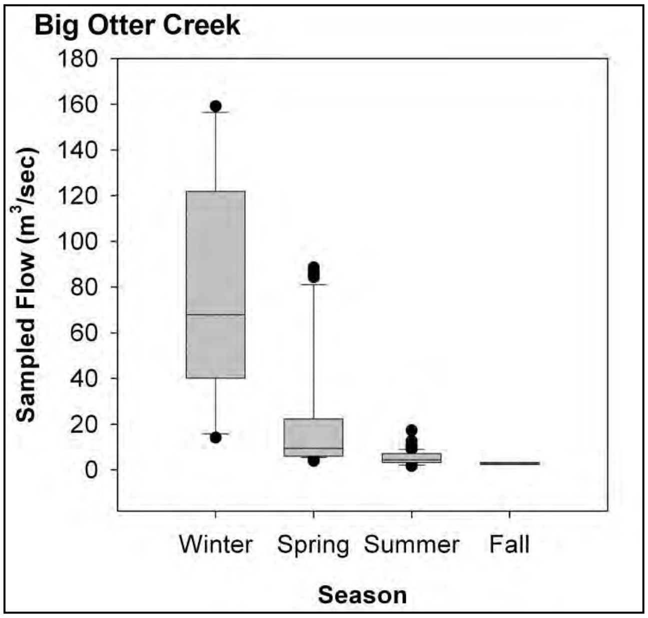

Figure 7: Boxplots of stream flows (m^3/sec) sampled between 2007 and 2009 plotted by season (winter, spring, summer, fall) at the mouth of Big Otter Creek.

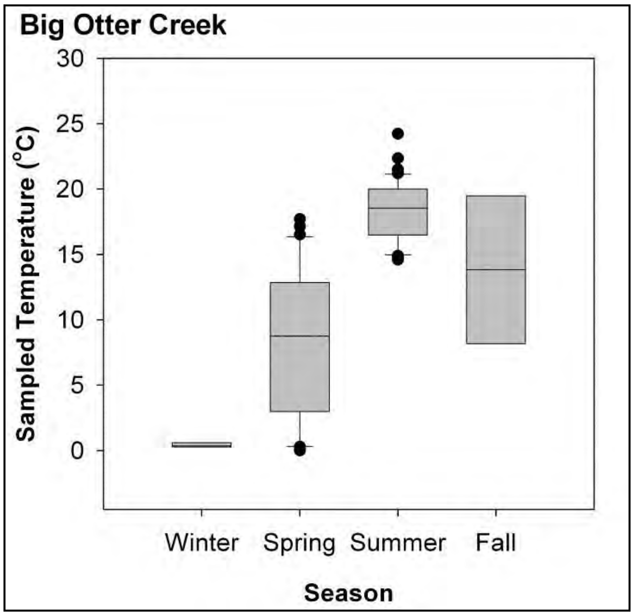

Figure 8: Boxplots of water temperature (°C) sampled between 2007 and 2009 plotted by season (winter, spring, summer, fall) at the mouth of Big Otter Creek.

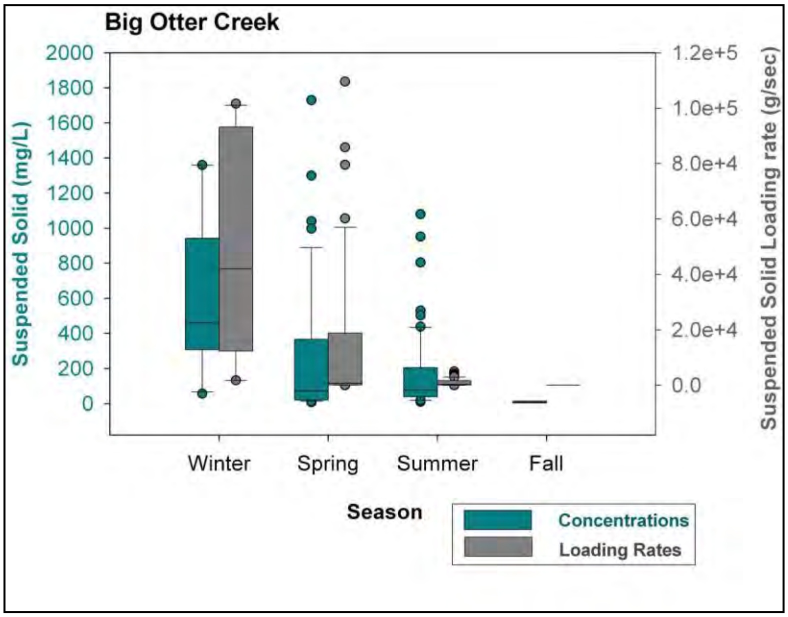

Figure 9: Boxplots of all observed suspended solids concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Big Otter Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.

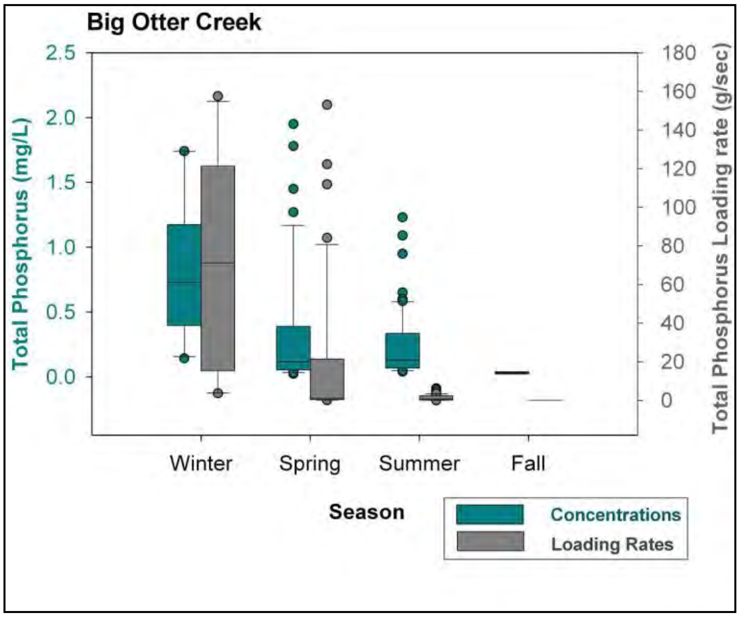

Figure 10: Boxplots of all observed total phosphorus concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Big Otter Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.

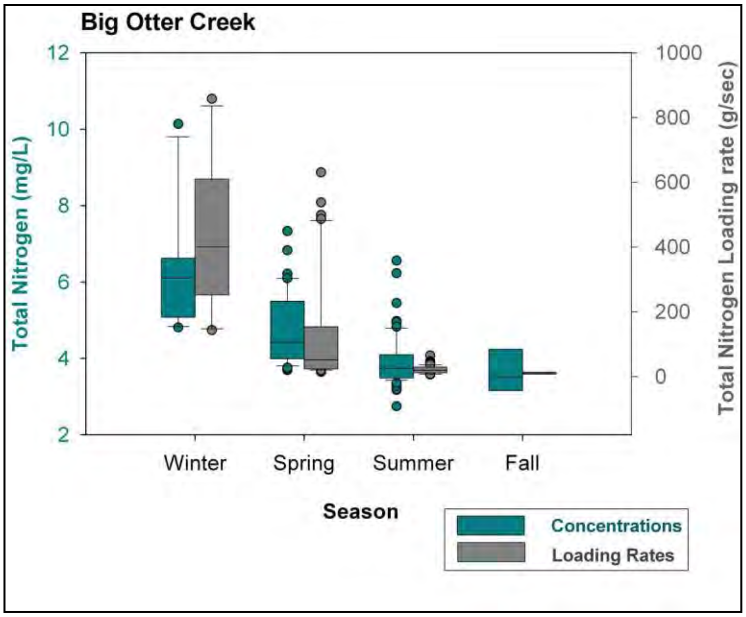

Figure 11: Boxplots of all observed total nitrogen concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Big Otter Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.

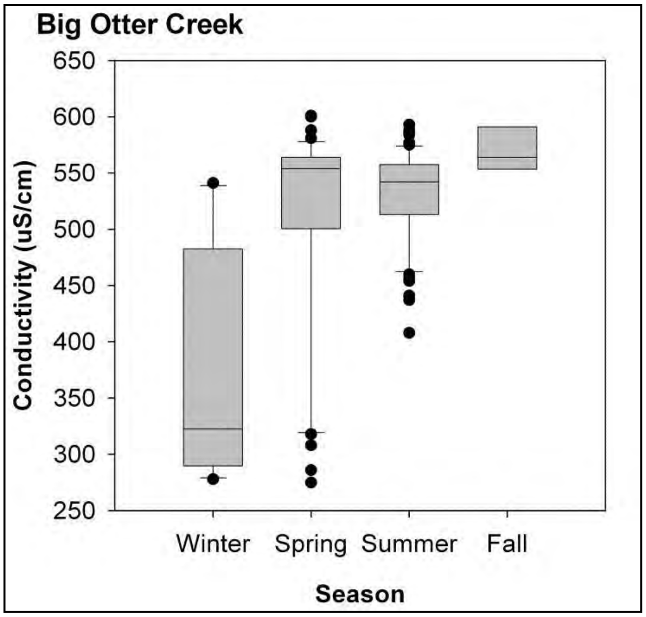

Figure 12: Boxplots of conductivity (µS/cm) sampled between 2007 and 2009 plotted by season (winter, spring, summer, fall) at the mouth of Big Otter Creek.

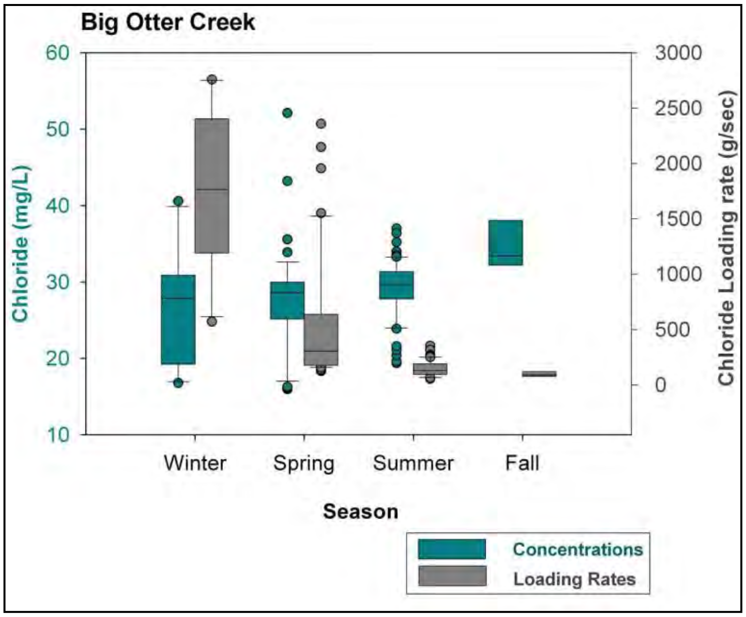

Figure 13: Boxplots of all observed chloride concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Big Otter Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.

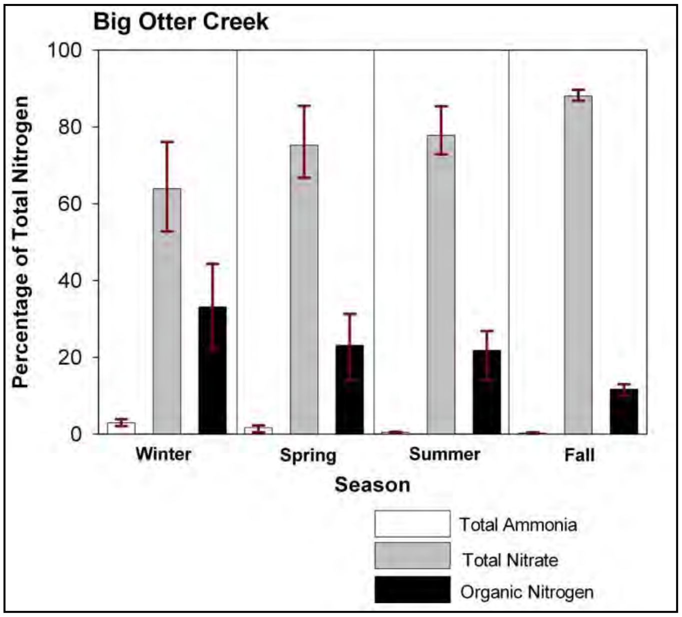

Figure 14: Bar graphs of the percentage of total ammonia, total nitrate, and organic nitrogen in total nitrogen values at the mouth of Big Otter Creek according to sample season (winter, spring, summer, fall) between 2007 and 2009. Error bars represent the 25th and 75th percentiles.

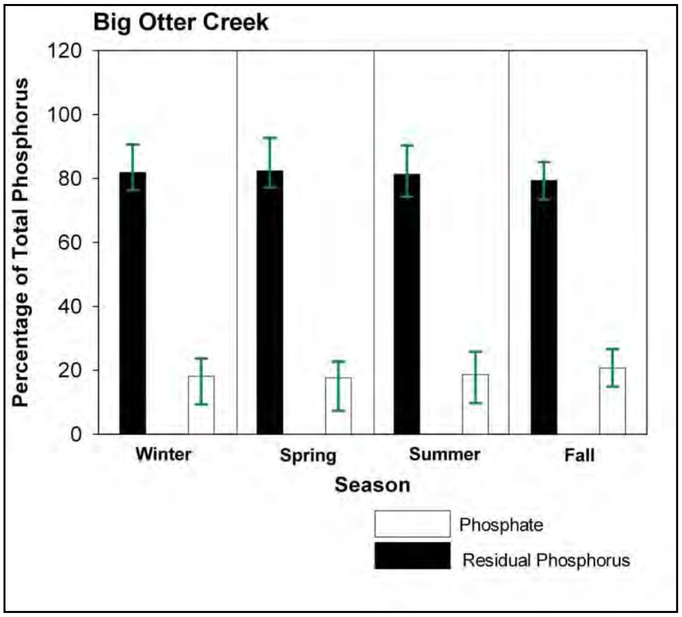

Figure 15: Bar graphs of the percentage of residual phosphorus and phosphate in total phosphorus values at the mouth of Big Otter Creek according to sample season (winter, spring, summer, fall) between 2007 and 2009. Error bars represent the 25th and 75th percentiles.

Correlations

Significant (*p* >0.001) positive results were observed for spring, summer, and full dataset correlations with suspended solids concentrations (Table 6: Non-parametric Spearman Correlation Coefficients (*p* values) for water quality parameter pairs across seasons (winter, spring, summer, fall) and in the full dataset.Table 6; Figure 16;Figure 17; Figure 18). The fall correlations were often weak due to a small sample size and low variation in the dataset. The weakest correlations with suspended solid concentrations occurred with total nitrogen and *E. coli* concentrations. The only negative correlations were observed between chloride and phosphate concentrations in both the full and seasonal datasets. Chloride and total nitrate concentrations were significantly correlated during the winter and fall but not in other seasons or in the full dataset (Figure 19).

Table 6: Non-parametric Spearman Correlation Coefficients (*p* values) for water quality parameter pairs across seasons (winter, spring, summer, fall) and in the full dataset.

	Spearman Correlation Coefficients				
Correlations	**Seasonal Datasets**				**Full dataset**
	Winter	**Spring**	**Summer**	**Fall**	
Chloride vs. Total Nitrate	*0.745 (0.013)*	-0.302 (0.055)	0.096 (0.463)	0.*925 (0.008)*	-0.113 (0.224)
Chloride vs. Phosphate	*-0.673 (0.033)*	*-0.540 (<0.001)*	*-0.597(<0.001)*	0.145 (0.784)	*-0.511 (<0.001)*
Suspended Solids vs. Turbidity	*0.952 (<0.001)*	*0.942 (<0.001)*	*0.972 (<0.001)*	0.714 (0.111)	*0.967 (<0.001)*
Suspended Solids vs. *E. coli*	0.467 (0.243)	*0.828 (<0.001)*	*0.593 (<0.001)*	0.600 (0.285)	*0.644 (<0.001)*
Suspended Solids vs. Total Nitrogen	-0.055 (0.881)	*0.610 (<0.001)*	*0.592 (<0.001)*	-0.086 (0.872)	*0.553 (<0.001)*
Suspended Solids vs. Organic Nitrogen	*0.685 (0.029)*	*0.719 (<0.001)*	*0.894 (<0.001)*	0.486 (0.329)	*0.879 (<0.001)*
Suspended Solids vs. Total Phosphorus	*0.818 (0.004)*	*0.883 (<0.001)*	*0.929 (<0.001)*	*0.829 (0.042)*	*0.932 (<0.001)*
Suspended Solids vs. Residual Phosphorus	*0.815 (0.004)*	*0.850 (<0.001)*	*0.935 (<0.001)*	0.*600 (0.207)*	*0.924 (<0.001)*
Suspended Solids vs. Phosphate	*0.624 (0.054)*	*0.813 (<0.001)*	*0.561 (<0.001)*	0.638 (0.173)	*0.746 (<0.001)*

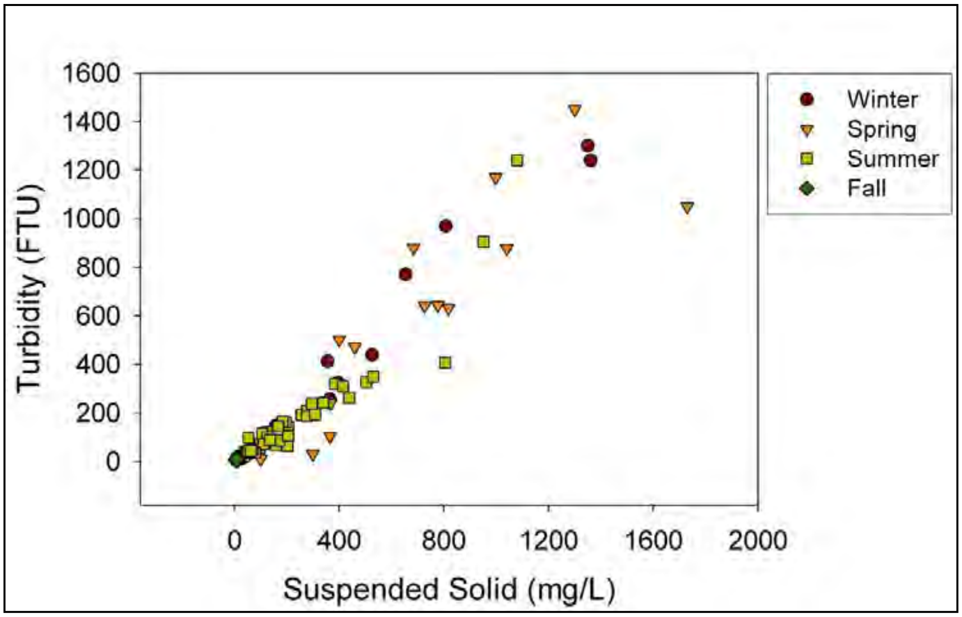

Figure 16: Turbidity (FTU) vs. suspended solids (mg/L) concentrations in water samples collected between 2007 and 2009 near the mouth of Big Otter Creek differentiated by season (winter, spring, summer, fall).

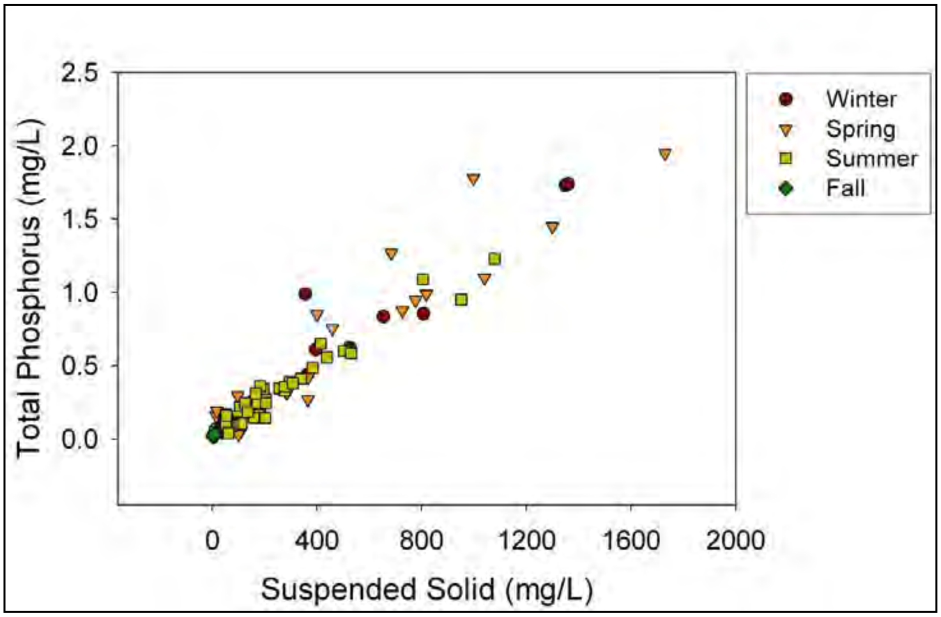

Figure 17: Total phosphorus (mg/L) vs. suspended solids (mg/L) concentrations in water samples collected between 2007 and 2009 near the mouth of Big Otter Creek differentiated by season (winter, spring, summer, fall).

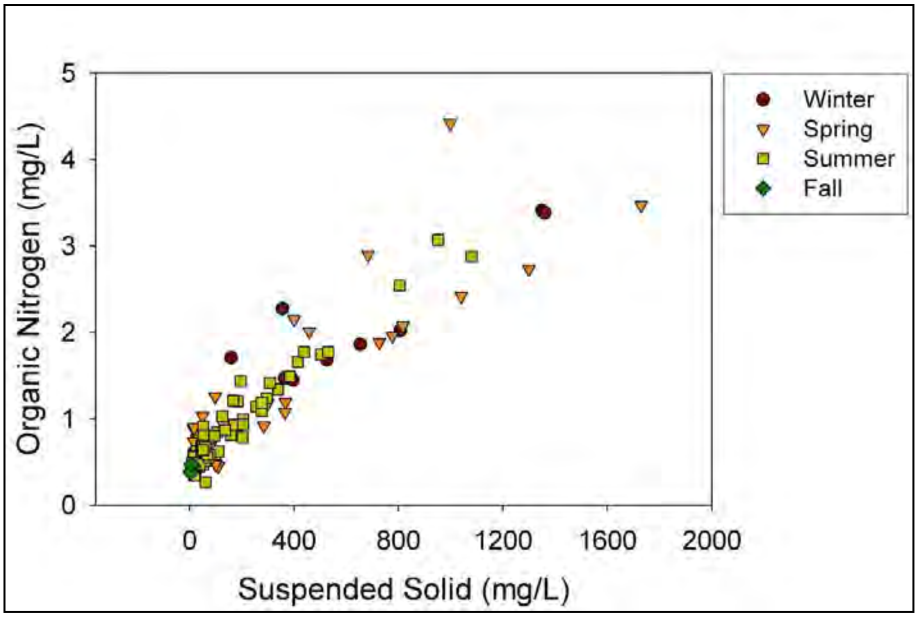

Figure 18: Organic nitrogen (mg/L) vs. suspended solids (mg/L) concentrations in water samples collected between 2007 and 2009 near the mouth of Big Otter Creek differentiated by season (winter, spring, summer, fall).

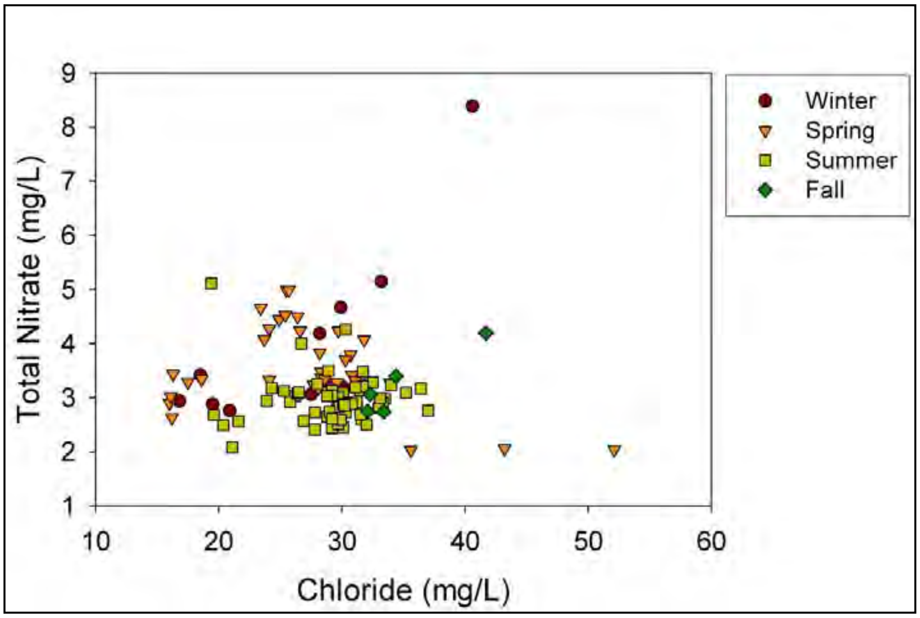

Figure 19: Total nitrate (mg/L) vs. chloride (mg/L) concentrations in water samples collected between 2007 and 2009 near the mouth of Big Otter Creek differentiated by season (winter, spring, summer, fall).

Load Estimates

Significant linear regressions (*p* <0.001; R^2 0.792 – 0.967) occurred between the *ln* transformed loading rate and the *ln* transformed flow for all parameters tested (Table 7: Linear equations generated from linear regressions performed on *ln* transformed sampled hourly flow (m^3/sec) and *ln* transformed loading rates (kg) for water quality parameters measured at the mouth of Big Otter Creek between 2007 and 2009.Table 7).

Table 7: Linear equations generated from linear regressions performed on *ln* transformed sampled hourly flow (m^3/sec) and *ln* transformed loading rates (kg) for water quality parameters measured at the mouth of Big Otter Creek between 2007 and 2009.

Parameter	y = m(± SE) x + b(± SE)	R^2 value	*p* value
Chloride	y = 0.895(± 0.014) x + 3.559(± 0.034)	0.971	<0.001
Total Ammonia	y = 1.856(± 0.063) x + -5.489(± 0.15)	0.882	<0.001
Total Nitrate	y = 1.024 (± 0.018) x + 1.108(± 0.042)	0.967	<0.001
Organic Nitrogen	y = 1.408(± 0.037) x + -0.995(± 0.087)	0.928	<0.001
Phosphate	y = 1.920(± 0.076) x + -5.775(± 0.180)	0.846	<0.001
Residual Phosphorus	y = 1.743(± 0.078) x + -3.59(± 0.185)	0.812	<0.001
Total Phosphorus	y = 1.766(± 0.072) x + -3.435(± 0.171)	0.840	<0.001
Suspended Solids	y = 1.904(± 0.091) x + 2.642(± 0.217)	0.792	<0.001

The linear equations from the regression analysis were used to calculate the monthly and annual loads of total nitrate, phosphate, and total phosphorus between 2007 and 2009 (Figure 20; Figure 21; Figure 22). For all three parameters, the total loading during 2007 was almost an order of magnitude lower than what was observed in 2008. The loading in 2007 was also much lower than the loads calculated for 2009 (January through to September). In general, winter and spring (December, January, February, March and April) monthly loads were highest in all three years.

The ratio of parameter mass over water weight and calculated export coefficients (tonnes/km^2) for Big Otter Creek for the various water quality parameters are listed in **Error! Reference source not found.**. In general, greater mass of constituents were exported from the Big Otter Creek watershed in 2008, due to the greater amount of precipitation and runoff.

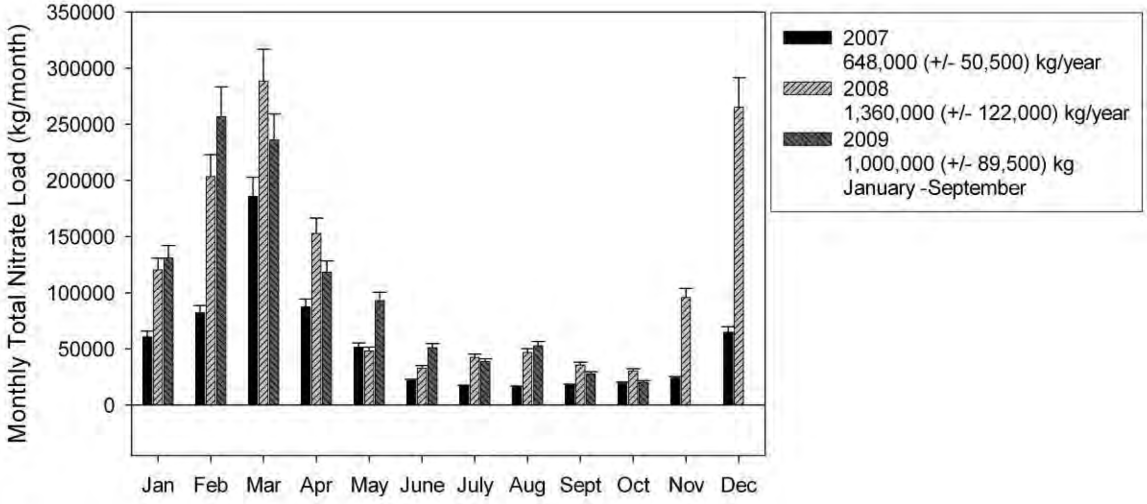

Figure 20: The estimated monthly total nitrate loads (kg/month) based on the linear regression equations generated from the water quality datasets collected at the mouth of Big Otter Creek between 2007 and 2009. Errors are presented as standard errors.

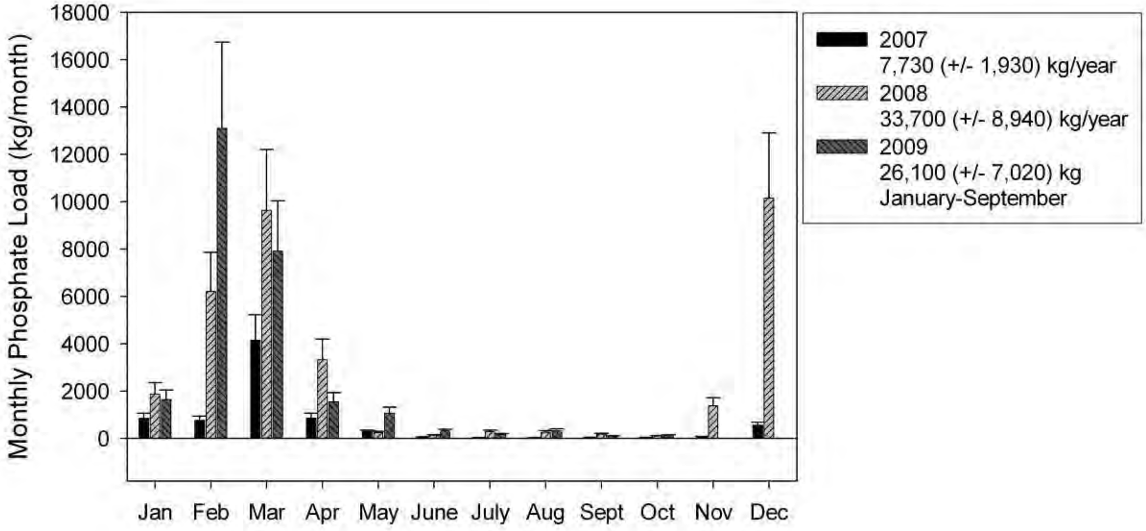

Figure 21: The estimated monthly phosphate loads (kg/month) based on the linear regression equations generated from the water quality datasets collected at the mouth of Big Otter Creek between 2007 and 2009. Errors are presented as standard errors.

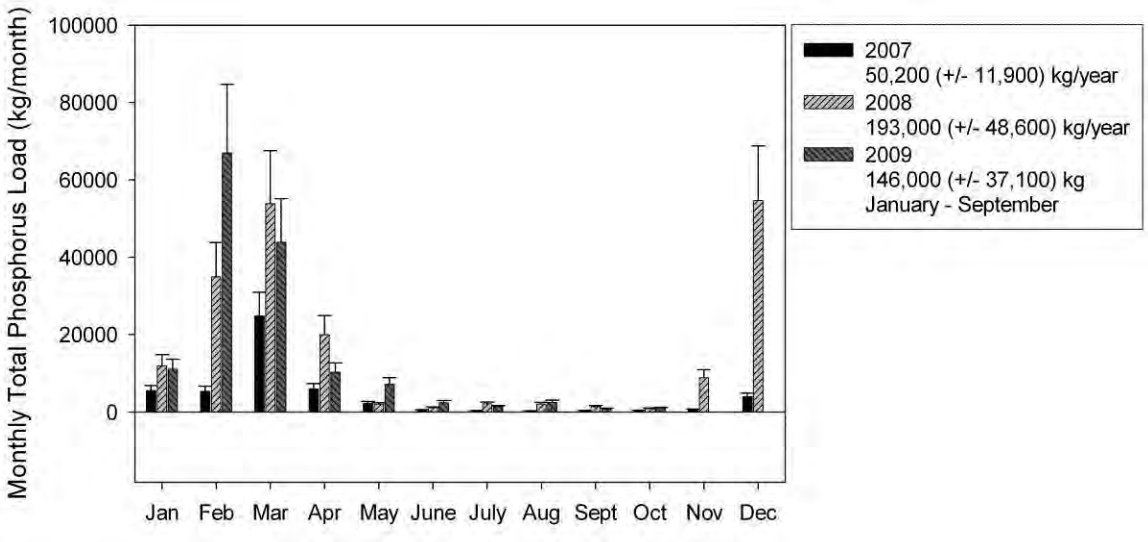

Figure 22: The estimated monthly total phosphorus loads (kg/month) based on the linear regression equations generated from the water quality datasets collected at the mouth of Big Otter Creek between 2007 and 2009. Errors are presented as standard errors.

Table 8. The ratio (± standard error) of parameter mass over water weight and export coefficients based on analysis of water quality datasets and flow data from the mouth of Big Otter Creek between 2007 and 2009.

Parameter	**Ratio of Total Parameter wt / Total Water wt (‰) Estimates**			**Export Coefficient (tonnes/km^2)**	
	2007-2009	**2007**	**2008**	**2007**	**2008**
Chloride	26.0 *(24.1 – 28.0)*	27.6 *(25.8 – 29.5)*	25.4 *(23.6 – 27.5)*	7.9 *(7.4 – 8.4)*	14.9 *(13.8 – 16.1)*
Total Ammonia	0.08 *(0.06 – 0.09)*	0.04 *(0.03 – 0.05)*	0.08 *(0.07 – 0.10)*	0.01 *(0.01 – 0.01)*	0.049 *(0.04 – 0.06)*
Total Nitrate	3.24 *(2.98 – 3.53)*	3.20 *(2.97 – 3.45)*	3.26 *(2.99 – 3.55)*	0.91 *(0.84 – 0.98)*	1.91 *(1.75 – 2.08)*
Organic Nitrogen	1.33 *(1.16 – 1.52)*	1.03 *(0.91 – 1.16)*	1.43 *(1.24 – 1.63)*	0.29 *(0.26 –0.33)*	0.84 *(0.73 – 0.96)*
Phosphate	0.073 *(0.057 – 0.092)*	0.038 *(0.031 – 0.048)*	0.081 *(0.064 – 0.102)*	0.011 *(0.009 – 0.014)*	0.047 *(0.038 – 0.060)*
Residual Phosphorus	0.328 *(0.259 – 0.416)*	0.198 *(0.158 – 0.249)*	0.363 *(0.286 – 0.461)*	0.056 *(0 .045 – 0.071)*	0.213 *(0.168 – 0.270)*
Total Phosphorus	0.418 *(0.334 – 0.523)*	0.248 *(0.200 – 0.307)*	0.310 *(0.224 – 0.429)*	0.071 *(0.057 – 0.087)*	0.181 *(0.131 - 0.252)*
Suspended Solids	308 *(235 – 404)*	164 *(126 – 213)*	343 *(262 – 451)*	47 *(36 – 61)*	201 *(153 – 264)*

Predicting Water Quality

The relative importance of the difference between the modeled and the predicted concentrations were summarized by calculating the percentage of each difference from the corresponding observed concentration (Table 9). The linear regression equations were most accurate in predicting observed chloride and total nitrate concentrations. For these two parameters the residuals were typically less than 20 percent of the observed concentration. In contrast, for total ammonia, phosphate, residual phosphorus, total phosphorus, and suspended solid concentrations many of the residuals approached or were greater than the observed concentrations indicating that the prediction was off by as much as double the observed concentration. When observed in time series relative to the hydrograph the greatest differences between the observed and the predicted concentrations corresponded with samples collected during a melt or storm event (e.g Chloride; Figure 23).

Table 9: The mean, median, and 75th percentile for the percent difference between the observed and the predicted concentrations calculated from the water quality datasets collected from Big Otter Creek between 2007 and 2009.

Parameter	Mean	Median	*75th* percentile
Chloride	11 %	5 %	13 %
Total Ammonia	72 %	48 %	79 %
Total Nitrate	14 %	9 %	22 %
Organic Nitrogen	31 %	22 %	41 %
Phosphate	99%	62%	87 %
Residual Phosphorus	88 %	49 %	83 %
Total Phosphorus	76 %	41 %	84 %
Suspended Solid	72 %	48 %	79 %

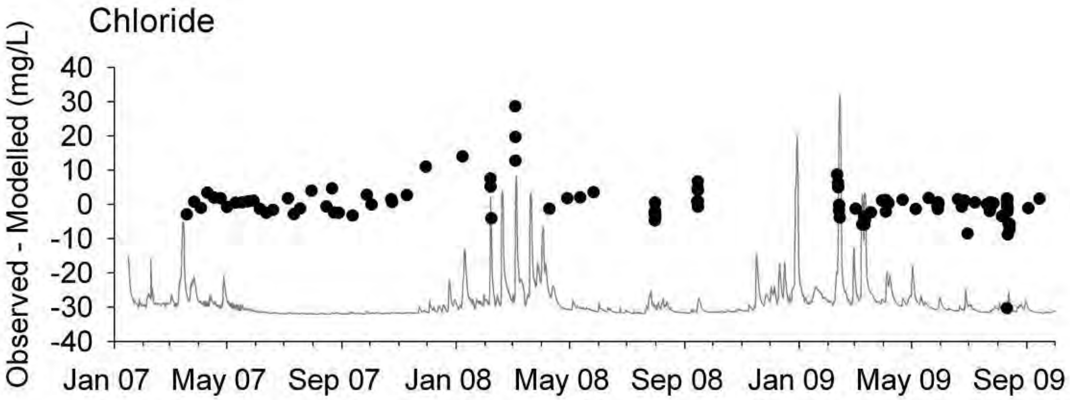

Figure 23: The difference between the observed chloride (mg/L) concentrations and the modeled concentrations plotted in time series relative to the hydrograph at the mouth of Big Otter Creek between 2007 and 2009.

The linear regression equation generated from the *ln* transformed loading rate and the *ln* transformed sampled flow did not predict observed *E. coli* concentrations very well in Big Otter Creek samples. Furthermore, no trend in how or when observed concentrations deviated from the predicted concentrations is observed. When concentrations are compared to the water quality guidelines set by the Canadian Council for Ministers of the Environment (CCME) for recreation (e.g. 200 CFU/100ml), samples frequently exceeded this guideline*)* across all seasons (Figure 24).

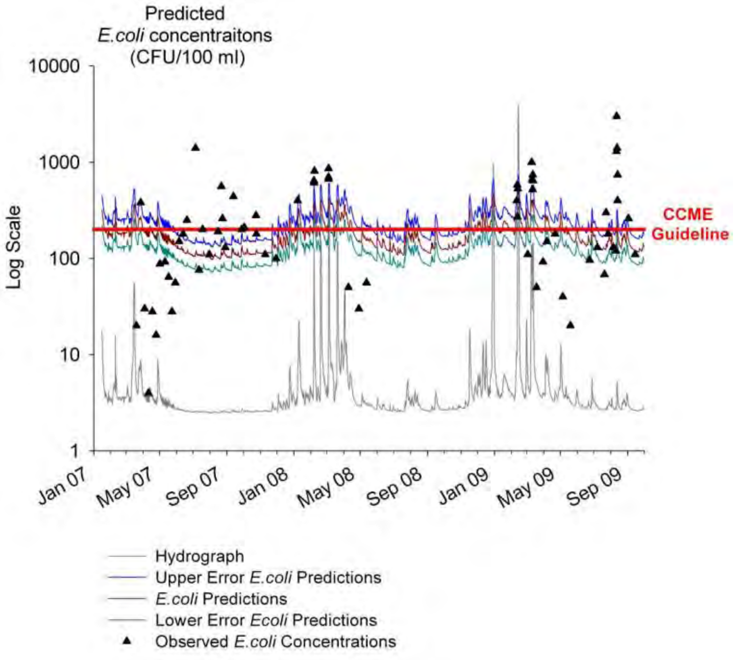

Figure 24: The observed *E. coli* (CFU/100ml) concentrations relative to the predicted concentrations, the flow record, and the CCME guideline for recreational water use at the mouth of Big Otter Creek between 2007 and 2009.

The hourly phosphate and total phosphorus loads calculated from observed concentrations fell within or just below the estimate predicted from the linear regression equation for the February 2009 melt event (Figure 25). During the March 2009 melt event, the hourly load predictions fell within the expected range in four of the six samples where the loads exceeded the predictions by approximately 20 kg/hr for phosphate and less than 200 kg/hr for total phosphorus (Figure 26). For the storm event sampled in August of 2009, the phosphate loads exceeded the range of the predicted hourly load in most samples by 1-2 kg/hr (Figure 27). However, the trend in observed phosphate loads corresponded with the trend in the predicted loads. Total phosphorus hourly loads were as predicted during the event hydrograph but prior to the rise in the event hydrograph the observed loads increased more rapidly than predicted.

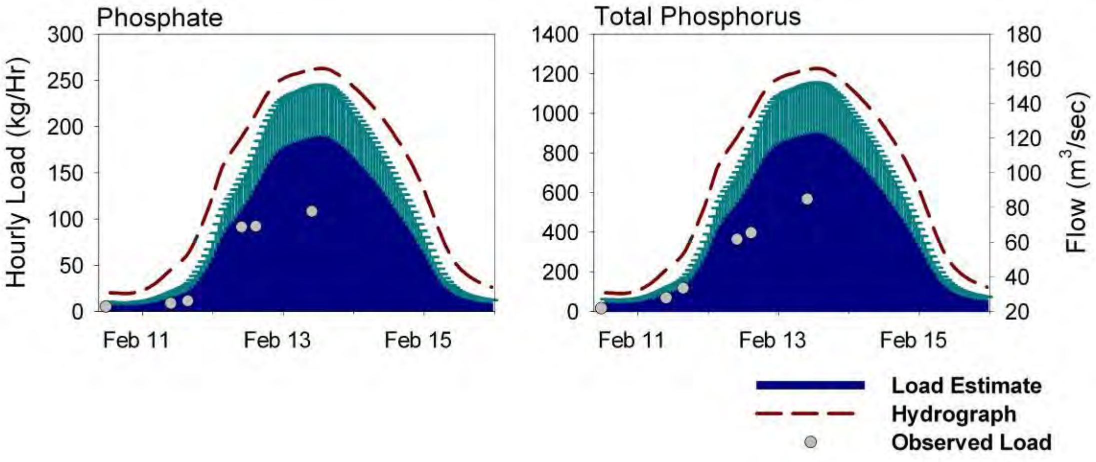

Figure 25: The predicted hourly load (kg/hr) of phosphate (left) and total phosphorus (right) relative to the observed hourly load calculated from water samples collected during a high flow event in February 2009 at the mouth of Big Otter Creek.

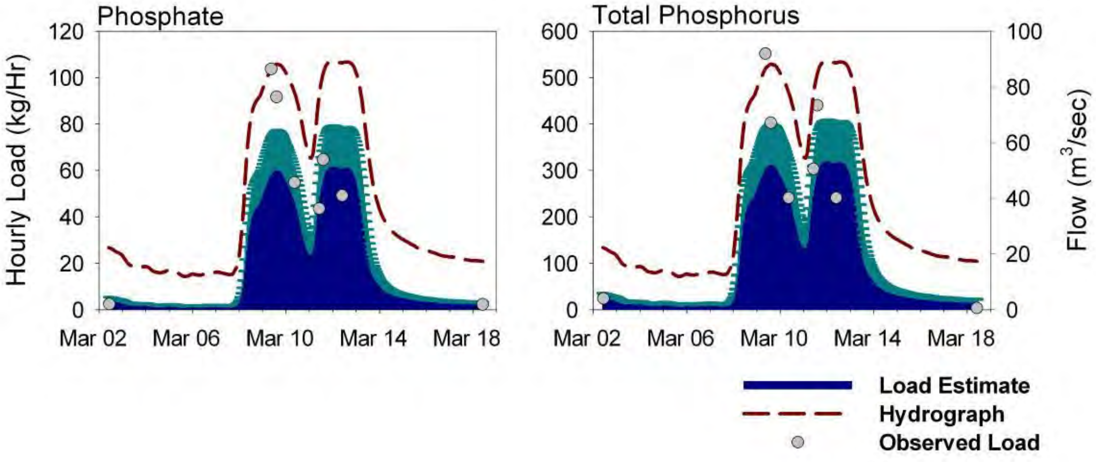

Figure 26: The predicted hourly load (kg/hr) of phosphate (left) and total phosphorus (right) relative to the observed hourly load calculated from water samples collected during a high flow event in March 2009 at the mouth of Big Otter Creek.

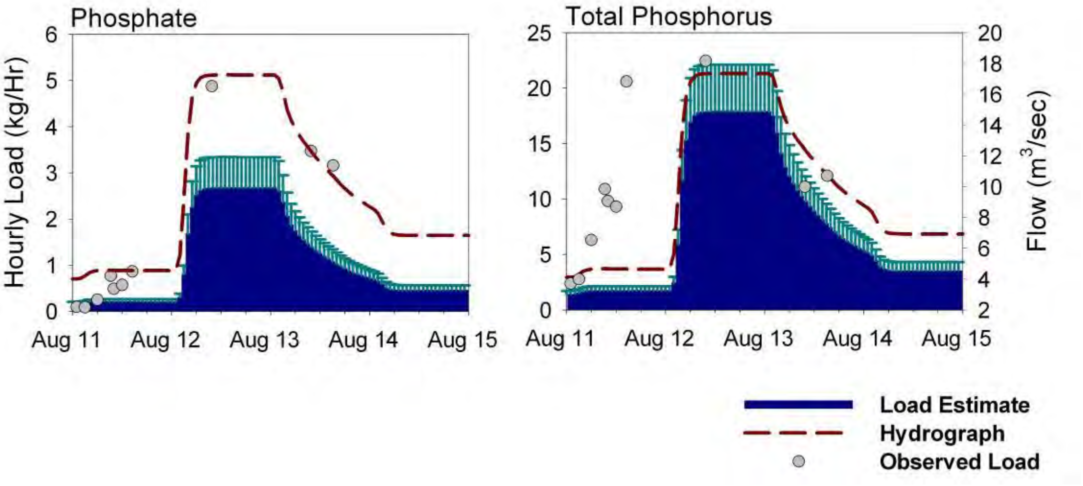

Figure 27. The predicted hourly load (kg/hr) of phosphate (left) and total phosphorus (right) relative to the observed hourly load calculated from water samples collected during a high flow event in August 2009 at the mouth of Big Otter Creek.

Catfish Creek

Watershed Characterization

Catfish Creek watershed drains 490 square kilometres in Elgin and Oxford Counties and discharges into Lake Erie at Port Bruce (Lake Erie Source Protection Region Technical Team, 2008). Like much of south western Ontario, the landscape in Catfish Creek has been shaped by glacial processes which created the three dominate geological features in the region: the Norfolk Sand Plain, the Ekfrid Clay Plain, and the Mount Elgin Ridges. The Norfolk Sand Plain is a large feature in the southern region of the watershed along the Lake Erie shoreline covering ~ 25% of the watershed (Table 10). The Ekfrid Clay Plain is a relatively flat area with high silt and clay soils representing approximately 12% of the drainage area located in the western/central portion of the watershed. The Mount Elgin Ridges are composed of various moraine complexes (Tillsonburg, St. Thomas, and Sparta) and located primarily at the periphery and in the upper reaches of the watershed. The highest point of the watershed occurs in the northern region of the watershed where elevation approaches 300 metres above sea level (masl). The lowest point occurs as the river valley approaches Lake Erie at approximately 175-180 masl.

Table 10: The percent of soil types occurring in the Catfish Creek watershed.

Surficial Geology Category	Percent Land Cover (%)
Clay	2
Silt	10
Diamicton (Till)	61
Gravel	1
Fill	<1.0
Organic Deposits	<1.0
Paleozoic Bedrock	0
Sand	25

Land use in this region is predominantly agricultural (79%) supporting both livestock and crop production (Table 11). Higher densities and overall abundance of cattle, swine, and poultry occur in the upper region of the watershed relative to the lower region of the watershed with densities of 0.33, 0.91, and 6.76 animals per hectare of farmed land for cattle, swine, and poultry, respectively, across the watershed as a whole. The dominant crops in the watershed are corn, soy, and grains which predominantly occur on the northwestern portion of the watershed where soils are of glacial till in origin. The agricultural character of the Norfolk Sand Plain differs from other regions as the coarse well drained soils are capable of supporting selective crops such as vegetables and tobacco. These crops do, however, have a high water requirement and irrigation is frequently employed in this region.

Urban development is limited in the Catfish Creek watershed with the highest densities occurring in Aylmer, Ontario in the centre of the watershed followed by Port Bruce, Ontario at the mouth of Catfish Creek. A single municipal waste water treatment plant serving the municipality of Aylmer discharges into Catfish Creek. Discharge from the lagoon system occurs during the spring and fall only.

Table 11: The percent of different land use categories occurring in the Catfish Creek watershed.

Land Use Category	Percent Land Cover (%)
Treed land	10.5
Wetland/ open water	3.7
Urban	5.8
Extraction	0.1
Agriculture	79.9

Long term flows records from the lower portion of Catfish Creek are characteristic of a run-off dominated system with extreme peak flows and low base flows (Lake Erie Source Protection Region Technical Team 2008). Across the entire watershed, annual contributions of surface run-off and ground water discharges to stream flow are equal, however, between sub-basins these quantities vary (AquaResource Inc. 2009). Flow regulation is limited in the watershed to the Springwater Reservoir and dam, which are located on a tributary to Catfish Creek in the centre of the watershed.

Methods

Water quality monitoring of Catfish Creek began in 2007 at a site near the mouth. In 2007 water quality samples were collected biweekly May through October in correspondence with nearshore sampling. During nearshore sampling, water samples were also collected from various locations between the intensively sampled site and the river mouth to ensure that the intensively sampled site was representative of conditions in the river discharge (Appendix A). In 2008, more intensive sampling was started to characterize spring melt conditions and summer rain events. The intensive sampling continued throughout the 2008 and 2009 seasons with increased focus on characterization of the observed range in environmental conditions, including peak and low flows across seasons. Sampling programs in 2008 and 2009 included both grab samples and the employment of ISCO samplers to characterize individual storm events.

Water samples were sent to the Ministry of the Environment (MOE) Laboratory in Etobicoke, Ontario and analyzed for a suite of physical, chemical, and biological water quality parameters (Table 12). Laboratory procedures are outlined in the Laboratory Information Management System (LIMS) (LIMS Project Team 1994; Todd 2006).

Table 12: List of water quality variables analyzed in water samples collected in Catfish Creek between 2007 and 2009.

Water Quality Variable Category	Water Quality Variable
Nutrients	Dissolved Nutrients: ammonia, nitrite, nitrate, phosphate, silicate Total Nutrients: total phosphorus, Kjeldahl nitrogen Dissolved Carbon: dissolved inorganic carbon, dissolved organic carbon
Solids	Suspended Solids
Major Ions	Chloride
Routine Chemistry	pH, alkalinity, conductivity
Routine Physical	Temperature, turbidity
Bacterial	*E. coli*
Productivity	Chlorophyll[1]

[1] Chlorophyll analysis was limited to those samples collected through the river survey by boat in 2007.

Hourly flow data for each watershed was collected as part of the Water Survey of Canada hydrological monitoring network (see www.wsc.gc.ca for more information). Because flow gauges were located at different points from the sampling locations, the sampled flow at the monitoring site was modeled from this record (Appendix B.)

Data Analysis

Sample Period

The sample period (2007-2009) was characterized relative to long term trends in flow and climate data from the Water Survey of Canada and the Environment Canada climate databases. The flow gauge used for this assessment was located near Sparta, Ontario in Big Otter Creek (02GC018). The air temperature was taken from the climate station at the Shand Dam in Fergus, Ontario within the Grand River watershed (see http://climate.weatheroffice.ec.gc.ca for more information).

Sample Program

Because water quality monitoring data cannot be used to describe environmental conditions which are not represented within the dataset (i.e. winter under ice conditions), a good understanding of the composition of the dataset is necessary to define the limitations of interpretation. The representation of environmental conditions which occurred between 2007 and 2009 in the dataset were evaluated in the water quality dataset through three methods:

1) The frequency of samples collected across months and years was calculated;
2) The sampled flow was plotted relative to the observed hydrograph between 2007 and 2009; and
3) The percent of flow sampled across seasons was calculated.

Note that most water quality parameters were analyzed within each sample; however, *E. coli* measurements were taken in fewer samples due to extended sample holding times.

Seasonal water quality summary

Water quality data from the tributary monitoring site was summarized by season with box and whisker plots and with descriptive statistics. Because few of the ISCO samples effectively captured the full event, these samples were included with the grab samples for analysis. Descriptive statistics used were: sample size, mean, median, range, and dataset skewness. Skewness in the dataset was assessed relative to two times the standard error of skewness (the square root of six divided by sample size; Appendix C). In a box and whisker plot the box encloses the 25th to 75th percentiles, the horizontal line bisecting the box represents the median, the error bars represent the 5th and 95th percentiles, and the circles represent the outliers in the dataset.

Water quality datasets were presented from as many as three perspectives depending on the parameter (Table 13). The direct measurements of parameters were presented which include physical measurements such as temperature, conductivity, and turbidity as well as concentrations. For concentrations, the datasets were also transformed into instantaneous loading rates by multiplying the observed concentration by the sampled flow taken from the modeled hourly flow record. The third type of transformation was performed on nitrogen and phosphorus species to assess how the proportions of nutrient species change across seasons. For this the percentage of nitrogen and phosphorus species in the total nitrogen and phosphorus concentrations were calculated for each sample.

Seasonal comparisons for each parameter and transformed dataset were performed using a non-parametric Kruskal Wallis group test paired with a bonniferrioni post hoc contrast.

Table 13: Equations for all transformations and calculations performed on the water quality dataset

Parameter	Equation
loading rate	
- mg/L → g/sec	[sampled flow (m^3/sec)]x [concentrations (mg/L)]
- CFU/100ml →CFU/sec	[sampled flow (m^3/sec)]x [concentrations (CFU/100ml)x10^3]
Total Nitrogen	Total Nitrate (mg/L) + Kjeldahl Nitrogen (mg/L)
Organic Nitrogen	Kjeldahl Nitrogen (mg/L) – total ammonia (mg/L)
Residual Phosphorus	Total phosphorus (mg/L) – phosphate (mg/L)
Nutrient Proportions	100 x [nutrient species (mg/L)/ total nutrient (mg/L)]

Correlations between parameters

Correlations between select parameter concentrations were assessed graphically and with a Spearman non-parametric correlation coefficient for each season and across the full dataset. The correlations investigated were: chloride vs. total nitrate, chloride vs. phosphate, suspended solids vs. turbidity, suspended solids vs. *E. coli*, suspended solids vs. total nitrogen, suspended solids vs. organic nitrogen, suspended solids vs. total phosphorus, suspended solids vs. residual phosphorus, and suspended solids vs. phosphate.

Load estimates

Parameters of concern to the nearshore (nutrients, sediments, and *E. coli*) were analyzed for relationships with sampled flows using *ln* transformed observed loading rates and the *ln* transformed sampled flows for samples collected between 2007 and 2009 from the intensive sampling site (Appendix D). The linear regression was assessed in SPSS v.14. The standard error for each constant in the equation was calculated and presented.

Monthly and annual load estimates for total nitrate, total phosphorus, and phosphate were calculated from the hourly flow record with the linear regression equation between January 2007 and September 2009.

The calculation of export coefficients is one method often used to correct load estimates from watershed areas allowing comparisons and contrasts between watersheds or drainage areas to occur. Export coefficients are calculated by dividing the total load by the drainage area producing a load per unit area. Unfortunately the numbers generated from the calculation can vary between years and across seasons due to variation in hydrological conditions between years. Considering the limitations of the approach, an alternative correction of load estimates was performed to allow comparison between watersheds. Given the importance of stream flow on the load estimates, the total load estimated was divided by the water load for the same period producing a ratio for each period and watershed. This ratio was expressed in parts per million and is equivalent to a concentration. These ratios were also determined for the standard error of the load estimate providing an error estimate on the ratio. The calculation of hourly water weight was determined from the flow data based on the following conversions:

$$1\ m^3/sec = 1000\ L/sec = 360{,}000\ kg/hr$$

From the linear regression equations, predicted concentrations were calculated. The difference between the observed concentrations and the predicted concentrations were plotted in time series relative to the hydrograph to see when stream flow did not predict water quality. Storm events showed the greatest deviation from predicted concentrations and two individual events sampled over the event period were identified. As a result a time series plot of the storm events, the estimated hourly loads, and the observed loading rates was created.

Results

Sampling Period

Environmental conditions during the sample period covered the range of conditions observed in the long term records. Annual average flows and total precipitation in 2007 fell at or below the 5th percentile of the long term record while in 2008 and 2009 these approached the 95th percentiles (Figure 28). Annual average temperature records indicate that while 2007 fell into the upper quartile of the distribution, 2008 was within the two middle quartiles of the distribution.

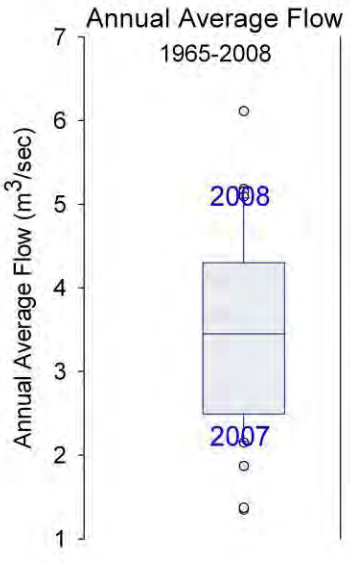

Figure 28: The annual average flows (m^3/sec) at the Sparta Gauge in the Catfish Creek watershed in 2007-2008 relative to annual averages from 1965-2008.

The distribution of monthly averages across years reflects the trends observed in the annual records (Figure 29). Average flows in 2007 most often fell within the lowest quartile of the distribution, while 2008 and 2009 fell into the upper most quartile of the distribution. In particular, peak summer flows during the later years were amongst the highest on record. Similarly, precipitation at a reference site (e.g. Shand Dam) was particularly low during the summer months of 2007 relative to the long term distribution, and 2008 and 2009 which typically fell within the upper half of the sample distribution (Figure 3). Monthly average temperature showed elevated temperatures occurring during the summer and fall relative to the long term average. Temperatures were often lower during the summer months of 2008 and 2009 (Figure 3).

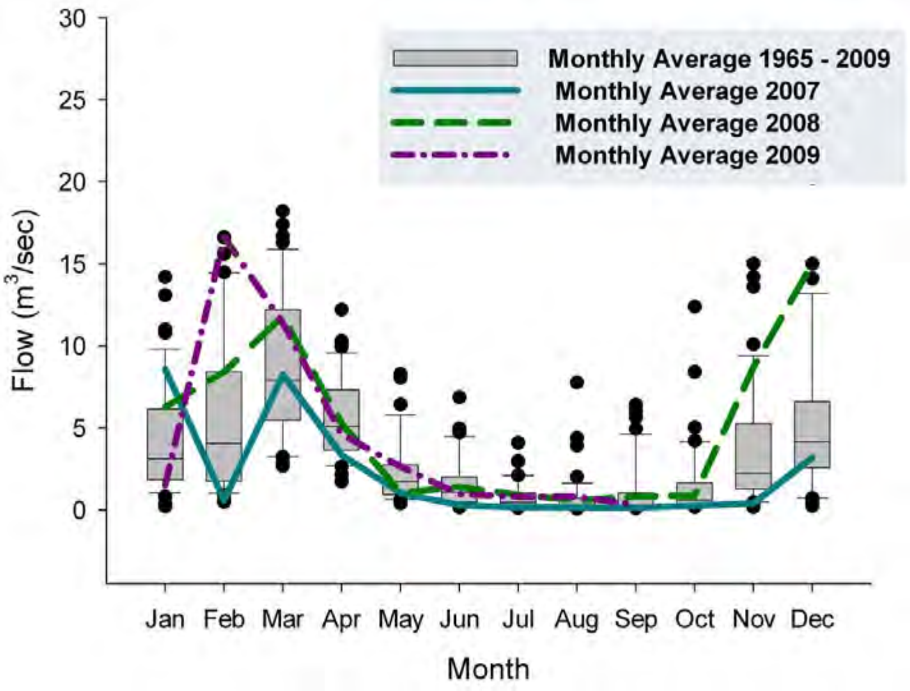

Figure 29: The monthly average flows (m^3/sec) at the Sparta Gauge in the Catfish Creek watershed in 2007-2009 relative to monthly averages from 1965-2009.

Sample Program

The spring and summer months were most strongly represented in the dataset with samples collected during 2009 being the greatest (Figure 30).

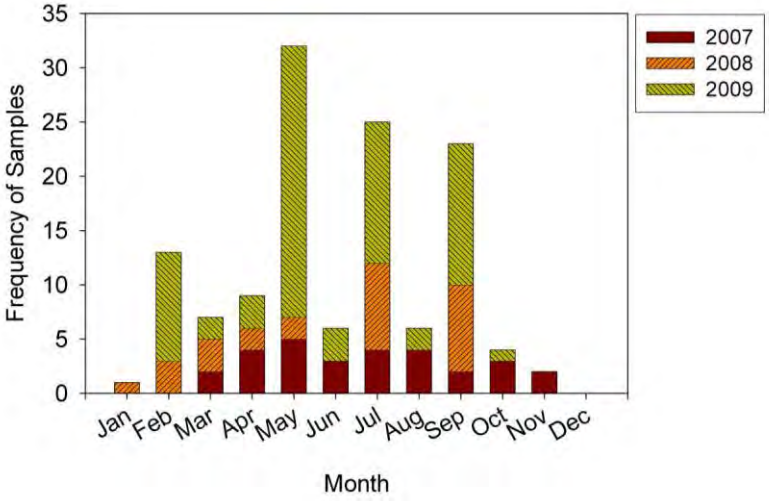

Figure 30: The monthly frequency of water quality samples collected at the mouth of Catfish Creek by year between 2007 and 2009.

Melt events were well sampled in Catfish Creek with peak flows being sampled in winter and spring months in 2008 and 2009 (Figure 31). Conditions which were not well represented were winter low flow and fall high flow conditions. These observations are reflected by the percent of the flow range sampled across seasons which shows good characterization of the range in flow from winter through summer but not during the fall (Table 14;Figure 32). The range of sampled temperatures is shown in Figure 33.

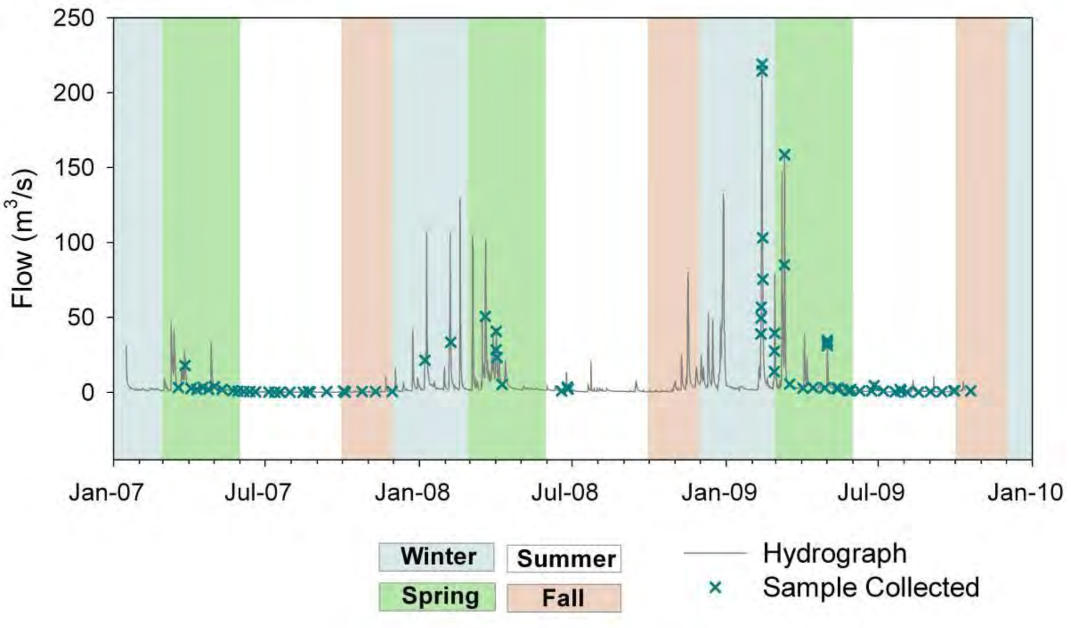

Figure 31: The stream flows (m^3/sec) sampled for water quality at the mouth of Catfish Creek relative to the hydrograph with the seasons identified (winter, spring, summer, fall) between 2007 and 2009.

Table 14: The percent of flow sampled at the mouth of Catfish Creek per season (winter, spring, summer, fall) in 2007, 2008, and 2009.

Year	Season Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
2007	n/a	37%	69%	7%
2008	9%	44%	13%	n/a
2009	93%	100%	42%	n/a
Total	71%	100%	21%	n/a

Water Quality Summary

The 25th and 75th percentile concentrations of turbidity, *E. coli*, suspended solids, total ammonia, organic nitrogen, nitrate, total phosphorus, residual phosphorus, and phosphate were distinctly greater in samples collected during the winter season when compared to the other seasons (e.g. Figure 32; Figure 33). The outliers in the spring and summer datasets had similar values to those observed in the winter dataset. Sampled flows demonstrated a similar seasonal pattern except the outliers to the spring and summer datasets were lower relative to values observed in the winter datasets. For dissolved organic carbon, silicate, and total nitrogen, the concentrations tended to be slightly higher or more variable during the winter but differences were less distinct.

Alkalinity, conductivity and dissolved inorganic carbon (e.g. Figure 36) concentrations were generally lower during the winter when compared to other seasons. In addition, chloride concentrations were lower during the winter but trends were not as distinct for this parameter. The loading rate for all parameters followed the same seasonal pattern as the sampled flows.

No seasonal trends in the proportion of the different nitrogen forms were observed (Figure 37). Most of the nitrogen pool across all seasons was in the form of nitrate. The proportion of phosphate (as estimated by soluble reactive phosphorus) remained consistent in all seasons (about 20-25 percent) (Figure 38).

When all concentration measurements were converted to loading rates, seasonal trends reflected those observed in the sampled flows with the exception of outliers to the spring loading dataset which were often some of the highest observations.

Box and whisker plots for all routine water chemistry parameters sampled in Catfish Creek are in Appendix E.

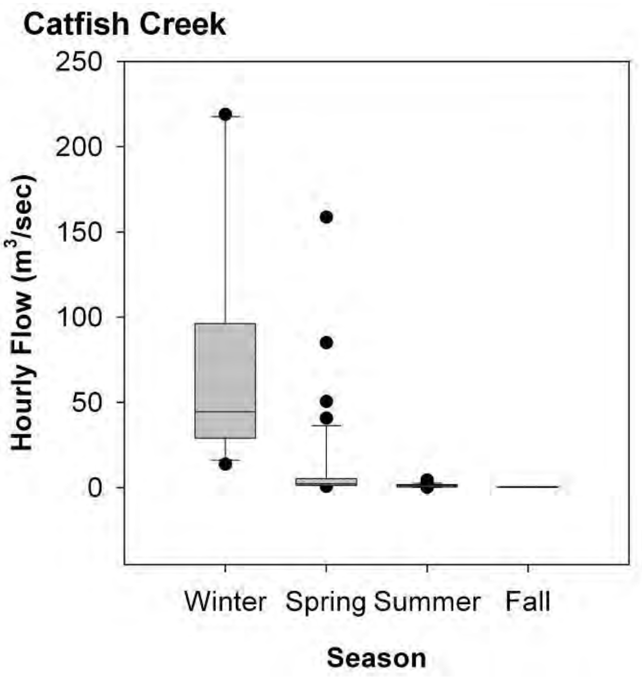

Figure 32: Boxplots of flows (m^3/sec) sampled between 2007 and 2009 plotted by season (winter, spring, summer, fall) at the mouth of Catfish Creek.

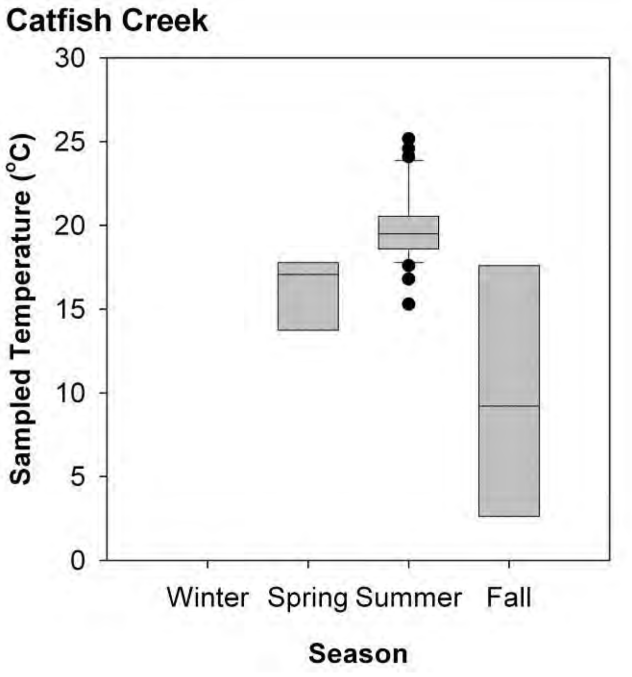

Figure 33: Boxplots of water temperature (°C) sampled between 2007 and 2009 plotted by season (winter, spring, summer, fall) at the mouth of Catfish Creek.

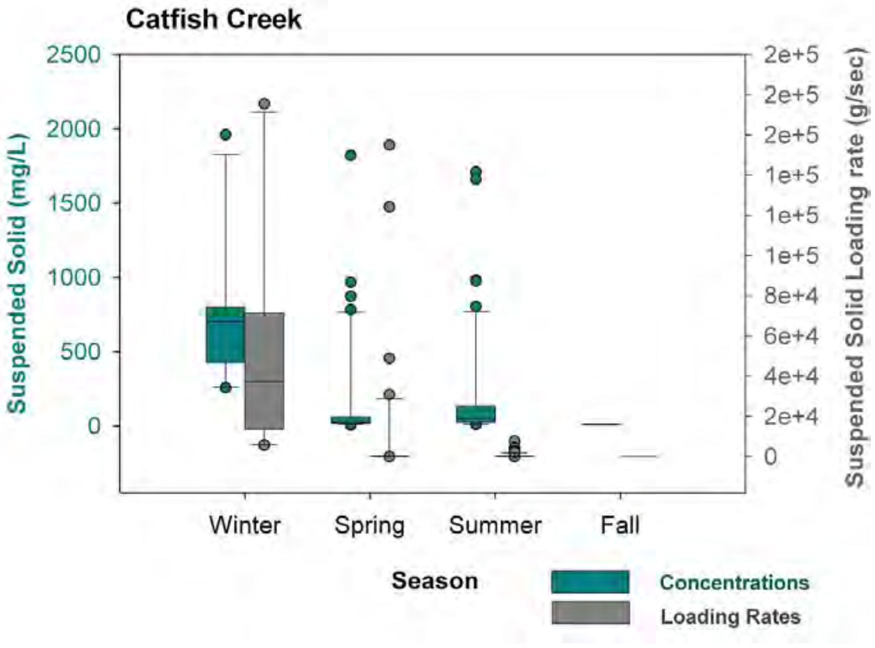

Figure 34: Boxplots of all observed suspended solids concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Catfish Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.

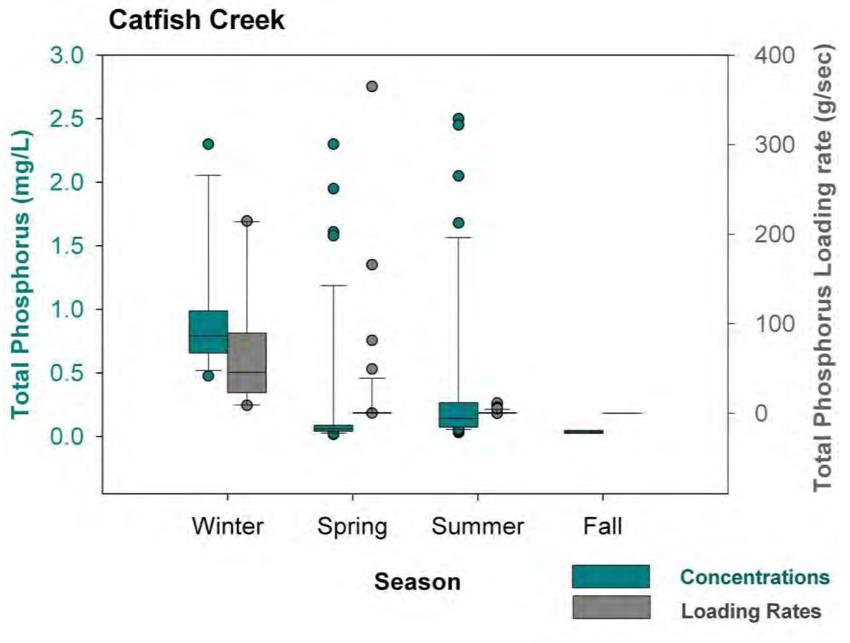

Figure 35: Boxplots of all observed total phosphorus concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Catfish Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.

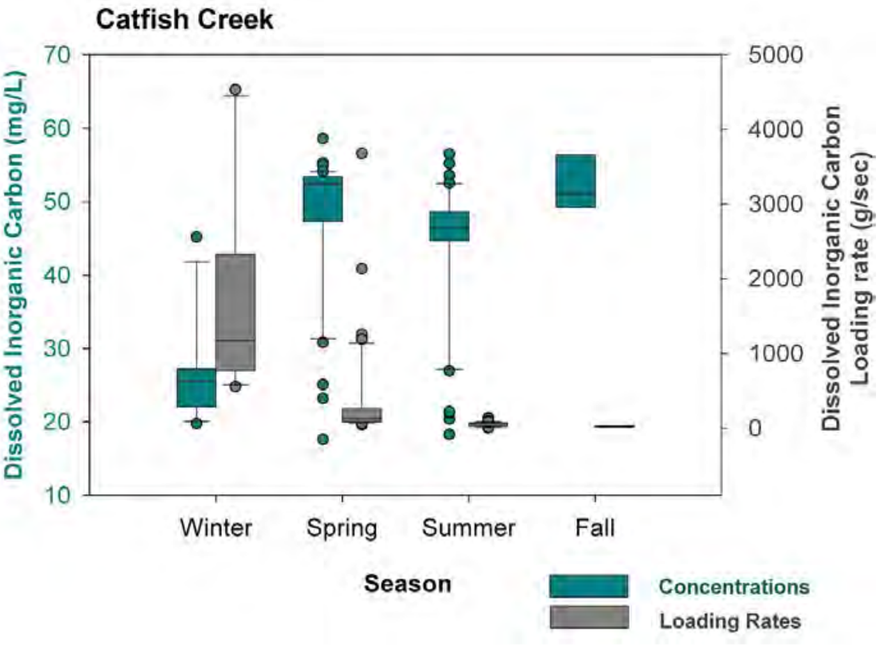

Figure 36: Boxplots of all observed dissolved inorganic carbon concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Catfish Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.

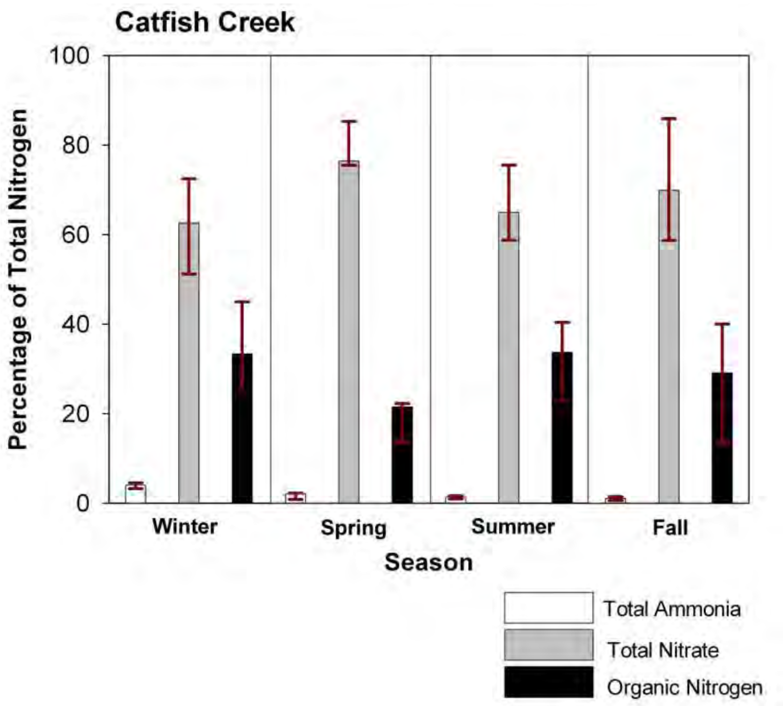

Figure 37: Bar graphs of the percentage of total ammonia, total nitrate, and organic nitrogen in total nitrogen values at the mouth of Catfish Creek according to sample season (winter, spring, summer, fall) between 2007 and 2009. Error bars represent the 25th and 75th percentiles.

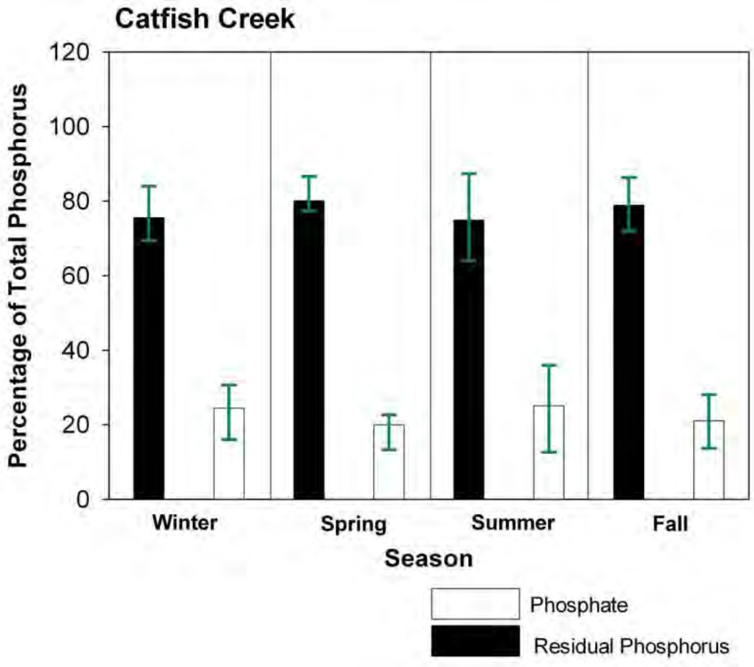

Figure 38: Bar graphs of the percentage of residual phosphorus and phosphate in total phosphorus values at the mouth of Catfish Creek according to sample season (winter, spring, summer, fall) between 2007 and 2009. Error bars represent the 25th and 75th percentiles.

Correlations

Correlations were strongest for suspended solids against turbidity, organic nitrogen, total phosphorus, and residual phosphorus (Table 15; e.g. Figure 39). The results were similar when run across for winter, spring, and summer as when they were run for the full dataset for these pairs of parameters. Weaker correlations were observed for the following pairs of parameters: chloride and phosphate, suspended solids and *E. coli*, and suspended solids and total nitrogen. The correlations observed were similar between spring, summer and the full datasets but no correlations were observed for the winter and fall datasets. The correlations between chloride and total nitrate during winter and summer and for the full dataset were relatively weak with a positive trend observed during the winter and a negative trend observed during the summer and in the full dataset.

Table 15: The non-parametric Spearman Correlation Coefficients (*p* values) for water quality parameter pairs across seasons (winter, spring, summer, fall) and in the full dataset. Red colour indicates significance of p = 0.05.

Correlations	Spearman Correlation Coefficients				
	Seasonal Datasets				Full dataset
	Winter	Spring	Summer	Fall	
Chloride vs. Total Nitrate	*0.636 (0.026)*	-0.145 (0.343)	*-0.381 (0.012)*	0.400 (0.505)	*-0.370 (<0.001)*
Chloride vs. Phosphate	-0.538 (0.071)	*-0.597 (<0.001)*	*-0.455 (0.002)*	0.600 (0.285)	*-0.422 (<0.001)*
Suspended Solids vs. Turbidity	*0.965 (<0.001)*	*0.911 (<0.001)*	*0.930 (<0.001)*	0.700 (0.188)	*0.993 (<0.001)*
Suspended Solids vs. *E. coli*	-0.800 (0.200)	*0.606 (0.001)*	*0.632 (0.001)*	0.100 (0.873)	*0.626 (<0.001)*
Suspended Solids vs. Total Nitrogen	-0.091 (0.779)	*0.521 (<0.001)*	*0.741 (<0.001)*	-0.500 (0.391)	*0.652 (<0.001)*
Suspended Solids vs. Organic N	*0.873 (<0.001)*	*0.614 (<0.001)*	*0.754 (<0.001)*	-0.100 (0.873)	*0.778 (<0.001)*
Suspended Solids vs. Total Phosphorus	*0.923 (<0.001)*	*0.803 (<0.001)*	*0.829 (<0.001)*	0.300 (0.624)	*0.852 (<0.001)*
Suspended Solids vs. Residual Phosphorus	*0.951 (<0.001)*	*0.809 (<0.001)*	*0.826 (<0.001)*	0.600 (0.285)	*0.892 (<0.001)*

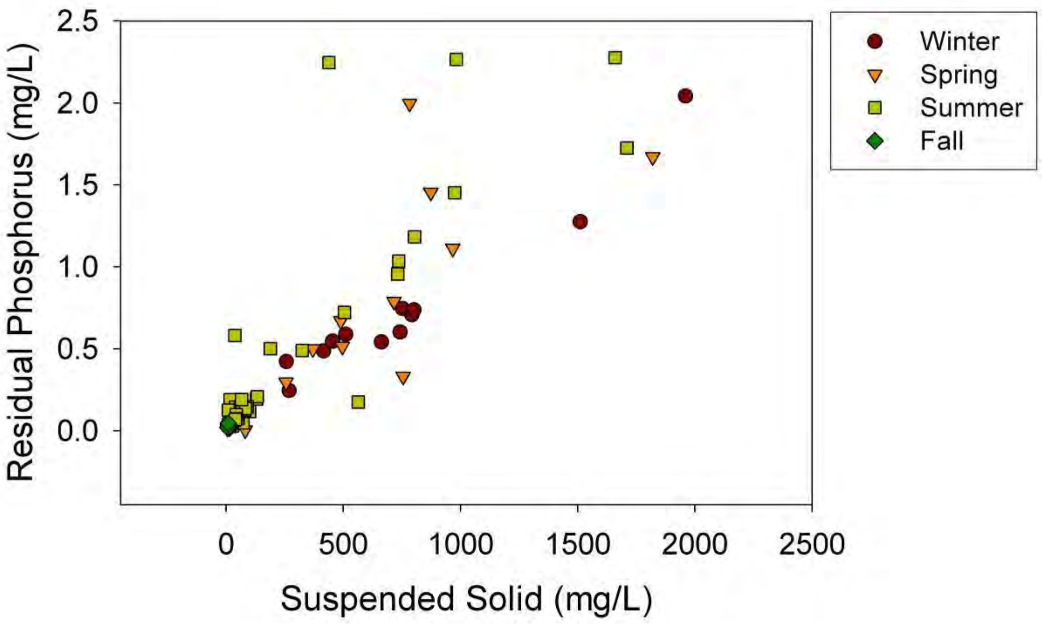

Figure 39: Residual phosphorus (mg/L) vs. suspended solids (mg/L) concentrations in water samples collected between 2007 and 2009 near the mouth of Catfish Creek differentiated by season (winter, spring, summer, fall).

Load Estimates

Significant regressions between the *ln* transformed loading rates and the *ln* transformed sampled flow were observed for all tested parameters (p <0.001; R^2 = 0.754 – 0.983) (Table 16).

Table 16: Linear equations generated from regressions performed on *ln* transformed sampled hourly flow (m^3/sec) and *ln* transformed loading rates (kg) for water quality parameters measured at the mouth of Catfish Creek between 2007 and 2009.

Parameter	y = m(± SE) x + b(± SE)	R^2 value	*p* value
Chloride	y = 0.915(± 0.011) x + 3.508(± 0.021)	0.983	<0.001
E. coli	y = 1.308(± 0.095) x + 14.112(± 0.155)	0.754	<0.001
Total Ammonia	y = 1.453(± 0.047) x + -3.36(± 0.089)	0.892	<0.001
Total Nitrate	y = 0.833 (± 0.020) x + 0.692(± 0.070)	0.913	<0.001
Organic Nitrogen	y = 1.268(± 0.031) x + -0.264(± 0.059)	0.935	<0.001
Phosphate	y = 1.584(± 0.062) x + -4.024(± 0.117)	0.851	<0.001
Residual Phosphorus	y = 1.547(± 0.061) x + -2.629(± 0.114)	0.851	<0.001
Total Phosphorus	y = 1.550(± 0.058) x + -2.355(± 0.109)	0.864	<0.001
Suspended Solids	y = 1.675(± 0.065) x + 3.619(± 0.122)	0.854	<0.001

Monthly and annual load estimates calculated from the linear regression equations for total nitrate, total phosphorus, and phosphate show that loads for these nutrients were typically highest during February and March. Total monthly loads were almost an order of magnitude lower in 2007 relative to 2008 or 2009 (Figure 40; Figure 41; Figure 42).

The ratio of parameter mass over water weight and calculated export coefficients (tonnes/km^2) for Catfish Creek for the various water quality parameters are listed in Table 17. In general, greater mass of constituents were exported from the Catfish Creek watershed in 2008, due to the greater amount of precipitation and runoff.

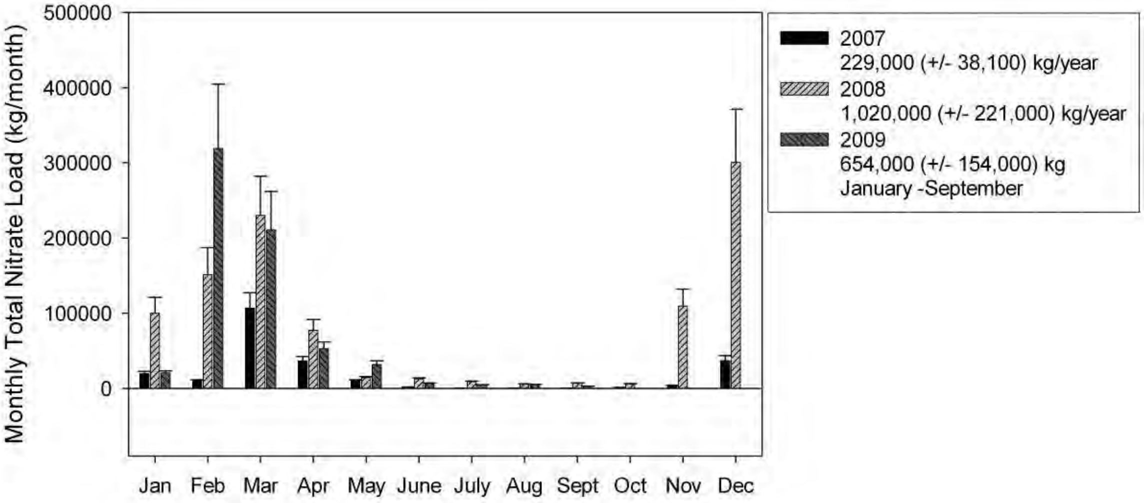

Figure 40: The estimated monthly total nitrate loads (kg/month) based on the linear regression equations generated from the water quality datasets collected at the mouth of Catfish Creek between 2007 and 2009. Errors are presented as standard errors.

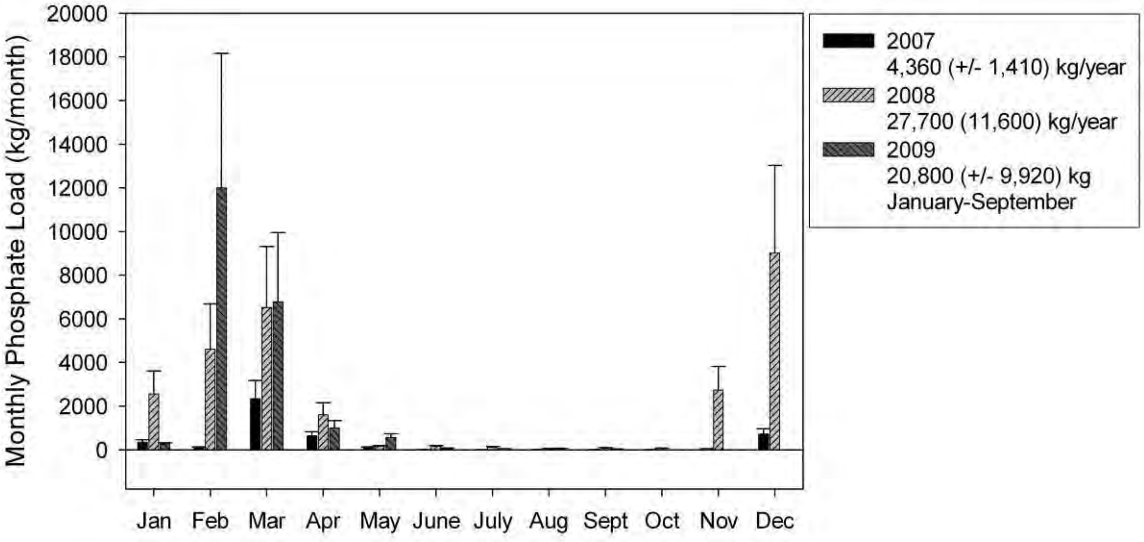

Figure 41: The estimated monthly phosphate loads (kg/month) based on the linear regression equations generated from the water quality datasets collected at the mouth of Catfish Creek between 2007 and 2009. Errors are presented as standard errors.

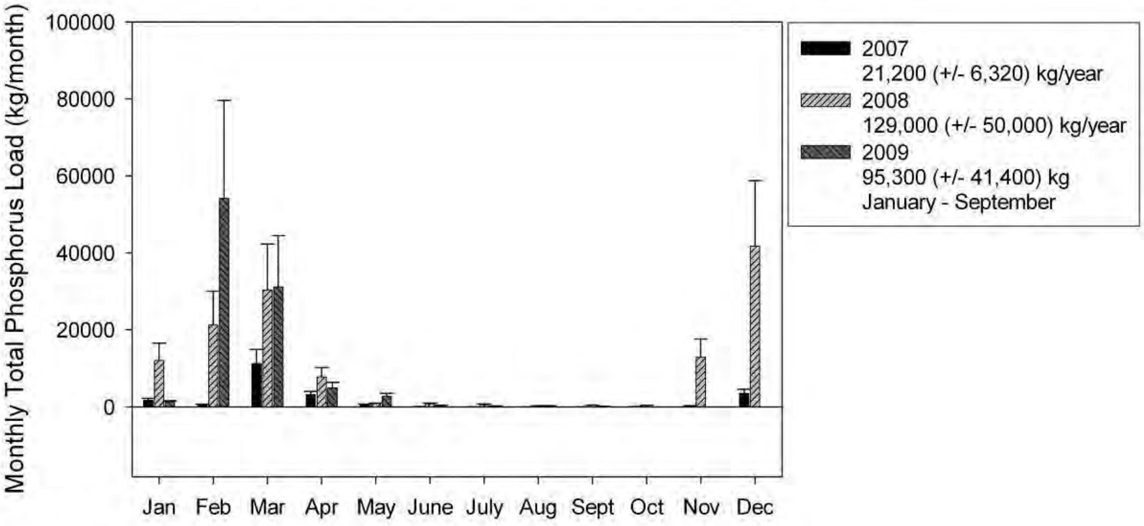

Figure 42: The estimated monthly total phosphorus loads (kg/month) based on the linear regression equations generated from the water quality datasets collected at the mouth of Catfish Creek between 2007 and 2009. Errors are presented as standard errors.

Table 17: The ratio (± standard error) of parameter mass over water weight and export coefficients based on analysis of water quality datasets and flow data from the mouth of Catfish Creek between 2007 and 2009.

Parameter	Ratio of Total Parameter wt / total Water wt (‰) Estimates			Export Coefficient (tonnes/km^2)	
	2007-2009	2007	2008	2007	2008
Chloride	26.5 *(25.2 – 27.9)*	28.8 *(27.7 – 29.9)*	26.1 *(24.8 – 27.5)*	4.8 *(4.7 – 5.0)*	14.3 *(13.6 – 15.1)*
Total Ammonia	0.15 *(0.12 – 0.20)*	0.09 *(0.08 – 0.11)*	0.16 *(0.12 – 0.20)*	0.02 *(0.01 – 0.02)*	0.09 *(0.07 – 0.11)*
Total Nitrate	4.68 *(3.85 – 5.69)*	3.49 *(3.00 – 4.08)*	4.77 *(3.93 – 5.81)*	0.59 *(0.50 – 0.69)*	2.62 *(2.15 – 3.19)*
Organic Nitrogen	1.75 *(1.49 – 2.07)*	1.32 *(1.16 – 1.50)*	1.79 *(1.52 – 2.11)*	0.22 *(0.20 –0.25)*	0.98 *(0.84 – 1.16)*
Phosphate	0.129 *(0.091 – 0.186)*	0.067 *(0.050 – 0.088)*	0.129 *(0.091 – 0.183)*	0.011 *(0.009 – 0.015)*	0.071 *(0.050 – 0.100)*
Residual Phosphorus	0.453 *(0.320 – 0.644)*	0.244 *(0.186 – 0.321)*	0.454 *(0.323 – 0.640)*	0.041 *(0 .031 – 0.054)*	0.249 *(0.177 – 0.351)*
Total Phosphorus	0.603 *(0.433 – 0.843)*	0.334 *(0.273 – 0.411)*	0.604 *(0.437 – 0.838)*	0.054 *(0.042 - 0.071)*	0.331 *(0.240 – 0.460)*
Suspended Solids	387 *(265 – 570)*	177 *(131 – 239)*	381 *(263 – 554)*	30 *(22 – 40)*	209 *(144 – 304)*

Predicting Water Quality

The relative importance of the difference between the modeled and the predicted concentrations were summarized by calculating the percentage of each difference from the corresponding observed concentration. The percentage between the observed and predicted concentrations was lowest for chloride (75th percentile = 25%) and highest for total phosphorus, residual phosphorus, and phosphate (75th percentile ranged from 93 – 105 %) (Table 18). The differences were plotted in time series and tended to be greatest in the sampled storm events. The sampled portion of a storm event from June 2008 showed much higher concentrations than predicted from the linear regressions. During the melt period and the summer of 2009 higher than predicted concentrations were often observed (e.g. Figure 43).

Table 18: The mean, median, and 75th percentile for the percent difference between the observed and the predicted concentrations calculated from the water quality datasets collected from Catfish Creek between 2007 and 2009.

Parameter	Mean	Median	*75th* percentile
Chloride	16%	13%	25%
Total Ammonia	89%	37%	77%
Total Nitrate	59%	38%	77%
Organic Nitrogen	40%	33%	54%
Phosphate	131%	64%	105%
Residual Phosphorus	117%	67%	102%
Total Phosphorus	101%	60%	93%
Suspended Solids	72%	48%	79%

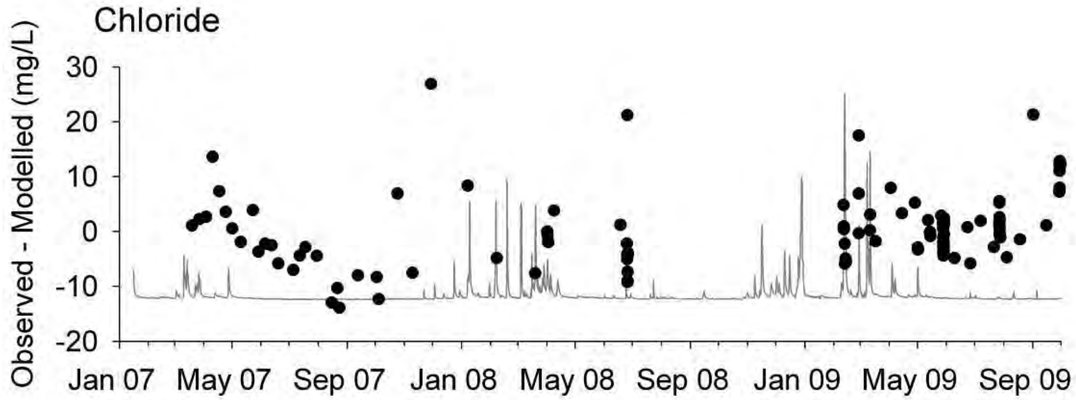

Figure 43: The difference between the observed chloride (mg/L) concentrations and the modeled concentrations plotted in time series relative to the hydrograph at the mouth of Catfish Creek between 2007 and 2009.

The linear regression equation generated from the *ln* transformed loading rate and the *ln* transformed sampled flow did not predict observed *E. coli* concentrations very well in Catfish Creek. Furthermore, there was no clear trend in how or when observed concentrations deviated from the predicted concentrations. When concentrations are compared to the water quality guidelines set by the CCME (200 CFU/100ml for recreational waters), samples frequently exceeded this guideline across all seasons (Figure 44).

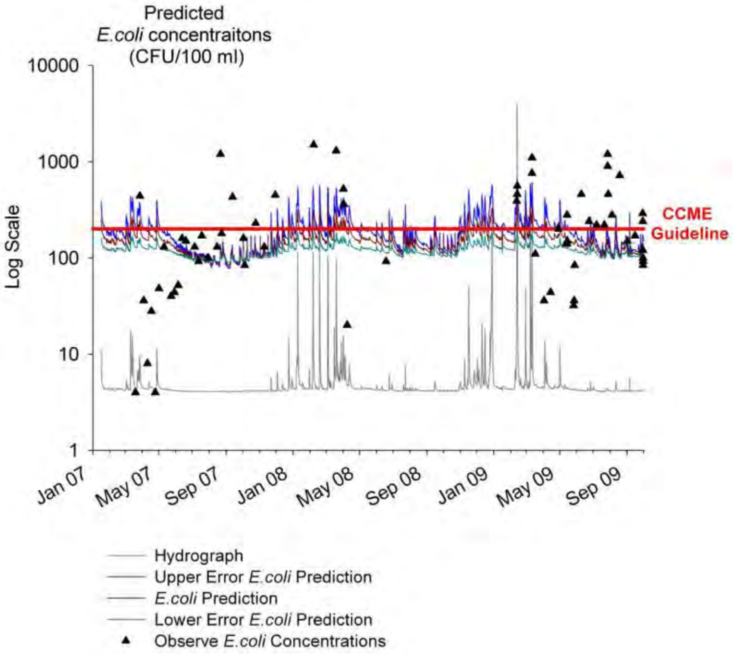

Figure 44: The observed *E. coli* (CFU/100ml) concentrations relative to the predicted concentrations, the flow record, and the Canadian Council for Ministers of the Environment (CCME) guideline for recreational water use at the mouth of Catfish Creek between 2007 and 2009.

A comparison between the predicted hourly loads and the calculated hourly loads for an event during the summer 2008 shows the observed loads were much higher than what was predicted for phosphate and total phosphorus during the falling limb of the hydrograph (Figure 45). In contrast, the observed loads fell within the predicted range for phosphate and total phosphorus across the melt event hydrograph from February 2009 (Figure 46).

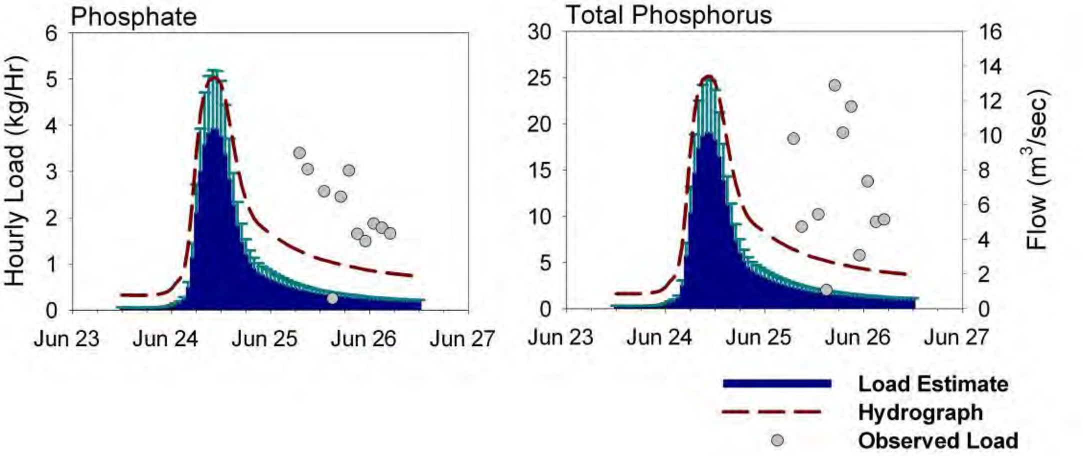

Figure 45: The predicted hourly load (kg/hr) of phosphate (left) and total phosphorus (right) relative to the observed hourly load calculated from water samples collected during a high flow event in June 2008 at the mouth of Catfish Creek.

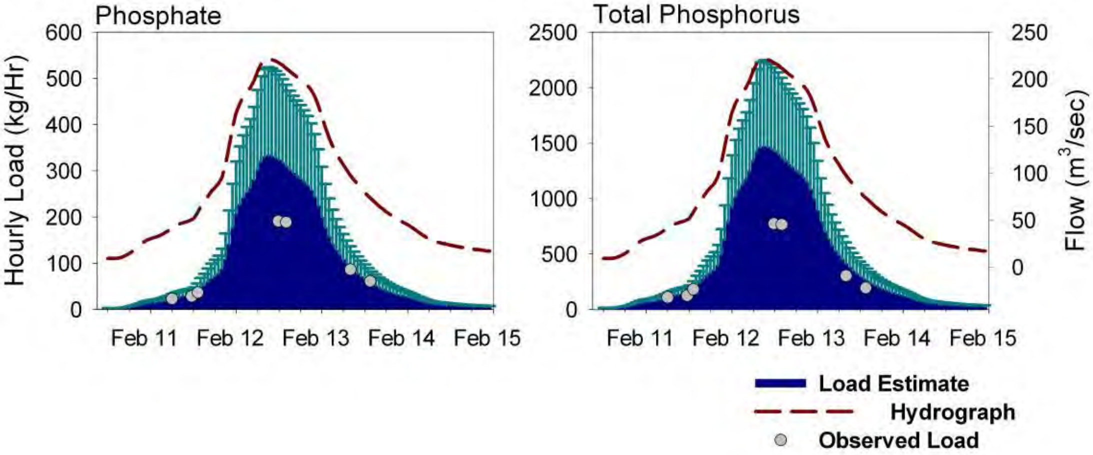

Figure 46: The predicted hourly load (kg/hr) of phosphate (left) and total phosphorus (right) relative to the observed hourly load calculated from water samples collected during a high flow event in February 2009 at the mouth of Catfish Creek.

Kettle Creek

Watershed Characterization

Kettle Creek drains an area of 520 square kilometres of land which includes the south-central portion of Middlesex County/City of London and the central portion of Elgin County, including the city of St. Thomas and discharges to Lake Erie at Port Stanley (Lake Erie Source Protection Region Technical Team 2008). The upper portion of Kettle Creek draining the northeast portion of the watershed is the highest region in the watershed approaching 300 m above sea level and contains a series of till moraine complexes. The Westminster moraine defines the northern border of the watershed while the St. Thomas moraine defines the border between Kettle Creek and Catfish Creek. In the middle of the watershed, Kettle Creek joins with Dodd Creek, a tributary which drains the western portion of the watershed. Soils in this portion of the watershed are part of the Ekfrid Clay Plain and the landscape is generally flat in nature and represents approximately nine percent of the watershed (Table 19). The lower portion of the watershed (~ 15%) drains a portion the Norfolk Sand Plain prior to discharging to Lake Erie (Table 19).

Table 19: The percent of soil types occurring in the Kettle Creek watershed.

Surficial Geology Category	Percent Land Cover (%)
Clay	<1.0
Silt	10
Diamicton (Till)	71
Gravel	4
Organic Deposits	< 1.0
Sand	15

Agricultural production is the dominant land use (78%; Table 20) in the watershed with most of the lands being used for crop production. Soy and corn are the dominant crop lands (34 and 34 %, respectively) although grain and vegetable production represents approximately 10% of crop lands each. Irrigation is not common across the watershed and concentrated to regions within the Norfolk Sand Plain in the lower portion of the watershed. Livestock production is prevalent across the watershed with the highest densities of cattle and swine observed in the upper portion of Kettle Creek (0.27 and 0.61 animals per hector of farmed land, respectively) and highest densities of poultry occur in the lower portion of the watershed (7.7 animals per hector of farmed land).

Urban development and population in the watershed are concentrated in the centre of the watershed where Dodd Creek joins with Kettle Creek in the municipality of St. Thomas, Ontario. One other small urban area occurs at the river mouth (Port Stanley, Ontario). Populations in the watershed are served by three municipal wastewater facilities. The St. Thomas Water Pollution Control Plant is the largest facility serving the municipality of St. Thomas and discharging directly to Kettle Creek downstream of St. Thomas. The town of Belmont, Ontario in the upper reaches of Kettle Creek and Port Stanley at the river mouth both employ lagoon treatment facilities which discharge continuously and between April and November, respectively. Two other small privately operated facilities serve individual organizations on the west side of the watershed. Although the Port Stanley facility discharges to a small creek which later discharges to Kettle Creek, the sites used in the longitudinal survey of Kettle Creek occur up and downstream of this tributary and give no indication that conditions differ in Kettle Creek due to this discharge.

Table 20: The percent of different land use categories occurring in the Kettle Creek watershed.

Land Use Category	Percent Land Cover (%)
Treed land	11
Wetland/ open water	2
Urban	9
Extraction	<1.0
Agriculture	78

Annually, stream flow in this watershed is sustained by a greater proportion of surface run-off compared to ground water discharges (AquaResource Inc. 2009). Extreme peak flows occur during spring melt and base flows are typically low. These flow patterns reflect that of an unregulated system; although, stream flows are regulated by various conservation authority and privately owned reservoirs and dams. The flow characteristics reflect the reduced capacity of precipitation to infiltrate clay based soils and packed tills which cover most of the watershed.

Methods

Water quality monitoring of Kettle Creek began in 2007 at a site near the mouth of the creek. In 2007 water quality samples were collected biweekly May through October in correspondence with nearshore sampling. During nearshore sampling, water samples were also collected from various locations between the intensively sampled site and the river mouth to ensure that the intensively sampled site was representative of conditions in the river discharge (Appendix A). In 2008, more intensive sampling was started to characterize spring melt conditions and summer rain events. The intensive sampling continued throughout the 2008 and 2009 seasons with increased focus on characterization of the observed range in environmental conditions, including peak and low flows across seasons. Sampling programs in 2008 and 2009 included both grab samples and the employment of ISCO samplers to characterize individual storm events.

Water samples were sent to the Ministry of the Environment (MOE) Laboratory in Etobicoke, Ontario and analyzed for a suite of physical, chemical, and biological water quality parameters (Table 21). Laboratory procedures are outlined in the Laboratory Information Management System (LIMS) (LIMS Project Team 1994; Todd 2006).

Table 21: List of water quality variables analyzed in water samples collected in Kettle Creek between 2007 and 2009.

Water Quality Variable Category	Water Quality Variable
Nutrients	Dissolved Nutrients: ammonia, nitrite, nitrate, phosphate, silicate Total Nutrients: total phosphorus, Kjeldahl nitrogen Dissolved Carbon: dissolved inorganic carbon, dissolved organic carbon
Solids	Suspended Solids
Major Ions	Chloride
Routine Chemistry	pH, alkalinity, conductivity
Routine Physical	Temperature, turbidity
Bacterial	*E. coli*
Productivity	Chlorophyll[1]

[1] Chlorophyll analysis was limited to those samples collected through the river survey by boat in 2007.

Hourly flow data for each watershed was collected as part of the Water Survey of Canada hydrological monitoring network (see www.wsc.gc.ca for more information). Because flow gauges were located at different points from the sampling locations, the sampled flow at the monitoring site was modeled from this record (see Appendix B).

Data Analysis

Sample Period

The sample period (2007-2009) was characterized relative to long term trends in flow and climate data from the Water Survey of Canada and the Environment Canada climate databases. The flow gauge used for this assessment was located at St. Thomas, Ontario in Kettle Creek (02GC002). The air temperature was taken from the climate station at the Shand Dam in Fergus, Ontario within the Grand River watershed (see http://climate.weatheroffice.ec.gc.ca for more information).

Sample Program

Because water quality monitoring data cannot be used to describe environmental conditions which are not represented within the dataset (i.e. winter under ice conditions), a good understanding of the composition of the dataset is necessary to define the limitations of interpretation. The representation of environmental conditions which occurred between 2007 and 2009 in the dataset were evaluated in the water quality dataset through three methods:

1) The frequency of samples collected across months and years was calculated;
2) The sampled flow was plotted relative to the observed hydrograph between 2007 and 2009; and
3) The percent of flow sampled across seasons was calculated.

Note that most water quality parameters were analyzed within each sample; however, *E. coli* measurements were taken in fewer samples due to extended sample holding times.

Seasonal water quality summary

Water quality data from the tributary monitoring site was summarized by season with box and whisker plots and with descriptive statistics. Because few of the ISCO samples effectively captured the full event, these samples were included with the grab samples for analysis. Descriptive statistics used were: sample size, mean, median, range, and dataset skewness. Skewness in the dataset was assessed relative to two times the standard error of skewness (the square root of six divided by sample size; Appendix C). In a box and whisker plot the box encloses the 25th to 75th percentiles, the horizontal line bisecting the box represents the median, the error bars represent the 5th and 95th percentiles, and the circles represent the outliers in the dataset.

Water quality datasets were presented from as many as three perspectives depending on the parameter (Table 22). The direct measurements of parameters were presented which include physical measurements such as temperature, conductivity, and turbidity as well as concentrations. For concentrations, the datasets were also transformed into instantaneous loading rates by multiplying the observed concentration by the sampled flow taken from the modeled hourly flow record. The third type of transformation was performed on nitrogen and phosphorus species to assess how the proportions of nutrient species change across seasons. For this the percentage of nitrogen and phosphorus species in the total nitrogen and phosphorus concentrations were calculated for each sample.

Seasonal comparisons for each parameter and transformed dataset were performed using a non-parametric Kruskal Wallis group test (Appendix C).

Table 22. Equations for all transformations and calculations performed on the water quality dataset

Parameter	Equation
loading rate	
- mg/L → g/sec	[sampled flow (m^3/sec)]x [concentrations (mg/L)]
- CFU/100ml →CFU/sec	[sampled flow (m^3/sec)]x [concentrations (CFU/100ml)x10^3]
Total Nitrogen	Total Nitrate (mg/L) + Kjeldahl Nitrogen (mg/L)
Organic Nitrogen	Kjeldahl Nitrogen (mg/L) – total ammonia (mg/L)
Residual Phosphorus	Total phosphorus (mg/L) – phosphate (mg/L)
Nutrient Proportions	100 x [nutrient species (mg/L)/ total nutrient (mg/L)]

Correlations between parameters

Correlations between select parameter concentrations were assessed graphically and with a Spearman non-parametric correlation coefficient for each season and across the full dataset. The correlations investigated were: chloride vs. total nitrate, chloride vs. phosphate, suspended solids vs. turbidity, suspended solids vs. *E. coli*, suspended solids vs. total nitrogen, suspended solids vs. organic nitrogen, suspended solids vs. total phosphorus, suspended solids vs. residual phosphorus, and suspended solids vs. phosphate.

Load estimates

Parameters of concern to the nearshore (nutrients, sediments, and *E. coli*) were analyzed for relationships with sampled flows using *ln* transformed observed loading rates and the *ln* transformed sampled flows for samples collected between 2007 and 2009 from the intensive sampling site (Appendix D). The linear regression was assessed in SPSS v.14. The standard error for each constant in the equation was calculated and presented.

Monthly and annual load estimates for total nitrate, total phosphorus, and phosphate were calculated from the hourly flow record with the linear regression equation between January 2007 and September 2009.

The calculation of export coefficients is one method often used to correct load estimates from watershed areas allowing comparisons and contrasts between watersheds or drainage areas to occur. Export coefficients are calculated by dividing the total load by the drainage area producing a load per unit area. Unfortunately the numbers generated from the calculation can vary between years and across seasons due to variation in hydrological conditions between years. Considering the limitations of the approach, an alternative correction of load estimates was performed to allow comparison between watersheds. Given the importance of stream flow on the load estimates, the total load estimated was divided by the water load for the same period producing a ratio for each period and watershed. This ratio was expressed in parts per million and is equivalent to a concentration. These ratios were also determined for the standard error of the load estimate providing an error estimate on the ratio. The calculation of hourly water weight was determined from the flow data based on the following conversions:

$$1\ \text{m}^3/\text{sec} = 1000\ \text{L/sec} = 360{,}000\ \text{kg/hr}$$

From the linear regression equations, the predicted concentrations were calculated. The difference between the observed concentrations and the predicted concentrations were plotted in time series relative to the hydrograph to see when stream flow did not predict water quality. Storm events showed the greatest deviation from predicted concentrations and three individual events sampled over the event period were identified. As a result a time series plot of the storm events, the estimated loading rates, and the observed loading rates was created.

Results

Sampling Period

Environmental conditions during the sample period covered the range of conditions observed in the long term records. Annual average flows and total precipitation in 2007 fell at or below the 5th percentile of the long term record while in 2008 and 2009 these parameters approached the 95th percentiles (Figure 47). For a reference site (e.g. Shand dam), annual average temperature records indicate that while 2007 fell into the upper quartile of the distribution, 2008 was within the two middle quartiles of the distribution (Figure 3).

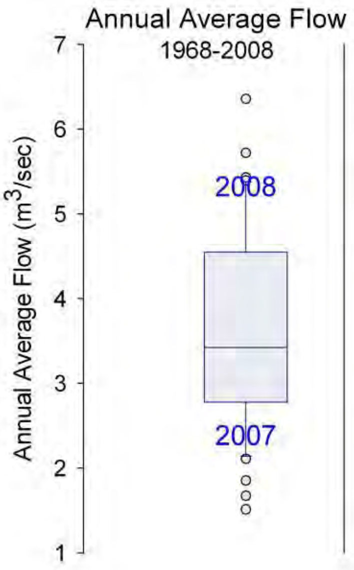

Figure 47: The annual average flows (m^3/sec) at the St. Thomas Gauge in the Kettle Creek watershed in 2007-2008 relative to annual averages from 1968-2008.

The distribution of monthly average flows across years reflects the trends observed in the annual records (Figure 48). Average flows in 2007 most often fell within the lowest quartile of the distribution, while 2008 and 2009 fell into the upper most quartile of the distribution. In particular, peak summer flows during the later years were amongst the highest on record.

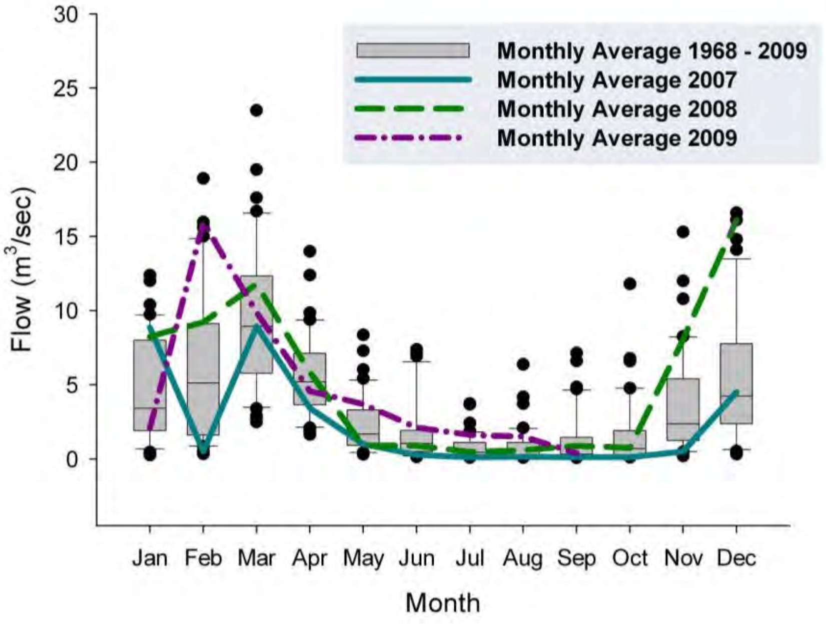

Figure 48: The monthly average flows (m^3/sec) at the St. Thomas Gauge in the Kettle Creek watershed in 2007-2009 relative to monthly averages from 1968-2009

Sampling Program

Sampling was focused on characterizing flows throughout the year (Figure 49). Although an attempt was made to characterize flows in each month between 2007 and 2009, some months were sampled more frequently than others. Winter months were not well characterized in 2007 and 2009.

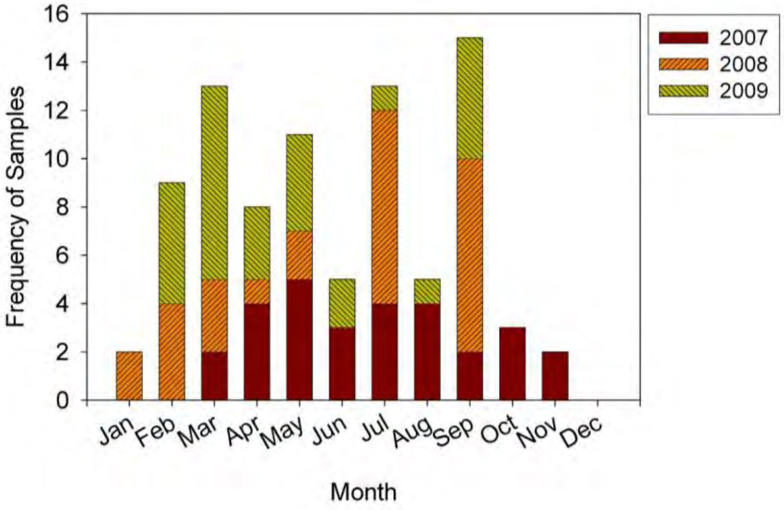

Figure 49: The monthly frequency of water quality samples collected at the mouth of Kettle Creek by year between 2007 and 2009.

A comparison of sampled flows relative to the hydrograph shows that the winter and spring melt events were well sampled in 2008 and 2009. Low flow summer conditions were well sampled in 2007 and a high flow event in 2008 was represented (Figure 50).

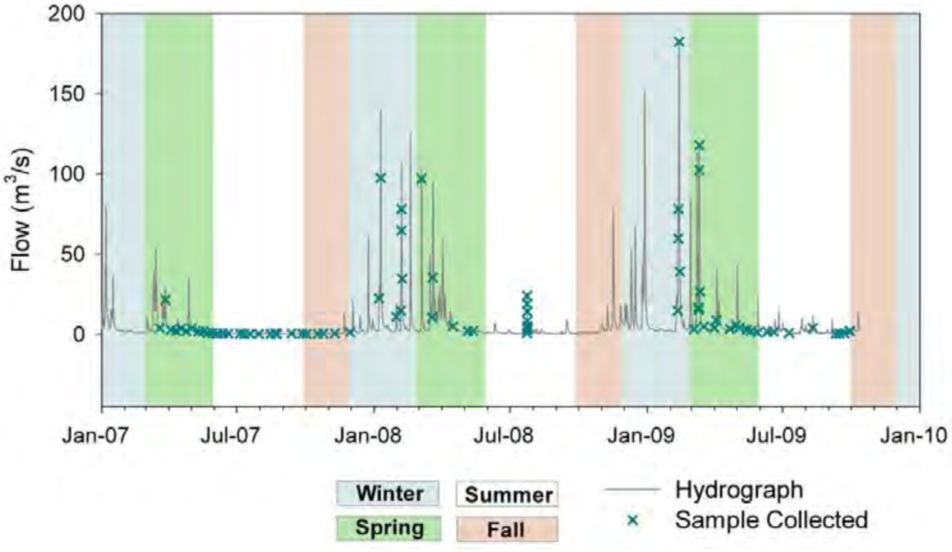

Figure 50: The stream flows (m^3/sec) sampled for water quality at the mouth of Kettle Creek relative to the hydrograph with the seasons identified (winter, spring, summer, fall) between 2007 and 2009.

The range of flow sampled by seasons and years shows that the spring and summer of 2008 and the winter of 2009 were the best sample periods (Table 23). Across years, a good representation of winter, spring and summer flows is observed. Fall conditions and winter low flows were not well represented in the dataset.

Table 23: The percent of flow sampled at the mouth of Kettle Creek per season (winter, spring, summer, fall) in 2007, 2008, and 2009.

	Season			
Year	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
2007	n/a	39%	26%	8%
2008	62%	94%	93%	n/a
2009	92%	72%	21%	n/a
Total	94%	82%	94%	n/a

Water Quality Summary

Higher sampled flows occurred during the winter relative to the spring, summer, and fall (Figure 51). Outliers of the spring dataset fell between the 75th and the 95th percentile of the winter dataset. Similarly, sampled summer flows were lower than the spring flows except the outliers fell between the 75th and the 95th percentile of the winter dataset. Sampled temperatures ranged from near zero to 24°C (Figure 52).

Turbidity, suspended solids, total phosphorus, and residual phosphorus concentrations tended to follow the same seasonal pattern (e.g. Figure 53; Figure 54). Although higher *E. coli* and organic nitrogen concentrations were observed during the winter, the difference between seasons was not as distinct. Also, outliers in the spring and summer *E. coli* concentration datasets approached or exceeded maximum concentrations observed for the winter dataset which was not observed in other datasets (Figure 55).

Seasonal patterns in alkalinity, conductivity, dissolved inorganic carbon, and chloride concentrations were opposite of sampled flows, where the lowest observations occurred during the winter and spring; summer, and fall observations where higher (Figure 56; Figure 57).

Seasonal trends in total nitrate concentrations showed an increasing trend from the winter through the fall. Because total nitrate represented the dominant nitrogen form, the total nitrogen concentration also showed this pattern (Figure 58). The percentage of total nitrate also followed this pattern while the percentage of organic nitrogen and total ammonia followed an opposite pattern.

All seasons were similar for silicate and nitrite and clear trends were not observable in dissolved organic carbon, total ammonia, and phosphate. Because trends in phosphate concentrations differed from those for total phosphorus, the proportion of residual phosphorus and phosphate differed seasonally with the highest proportions of approximately 80% occurring in the fall (Figure 59). This is distinct from the winter samples where the proportion of residual phosphorus is approximately 65%.

Once converted to loading rates, all parameters followed a seasonal trend similar to that of the sampled flows.

Box and whisker plots for all routine water chemistry parameters sampled in Kettle Creek are in Appendix E.

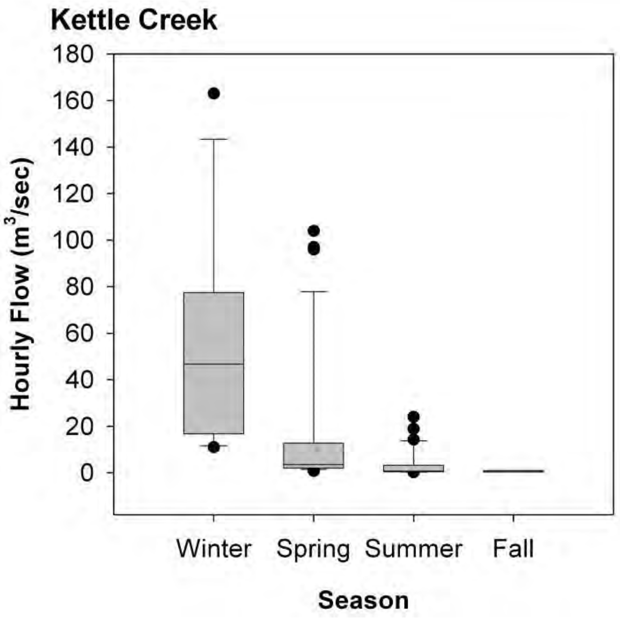

Figure 51: Boxplots of flows (m^3/sec) sampled between 2007 and 2009 plotted by season (winter, spring, summer, fall) at the mouth of Kettle Creek.

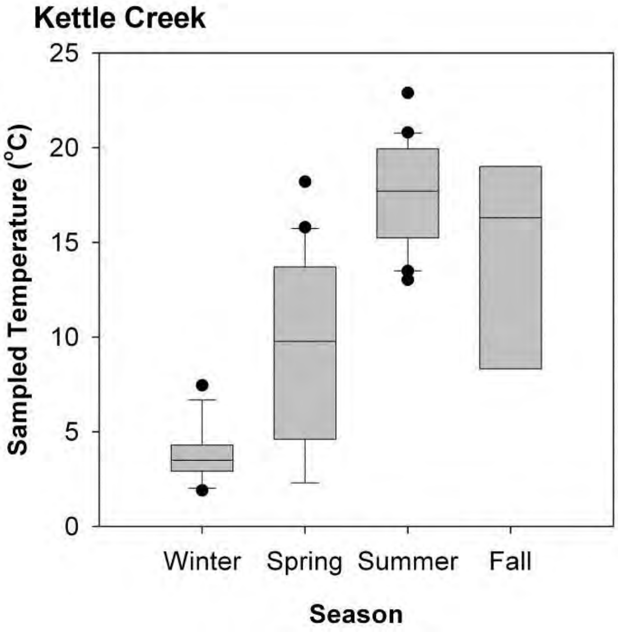

Figure 52: Boxplots of water temperature (°C) sampled between 2007 and 2009 plotted by season (winter, spring, summer, fall) at the mouth of Kettle Creek.

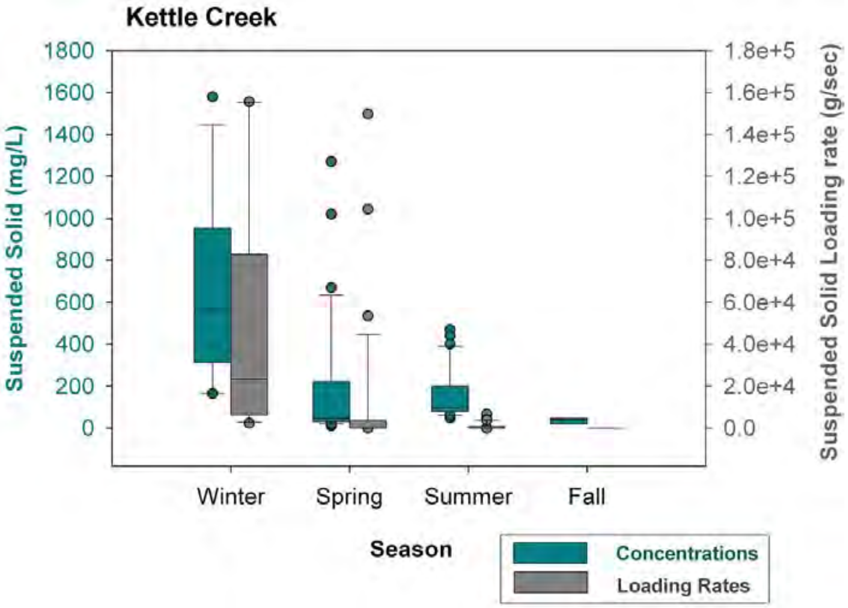

Figure 53: Boxplots of all observed suspended solids concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Kettle Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.

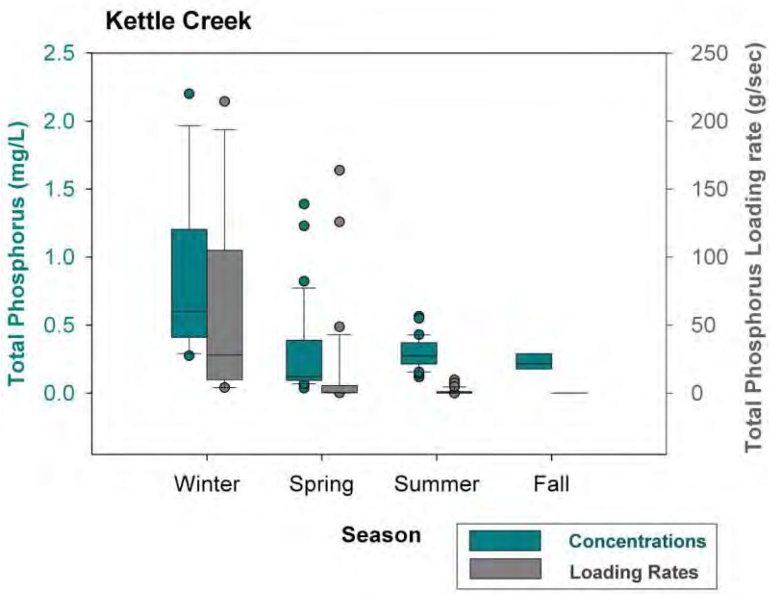

Figure 54: Boxplots of all observed total phosphorus concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Kettle Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.

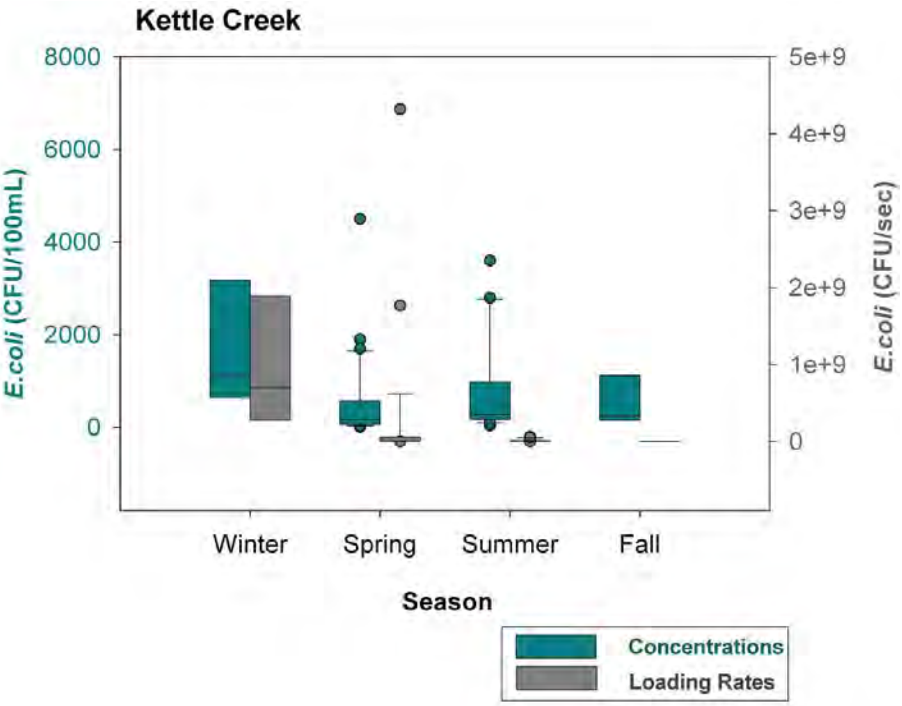

Figure 55: Boxplots of all observed *E. coli* (CFU/100ml) concentrations (CFU/100ml; left axis) and loading rates (CFU/100ml/sec; right axis) at the mouth of Kettle Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.

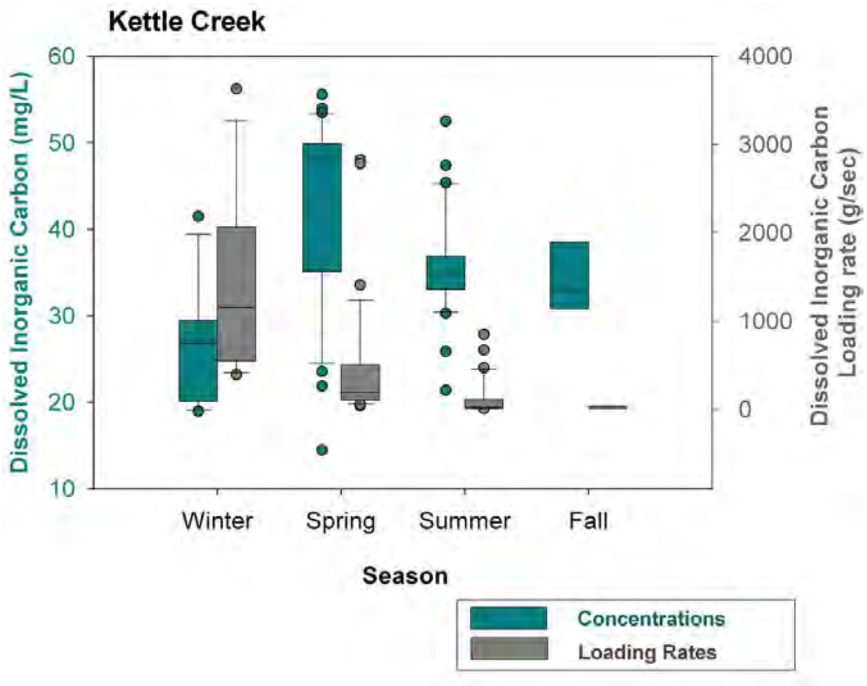

Figure 56: Boxplots of all observed dissolved inorganic carbon concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Kettle Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.

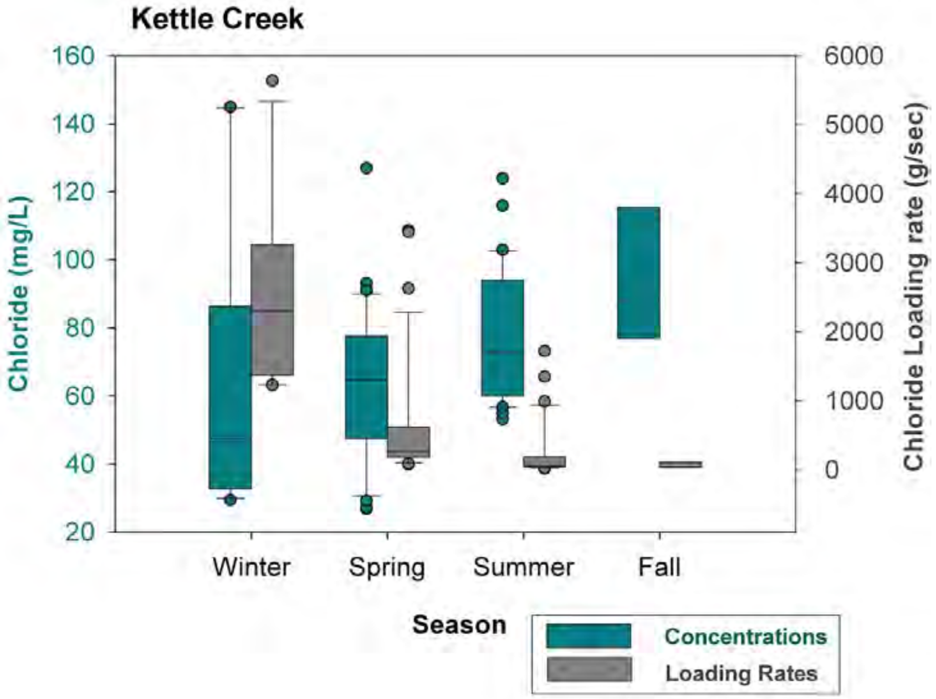

Figure 57: Boxplots of all observed chloride concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Kettle Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.

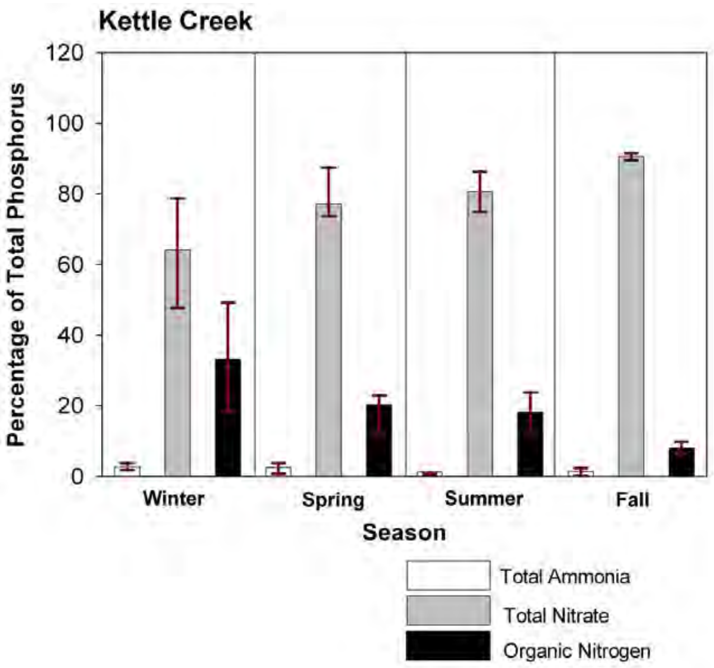

Figure 58: Bar graphs of the percentage of total ammonia, total nitrate, and organic nitrogen in total nitrogen values at the mouth of Kettle Creek according to sample season (winter, spring, summer, fall) between 2007 and 2009. Error bars represent the 25th and 75th percentiles.

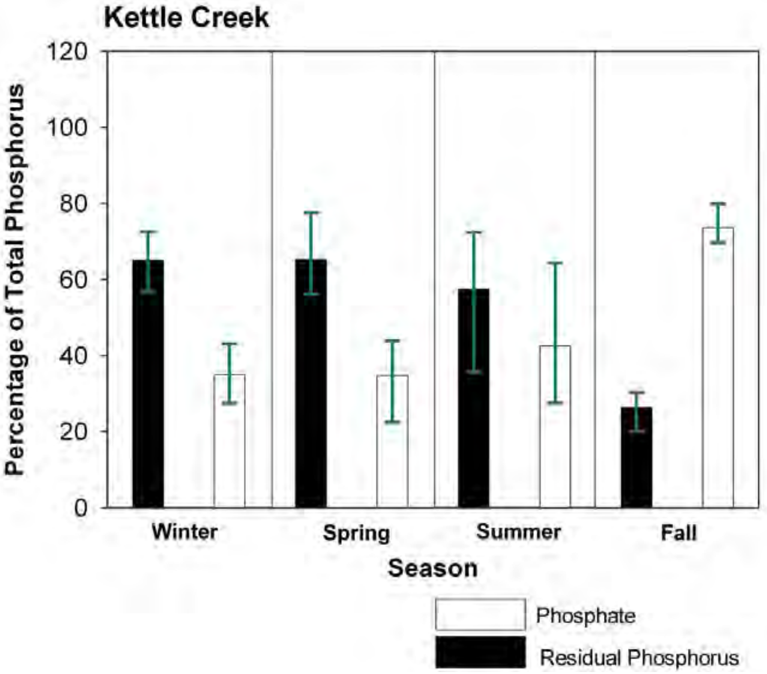

Figure 59: Bar graphs of the percentage of residual phosphorus and phosphate in total phosphorus values at the mouth of Kettle Creek according to sample season (winter, spring, summer, fall) between 2007 and 2009. Error bars represent the 25th and 75th percentiles.

Correlations

Correlation results for suspended solids vs. turbidity, organic nitrogen, and total and residual phosphorus were all strong (p <0.001; r = 0.832 – 1.000) during the winter, spring, and fall as well as in the full dataset (Table 24; e.g. Figure 60). For these pairs of parameters, the summer correlations were also significant (p <0.001) but the results for organic nitrogen and total and residual phosphorus were weaker (r = 0.577 - 0.668) while the turbidity results were similar to the other season (r = 0.967). *E. coli* concentrations correlated with suspended solids concentrations in spring and summer as well as in the full dataset but not in the winter and fall datasets. Total nitrogen showed a weak correlation with suspended solids in the summer only. Moderate negative correlations for chloride vs. total nitrate and phosphate were observed in the spring (p <0.001; r = -0.707 and -0.691) and weaker positive correlations were observed in the summer (p <0.001; r = 0.585 and 0.379). Of the two, only the chloride and nitrate correlation was significant for the full dataset and this correlation was weakly positive (Figure 61).

Table 24. The non-parametric Spearman Correlation Coefficients (p values) for water quality parameter pairs across seasons (winter, spring, summer, fall) and in the full dataset

Correlations	Spearman Correlation Coefficients				
	Seasonal Datasets				Full dataset
	Winter	Spring	Summer	Fall	
Chloride vs. Total Nitrate	0.483 (0.112)	*-0.707 (<0.001)*	*0.585 (<0.001)*	-0.100 (0.873)	0.*534 (<0.001)*
Chloride vs. Phosphate	-0.154 (0.633)	*-0.691(<0.001)*	*0.379 (0.025)*	0.300 (0.624)	-0.164 (0.148)
Suspended Solids vs. Turbidity	*1.000 (<0.001)*	*0.979 (<0.001)*	*0.967 (<0.001)*	*1.000 (<0.001)*	*0.976 (<0.001)*
Suspended Solids vs. *E. coli*	0.214 (0.610)	*0.811 (<0.001)*	*0.492 (0.011)*	-0.700 (0.188)	*0.721 (<0.001)*
Suspended Solids vs. Total Nitrogen	0.077 (0.812)	0.050 (<0.786)	*-0.347 (0.041)*	0.300 (0.624)	-0.050 (0.662)
Suspended Solids vs. Organic Nitrogen	*0.902 (<0.001)*	*0.897 (<0.001)*	*0.577 (<0.001)*	*1.000 (<0.001)*	*0.832 (<0.001)*
Suspended Solids vs. Total Phosphorus	*0.958 (<0.001)*	*0.938 (<0.001)*	*0.668 (<0.001)*	0.700 (0.188)	*0.916 (<0.001)*
Suspended Solids vs. Residual Phosphorus	*0.909 (<0.001)*	*0.891 (<0.001)*	*0.666 (<0.001)*	*1.000 (<0.001)*	*0.874 (<0.001)*

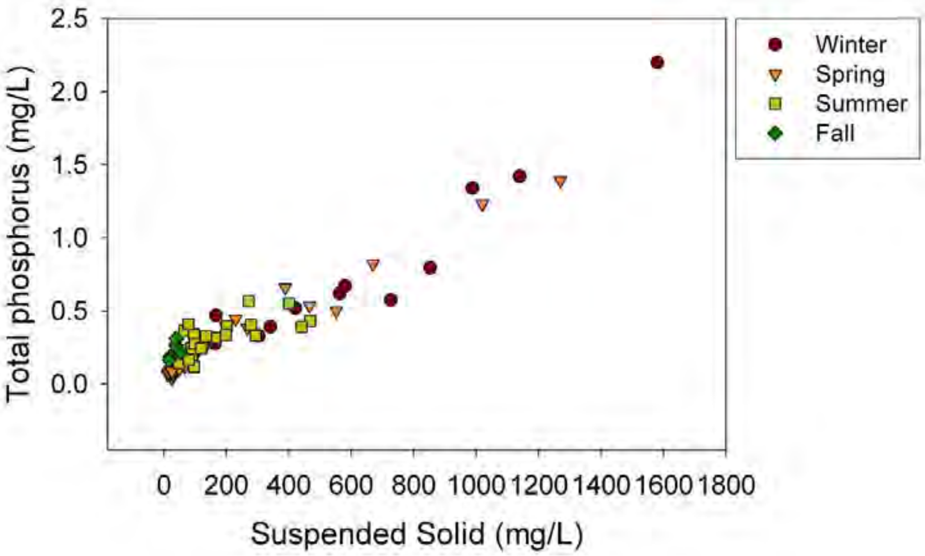

Figure 60: Total phosphorus (mg/L) vs. suspended solids (mg/L) concentrations in water samples collected between 2007 and 2009 near the mouth of Kettle Creek differentiated by season (winter, spring, summer, fall).

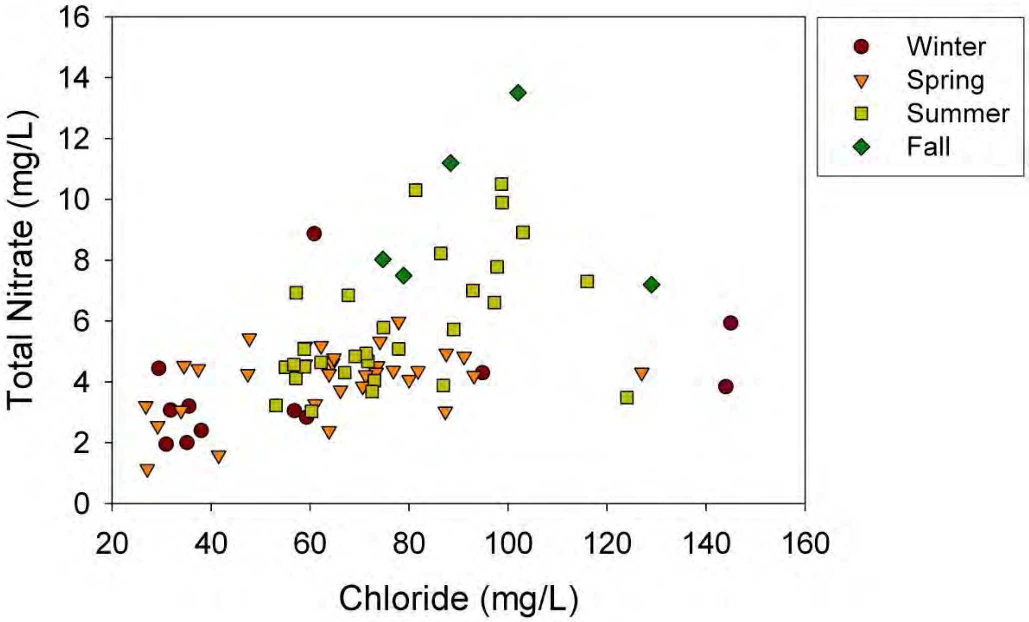

Figure 61: Total nitrate (mg/L) vs. chloride (mg/L) concentrations in water samples collected between 2007 and 2009 near the mouth of Kettle Creek differentiated by season (winter, spring, summer, fall).

Load Estimates

All linear regressions performed between the *ln* transformed load rate and the *ln* transformed sampled flow were significant (p <0.001; R^2 = 0.754 - 0.968) (Table 25).

Table 25: Linear equations generated from linear regressions performed on the *ln* transformed sampled hourly flow (m3/sec) and *ln* transformed loading rates (kg) for water quality parameters measured at the mouth of Kettle Creek between 2007 and 2009.

Parameter	y = m(± SE) x + b(± SE)	R^2 value	*p* value
Chloride	y = .843(± 0.018) x + 4.395(± 0.039)	0.968	<0.001
E. coli	y = 1.308(± 0.095) x + 14.634(± 0.200)	0.754	<0.001
Total Ammonia	y = 1.236(± 0.063) x + -3.053(± 0.138)	0.835	<0.001
Total Nitrate	y = 0.833 (± 0.020) x + 1.74(± 0.044)	0.957	<0.001
Organic Nitrogen	y = 1.127(± 0.026) x + -0.089(± 0.057)	0.961	<0.001
Phosphate	y = 1.155(± 0.063) x + -2.594(± 0.139)	0.814	<0.001
Residual Phosphorus	y = 1.348(± 0.056) x + -2.441(± 0.126)	0.887	<0.001
Total Phosphorus	y = 1.250(± 0.043) x + -1.687(± 0.094)	0.917	<0.001
Suspended Solids	y = 1.456(± 0.055) x + 4.153(± 0.122)	0.900	<0.001

The monthly and annual total nitrate, total phosphorus, and phosphate loads calculated between 2007 and 2009 from the linear regression equations show in all three parameters that monthly loads were highest during the winter and early spring, and annually, loads were lowest during 2007 and approximately double in 2008 (Figure 62; Figure 63; Figure 64).

The ratio of parameter mass over water weight and calculated export coefficients (tonnes/km^2) for Kettle Creek for the various water quality parameters are listed in Table 26. In general, greater mass of constituents were exported from the Kettle Creek watershed in 2008, due to the greater amount of precipitation and runoff.

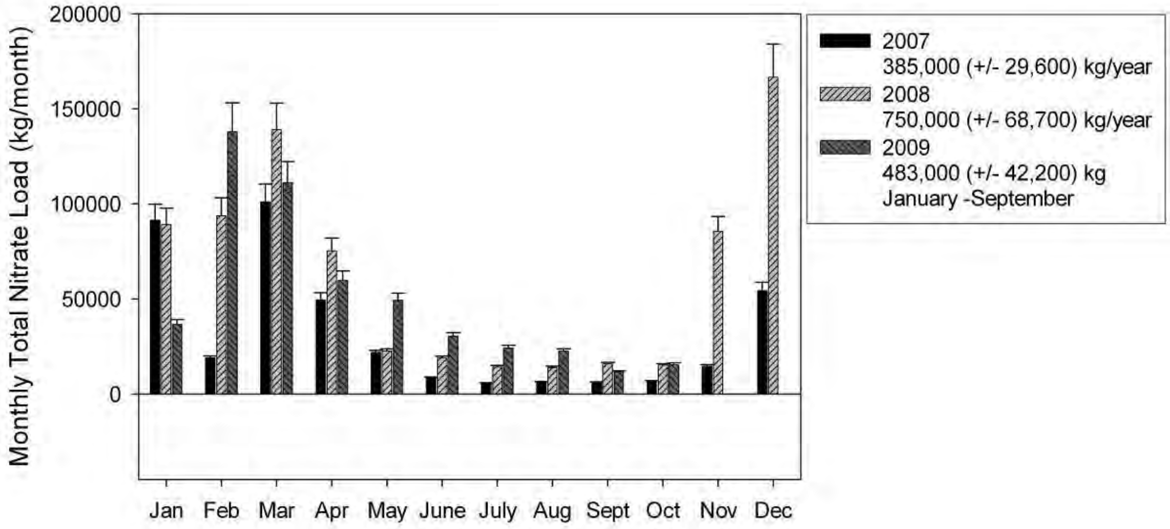

Figure 62: The estimated monthly total nitrate loads (kg/month) based on the linear regression equations generated from the water quality datasets collected at the mouth of Kettle Creek between 2007 and 2009. Errors are presented as standard errors.

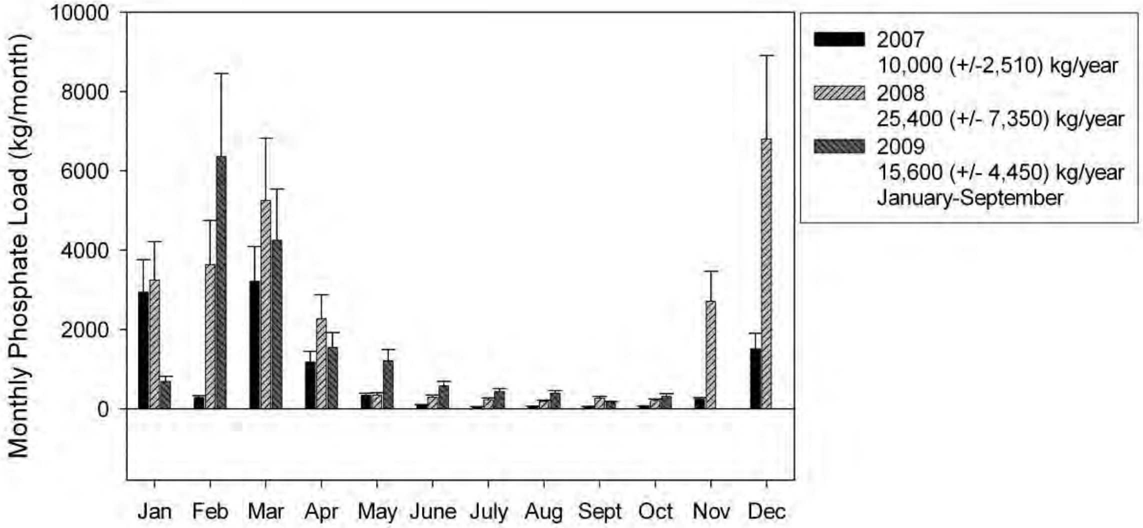

Figure 63: The estimated monthly phosphate loads (kg/month) based on the linear regression equations generated from the water quality datasets collected at the mouth of Kettle Creek between 2007 and 2009. Errors are presented as standard errors.

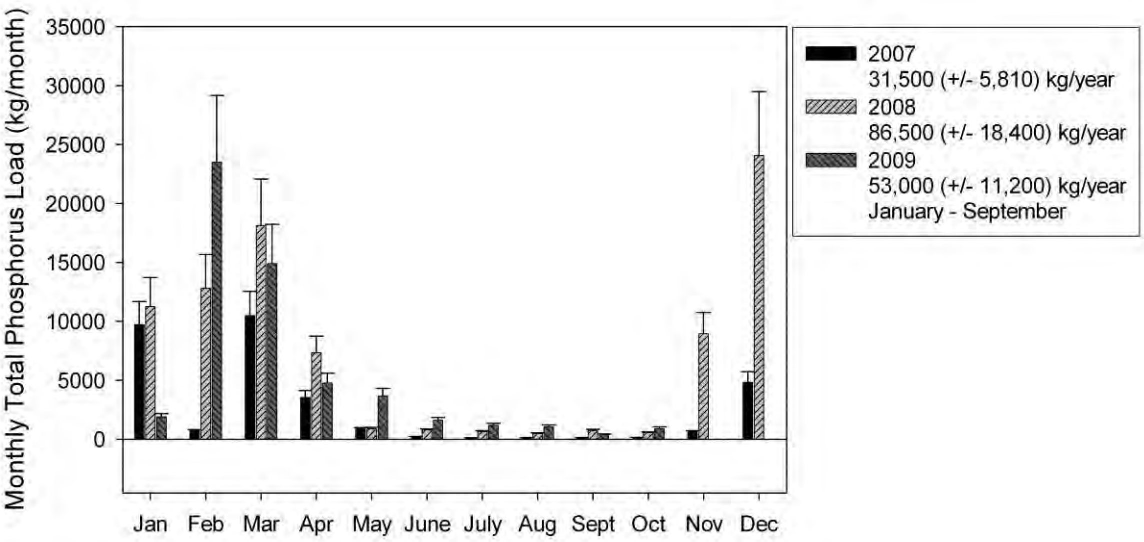

Figure 64: The estimated monthly total phosphorus loads (kg/month) based on the linear regression equations generated from the water quality datasets collected at the mouth of Kettle Creek between 2007 and 2009. Errors are presented as standard errors.

Table 26: The ratio (± standard error) of parameter mass over water weight and export coefficients based on analysis of water quality datasets and flow data from the mouth of Kettle Creek between 2007 and 2009.

Parameter	Ratio of Total Parameter wt / Total Water wt (‰)Estimates			Export Coefficient (tonnes/km^2)	
	2007-2009	2007	2008	2007	2008
Chloride	54.2 *(50.0 – 58.8)*	59.2 *(55.1 – 63.7)*	52.0 *(47.7 – 56.8)*	13.3*(12.4 – 14.3)*	26.0 *(23.9 – 28.4)*
Total Ammonia	0.10 *(0.07 – 0.13)*	0.08 *(0.06 – 0.11)*	0.10 *(0.07 – 0.14)*	0.02 *(0.01 – 0.03)*	0.05 *(0.04 – 0.07)*
Total Nitrate	3.72 *(3.40 – 4.08)*	4.09 *(3.77 – 4.43)*	3.56 *(3.23 – 3.92)*	0.92 *(0.85 – 1.00)*	1.78 *(1.62 – 1.96)*
Organic Nitrogen	1.31 *(1.15 – 1.50)*	1.21 *(1.08 – 1.37)*	1.35 *(1.17 – 1.55)*	0.27 *(0.24 –0.31)*	0.68 *(0.59 – 0.78)*
Phosphate	0.117 *(0.084 – 0.163)*	0.106 *(0.080 – 0.143)*	0.121 *(0.086 – 0.171)*	0.024 *(0.018 – 0.032)*	0.061 *(0.043 – 0.086)*
Residual Phosphorus	0.255 *(0.186 – 0.352)*	0.204 *(0.154 – 0.270)*	0.272 *(0.197 – 0.377)*	0.046 *(0 .035 – 0.061)*	0.136 *(0.099 – 0.189)*
Total Phosphorus	0.391 *(0.310 – 0.495)*	0.334 *(0.273 – 0.411)*	0.411 *(0.324 – 0.524)*	0.075 *(0.061 – 0.092)*	0.206 *(0.162 - 0.262)*
Suspended Solids	273 *(198 – 376)*	201 *(152 – 267)*	294 *(212 – 407)*	45 *(34 – 60)*	147 *(106 – 204)*

Predicting Water Quality

The relative importance of the difference between the modeled and the predicted concentrations were summarized by calculating the percentage of each difference from the corresponding observed concentration (**Error! Reference source not found.**. The summary of these datasets shows that half of the predictions for all water quality parameters differed from the observed concentration by less than 60% of the observed concentration with the lowest median value being 16% for chloride and the highest being 60% for total ammonia. Overall, predictions for chloride, total nitrate, and organic nitrogen were most accurate while the predictions for total ammonia, phosphate, residual phosphorus, total phosphorus, and suspended solids concentrations differed by as much double the observed concentration. The largest percent differences occurred because the observed concentrations were very small and approached an order of magnitude lower than the predicted concentration.

In Kettle Creek, across all water quality parameters, deviations from predicted concentrations were observed during melt events and summer storm events in 2008 and 2009 (e.g. chloride **Error! Reference source not found.**) . During the summer of 2007, across all water quality parameters, the observed concentrations differed from the predicted concentrations.

Table 27. The mean, median, and 75th percentile for the percent difference between the observed and the predicted concentrations calculated from the water quality datasets collected from Kettle Creek between 2007 and 2009.

Parameter	Mean	Median	*75th* percentile
Chloride	20%	16%	30%
Total Ammonia	127%	60%	130%
Total Nitrate	25%	18%	31%
Organic Nitrogen	33%	24%	46%
Phosphate	123%	58%	98%
Residual Phosphorus	162%	42%	70%
Total Phosphorus	66%	40%	74%
Suspended Solids	97%	57%	98%

The linear regression equation generated from the *ln* transformed loading rate and the *ln* transformed sampled flow did not predict observed *E. coli* concentrations very well in Kettle Creek. It was not possible to observe a trend in how or when observed concentrations deviated from the predicted concentrations. When concentrations are compared to the water quality guidelines set by the Canadian Council for Ministers of the Environment (CCME), samples frequently exceeded this guideline (200 CFU/100ml of *E. coli* for recreational water use*)* across all seasons (Figure 65).

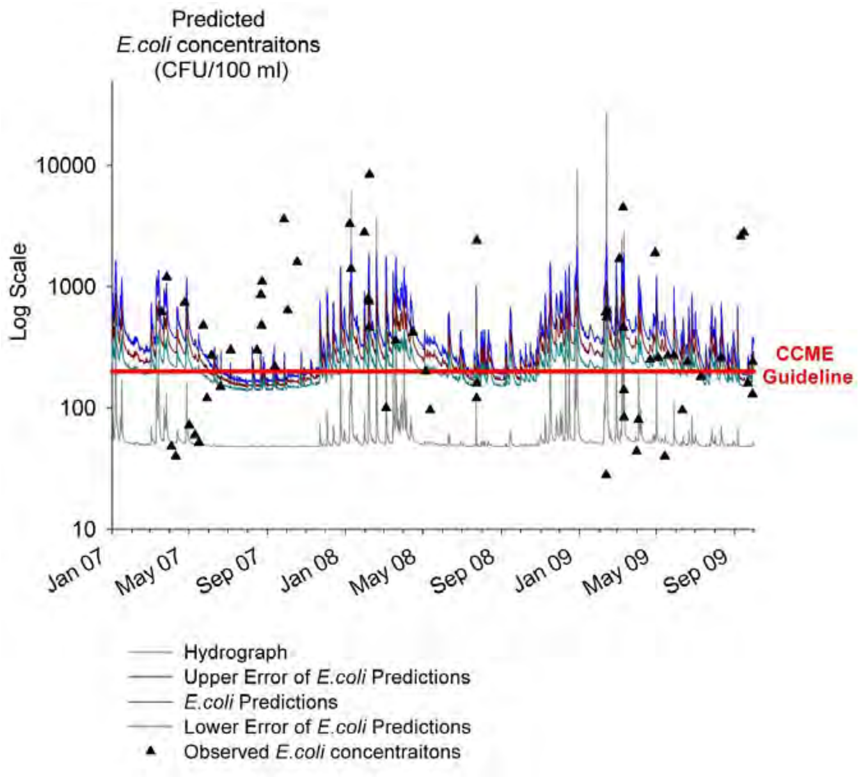

Figure 65: The observed *E. coli* (CFU/100ml) concentrations relative to the predicted concentrations, the flow record, and the CCME guideline for recreational water use at the mouth of Kettle Creek between 2007 and 2009.

The predicted hourly load estimates for phosphate and total phosphorus during the summer storm event in July 2008 and the melt event in February 2009 corresponded well with the observed hourly load estimates (Figure 66; Figure 67). However, for the March 2009 high flow event, observed hourly loads during the peak of the event exceeded the predicted hourly loads (Figure 68).

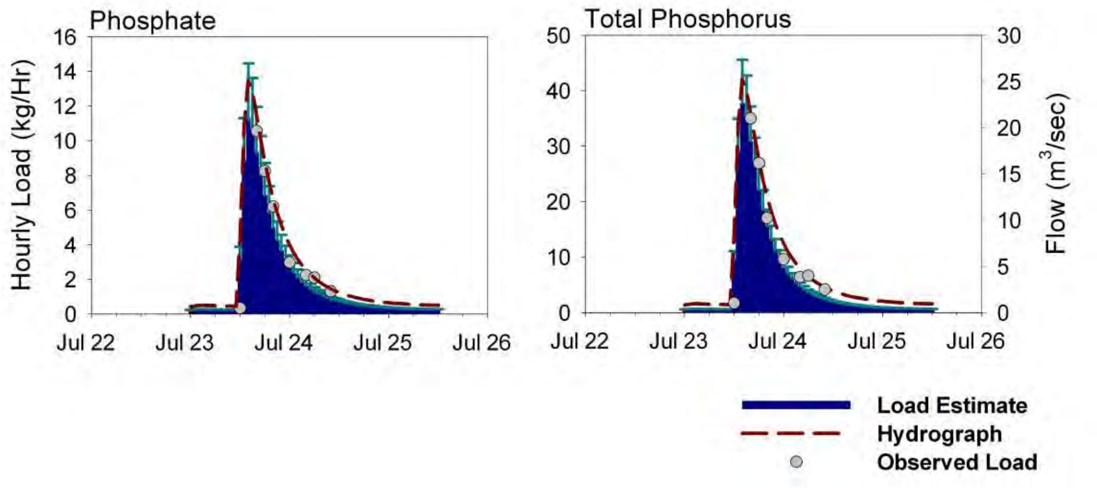

Figure 66: The predicted hourly load (kg/hr) of phosphate (left) and total phosphorus (right) relative to the observed hourly load calculated from water samples collected during a high flow event in July 2008 at the mouth of Kettle Creek.

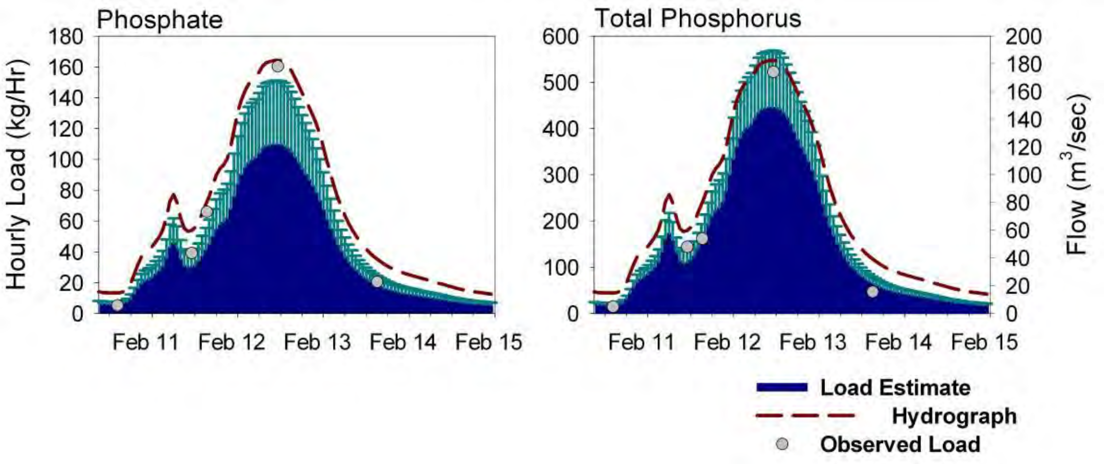

Figure 67: The predicted hourly load (kg/hr) of phosphate (left) and total phosphorus (right) relative to the observed hourly load calculated from water samples collected during a high flow event in February 2009 at the mouth of Kettle Creek.

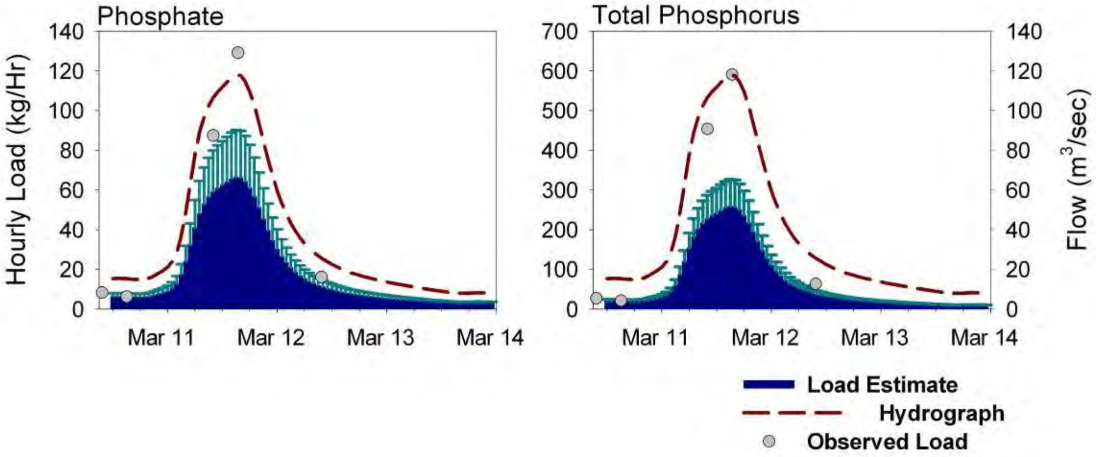

Figure 68: The predicted hourly load (kg/hr) of phosphate (left) and total phosphorus (right) relative to the observed hourly load calculated from water samples collected during a high flow event in March 2009 at the mouth of Kettle Creek.

Discussion

Tributary water quality is generally influenced by stream flow, season, in-river processes and watershed characteristics (e.g. land cover, point source discharges etc). The objective of this study was to develop a large water quality dataset with samples collected across all seasons and hydrologic regimes to characterize tributary water quality; explore relationships between a select number of water quality parameters or between stream flow and a select number of water quality parameters that are of importance to the nearshore environment of the central basin of Lake Erie. This region supports many human uses and values including recreation (e.g. cottage development, swimming at public beaches) and drinking water supplies. Many of these values, such as recreation, are most influenced by the growth of nuisance algae along the nearshore in the summer. Algal growth is likely a result of a high nutrient flux from local tributaries, especially during the spring and following significant rainfall events. To fully understand the relationship between algal growth and tributary water quality, it is important to characterize the nutrient flux from watersheds to the nearshore during important hydrologic events such as spring runoff. However, uses such as drinking water supplies, are influenced by lake and tributaries year-round and consequently, characterizing tributary water quality and their influence on the nearshore, is critical during all seasons.

The objective of this study was to fully characterize tributary water quality across seasons. As a result, intensive, flow-proportionate water quality sampling was completed to characterize seasons and key hydrologic events. A fairly robust dataset was developed that enabled the characterization of key hydrologic events as well as low flows during the winter, spring, and summer between 2007 and 2009. However, fall or winter low flow conditions were not well characterized.

When monitoring water quality, understanding which parameters behave similarly across environmental conditions is useful to determine if one or a few parameters are suited to be indicators of overall water quality. The two factors which are important for choosing an indicator are: 1) a relationship between the indicator and the parameter of interest is understood so that changes in the indicator can be translated into changes in the parameter of interest; and 2) measuring the indicator is more feasible than measuring the parameters of interest. Correlations between parameters were explored to evaluate significant relationships. Significant relationships in all creeks for the full datasets were seen for suspended solids and turbidity; suspended solids and total phosphorus; and suspended solids and residual phosphorus. Consequently, turbidity may be an important indicator or measure to infer suspended solids and phosphorus concentrations in these creeks.

Linear regression was used to assess relationships between flow and water quality. Because flows are inherently related to observed concentrations due to the shared volume component in each measurement (m^3 for flow and mL for concentration), it is known that flows affect water quality. To illustrate, if the quantity of solute was held constant, a change in flow or the amount of water will “cause” a change in solute concentration or water quality. Therefore, any assessment of relationships between stream flow and water quality is complicated by this causal relationship. However, the processes which alter the stream flows (i.e. surface run-off or ground water discharge) also alter the load of solute. In this situation, stream flow and water quality co-vary as a result of watershed processes (i.e. hydrology, geology, land use) and the relationship between stream flow and water quality is a correlation. This distinction is why it was necessary to transform the concentrations into loading rates for the linear regression analysis. Through this transformation the "cause" relationship between stream flow and water quality is removed so the correlation can be assessed.

The linear regression analysis of water quality parameters and stream flow showed that the two were significantly related. When the relationships were used to predict concentrations of various water quality parameters and the predicted concentrations were compared with the observed concentrations, it was determined that an individual flow value would not necessarily predict the corresponding water quality concentration. However, the difference between the observed and predicted concentrations when plotted in time series relative to the hydrograph showed that the observed concentrations tended to deviate from the predicted concentrations during key hydrological periods.

The problem with using a single regression-based model to predict water quality from flows is that the model assumes the relationship between water quality and flows is consistent across environmental conditions. Across the seasons, different processes are responsible for observed stream flows as well as the movement of solutes such as melt events during the spring, surface run-off during summer, and groundwater or reservoir discharges during the low flows. In addition, in-stream processing and cycling of select parameters such as nutrients or sediments can also affect the load of these parameters discharged from a river system (Birgand, Skaggs et al. 2007). To accurately predict water quality, understanding and defining each of these relationships is required. Within the current dataset sufficient data was not available to assess relationships which occur in each category of environmental conditions.

The contamination of beaches with *E. coli* originating from watersheds of nearby creeks and tributaries has been shown in Lake Michigan (e.g. (Nevers, Whitman et al. 2007) and is a concern for many Canadian beaches in the Great Lakes basin. Concentrations of *E. coli* observed in this study frequently exceeded the recreational guidelines of 200 CFU/100mL in spring and summer samples. Unlike other water quality parameters, *E. coli* concentrations varied considerably with no relationship with tributary flow nor did it correlate strongly with other water quality parameters. While concentrations observed in Kettle Creek were the highest, *E. coli* concentrations frequently exceeded the water quality objectives in all three creeks with no observable temporal trend. It is for this reason that it is necessary to understand the fate of the tributary discharge in the nearshore during summer periods when local beaches are used.

Contrasts between the observations made in each of the datasets reveal strong similarities between parameters among the three study watersheds. Seasonal trends for water quality parameters such as turbidity, suspended solids, total phosphorus, conductivity, alkalinity, and dissolved inorganic carbon were similar. In all three watersheds, a strong connection between sampled flow and water quality was observed. Overlap in the standard errors of the weight ratios were observed across watersheds for all parameters investigated except chloride which was much higher in Kettle Creek than in Big Otter Creek and Catfish Creek. The elevated chloride concentrations in Kettle Creek are likely due to the influence of a large urban area (e.g. St. Thomas). Predicted concentrations based on the relationships between sampled flow and water quality were least able to predict concentrations during summer storm events in all three watersheds.

Although differences in the geology, agricultural profile, and the urban landscape were described between the three watersheds, the relevance of these differences to the observed water quality of their associated tributary discharges is not large. The clearest difference occurs during low summer flows in Kettle Creek where concentrations are higher, less predictable, and affect the seasonal trends in water quality relative to Big Otter and Catfish Creek. One likely explanation for the distinctive trends in water quality in Kettle Creek is the influence of the municipal waste water discharge in St. Thomas which is most likely to be observed during summer low flows. The similarity between the watersheds is most likely a reflection of their shared climate, agricultural land use, and elevation.

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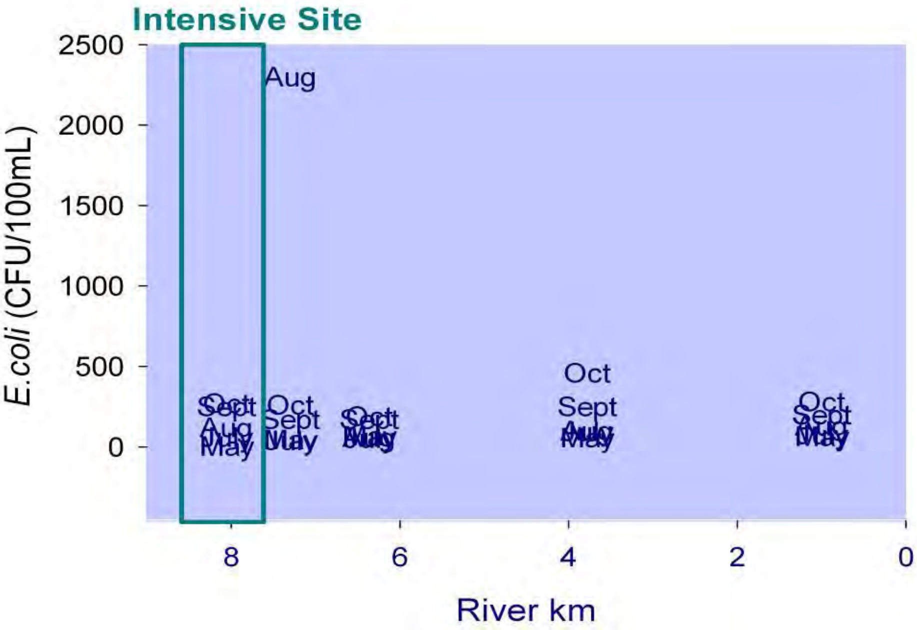
Appendix A:

During nearshore sampling of Lake Erie, water samples were also collected from various locations between the intensively sampled tributary site and the river mouth to ensure that the intensively sampled site was representative of conditions in the river discharge.

The following are figures that illustrate the concentrations of the various water quality parameters (Y axis) and at sampling locations within the river. Samples were collected by boat by the Ministry of the Environment during a nearshore sampling survey. In general, the tributary monitoring site likely underestimates most parameters in Big Otter and Catfish while parameters tend to be lower than those collected by boat near the mouth of Kettle Creek.

Big Otter Creek

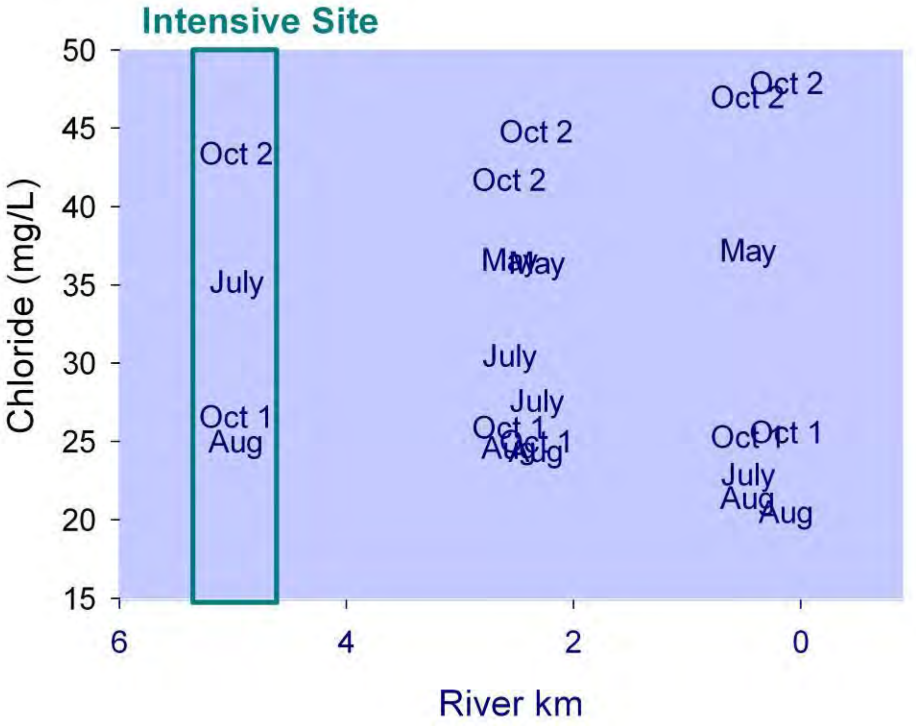

Intensive Site
Suspended Solid (mg/L)
60
50
40
30
20
10
0
July
Sept
Sept
May
July
Sept
Oct
Aug
May
Oct
Aug
July
Sept
May
Aug
Oct
May
July
Aug
Sept
July
May
Aug
Oct
8
6
4
2
0
River km

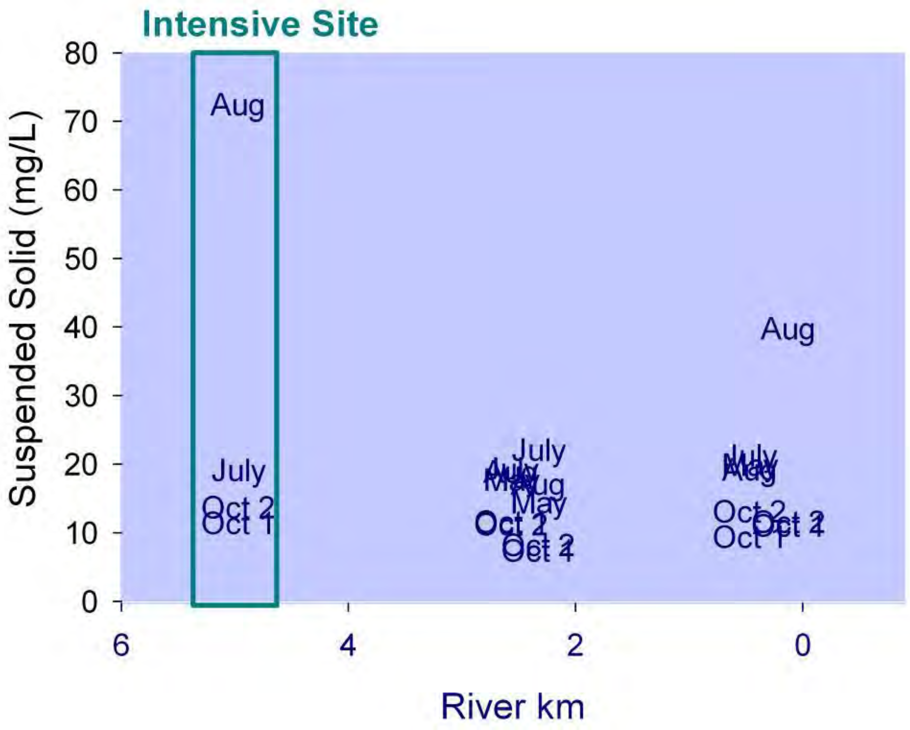

Intensive Site
E.coli (CFU/100mL)
2500
2000
1500
1000
500
0
Aug
Oct
Sept
Aug
July
May
Oct
Sept
May
Sept
July
Oct
Sept
Aug
May
Oct
Sept
Aug
May
8
6
4
2
0
River km

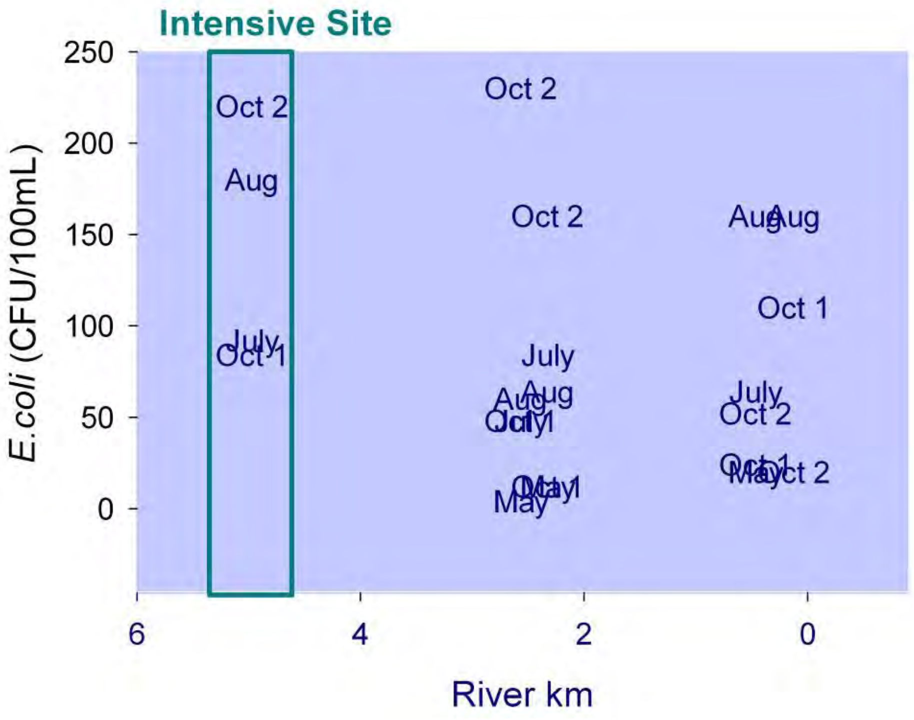

Intensive Site
Total Nitrate (mg/L)
3.4
3.2
3.0
2.8
2.6
2.4
July
Sept
Aug
Sept
Sept
July
Sept
May
July
July
May
May
Aug
Aug
May
Sept
May
Oct
Oct
Oct
Aug
Oct
Oct
Aug
Oct
8
6
4
2
0
River km

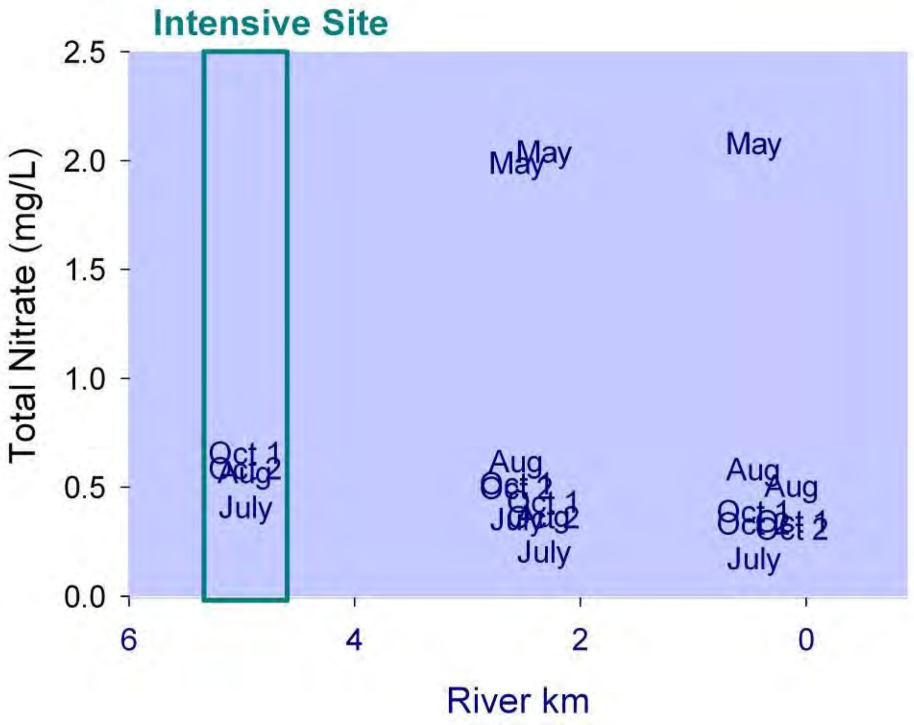

Intensive Site
Total Phosphorus (mg/L)
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
Sept
July
July
Sept
July
May
May
May
May
May
Aug
May
Sept
Aug
Aug
Sept
Aug
Aug
Sept
July
July
Oct
Oct
Oct
Oct
Oct
8
6
4
2
0
River km

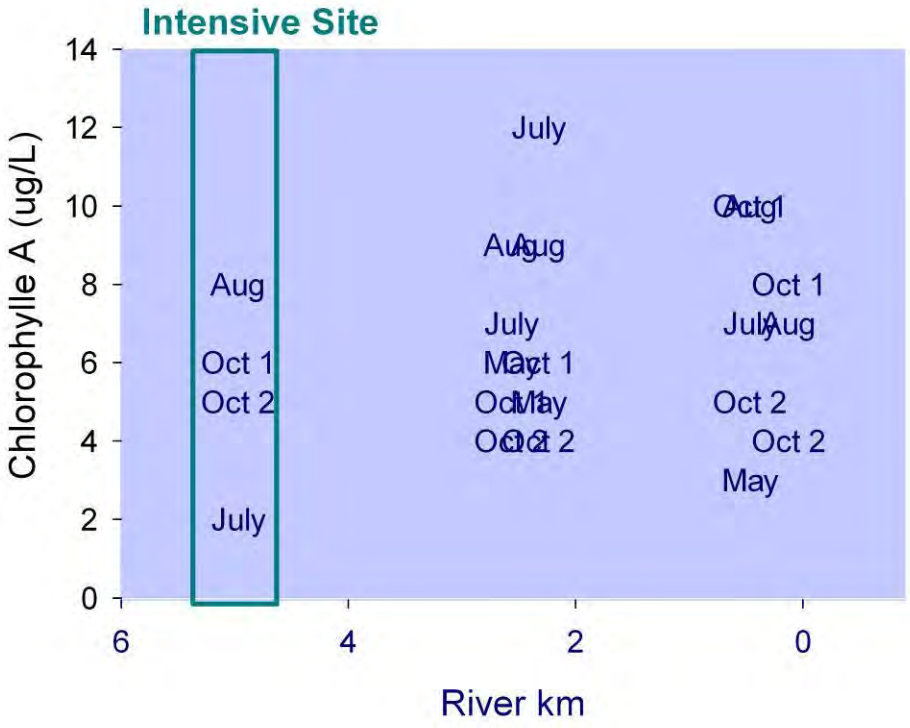
Catfish Creek



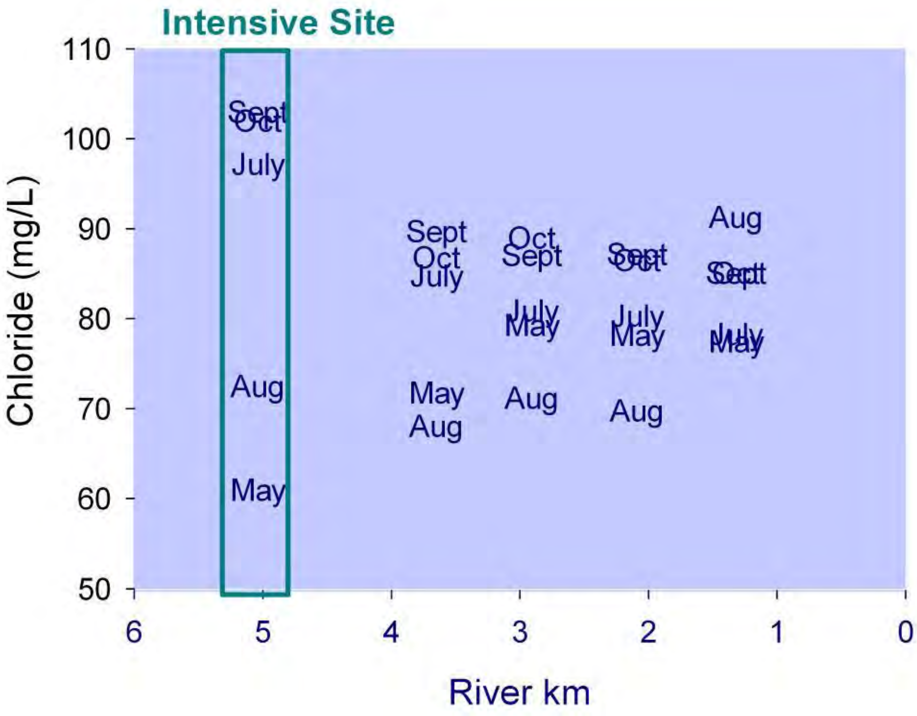

Intensive Site
Suspended Solid (mg/L)
80
70
60
50
40
30
20
10
0
6
4
2
0
River km
Aug
July
Oct 2
Oct 1
July
Aug
May
Aug
May
Oct 2
Oct 3
Oct 4
Aug
July
May
Aug
Oct 2
Oct 1
Oct 3
Oct 4

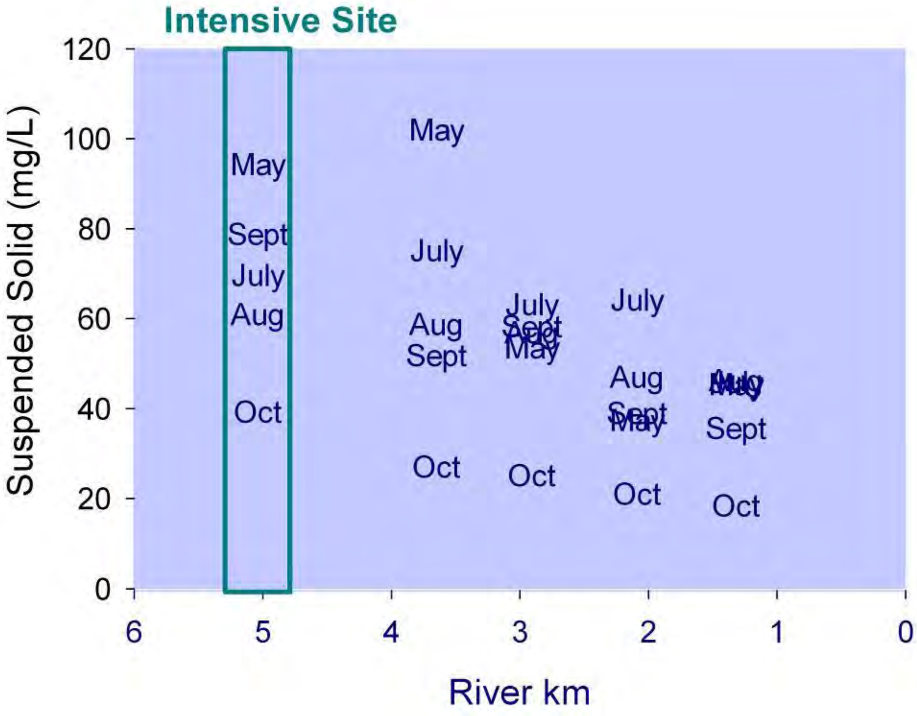

Intensive Site
E.coli (CFU/100mL)
250
200
150
100
50
0
6
4
2
0
River km
Oct 2
Aug
July
Oct 1
Oct 2
Oct 2
July
Aug
Aug
July
Oct 1
Oct 1
May
Aug
Aug
Oct 1
July
Oct 2
Oct 1
May
Oct 2

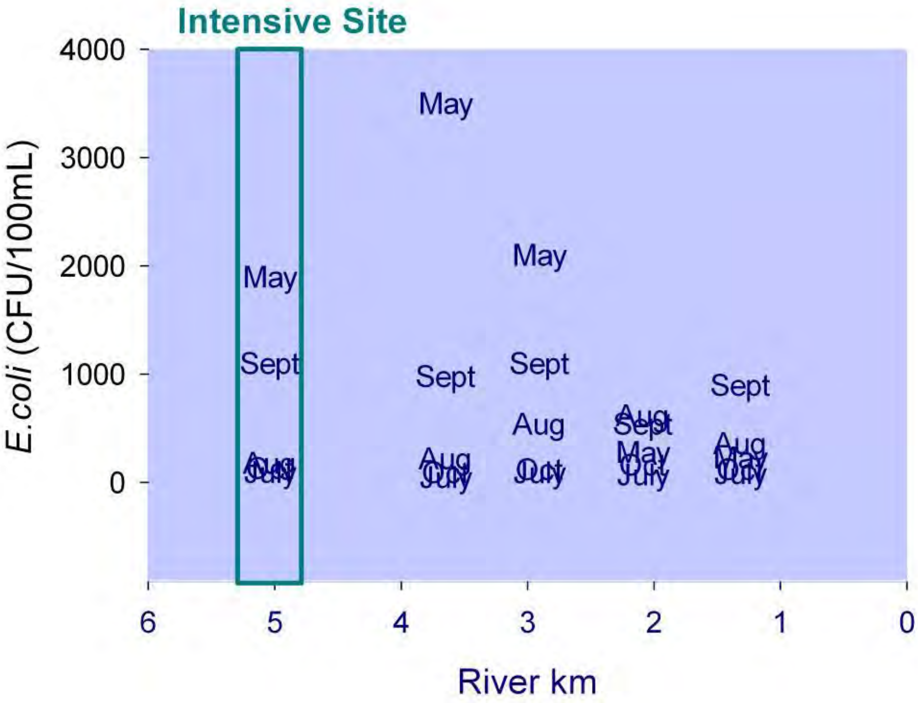

Intensive Site
Total Nitrate (mg/L)
2.5
2.0
1.5
1.0
0.5
0.0
May
May
May
Oct 1
Oct 2
Aug
July
Aug
Oct 2
Oct 1
July
Aug
July
Aug
Aug
Oct 1
Oct 1
Oct 2
July
6
4
2
0
River km

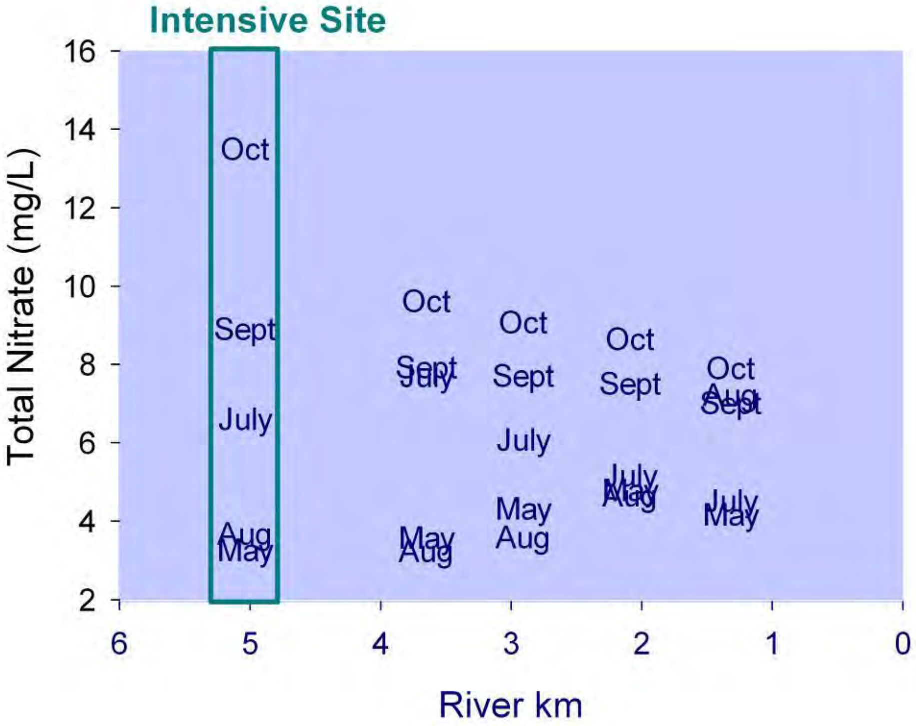

Intensive Site
Chlorophylle A (ug/L)
14
12
10
8
6
4
2
0
Aug
Oct 1
Oct 2
July
July
Aug
Aug
July
May
Oct 1
Oct 1
May
Oct 2
Oct 2
Oct 1
Aug
Oct 1
July
Aug
Oct 2
Oct 2
May
6
4
2
0
River km

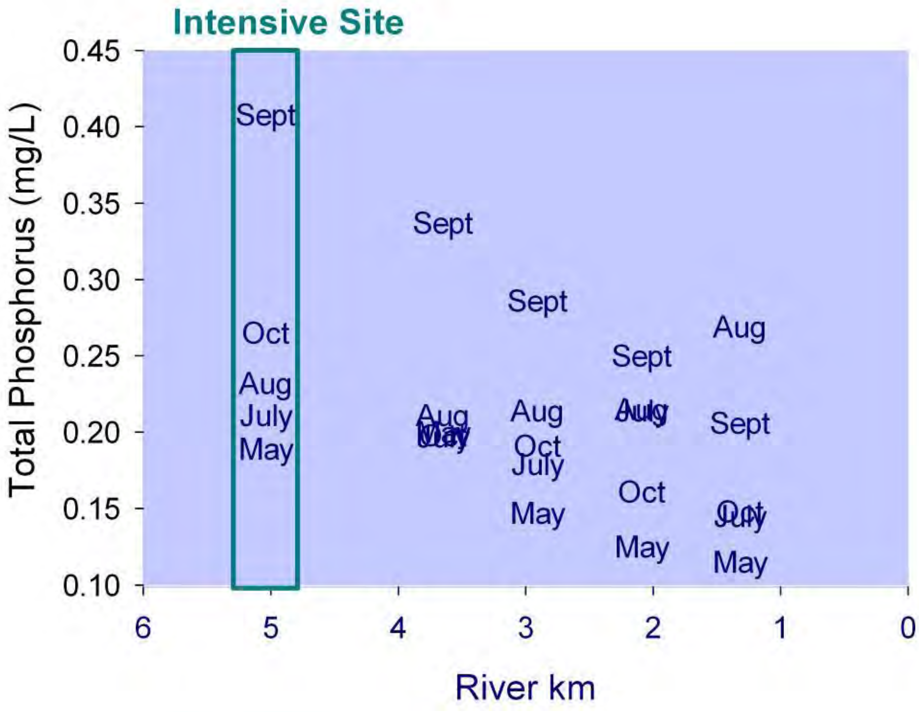
Kettle Creek

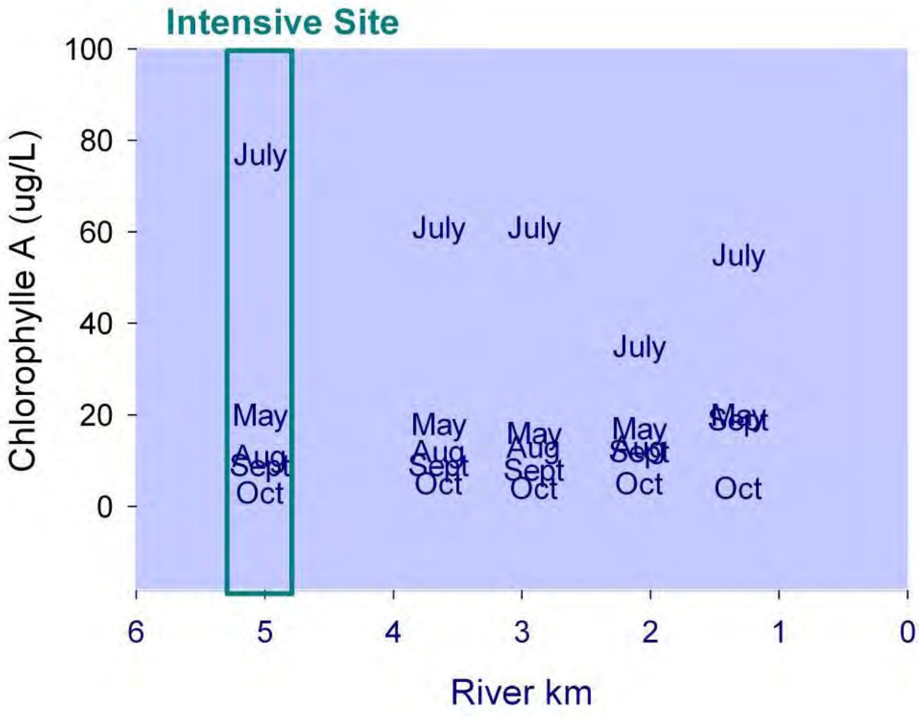





Intensive Site
4000
3000
2000
1000
0
E.coli (CFU/100mL)
May
May
May
Sept
Sept
Sept
Sept
Aug
Aug
Sept
May
July
Aug
Oct
July
Aug
Oct
July
Oct
July
Aug
May
Oct
July
6
5
4
3
2
1
0
River km


Intensive Site
16
14
12
10
8
6
4
2
Total Nitrate (mg/L)
Oct
Oct
Oct
Oct
Oct
Sept
Sept
July
Sept
Sept
Aug
Sept
July
July
July
July
May
Aug
May
Aug
May
Aug
May
Aug
May
6
5
4
3
2
1
0
River km


Intensive Site
Total Phosphorus (mg/L)
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
6
5
4
3
2
1
0
River km
Sept
Oct
Aug
July
May
Sept
Aug
May
Oct
Sept
Aug
Oct
July
May
Sept
Aug
July
Oct
May
Aug
Sept
Oct
July
May


Intensive Site
Chlorophylle A (ug/L)
100
80
60
40
20
0
6
5
4
3
2
1
0
River km
July
May
Aug
Sept
Oct
July
May
Aug
Sept
Oct
July
May
Aug
Sept
Oct
July
May
Aug
Sept
Oct
July
May
Sept
Oct

Appendix B:

The methods used for modeling the flow at the intensively sampled sites from flow data provided by the water survey of Canada's upstream gauges.

Stephanie Shifflett, M.Sc, EIT,

Surface Water Resources, Grand River Conservation Authority, Cambridge.

To provide an estimate of stream flow at the sampling location, hourly flow data from the closest gauge upstream to the sampling location was input into the corresponding watershed hydrologic model. The four hydrologic models are built on the GAWSER platform (Schroeter, Boyd and Whiteley 2000). The watershed models were used to route stream flow from the upstream gauges downstream to the sampling locations on an hourly basis using the Muskingum-Cunge method. In addition daily meteorological data and hourly rainfall was input into the watershed models to include an estimate of local runoff between the gauge and the downstream sampling point. Runoff is calculated in the hydrologic models by subtracting infiltration and depression storage from rainfall, where infiltration is calculated using the Green-Ampt formula.

Grand River

The Grand River continuous hydrologic model was developed and tested with upwards of 40 years of hydrologic data. The most recent calibration update to the model was completed during the first phase of the Tier 2 Water Budget completed in March 2007.

Hourly stream flow data was input into the model from the Grand River at York stream gauge and the McKenzie Creek near Caledonia (02GB010) stream gauge, operated by the GRCA and the WSC respectively. The combination of these two gauges is the most downstream continuously gauged location in the Grand River watershed. Stream flow rates from both gauges are considered provisional for the period used. Temperature and rainfall data inputs from the GRCA head office in Cambridge were used to estimate local runoff to Dunnville.

Hourly and daily stream flow at the sampling point (bridge at Dunnville) was output from the model from January 2006 to September 2008. The sampling point is approximately 33km downstream from the confluence of McKenzie Creek with the Grand River with 387 km^2 of watershed area between the confluence and the sampling point.

Long Point Region

The Long Point Region continuous hydrologic model was developed for the LPRCA Water Budget in May 2006 (Schroeter & Associates 2006a). The Big Otter Creek watershed was split out of the greater regional model to facilitate routing calculations between the gauged location and the sampling point.

Hourly stream flow data was input into the model from the Big Otter Creek near Calton gauge (02GC026) operated by the Water Service of Canada (WSC). Stream flows are considered provisional for the period used. Daily temperature readings from the GRCA head office in Cambridge and hourly rainfall from the LPRCA gauge at Otterville were used to estimate local runoff to Vienna.

Hourly and daily stream flow at the sampling point at Vienna was output from the model from January 2007 to September 2008. The gauge is only 8.7km upstream from the sampling point with 24km^2 of watershed area between the two locations; therefore output flow rates were very similar to the input values.

Catfish Creek

The Catfish Creek continuous hydrologic model was developed for the Catfish Creek Water Budget in June 2006 (Schroeter & Associates 2006b).

Hourly stream flow data was input into the model from the Catfish Creek near Sparta (02GC018) gauge operated by the Water Service of Canada (WSC). Stream flows are considered provisional for the period used. Daily temperature readings from the GRCA head office in Cambridge and hourly rainfall from the LPRCA gauge at Otterville were used to estimate local runoff to the sampling point.

Hourly and daily stream flow at the sampling point at Jamestown Line upstream of Port Bruce was output from the model from January 2007 to September 2008. The gauge is approximately 15km upstream from the sampling point with about 80km^2 of watershed area between the two locations.

Kettle Creek

The Kettle Creek continuous hydrologic model was developed for the Kettle Creek Water Budget in June 2006 (Schroeter & Associates 2006c).

Hourly stream flow data was input into the model from the Kettle Creek at St. Thomas gauge (02GC002) operated by the Water Service of Canada (WSC). Stream flows are considered provisional for the period used. Daily temperature readings from the GRCA head office in Cambridge and hourly rainfall from the LPRCA gauge at Otterville were used to estimate local runoff to the sampling point.

Hourly and daily stream flow at the sampling point at Sparta Line upstream of Port Stanley was output from the model from January 2007 to September 2008. The gauge is approximately 17km upstream from the sampling point with about 60km^2 of watershed area between the two locations.

References

Schroeter & Associates. 2006a. Long Point Region Watershed Hydrology Model: Set-up, validation and application. Prepared for the Long Point Region Conservation Authority.

Schroeter & Associates. 2006b. Catfish Creek Watershed Hydrology Model: Set-up, validation and application. Prepared for the Catfish Creek Conservation Authority.

Schroeter & Associates. 2006c. Kettle Creek Watershed Hydrology Model: Set-up, validation and application. Prepared for the Kettle Creek Conservation Authority.

Schroeter, HO, DK Boyd and HR Whiteley. 2000. GAWSER: A Versatile Tool for Water Management Planning. Presented at the Ontario Water Conference 2000.
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Appendix C:

Summary statistics for water quality parameters collected in Big Otter, Catfish and Kettle Creeks from 2007-2009

Big Otter Creek

Flow (m^3/sec)

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
N	10	41	62	5
Mean	76.07	23.80	5.31	2.76
Median	67.86	11.57	4.39	2.64
Range (min-max)	145.05 (14.11 -159.16)	84.64 (3.99 - 88.63)	15.60 (1.74 - 17.33)	1.35 (2.20 - 3.55)
Skewness	0.61	-0.58	1.78	-0.36
2(standard error of skewness)	1.55	0.77	0.62	2.19
seasonal comparison: *p* value	<0.001			

Temperature (ºC)

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
N	6	30	46	5
Mean	0.40	8.45	18.40	13.82
Median	0.35	8.75	18.55	13.83
Range	0.40 (0.20 - 0.60)	17.68 (0.02 - 17.70)	9.64 (14.60 - 24.24)	19.49 (4.06 - 23.55)
Skewness	0.38	1.53	-0.73	3.83
2(standard error of skewness)	2.00	0.89	0.07	2.19
seasonal comparison: *p* value	<0.001			

Significant Figures for Flow and Temperature is 2

pH

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
N	10	41	61	5
Mean	8.1	8.3	8.3	8.4
Median	8.1	8.3	8.3	8.5
Range	0.2 (8.0 - 8.2)	0.5 (8.0 - 8.5)	0.4 (8.1 - 8.5)	0.2 (8.3 - 8.5)
Skewness	0.02	0.92	1.96	0.60
2(standard error of skewness)	1.55	0.77	0.63	2.19
seasonal comparison: *p* value	<0.001			

Alkalinity (mg/L)

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
N	10	41	61	5
Mean	126	192	203	220
Median	107	215	206	220
Range	84.5 (92.5 - 177)	153.8 (85.2 - 239)	84 (157 - 241)	13 (213 - 226)
Skewness	0.67	-0.05	1.58	0.27
2(standard error of skewness)	1.55	0.77	0.63	2.19
seasonal comparison: *p* value	<0.001			

Conductivity (µS/cm)

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
N	10	41	61	5
Mean	376	503	531	570
Median	322	552	542	564
Range	263 (278 - 541)	326 (275 - 601)	185 (408 - 593)	60 (550 - 610)
Skewness	0.68	0.92	-0.40	-0.01
2(standard error of skewness)	1.55	0.77	0.63	2.19
seasonal comparison: *p* value	<0.001			

Turbidity (FTU)

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
N	10	41	61	5
Mean	590	238	129	8.07
Median	425	47.3	54.7	8.67
Range	1250 (46.4 - 1300)	1440 (4.88 - 1450)	1230 (7.87 - 1240)	8.44 (4.36 - 12.8)
Skewness	0.57	-0.26	2.44	0.14
2(standard error of skewness)	1.55	0.77	0.63	2.19
seasonal comparison: *p* value	<0.001			

Chloride

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
Concentration (mg/L)				
N	10	41	61	5
Mean	26.5	27.7	29.1	34.7
Median	27.8	28.3	29.7	33.4
Range	23.8 (16.8 - 40.6)	36.1 (16.0 - 52.1)	17.6 (19.4 - 37.0)	9.6 (32.1 - 41.7)
Skewness	0.40	-1.32	0.01	0.92
2(standard error of skewness)	1.55	0.77	0.63	2.19
seasonal comparison: *p* value	0.001			
Loading Rate (g/sec)				
N	10	41	61	5
Mean	1740	575	148	97.3
Median	1760	305	129	90.6
Range	2180 (573 - 2750)	2230 (125 - 2350)	297 (56.4 - 353)	77 (70.8 - 147)
Skewness	-0.05	1.60	0.90	1.41
2(standard error of skewness)	1.55	0.77	0.63	2.19
seasonal comparison: *p* value	<0.001			

E. coli

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
Concentration (CFU/100ml)				
N	8	29	27	5
Mean	530	254	450	170
Median	550	88	200	180
Range	540 (270 - 810)	996 (4 - 1000)	2900 (68 - 3000)	180 (100 - 280)
Skewness	0.08	0.90	-2.86	0.74
2(standard error of skewness)	1.73	0.77	0.94	2.19
seasonal comparison: *p* value	0.005			
Loading Rate (CFU/100ml/sec)				
N	8	29	27	5
Mean	3.3 x10^{8}	1.5 x10^{8}	2.7 x10^{7}	460
Median	3.3 x10^{8}	8.6 x10^{6}	5.5 x10^{6}	460
Range	5.7 x10^{8} (5.6 x10^{7} - 6.2 x10^{8})	8.8 x10^{8} (3.0x10^{5} - 8.8x10^{8})	2.4 x10^{8} (1.5 x10^{6} - 2.4 x10^{8})	410 (280 – 700)
Skewness	0.56	1.25	1.10	1.47
2(standard error of skewness)	1.73	0.77	0.94	2.19
seasonal comparison: *p* value	0.002			

Dissolved Organic Carbon

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
Concentration (mg/L)				
N	10	41	61	5
Mean	4.2	4.0	4.0	2.8
Median	4.3	3.8	3.6	2.7
Range	1.6 (3.6 - 5.2)	3.1 (3.0 - 6.1)	9.6 (2.3 - 11.9)	0.8 (2.5 - 3.3)
Skewness	0.27	-1.34	-1.10	1.94
2(standard error of skewness)	1.55	0.77	.63	2.19
seasonal comparison: *p* value	0.004			
Loading Rate (g/sec)				
N	10	41	61	5
Mean	330	110	23	7.9
Median	240	43	16	6.8
Range	750 (56 - 810)	510 (12 - 520)	70 (4.1 - 74)	6 (5.7 – 11)
Skewness	0.98	1.72	1.17	1.7412
2(standard error of skewness)	1.55	0.77	0.63	2.19
seasonal comparison: *p* value	<0.001			

Dissolved Inorganic Carbon

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
Concentration (mg/L)				
N	10	41	61	5
Mean	29.8	44.5	46.2	51.1
Median	25.2	49.4	46.9	51.1
Range	20.4 (21.3 - 41.7)	34.2 (20 - 54.2)	44 (11.5 - 55.5)	1 (50.7 - 51.7)
Skewness	0.53	-1.31	-0.78	-0.26
2(standard error of skewness)	1.55	0.77	0.63	2.19
seasonal comparison: *p* value	<0.001			
Loading Rate (g/sec)				
N	10	41	61	5
Mean	2030	805	241	141
Median	1750	574	215	134
Range	3230 (550 - 3780)	2370 (201 - 2570)	774 (36.9 - 811)	70 (111 - 181)
Skewness	0.56	1.52	1.78	1.07
2(standard error of skewness)	1.55	0.77	0.63	2.19
seasonal comparison: *p* value	<0.001			

Silicate

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
Concentration (mg/L)				
N	10	41	61	5
Mean	2.30	2.52	3.64	3.70
Median	2.10	2.52	3.66	3.64
Range	1.66 (1.56 - 3.22)	1.84 (1.44 - 3.28)	2.52 (1.96 - 4.48)	0.36 (3.58 - 3.94)
Skewness	0.38	1.91	2.23	0.09
2(standard error of skewness)	1.55	0.77	0.63	2.19
seasonal comparison: *p* value	<0.001			
Loading Rate (g/sec)				
N	10	41	61	5
Mean	159	54.3	19.9	10.2
Median	125	26.0	14.2	9.43
Range	279 (45.4 - 324)	201 (9.34 - 210)	53.2 (3.57 - 56.8)	5.3 (7.98 - 13.3)
Skewness	0.84	1.64	1.03	-1.95
2(standard error of skewness)	1.55	0.77	0.63	2.19
seasonal comparison: *p* value	<0.001			

Suspended Solids

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
Concentration (mg/L)				
N	10	41	61	5
Mean	602	281	174	9
Median	460	85	78	6
Range	1300 (57 - 1360)	1720 (8 - 1730)	1070 (10 - 1080)	10.9 (4 - 15)
Skewness	0.86	1.68	2.43	0.25
2(standard error of skewness)	1.55	0.77	0.63	2.19
seasonal comparison: *p* value	<0.001			
Loading Rate (g/sec)				
N	10	41	61	5
Mean	50600	14300	1100	23
Median	42000	724	334	22
Range	99800 (1780 - 101000)	109000 (47 - 109000)	7790 (28 - 7810)	26 (11 – 37)
Skewness	0.09	2.15	2.33	1.30
2(standard error of skewness)	1.55	0.77	0.63	2.19
seasonal comparison: *p* value	<0.001			

Total Nitrogen

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
Concentration (mg/L)				
N	10	41	61	5
Mean	6.23	4.77	3.90	3.66
Median	6.11	4.47	3.74	3.52
Range	5.33 (4.81 - 10.14)	3.63 (3.70 - 7.33)	3.81 (2.75 - 6.56)	1.55 (3.15 - 4.7)
Skewness	2.06	1.79	1.95	1.28
2(standard error of skewness)	1.55	0.77	0.63	2.19
seasonal comparison: *p* value	<0.001			
Loading Rate (g/sec)				
N	10	41	61	5
Mean	431	129	21.4	10.2
Median	400	51.2	18.2	9.1
Range	714 (143 - 857)	615 (14.8 - 630)	59.0 (5.79 - 64.8)	8.9 (7.7 - 16.6)
Skewness	0.60	1.76	1.31	1.85
2(standard error of skewness)	1.55	0.77	0.63	2.19
seasonal comparison: *p* value	<0.001			

Total Ammonia

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
Concentration (mg/L)				
N	10	41	61	5
Mean	0.17	0.08	0.01	0.010
Median	0.18	0.03	0.01	0.005
Range	0.222 (0.042 - 0.264)	0.350 (0.003 - 0.353)	0.047 (0.002 - 0.049)	0.029 (0.002 - 0.031)
Skewness	-0.80	1.12	3.17	1.03
2(standard error of skewness)	1.55	0.77	0.63	2.19
seasonal comparison: *p* value	<0.001			
Loading Rate (g/sec)				
N	10	41	61	5
Mean	13	4.3	0.10	0.032
Median	9.6	0.26	0.082	0.014
Range	27 (0.59 - 28)	26 (0.013 - 26)	0.84 (0.004 - 0.84)	0.104 (0.005 - 0.109)
Skewness	0.61	1.64	4.11	0.86
2(standard error of skewness)	1.55	0.77	0.63	2.19
seasonal comparison: *p* value	<0.001			
Proportion of Total Nitrogen				
N	10	41	53	5
Mean	2.9	1	0.4	0.25
Median	3.07	0.65	0.37	0.15
Range	3.86 (0.41 - 4.27)	7.82 (0.07 - 7.89)	1.39 (0.05 - 1.44)	0.60 (0.052 - 0.65)
Skewness	0.51	-0.11	1.19	1.54
2(standard error of skewness)	1.55	0.77	0.67	2.19
seasonal comparison: *p* value	<0.001			

Organic Nitrogen

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
Concentration (mg/L)				
N	10	41	61	5
Mean	2.0	1.1	0.91	0.42
Median	1.78	0.77	0.69	0.41
Range	2.65 (0.75 - 3.41)	4.02 (0.39 - 4.42)	2.80 (0.26 - 3.06)	0.091 (0.38 - 0.47)
Skewness	0.74	1.67	2.17	2.23
2(standard error of skewness)	1.55	0.77	0.63	2.19
seasonal comparison: *p* value	Missing p value			
Loading Rate (g/sec)				
N	10	41	61	5
Mean	162	48.6	5.51	1.1691
Median	165	6.85	3.32	1.0463
Range	338 (23.5 - 361)	378 (1.70 - 380)	24.5 (0.595 - 25.1)	0.6 (0.99 - 1.6)
Skewness	0.24	2.29	1.68	2.23
2(standard error of skewness)	1.55	0.77	0.63	2.19
seasonal comparison: *p* value	<0.001			
Proportion of Total Nitrogen				
N	10	41	53	5
Mean	33	23	21	11
Median	33	18	17	12
Range	39 (12 - 51)	52 (8.7 - 60.)	48 (9.4 - 57)	3 (9.9 – 13)
Skewness	-1.05	1.93	1.67	1.84
2(standard error of skewness)	1.55	0.77	0.67	2.19
seasonal comparison: *p* value	0.001			

Total Nitrate

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
Concentration (mg/L)				
N	10	41	61	5
Mean	4.07	3.51	2.97	3.23
Median	3.31	3.33	2.94	3.06
Range	5.63 (2.76 - 8.39)	2.96 (2.03 - 4.99)	3.03 (2.08 - 5.11)	1.46 (2.74 - 4.2)
Skewness	2.03	2.01	2.16	1.69
2(standard error of skewness)	1.55	0.77	0.63	2.19
seasonal comparison: *p* value	<0.001			
Loading Rate (g/sec)				
N	10	41	61	5
Mean	254	76.8	15.7	9.09
Median	223	41.6	12.2	7.99
Range	349 (118 - 467)	278 (13.0 - 291)	40.4 (5.03 - 45.4)	8.1 (6.71 - 14.8)
Skewness	0.95	1.56	1.33	1.94
2(standard error of skewness)	1.55	0.77	0.63	2.19
seasonal comparison: *p* value	<0.001			
Proportion of Total Nitrogen				
N	10	41	53	5
Mean	63.9	75.2	77.7	88.0
Median	62.4	81.1	82.0	87.3
Range	36.9 (46.5 - 83.45)	55.1 (35.8 - 91.0)	48.5 (41.7 - 90.3)	3.2 (86.7 - 89.9)
Skewness	1.26	-0.27	-1.44	-0.60
2(standard error of skewness)	1.55	0.77	0.67	2.19
seasonal comparison: *p* value	<0.001			

Nitrite

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
Concentration (mg/L)				
N	10	41	61	5
Mean	0.057	0.045	0.02	0.038
Median	0.060	0.028	0.017	0.015
Range	0.048 (0.032 - 0.080)	0.179 (0.011 - 0.190)	0.064 (0.006 - 0.070)	0.116 (0.015 - 0.131)
Skewness	-0.23	0.71	0.13	2.05
2(standard error of skewness)	1.55	0.77	0.63	2.19
seasonal comparison: *p* value	<0.001			
Loading Rate (g/sec)				
N	10	41	61	5
Mean	4.6	2.1	0.12	0.12
Median	3.6	0.25	0.070	0.039
Range	9.5 (0.99 - 10)	16 (0.075 - 16)	0.70 (0.020 - 0.72)	0.43 (0.032 - 0.46)
Skewness	0.64	2.20	2.35	2.17
2(standard error of skewness)	1.55	0.77	0.63	2.19
seasonal comparison: *p* value	<0.001			
Proportion of Total Nitrogen				
N	10	41	53	5
Mean	0.96	0.90	0.5	0.91
Median	0.91	0.59	0.4	0.47
Range	1.1 (0.51 - 1.6)	2.3 (0.24 - 2.5)	1.0 (0.1 - 1.1)	2.3 (0.39 - 2.7)
Skewness	0.43	0.27	1.44	0.60
2(standard error of skewness)	1.55	0.77	0.67	2.19
seasonal comparison: *p* value	<0.001			

Total Phosphorus

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
Concentration (mg/L)				
N	10	41	61	5
Mean	0.823	0.38	0.23	0.030
Median	0.730	0.115	0.129	0.029
Range	1.59 (0.144 - 1.74)	1.92 (0.024 - 1.95)	1.19 (0.04 - 1.23)	0.029 (0.016 - 0.045)
Skewness	0.81	2.10	0.49	-0.76
2(standard error of skewness)	1.55	0.77	0.63	2.19
seasonal comparison: *p* value	<0.001			
Loading Rate (g/sec)				
N	10	41	61	5
Mean	71.8	20.	1.4	0.081
Median	71.2	1.1	0.65	0.085
Range	153 (3.72 - 157)	150 (0.13 - 150)	7.7 (0.076 - 7.8)	0.060 (0.042 - 0.10)
Skewness	0.11	2.1	1.67	0.89
2(standard error of skewness)	1.55	0.77	0.63	2.19
seasonal comparison: *p* value	<0.001			

Residual Phosphorus

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
Concentration (mg/L)				
N	10	41	61	5
Mean	0.70	0.31	0.20	0.024
Median	0.602	0.099	0.099	0.023
Range	1.517 (0.095 - 1.613)	1.90 (0.013 - 1.92)	1.14 (0.028 - 1.17)	0.023 (0.012 - 0.035)
Skewness	1.06	1.75	-0.25	1.37
2(standard error of skewness)	1.55	0.77	0.63	2.19
seasonal comparison: *p* value	<0.001			
Loading Rate (g/sec)				
N	10	41	61	5
Mean	60	15	1.2	0.064
Median	54.4	1.0	0.55	0.070
Range	124.5 (2.897 - 127.4)	124.2 (0.085 - 124.2)	7.3 (0.057 - 7.3)	0.045 (0.032 - 0.078)
Skewness	0.17	2.25	1.88	1.91
2(standard error of skewness)	1.55	0.77	0.63	2.19
seasonal comparison: *p* value	<0.001			
Proportion of Total Phosphorus				
N	10	41	53	5
Mean	81	82	81	79
Median	80	85	82	79
Range	26 (66 – 92)	64 (34 - 98)	43 (52.2 - 96)	18 (68 - 86)
Skewness	0.22	-1.18	-1.54	2.22
2(standard error of skewness)	1.55	0.77	0.67	2.19
seasonal comparison: *p* value	0.417			

Phosphate

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
Concentration (mg/L)				
N	10	41	61	5
Mean	0.121	0.069	0.031	0.006
Median	0.125	0.014	0.021	0.006
Range	0.165 (0.048 - 0.214)	0.359 (0.001 - 0.360)	0.078 (0.003 - 0.081)	0.006 (0.004 - 0.009)
Skewness	0.20	-0.43	2.04	0.21
2(standard error of skewness)	1.55	0.77	0.63	2.19
seasonal comparison: *p* value	<0.001			
Loading Rate (g/sec)				
N	10	41	61	5
Mean	11.6	4.18	0.224	0.017
Median	8.88	0.157	0.096	0.014
Range	29.2 (0.828 - 30.08)	28.81 (0.004 - 28.81)	1.344 (0.009 - 1.353)	0.023 (0.009 - 0.032)
Skewness	0.78	1.80	1.86	1.98
2(standard error of skewness)	1.55	0.77	0.63	2.19
seasonal comparison: *p* value	<0.001			
Proportion of Total Phosphorus				
N	10	41	53	5
Mean	18	17	18	20
Median	19.6	14.0	17.0	20
Range	26.1 (7.29 - 33.4)	64.1 (1.14 - 65.2)	44.4 (3.29 - 47.7)	18 (13 - 31)
Skewness	0.87	1.47	0.68	-0.52
2(standard error of skewness)	1.55	0.77	0.67	2.19
seasonal comparison: *p* value	0.417			

Catfish Creek

Flow (m^3/sec)

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
N	12	46	54	4
Mean	74.47	12.64	1.36	0.47
Median	44.58	2.25	1.15	0.56
Range (min-max)	205.19 (13.86 - 219.06)	157.80 (0.84 - 158.64)	4.53 (0.11 - 4.63)	0.45 (0.16 - 0.62)
Skewness	1.58	3.90	0.99	-1.75
2(standard error of skewness)	1.41	0.72	0.67	2.45
seasonal comparison: *p* value	<0.001			

Temperature (ºC)

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
N	N/A	7	35	4
Mean	N/A	16.3	19.7	9.8
Median	N/A	17.0	19.5	9.2
Range	N/A	5.5 (12.9 - 18.5)	9.8 (15.3 - 25.1)	16.3 (2.2 - 18.5)
Skewness	N/A	-0.97	0.86	0.17
2(standard error of skewness)	N/A	1.85	0.83	2.45
seasonal comparison: *p* value	<0.001			

pH

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
N	12	45	54	5
Mean	8.04	8.23	8.19	8.45
Median	8.04	8.24	8.22	8.48
Range	0.15 (7.96 - 8.12)	0.38 (8.00 - 8.38)	0.60 (7.92 - 8.52)	0.33 (8.25 - 8.58)
Skewness	0.27	-0.92	0.07	-1.31
2(standard error of skewness)	1.41	0.73	0.67	2.19
seasonal comparison: *p* value	0.012			

Alkalinity (mg/L)

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
N	12	45	54	5
Mean	110	204	192	227
Median	105	224	204	219
Range	108.1 (79.9 - 188)	179.8 (74.2 - 254)	176.4 (92.6 - 269)	43 (215 - 258)
Skewness	1.86	-1.61	-1.04	1.78
2(standard error of skewness)	1.41	0.73	0.67	2.19
seasonal comparison: *p* value	<0.001			

Conductivity (µS/cm)

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
N	12	45	54	5
Mean	339	539	532	608
Median	315	577	542	585
Range	342 (227 - 569)	432 (203 - 635)	354 (300 - 654)	161 (536 - 697)
Skewness	1.24	-1.93	-1.04	0.42
2(standard error of skewness)	1.41	0.73	0.67	2.19
seasonal comparison: *p* value	<0.001			

Turbidity (FTU)

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
N	12	45	54	5
Mean	714	211	287	10.0
Median	495	19.4	49.0	11.0
Range	1780 (215 - 2000)	1990(4.39 - 2000)	1986 (13.9 - 2000)	6.47 (7.13 - 13.6)
Skewness	1.63	2.88	2.34	0.08
2(standard error of skewness)	1.41	0.73	0.67	2.19
seasonal comparison: *p* value	0.019			

Chloride

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
Concentration (mg/L)				
N	12	45	54	5
Mean	25.1	30.3	34.3	39.5
Median	24.2	30.7	33.5	40.0
Range	28.9 (15.3 - 44.2)	28.8 (16.3 - 45.1)	35.2 (21.7 - 56.9)	35.2 (26.6 - 61.8)
Skewness	1.04	-0.16	0.65	1.04
2(standard error of skewness)	1.41	0.73	0.67	2.19
seasonal comparison: *p* value	0.001			
Loading Rate (g/sec)				
N	12	45	54	4
Mean	1510	312	44.2	20.2
Median	1170	78.6	48.7	19.9
Range	3520 (612 - 4140)	3900 (25.4 - 3930)	142 (2.93 - 145)	32.4 (4.35 - 36.7)
Skewness	1.76	4.24	0.78	0.09
2(standard error of skewness)	1.41	0.73	0.67	2.45
seasonal comparison: *p* value	<0.001			

E. coli

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
Concentration (CFU/100ml)				
N	4	27	32	5
Mean	720	220	280	180
Median	510	840	160	130
Range	1110 (390 - 1500)	1296 (4 - 1300)	1148 (52 - 1200)	418 (32 - 450)
Skewness	1.89	2.19	2.14	1.28
2(standard error of skewness)	2.45	0.94	0.87	2.19
seasonal comparison: *p* value	0.008			
Loading Rate (CFU/100ml/sec)				
N	4	27	32	4
Mean	7.3 x10^{8}	1.2 x10^{8}	2.3 x10^{6}	1.2 x10^{6}
Median	7.5 x10^{8}	1.8 x10^{6}	1.0 x10^{6}	1.0 x10^{6}
Range	9.7 x10^{8} (2.2 x10^{8} - 1.2 x10^{9})	1.7 x10^{9} (8.1 x10^{4} – 1.7 x10^{9})	2.0 x10^{7} (0.94 – 2.0 x10^{7})	2.5 x10^{6} (1.3 x10^{5} – 2.6 x10^{6})
Skewness	-0.16	3.74	3.46	0.80
2(standard error of skewness)	2.45	0.94	0.87	2.45
seasonal comparison: *p* value	0.068			

Dissolved Organic Carbon

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
Concentration (mg/L)				
N	11	45	54	5
Mean	5.4	4.3	4.9	4.1
Median	5.5	3.8	4.9	3.9
Range	3.3 (3.9 - 7.2)	5.6 (3.0 - 8.6)	7.4 (3.7 - 11.1)	1.5 (3.6 - 5.1)
Skewness	0.36	2.11	4.05	0.77
2(standard error of skewness)	1.48	0.73	0.67	2.19
seasonal comparison: *p* value	<0.001			
Loading Rate (g/sec)				
N	11	45	54	4
Mean	490	77	6.8	2.0
Median	240	8.8	5.8	2.2
Range	1501 (54 - 1555)	1138 (3.7 - 1142)	21 (0.39 - 21)	2.5 (0.63 - 3.1)
Skewness	1.54	4.35	0.80	-0.81
2(standard error of skewness)	1.48	0.73	0.67	2.45
seasonal comparison: *p* value	<0.001			

Dissolved Inorganic Carbon

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
Concentration (mg/L)				
N	12	45	54	5
Mean	26.8	47.5	43.0	52.4
Median	25.5	52.4	46.3	51.1
Range	25.4 (19.8.- 45.2)	41.0 (17.6 - 58.6)	38.2 (18.3 - 56.5)	11.1 (48.9 - 60)
Skewness	1.96	-1.58	-1.21	1.64
2(standard error of skewness)	1.41	0.73	0.67	2.19
seasonal comparison: *p* value	<0.001			
Loading Rate (g/sec)				
N	12	45	54	4
Mean	1730	392	51.9	23.9
Median	1170	122	52.4	28.1
Range	3970 (557 - 4530)	3630 (46.5 - 3680)	131 (5.20 - 136)	23.3 (8.10 - 31.4)
Skewness	1.43	3.33	0.37	-1.84
2(standard error of skewness)	1.41	0.73	0.67	2.45
seasonal comparison: *p* value	<0.001			

Silicate

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
Concentration (mg/L)				
N	12	45	54	5
Mean	2.23	1.87	2.78	3.00
Median	2.18	1.98	2.99	2.94
Range	1.08 (1.68 - 2.76)	2.44 (0.64 - 3.08)	2.62 (1.12 - 3.74)	0.74 (2.7 - 3.44)
Skewness	0.15	-0.22	-0.65	1.12
2(standard error of skewness)	1.41	0.73	0.67	2.19
seasonal comparison: *p* value	<0.001			
Loading Rate (g/sec)				
N	12	45	54	4
Mean	159	29.4	3.54	1.38
Median	98.4	3.52	3.37	1.66
Range	412 (38.2 - 450)	376 (0.73 - 377)	11.39 (0.29 - 11.68)	1.33 (0.44 - 1.77)
Skewness	1.54	3.87	0.85	-1.88
2(standard error of skewness)	1.41	.73	.67	2.45
seasonal comparison: *p* value	<0.001			

Suspended Solids

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
Concentration (mg/L)				
N	12	45	54	5
Mean	760	186	212	9.5
Median	702	25.3	45.9	9.9
Range	1700 (257 - 1960)	1810(6 - 1820)	1700 (10 - 1710)	4 (8 - 11)
Skewness	1.55	2.75	2.59	-0.23
2(standard error of skewness)	1.41	0.73	0.67	2.19
seasonal comparison: *p* value	0.045			
Loading Rate (g/sec)				
N	12	45	54	4
Mean	55600	10100	565	4.62
Median	37300	47.1	38.8	4.87
Range	169000 (5760 - 175000)	154000 (12 - 154000)	7690 (3 - 7690)	5 (2 - 7)
Skewness	1.51	3.94	3.70	-0.47
2(standard error of skewness)	1.41	0.73	0.67	2.45
seasonal comparison: *p* value	<0.001			

Total Nitrogen

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
Concentration (mg/L)				
N	12	45	54	5
Mean	6.46	4.78	4.74	2.57
Median	5.90	4.10	3.31	1.74
Range	8.41 (4.67 - 13.08)	9.97 (2.04 - 12.01)	13.7 (1.06 - 14.8)	4.74 (1.01 - 5.76)
Skewness	2.51	1.38	1.19	1.28
2(standard error of skewness)	1.41	0.73	0.67	2.19
seasonal comparison: *p* value	<0.001			
Loading Rate (g/sec)				
N	12	45	54	4
Mean	406	94.5	9.98	1.28
Median	287	10.8	3.16	0.76
Range	966 (88.8 - 1050)	1070 (1.71 - 1070)	61.1 (0.130 - 61.3)	3.25 (0.173 - 3.42)
Skewness	1.56	3.23	1.92	1.74
2(standard error of skewness)	1.41	0.73	0.67	2.45
seasonal comparison: *p* value	<0.001			

Total Ammonia

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
Concentration (mg/L)				
N	12	45	54	5
Mean	0.241	0.108	0.0599	0.0284
Median	0.226	0.063	0.0405	0.0140
Range	0.527 (0.090 - 0.617)	1.315 (0.005 - 1.32)	0.263 (0.002 - 0.265)	0.082 (0.01 - 0.092)
Skewness	2.08	5.42	1.77	2.21
2(standard error of skewness)	1.41	0.73	0.67	2.19
seasonal comparison: *p* value	<0.001			
Loading Rate (g/sec)				
N	12	45	54	4
Mean	14.6	2.37	0.120	17.5
Median	10.5	0.0994	0.0409	16.5
Range	32.2 (1.92 - 34.1)	26.9 (0.0136 - 26.9)	0.680 (0.000332 - 0.680)	8.9 (13.9 - 22.9)
Skewness	1.05	3.18	1.88	1.22
2(standard error of skewness)	1.41	0.73	0.67	2.45
seasonal comparison: *p* value	<0.001			
Proportion of Total Nitrogen				
N	12	45	54	4
Mean	14.6	2.37	0.120	0.0173
Median	10.5	0.0994	0.0409	0.0059
Range	32.2 (1.92 - 34.1)	26.9 (0.0136 - 26.9)	0.680 (0.000332 - 0.680)	0.0523 (0.00245 - 0.0547)
Skewness	1.05	3.18	1.88	1.97
2(standard error of skewness)	1.41	0.73	0.67	2.45
seasonal comparison: *p* value	0.007			

Organic Nitrogen

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
Concentration (mg/L)				
N	12	45	54	5
Mean	2.05	1.08	1.42	0.49
Median	1.82	0.64	0.81	0.46
Range	3.53 (0.76 - 4.29)	3.66 (0.41 - 4.08)	5.84 (0.40 - 6.24)	0.26 (0.38 - 0.64)
Skewness	1.58	2.01	1.96	1.10
2(standard error of skewness)	1.41	0.73	0.67	2.19
seasonal comparison: *p* value	0.036			
Loading Rate (g/sec)				
N	12	45	54	4
Mean	153	37.2	3.01	0.248
Median	77.1	1.22	0.751	0.272
Range	499 (24.7 - 524)	646 (0.463 - 647)	27.4 (0.049 - 27.5)	0.322 (0.063 - 0.385)
Skewness	1.74	4.52	2.88	-0.87
2(standard error of skewness)	1.41	0.73	0.67	2.45
seasonal comparison: *p* value	<0.001			
Proportion of Total Nitrogen				
N	12	45	54	4
Mean	33.3	21.5	32.0	30.8
Median	32.0	21.0	31.9	31.0
Range	45.3 (12.1 - 57.5)	51.1 (8.94 - 60.0)	68.4 (8.14 - 76.6)	38.8 (11.2 - 50.1)
Skewness	0.25	2.26	0.82	-0.06
2(standard error of skewness)	1.41	0.73	0.67	2.45
seasonal comparison: *p* value	<0.001			

Total Nitrate

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
Concentration (mg/L)				
N	12	45	54	5
Mean	4.17	3.59	3.25	2.05
Median	3.72	2.91	1.74	1.28
Range	9.13 (2.27 - 11.40)	7.27 (1.44 - 8.71)	11.0 (0.408 - 11.5)	4.52 (0.497 - 5.02)
Skewness	2.85	1.20	1.24	1.19
2(standard error of skewness)	1.41	0.73	0.67	2.19
seasonal comparison: *p* value	<0.001			
Loading Rate (g/sec)				
N	12	45	54	4
Mean	238	54.9	6.84	1.01
Median	199	9.33	1.70	0.482
Range	452 (55.5 - 508)	401 (1.21 - 402)	37.6 (0.055 - 37.6)	2.88 (0.107 - 2.98)
Skewness	0.90	2.01	1.87	1.83
2(standard error of skewness)	1.41	0.73	0.67	2.45
seasonal comparison: *p* value	<0.001			
Proportion of Total Nitrogen				
N	12	45	54	4
Mean	62	76	66.5	67.9
Median	63	76	66.5	67.8
Range	48.0 (39.0 - 87.1)	55.4 (34.4 - 89.9)	69.4 (21.9 - 91.4)	38.2 (48.8 - 87.1)
Skewness	0.06	-2.11	-0.75	0.02
2(standard error of skewness)	1.41	0.73	0.67	2.45
seasonal comparison: *p* value	<0.001			

Nitrite

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
Concentration (mg/L)				
N	12	45	54	5
Mean	0.065	0.063	0.056	0.016
Median	0.057	0.056	0.038	0.0070
Range	0.060 (0.046 - 0.106)	0.145 (0.015 - 0.160)	0.184 (0.007 - 0.191)	0.043 (0.006 - 0.049)
Skewness	1.07	1.18	1.23	2.07
2(standard error of skewness)	1.41	0.73	0.67	2.19
seasonal comparison: *p* value	<0.001			
Loading Rate (g/sec)				
N	12	45	54	4
Mean	5.4	1.3	0.12	0.010
Median	2.6	0.10	0.037	0.004
Range	19 (0.67 - 19)	25 (0.030 - 25)	0.81 (0.001 - 0.81)	0.028 (0.001 - 0.029)
Skewness	1.83	4.81	1.96	1.92
2(standard error of skewness)	1.41	0.73	0.67	2.45
seasonal comparison: *p* value	<0.001			
Proportion of Total Nitrogen				
N	12	45	54	4
Mean	1.09	1.50	1.11	0.627
Median	1.03	1.70	1.13	0.627
Range	1.58 (0.38 - 1.97)	2.67 (0.39 - 3.07)	2.48 (0.287 - 2.77)	0.448 (0.402 - 0.850)
Skewness	0.65	0.06	0.96	-0.01
2(standard error of skewness)	1.41	0.73	0.67	2.45
seasonal comparison: *p* value	0.004			

Total Phosphorus

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
Concentration (mg/L)				
N	12	45	54	5
Mean	0.95	0.29	0.42	0.03
Median	0.79	0.06	0.14	0.03
Range	1.8 (0.478 - 2.3)	2.2 (0.018 - 2.3)	2.4 (0.033 - 2.5)	0.035 (0.023 - 0.058)
Skewness	2.16	2.49	2.14	1.14
2(standard error of skewness)	1.41	0.73	0.67	2.19
seasonal comparison: *p* value	0.011			
Loading Rate (g/sec)				
N	12	45	54	4
Mean	70	17	1.0	0.018
Median	45	0.10	0.11	0.017
Range	200 (8.8 - 210)	360 (0.030 - 360)	11 (0.006 - 11)	0.029 (0.005 - 0.034)
Skewness	1.52	4.97	2.92	0.32
2(standard error of skewness)	1.41	0.73	0.67	2.45
seasonal comparison: *p* value	0.001			

Residual Phosphorus

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
Concentration (mg/L)				
N	12	45	54	5
Mean	0.75	0.24	0.35	0.028
Median	0.60	0.05	0.095	0.023
Range	1.798 (0.245 - 2.043)	1.991 (0.005 - 1.996)	2.250 (0.026 - 2.276)	0.025 (0.019 - 0.045)
Skewness	2.13	2.61	2.31	1.18
2(standard error of skewness)	1.41	0.73	0.67	2.19
seasonal comparison: *p* value	0.039			
Loading Rate (g/sec)				
N	12	45	54	4
Mean	54	14	0.89	0.015
Median	36	0.097	0.076	0.015
Range	156 (5.2 - 160)	310 (0.012 - 310)	10.5 (0.004 - 10.5)	0.023 (0.004 - 0.027)
Skewness	1.43	5.08	3.17	0.02
2(standard error of skewness)	1.41	0.73	0.67	2.45
seasonal comparison: *p* value	<0.001			
Proportion of Total Phosphorus				
N	12	45	54	4
Mean	75.5	80.0	73.9	82.4
Median	76.3	84.0	74.4	83.4
Range	37.5 (51.2 - 88.8)	67.0 (26.6 - 93.7)	52.0 (44.4-96.5)	8.9 (77.0-86.0)
Skewness	-1.11	-2.28	-0.26	-1.21
2(standard error of skewness)	1.41	0.73	0.67	2.45
seasonal comparison: *p* value	0.163			

Phosphate

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
Concentration (mg/L)				
N	12	45	54	5
Mean	0.202	0.052	0.075	0.009
Median	0.213	0.011	0.044	0.005
Range	0.163 (0.094 - 0.257)	0.494 (0.003 - 0.497)	0.321 (0.004 - 0.325)	0.012 (0.004 - 0.016)
Skewness	-1.10	2.97	1.46	0.65
2(standard error of skewness)	1.41	0.73	0.67	2.19
seasonal comparison: *p* value	0.007			
Loading Rate (g/sec)				
N	12	45	54	4
Mean	16.5	2.81	0.168	0.004
Median	8.96	0.017	0.050	0.003
Range	51.7 (1.30 - 53.0)	48.2 (0.003 - 48.2)	0.942 (0.001 - 0.943)	0.007 (0.001 - 0.008)
Skewness	1.61	4.10	1.78	1.41
2(standard error of skewness)	1.41	0.73	0.67	2.45
seasonal comparison: *p* value	0.001			
Proportion of Total Phosphorus				
N	12	45	54	4
Mean	24.4	19.9	26.0	17.5
Median	23.6	15.9	25.5	16.5
Range	37.5 (11.1 - 48.7)	67.0 (6.27 - 73.3)	52.0 (3.46 - 55.5)	8.9 (13.9 - 22.9)
Skewness	1.11	2.28	0.263	1.216
2(standard error of skewness)	1.41	0.73	0.67	2.45
seasonal comparison: *p* value	0.163			

Kettle Creek

Flow (m^3/sec)

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
N	12	32	35	5
Mean	55.40	15.03	2.90	0.62
Median	46.73	3.60	0.60	0.44
Range (min-max)	152.01 (10.99 - 163.00)	103.12 (0.89 - 104.00)	23.74 (0.27-24.01)	0.96 (0.35-1.31)
Skewness	1.29	-0.23	3.49	0.02
2(standard error of skewness)	1.41	0.87	0.83	2.19
seasonal comparison: *p* value	<0.001			

Temperature (ºC)

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
N	12	26	25	5
Mean	3.7	9.3	16.8	14.1
Median	3.5	9.7	17.6	16.2
Range	5.5 (1.9-7.4)	15.9 (2.3-18.2)	16.5 (6.3-22.9)	12.7 (6.3-19.1)
Skewness	1.48	2.61	3.04	0.44
2(standard error of skewness)	1.41	0.96	0.98	2.19
seasonal comparison: *p* value	<0.001			

pH

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
N	12	32	35	5
Mean	8.1	8.3	8.3	8.4
Median	8.1	8.3	8.3	8.4
Range	0.1 (8.0-8.1)	0.4 (8.0-8.5)	0.5 (8.1-8.6)	0.2 (8.3-8.5)
Skewness	-0.39	2.09	0.29	0.23
2(standard error of skewness)	1.41	0.87	0.83	2.19
seasonal comparison: *p* value	<0.001			

Alkalinity (mg/L)

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
N	12	32	35	5
Mean	128	183	155	150
Median	104	204	150	142
Range	235.5 (79.5-315)	186.7 (58.3-245)	111 (112-223)	55 (134-189)
Skewness	2.46	2.62	2.87	1.82
2(standard error of skewness)	1.41	0.87	0.83	2.19
seasonal comparison: *p* value	<0.001			

Conductivity (µS/cm)

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
N	12	32	35	5
Mean	482	602	668	740
Median	387	664	632	749
Range	939 (251 - 1190)	648 (211 - 859)	392 (513 - 905)	239 (620 - 859)
Skewness	1.64	-1.01	1.21	1.76
2(standard error of skewness)	1.41	0.87	0.83	2.19
seasonal comparison: *p* value	0.014			

Turbidity (FTU)

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
N	12	32	35	5
Mean	898	266	136	46
Median	700	54.7	122	46
Range	1840 (159 - 2000)	1990 (9 - 2000)	518 (10 - 528)	48 (25 - 74)
Skewness	0.71	2.40	1.69	0.00
2(standard error of skewness)	1.41	0.87	0.83	2.19
seasonal comparison: *p* value	<0.001			

Chloride

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
Concentration (mg/L)				
N	12	32	35	5
Mean	63.4	64.2	80.2	94.6
Median	47.4	64.6	74.8	88.4
Range	115 (29.4 - 145)	100 (26.8 - 127)	75.9 (53.1 - 129)	54.3 (74.7 - 129)
Skewness	1.34	0.00	-1.06	-0.69
2(standard error of skewness)	1.41	0.87	0.83	2.19
seasonal comparison: *p* value	0.009			
Loading Rate (g/sec)				
N	12	32	35	5
Mean	2550	619	199	63.8
Median	2290	261	58.5	38.7
Range	4400 (1230 - 5630)	3380 (80.5 - 3470)	1701 (20.1 - 1720)	141 (27.6 - 168)
Skewness	-1.16	1.15	-0.74	0.40
2(standard error of skewness)	1.41	0.87	0.83	2.19
seasonal comparison: *p* value	<0.001			

E. coli

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
Concentration (CFU/100ml)				
N	8	30	26	5
Mean	2300	500	740	550
Median	1100	170	270	240
Range	7940 (460 - 8400)	4492 (8 - 4500)	3560 (40 - 3600)	1470 (130 - 1600)
Skewness	2.06	-0.99	0.73	1.55
2(standard error of skewness)	1.73	0.89	0.96	2.19
seasonal comparison: *p* value	0.005			
Loading Rate (CFU/100ml/sec)				
N	8	29	26	5
Mean	1.4 x10^{9}	2.6 x10^{8}	9.0 x10^{6}	5.4 x10^{6}
Median	6.9 x10^{8}	4.6 x10^{6}	1.0 x10^{6}	1.0 x10^{6}
Range	6.2 x10^{9} (1.0 x10^{8} - 6.3 x10^{9})	4.3 x10^{9} (1.6 x10^{5} – 4.3 x10^{9})	6.0 x10^{7} (2.1 x10^{5} - 6.0 x10^{7})	2.0 x10^{7} (4.6 x10^{5} - 2.0 x10^{7})
Skewness	1.19	2.82	2.93	2.08
2(standard error of skewness)	1.73	0.91	0.96	2.19
seasonal comparison: *p* value	<0.001			

Dissolved Organic Carbon

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
Concentration (mg/L)				
N	12	32	35	5
Mean	5.1	4.6	5.5	5.3
Median	4.8	4.6	5.5	5.3
Range	6.1 (3.3 - 9.4)	2.5 (3.5 - 6.0)	3 (4.6 - 7.6)	1.0 (4.9 - 5.9)
Skewness	2.02	-1.00	0.52	-0.08
2(standard error of skewness)	1.41	0.87	0.83	2.19
seasonal comparison: *p* value	<0.001			
Loading Rate (g/sec)				
N	12	32	35	5
Mean	320	82	16	3.2
Median	230	15	3.6	2.5
Range	1000 (49 - 1000)	670 (4.8 - 680)	145 (1.4 - 140)	5.0 (1.7 - 6.7)
Skewness	1.25	2.64	3.00	2.08
2(standard error of skewness)	1.41	0.87	0.83	2.19
seasonal comparison: *p* value	<0.001			

Dissolved Inorganic Carbon

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
Concentration (mg/L)				
N	12	32	35	5
Mean	26.6	42.4	35.4	34.3
Median	26.8	48.0	34.7	32.8
Range	22.5 (19 - 41.5)	41.1 (14.5 - 55.6)	31.1 (21.4 - 52.5)	11.6 (30.5 - 42.1)
Skewness	0.92	0.28	0.68	1.15
2(standard error of skewness)	1.41	0.87	0.83	2.19
seasonal comparison: *p* value	<0.001			
Loading Rate (g/sec)				
N	12	32	35	5
Mean	1370	448	101	22.4
Median	1150	198	24.9	13.6
Range	3230 (396 - 3630	2780 (40.5 - 2820)	840 (9.13 - 850)	43.5 (11.4 - 55.0)
Skewness	1.15	2.52	3.07	2.15
2(standard error of skewness)	1.41	0.87	0.83	2.19
seasonal comparison: *p* value	<0.001			

Silicate

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
Concentration (mg/L)				
N	12	32	35	5
Mean	2.16	1.56	1.76	1.46
Median	2.18	1.41	1.98	1.22
Range	1.50 (1.50 - 3.00)	2.68 (0.24 - 2.92)	3.02 (0.02 - 3.04)	1.42 (0.80 - 2.22)
Skewness	0.28	2.21	0.87	0.56
2(standard error of skewness)	1.41	0.87	0.83	2.19
seasonal comparison: *p* value	0.095			
Loading Rate (g/sec)				
N	12	32	35	5
Mean	122	30.7	6.72	1.03
Median	92.8	9.18	1.03	0.639
Range	325 (24.9 - 350)	263 (0.412 - 264)	59.5 (0.009 - 59.5)	2.62 (0.280 - 2.90)
Skewness	1.37	3.48	3.11	1.24
2(standard error of skewness)	1.41	0.87	0.83	2.19
seasonal comparison: *p* value	<0.001			

Suspended Solids

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
Concentration (mg/L)				
N	12	32	35	5
Mean	652	187	135	34.4
Median	571	46.2	92.6	39.3
Range	1410 (164 - 1580)	1250 (12 - 1270)	451 (18 - 469)	35.0 (18 - 53)
Skewness	0.90	2.60	1.02	0.46
2(standard error of skewness)	1.41	0.87	0.83	2.19
seasonal comparison: *p* value	<0.001			
Loading Rate (g/sec)				
N	12	32	35	5
Mean	49600	11300	660.	17.4
Median	23200	167	51.2	17.7
Range	153000 (2410 - 155000)	149000 (25 - 149000)	6685 (14 - 6690)	10 (14 - 23)
Skewness	1.06	3.77	2.98	0.32
2(standard error of skewness)	1.41	0.87	0.83	2.19
seasonal comparison: *p* value	<0.001			

Total Nitrogen

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
Concentration (mg/L)				
N	12	32	35	5
Mean	5.89	5.22	7.56	10.45
Median	4.92	5.30	6.98	8.88
Range	6.51 (3.87 - 10.38)	3.62 (3.05 - 6.67)	10.65 (4.08 - 14.73)	6.85 (7.88 - 14.73)
Skewness	1.45	1.89	0.01	-0.17
2(standard error of skewness)	1.41	0.87	0.83	2.19
seasonal comparison: *p* value	<0.001			
Loading Rate (g/sec)				
N	12	32	35	5
Mean	322	81.1	17.9	5.92
Median	255	20.8	5.40	5.40
Range	921 (79.3 - 1000)	697 (5.13 - 702)	146 (1.67 - 147)	7.3 (2.95 - 10.3)
Skewness	1.69	3.28	3.17	1.47
2(standard error of skewness)	1.41	0.87	0.83	2.19
seasonal comparison: *p* value	<0.001			

Total Ammonia

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
Concentration (mg/L)				
N	12	32	35	5
Mean	0.136	0.120	0.083	0.169
Median	0.132	0.093	0.037	0.148
Range	0.185 (0.049 - 0.234)	0.323 (0.007 - 0.330)	0.598 (0.009 - 0.607)	0.448 (0.013 - 0.461)
Skewness	0.02	0.24	1.13	0.48
2(standard error of skewness)	1.41	0.87	0.83	2.19
seasonal comparison: *p* value	0.002			
Loading Rate (g/sec)				
N	12	32	35	5
Mean	8.03	3.55	0.111	0.076
Median	4.54	0.397	0.0562	0.089
Range	27.3 (1.25 - 28.6)	32.0 (0.015 - 32.0)	0.541 (0.004 - 0.545)	0.160 (0.005 - 0.164)
Skewness	1.59	2.79	2.98	1.73
2(standard error of skewness)	1.41	0.87	0.83	2.19
seasonal comparison: *p* value	<0.001			
Proportion of Total Nitrogen				
N	12	32	35	5
Mean	2.70	2.51	1.23	1.37
Median	2.70	1.65	0.52	1.63
Range	4.80 (0.477 - 5.28)	10.6 (0.140 - 10.8)	11.60 (0.11 - 11.71)	2.97 (0.15 - 3.12)
Skewness	0.11	-0.73	2.99	0.79
2(standard error of skewness)	1.41	0.87	0.83	2.19
seasonal comparison: *p* value				

Organic Nitrogen

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
Concentration (mg/L)				
N	12	32	35	5
Mean	1.93	1.02	1.14	0.80
Median	1.43	0.81	1.13	0.76
Range	5.09 (0.69 - 5.78)	2.71 (0.44 - 3.16)	1.45 (0.44 - 1.89)	0.28 (0.65 - 0.94)
Skewness	2.40	-0.99	0.95	0.93
2(standard error of skewness)	1.41	0.87	0.83	2.19
seasonal comparison: *p* value	<0.001			
Loading Rate (g/sec)				
N	12	32	35	5
Mean	137	31.9	3.64	0.464
Median	62.8	2.49	0.733	0.406
Range	550 (12.6 - 563)	371 (0.743 - 372)	35.0 (0.123 - 35.1)	0.585 (0.274 - 0.860)
Skewness	1.23	2.99	2.93	1.22
2(standard error of skewness)	1.41	0.87	0.83	2.19
seasonal comparison: *p* value	<0.001			
Proportion of Total Nitrogen				
N	12	32	35	5
Mean	33.1	20.3	16.7	8.04
Median	30.5	15.3	17.2	7.90
Range	42.2 (14.0 - 56.2)	44.4 (8.60 - 53.0)	25.5 (4.26 - 29.8)	5.98 (5.22 - 11.2)
Skewness	-0.24	-1.58	0.0555	-1.4136
2(standard error of skewness)	1.41	0.87	0.83	2.19
seasonal comparison: *p* value	0.025			

Total Nitrate

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
Concentration (mg/L)				
N	12	32	35	5
Mean	3.82	4.08	6.33	9.48
Median	3.14	4.31	5.72	8.03
Range	6.92 (1.95 - 8.87)	4.84 (1.14 - 5.98)	10.4 (3.03 - 13.5)	6.3 (7.2 - 13.5)
Skewness	1.77	1.92	2.97	1.70
2(standard error of skewness)	1.41	0.87	0.83	2.19
seasonal comparison: *p* value	<0.001			
Loading Rate (g/sec)				
N	12	32	35	5
Mean	176	45.6	14.2	5.38
Median	155	17.7	4.82	4.90
Range	375 (57.0 - 432)	308 (4.27 - 313)	110 (1.29 - 112)	6.79 (2.62 - 9.41)
Skewness	1.59	2.56	2.64	1.42
2(standard error of skewness)	1.41	0.87	0.83	2.19
seasonal comparison: *p* value	<0.001			
Proportion of Total Nitrogen				
N	12	32	35	5
Mean	64.1	77.2	82.0	90.5
Median	65.4	82.9	80.4	90.8
Range	44.3 (41.1 - 85.4)	52.2 (37.3 - 89.6)	25.5 (70.0 - 95.5)	3.0 (88.6 - 91.6)
Skewness	2.55	0.73	2.88	1.97
2(standard error of skewness)	1.41	0.87	0.83	2.19
seasonal comparison: *p* value	<0.001			

Nitrite

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
Concentration (mg/L)				
N	12	32	35	5
Mean	0.065	0.075	0.065	0.100
Median	0.057	0.066	0.060	0.079
Range	0.076 (0.034 - 0.110)	0.173 (0.017 - 0.190)	0.192 (0.019 - 0.211)	0.183 (0.028 - 0.211)
Skewness	0.60	0.16	1.78	0.21
2(standard error of skewness)	1.41	0.87	0.83	2.19
seasonal comparison: *p* value	0.434			
Loading Rate (g/sec)				
N	12	32	35	5
Mean	4.45	1.99	0.181	0.051
Median	2.61	0.253	0.042	0.051
Range	15.1 (0.501 - 15.6)	22.3 (0.036 - 22.4)	1.08 (0.008 - 1.09)	0.083 (0.010 - 0.092)
Skewness	1.12	2.37	1.90	1.38
2(standard error of skewness)	1.41	0.87	0.83	2.19
seasonal comparison: *p* value	<0.001			
Proportion of Total Nitrogen				
N	12	32	35	5
Mean	1.22	1.48	0.933	0.883
Median	1.22	1.21	0.850	0.889
Range	1.61 (0.481 - 2.09)	3.06 (0.349 - 3.40)	2.21 (0.301 - 2.51)	1.37 (0.331 - 1.71)
Skewness	0.03	1.68	3.92	0.53
2(standard error of skewness)	1.41	0.87	0.83	2.19
seasonal comparison: *p* value	0.025			

Total Phosphorus

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
Concentration (mg/L)				
N	12	32	35	5
Mean	0.800	0.277	0.284	0.229
Median	0.597	0.117	0.265	0.215
Range	1.925 (0.275 - 2.2)	1.353 (0.037 - 1.390)	0.447 (0.118 - 0.565)	0.147 (0.165 - 0.312)
Skewness	1.61	2.42	1.29	0.86
2(standard error of skewness)	1.41	0.87	0.83	2.19
seasonal comparison: *p* value	<0.001			
Loading Rate (g/sec)				
N	12	32	35	5
Mean	58.3	13.1	1.01	0.128
Median	28.1	0.376	0.166	0.120
Range	210 (4.05 - 214)	163 (0.101 - 163)	9.69 (0.033 - 9.72)	0.140 (0.075 - 0.215)
Skewness	2.10	2.67	2.89	1.22
2(standard error of skewness)	1.41	0.87	0.83	2.19
seasonal comparison: *p* value	<0.001			

Residual Phosphorus

	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
Concentration (mg/L)				
N	12	32	31	3
Mean	0.556	0.189	0.159	0.060
Median	0.392	0.087	0.142	0.057
Range	1.316 (0.133 - 1.449)	1.084 (0.001 - 1.086)	0.421 (0.033 - 0.454)	0.057 (0.033 - 0.090)
Skewness	1.12	-0.28	0.67	-0.50
2(standard error of skewness)	1.41	0.87	0.88	2.89
seasonal comparison: *p* value	<0.001			
Loading Rate (g/sec)				
N	12	32	31	3
Mean	41.6	9.17	0.743	0.040
Median	19.1	0.248	0.101	0.039
Range	139 (1.46 - 141)	128 (0.005 - 128)	6.777 (0.017 - 6.795)	0.007 (0.036 - 0.043)
Skewness	1.56	2.63	2.88	1.83
2(standard error of skewness)	1.41	0.87	0.88	2.89
seasonal comparison: *p* value	<0.001			
Proportion of Total Phosphorus				
N	12	32	31	3
Mean	65.0	65.2	54.4	26.3
Median	67.5	69.5	63.6	28.8
Range	50.7 (15.2 - 66.0)	89.9 (5.68 - 95.6)	74.9 (19.7 - 94.7)	10.3 (20.0 - 30.3)
Skewness	0.41	1.58	0.96	0.88
2(standard error of skewness)	1.41	0.87	0.88	2.89
seasonal comparison: *p* value	<0.001			

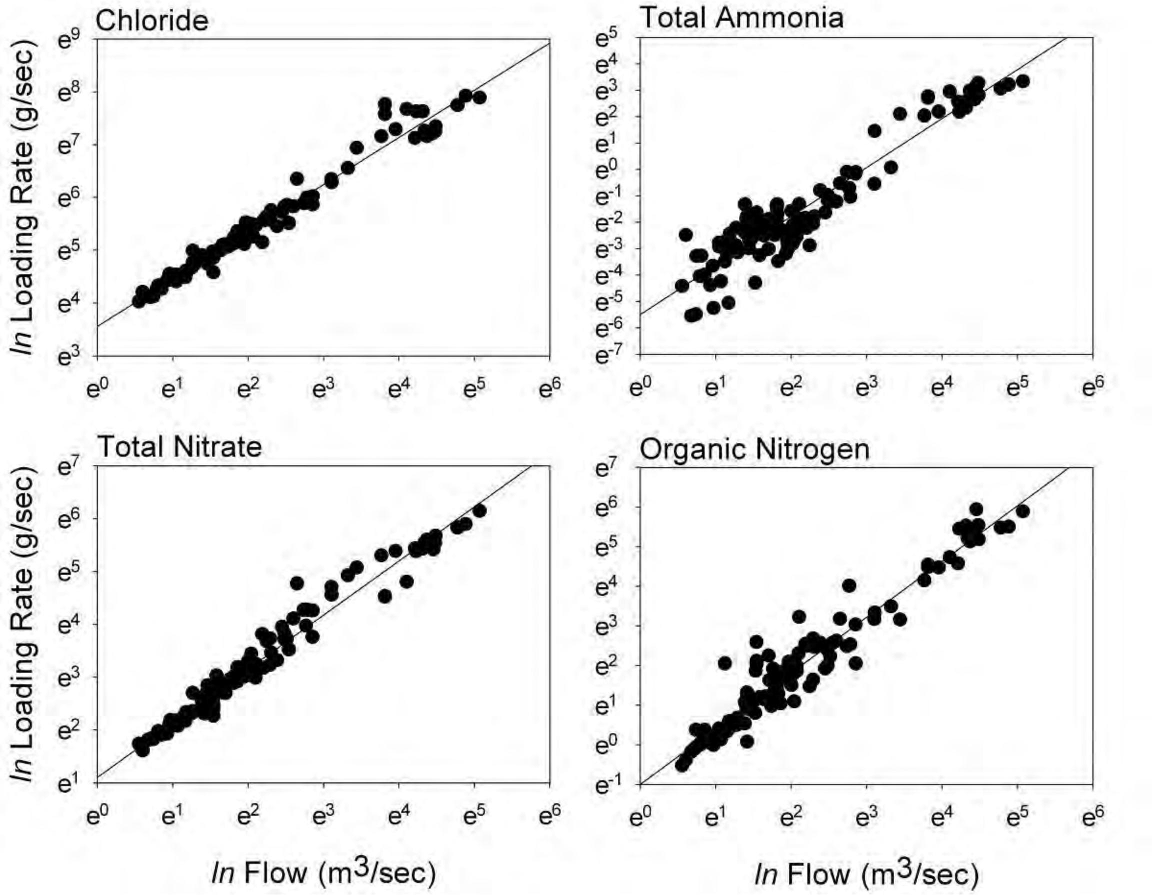
Phosphate

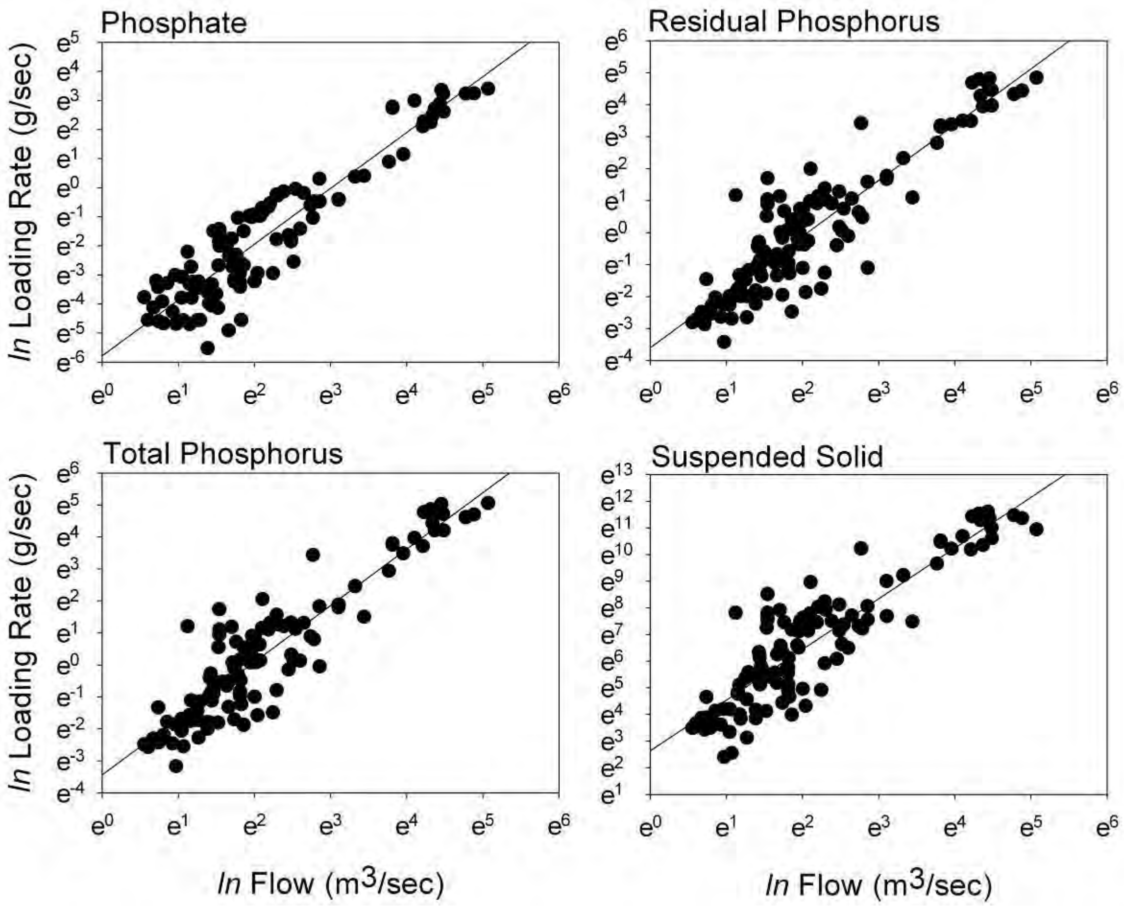
	Season			
	Winter (Dec – Feb)	Spring (Mar – May)	Summer (June – Sept)	Fall (Oct – Nov)
Concentration (mg/L)				
N	12	32	35	5
Mean	0.243	0.088	0.152	0.215
Median	0.211	0.044	0.132	0.222
Range	0.652 (0.099-0.751)	0.498 (0.005-0.503)	0.470 (0.010-0.481)	0.226 (0.131-0.357)
Skewness	2.84	-0.80	0.98	0.901
2(standard error of skewness)	1.41	0.87	0.83	2.19
seasonal comparison: *p* value	<0.001			
Loading Rate (g/sec)				
N	12	32	35	5
Mean	16.7	3.97	0.359	0.112
Median	8.57	0.154	0.104	0.097
Range	71.7 (1.46-73.2)	35.8 (0.010-35.8)	2.92 (0.005-2.92)	0.090 (0.082-0.172)
Skewness	1.62	3.14	2.98	1.24
2(standard error of skewness)	1.41	0.87	0.83	2.19
seasonal comparison: *p* value	<0.001			
Proportion of Total Phosphorus				
N	12	32	31	3
Mean	34.9	34.7	45.5	73.6
Median	32.4	30.4	36.3	71.1
Range	50.7 (15.2 -66.0)	89.9 (4.32 - 94.3)	74.9 (5.30-80.2)	10.3 (69.6-80.0)
Skewness	0.41	1.20	-0.04	0.38
2(standard error of skewness)	1.41	0.87	0.88	2.89
seasonal comparison: *p* value	0.036			

Appendix D:

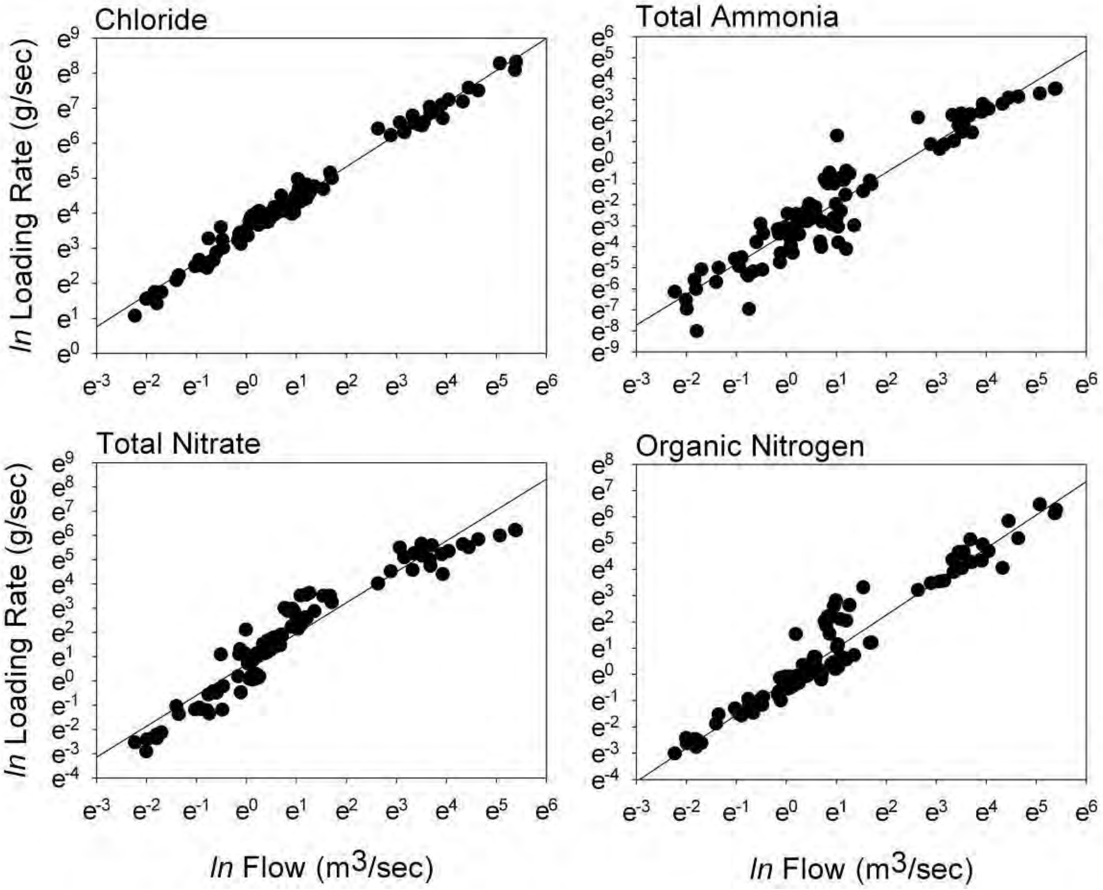
Regression plots for parameter loading rates vs. flows for Big Otter, Catfish and Kettle Creeks.

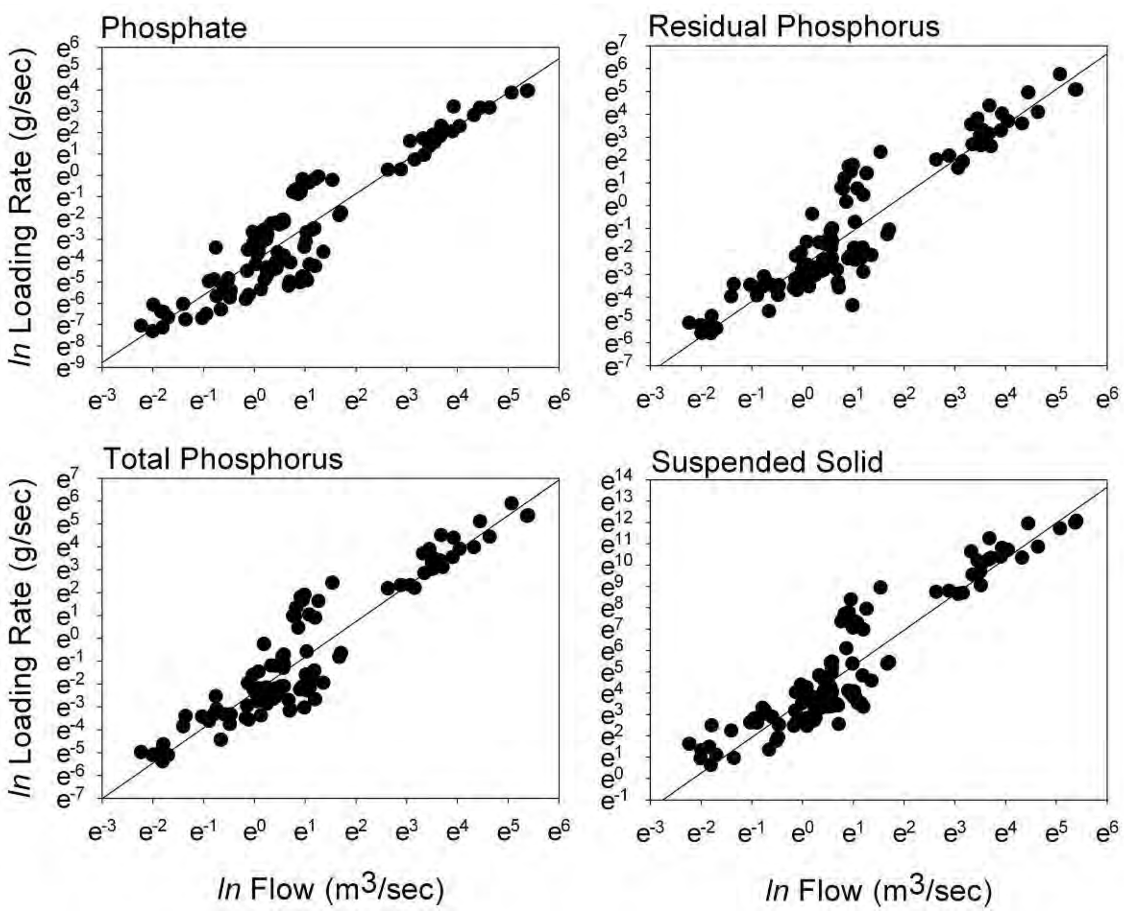
Big Otter



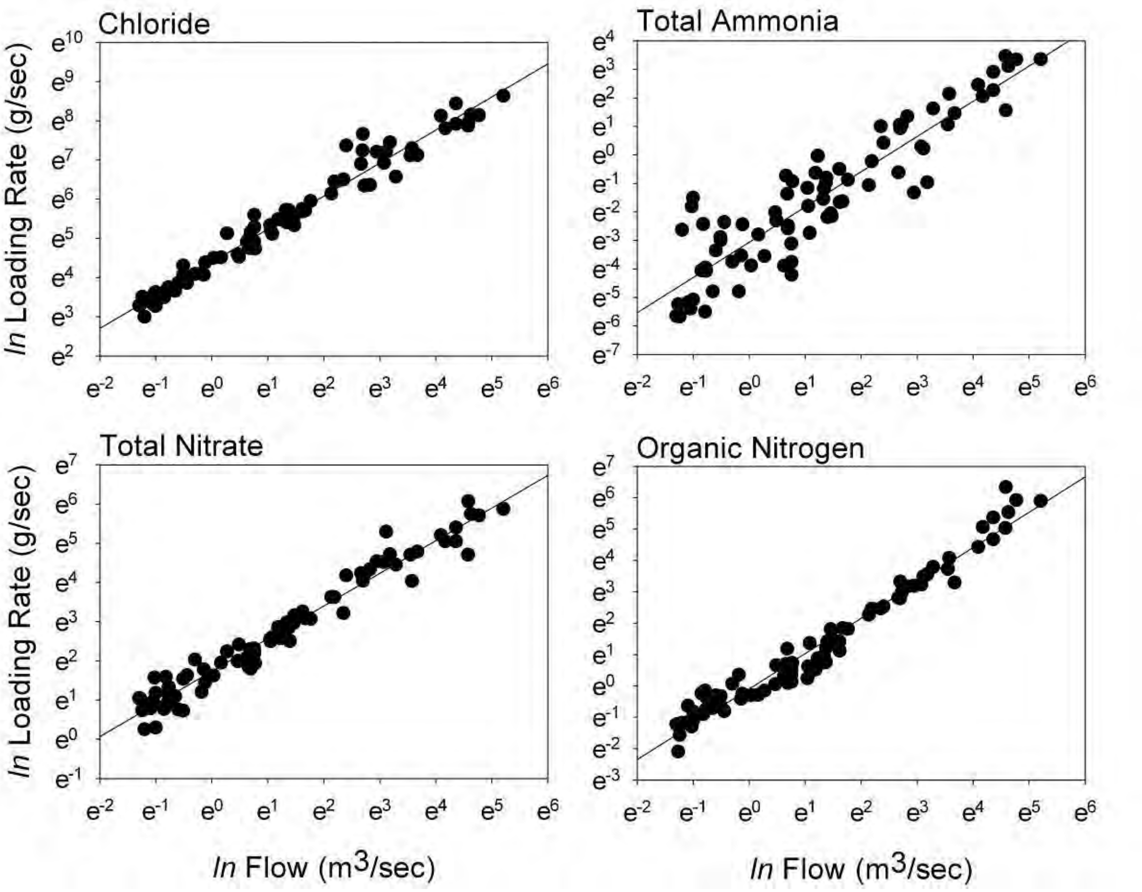

Phosphate
Residual Phosphorus
Total Phosphorus
Suspended Solid
ln Loading Rate (g/sec)
ln Loading Rate (g/sec)
ln Flow (m^3/sec)
ln Flow (m^3/sec)
e^5
e^4
e^3
e^2
e^1
e^0
e^{-1}
e^{-2}
e^{-3}
e^{-4}
e^{-5}
e^{-6}
e^6
e^{13}
e^{12}
e^{11}
e^{10}
e^9
e^8
e^7

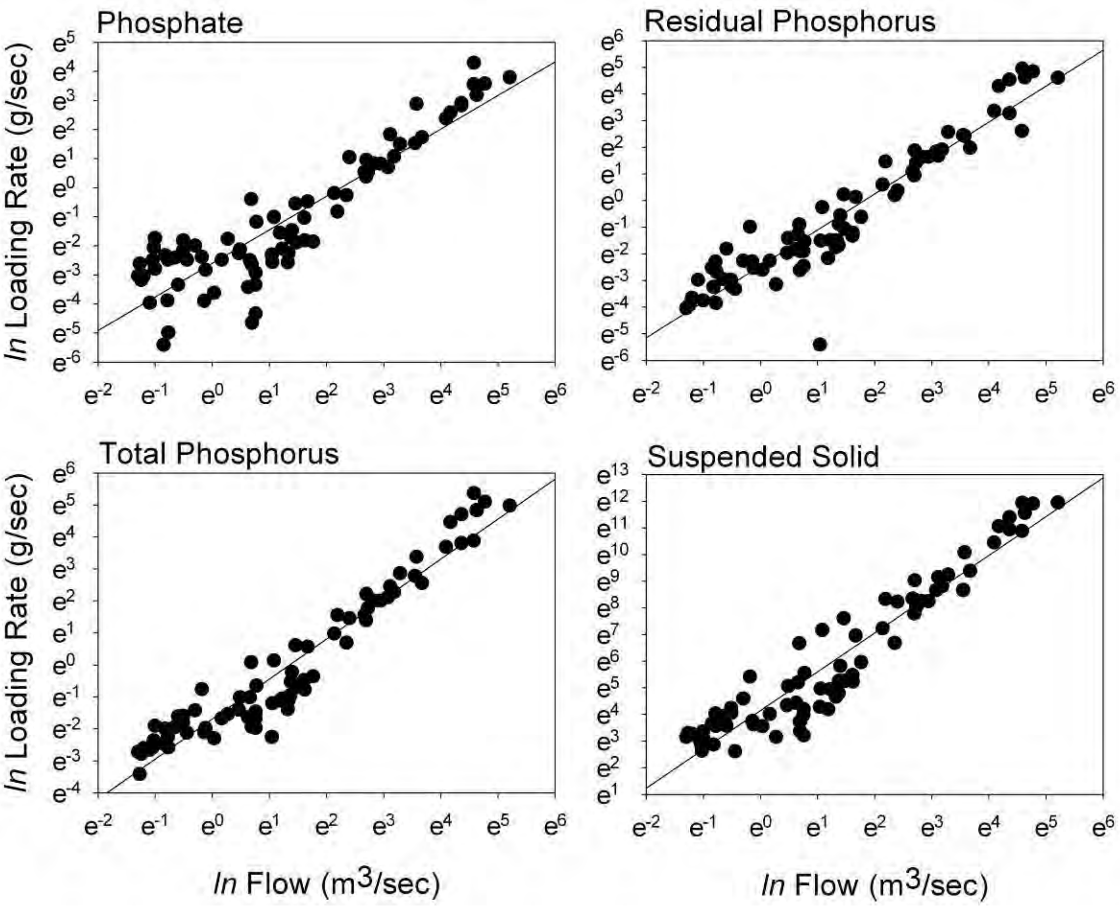
Catfish Creek




Phosphate
Residual Phosphorus
Total Phosphorus
Suspended Solid
ln Loading Rate (g/sec)
ln Flow (m3/sec)
e^{-9} e^{-8} e^{-7} e^{-6} e^{-5} e^{-4} e^{-3} e^{-2} e^{-1} e^{0} e^{1} e^{2} e^{3} e^{4} e^{5} e^{6}
e^{-7} e^{-6} e^{-5} e^{-4} e^{-3} e^{-2} e^{-1} e^{0} e^{1} e^{2} e^{3} e^{4} e^{5} e^{6} e^{7}
e^{-1} e^{0} e^{1} e^{2} e^{3} e^{4} e^{5} e^{6} e^{7} e^{8} e^{9} e^{10} e^{11} e^{12} e^{13} e^{14}
e^{-3} e^{-2} e^{-1} e^{0} e^{1} e^{2} e^{3} e^{4} e^{5} e^{6}

Kettle Creek

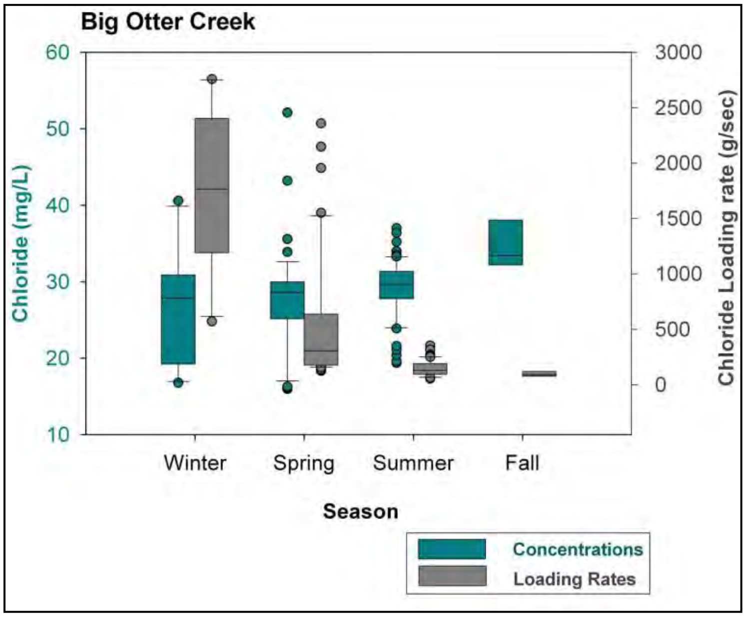



Phosphate
Residual Phosphorus
Total Phosphorus
Suspended Solid
ln Loading Rate (g/sec)
ln Loading Rate (g/sec)
e^{5} e^{4} e^{3} e^{2} e^{1} e^{0} e^{-1} e^{-2} e^{-3} e^{-4} e^{-5} e^{-6}
e^{6} e^{5} e^{4} e^{3} e^{2} e^{1} e^{0} e^{-1} e^{-2} e^{-3} e^{-4} e^{-5} e^{-6}
e^{6} e^{5} e^{4} e^{3} e^{2} e^{1} e^{0} e^{-1} e^{-2} e^{-3} e^{-4}
e^{13} e^{12} e^{11} e^{10} e^{9} e^{8} e^{7} e^{6} e^{5} e^{4} e^{3} e^{2} e^{1}
e^{-2} e^{-1} e^{0} e^{1} e^{2} e^{3} e^{4} e^{5} e^{6}
ln Flow (m^3/sec)
ln Flow (m^3/sec)

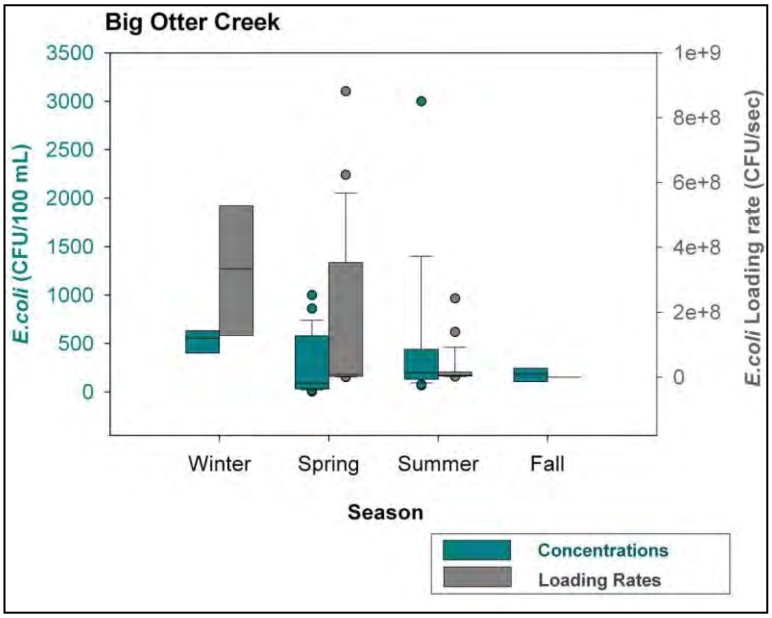
Appendix E.

Big Otter Creek

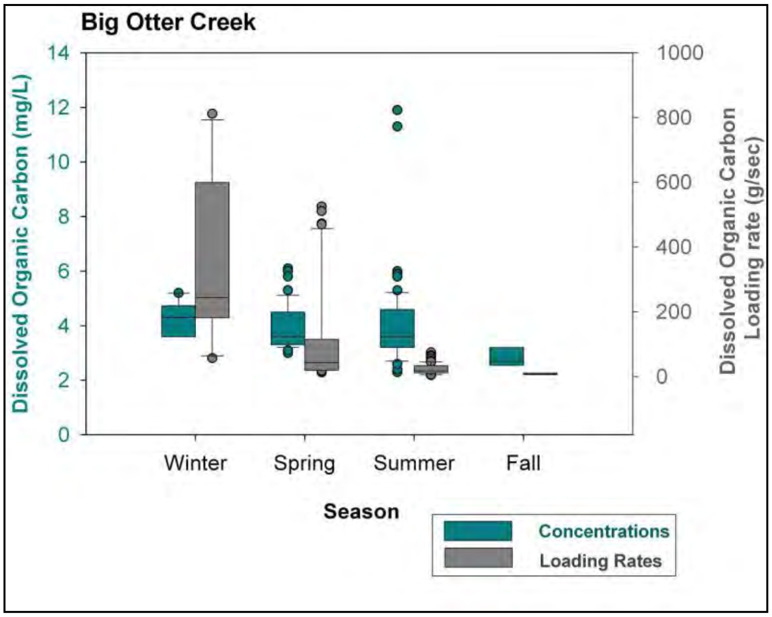
Box and whisker plots of routine water chemistry parameters for Big Otter Creek



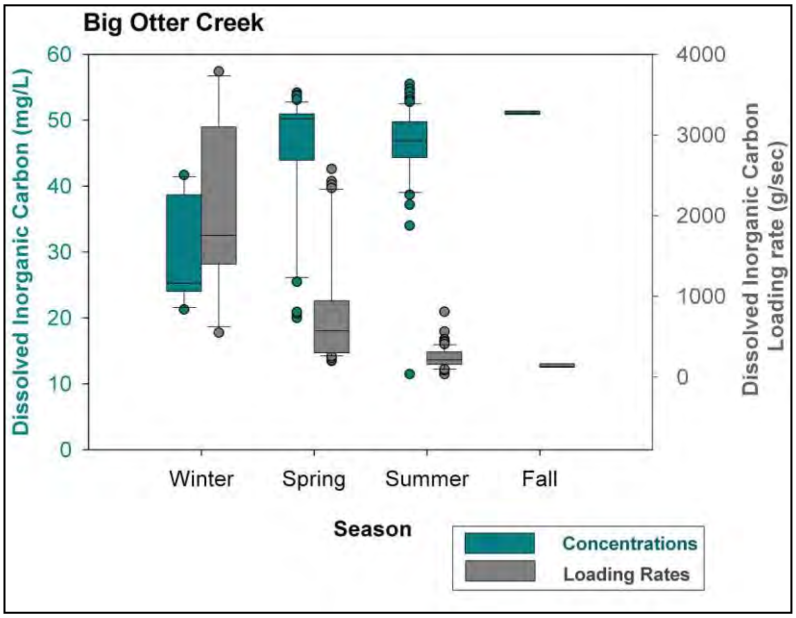
E 1. Boxplots of all observed chloride concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Big Otter Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.



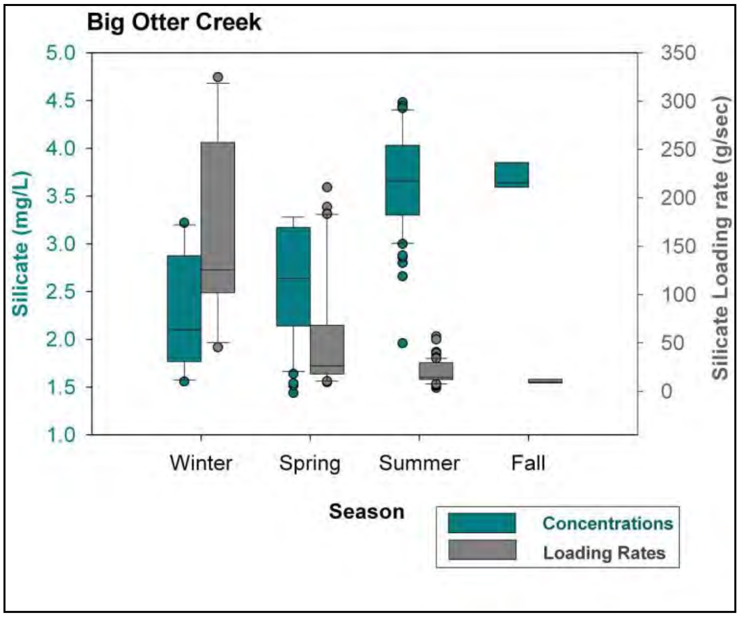
E 2Boxplots of all observed E. coli concentrations (CFU/100ml; left axis) and loading rates (CFU/100ml/sec; right axis) at the mouth of Big Otter Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.



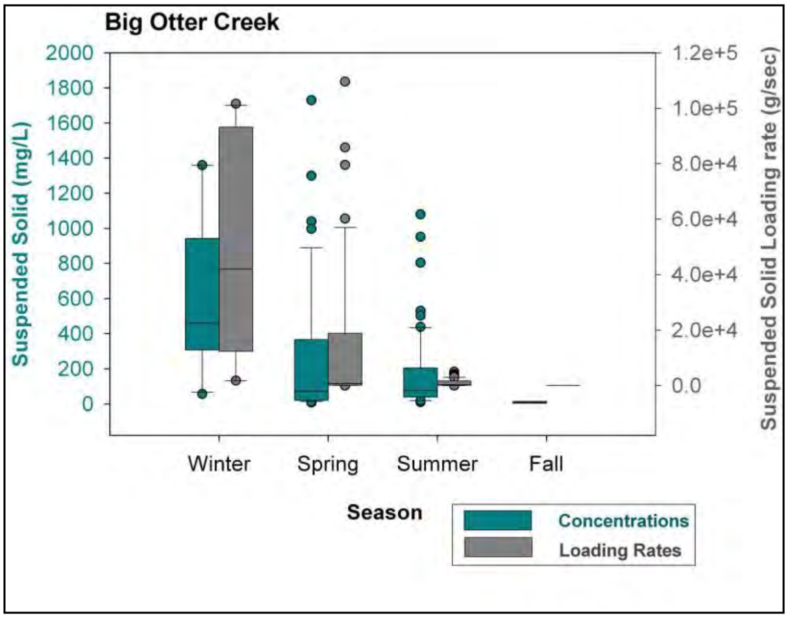
E 3Boxplots of all observed dissolved organic carbon concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Big Otter Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.



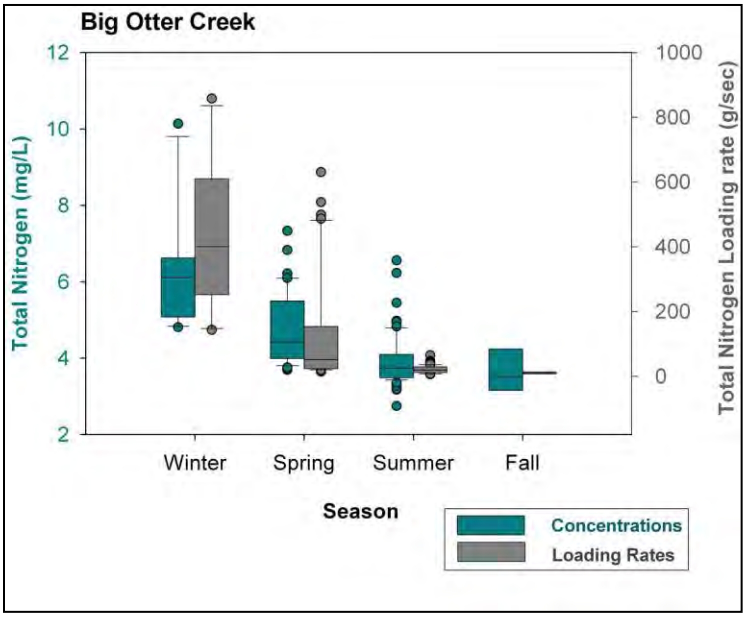
E 4Boxplots of all observed dissolved inorganic carbon concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Big Otter Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.



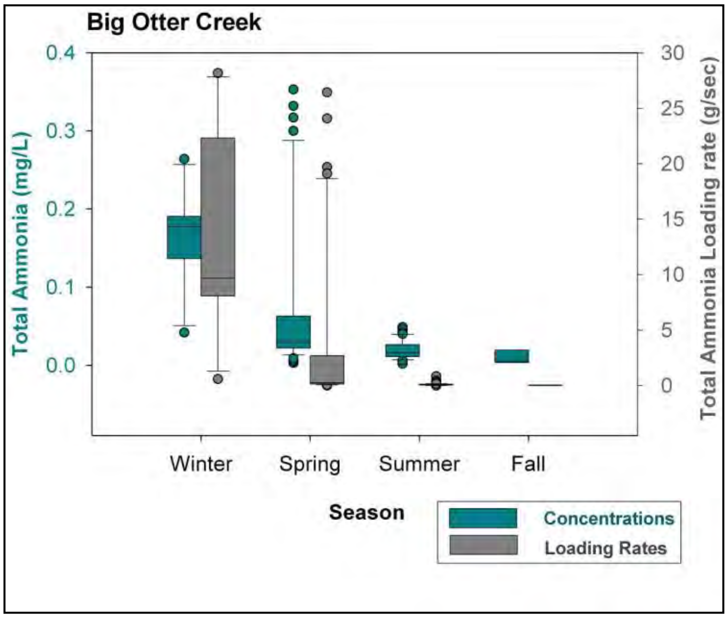
E 5Boxplots of all observed silicate concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Big Otter Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.



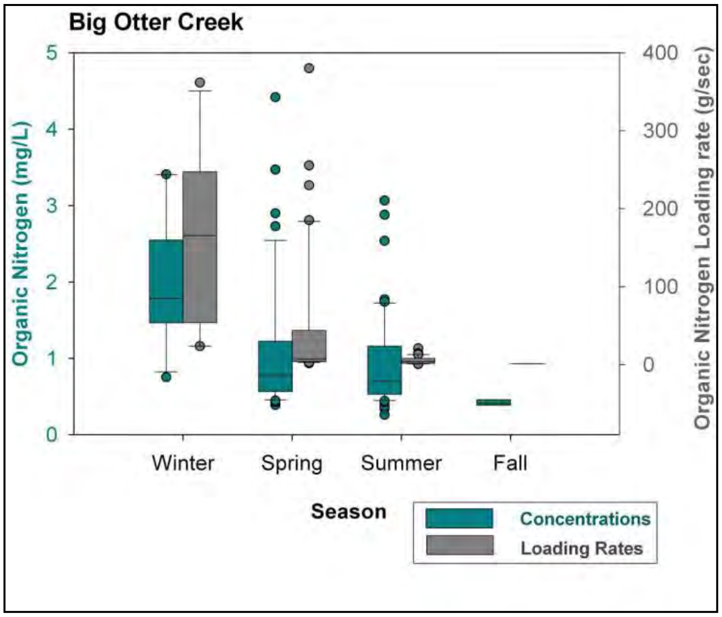
E 6. Boxplots of all observed suspended solids concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Big Otter Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.



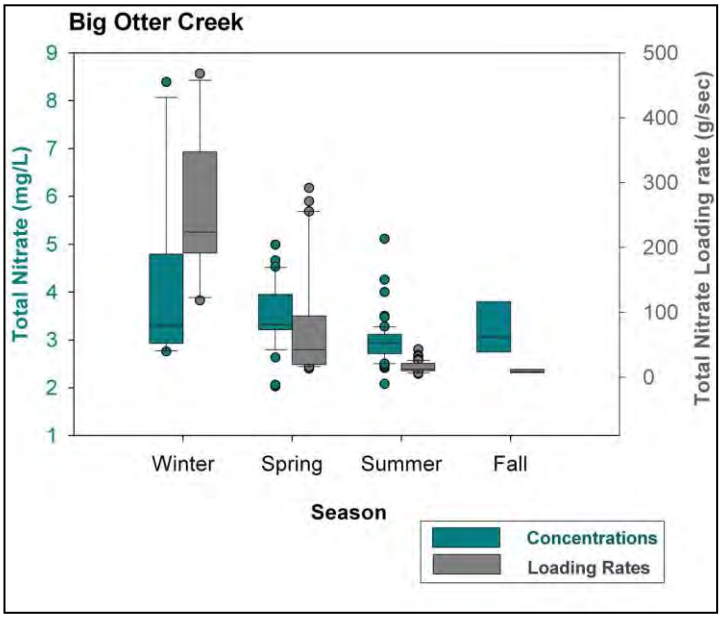
E 7. Boxplots of all observed total nitrogen concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Big Otter Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.



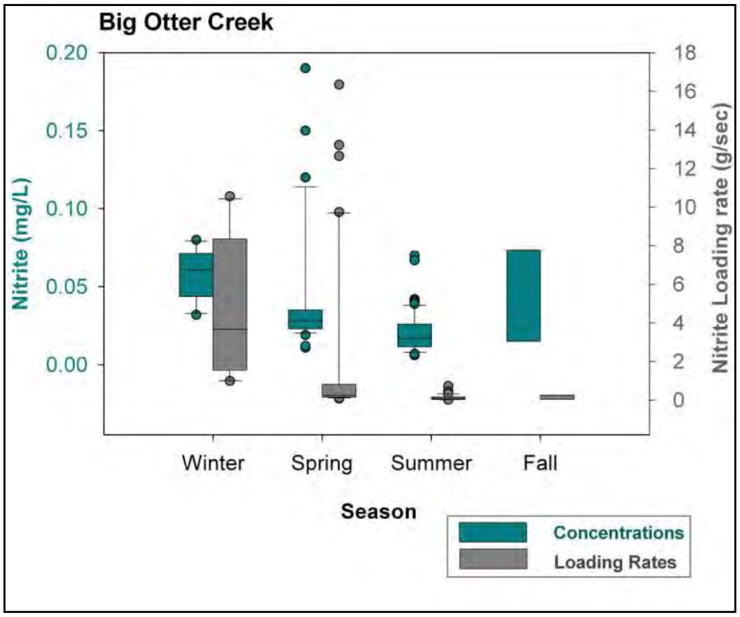
E 8. Boxplots of all observed total ammonia concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Big Otter Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.



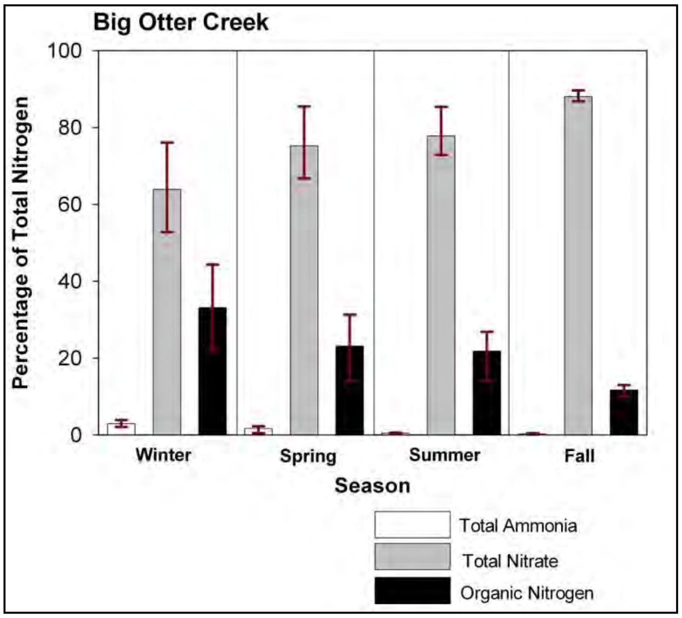
E 9. Boxplots of all observed organic nitrogen concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Big Otter Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.



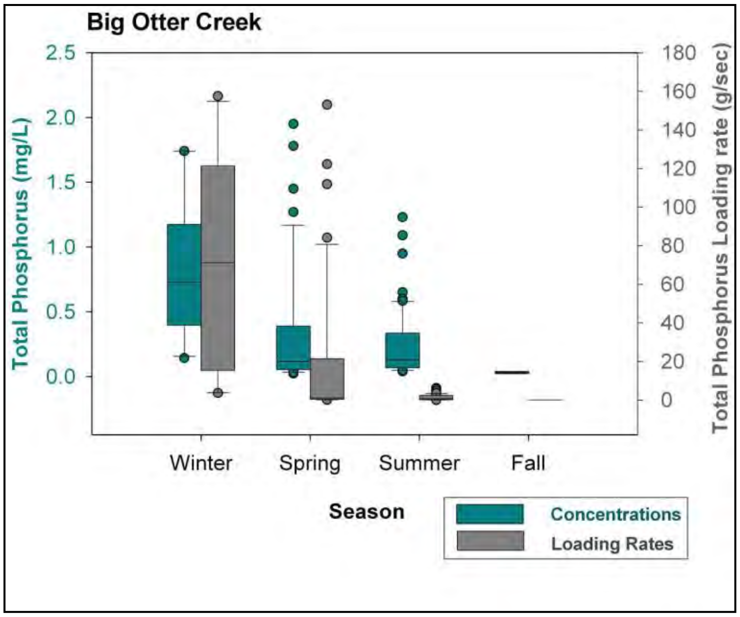
E 10. Boxplots of all observed total nitrate concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Big Otter Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.



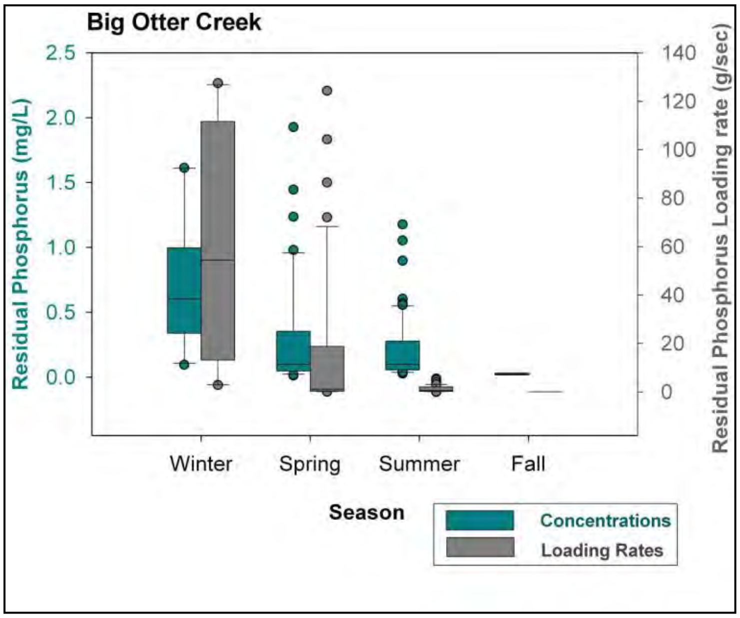
E 11. Boxplots of all observed nitrite concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Big Otter Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.



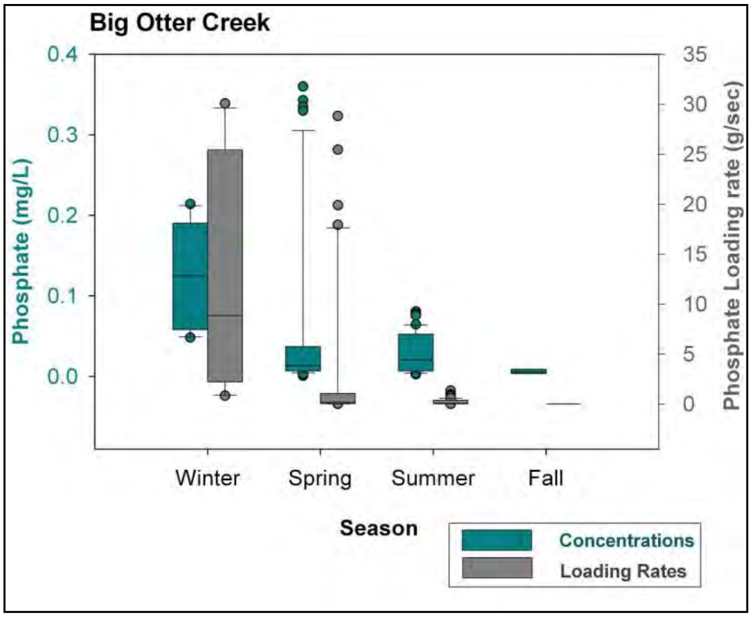
E 12. Bar graphs of the percentage of total ammonia, total nitrate, and organic nitrogen in total nitrogen values at the mouth of Big Otter Creek according to sample season (winter, spring, summer, fall) between 2007 and 2009. Error bars represent the 25th and the 75th percentile.



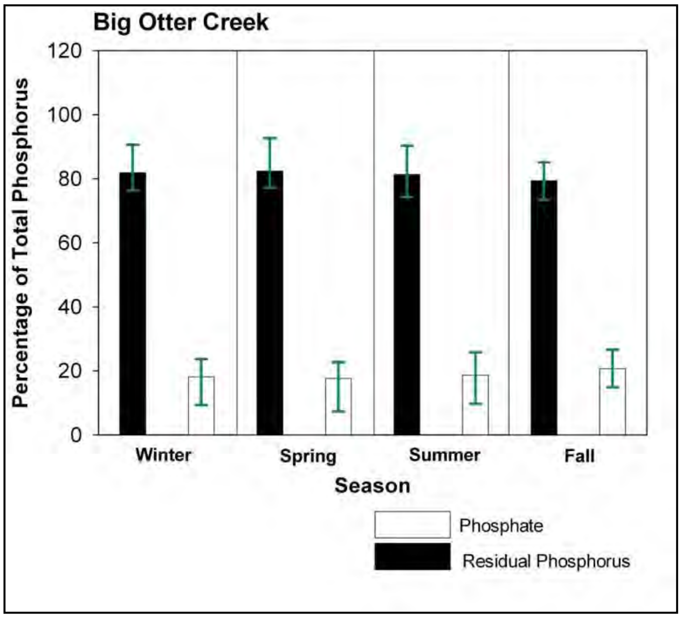
E 13. Boxplots of all observed total phosphorus concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Big Otter Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.



E 14. Boxplots of all observed residual phosphorus concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Big Otter Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.



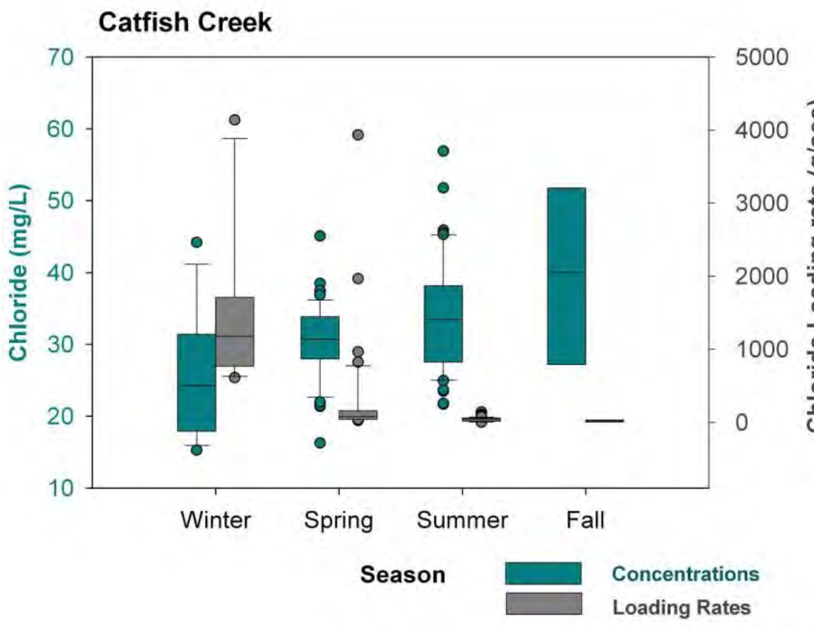
E 15. Boxplots of all observed phosphate concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Big Otter Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.



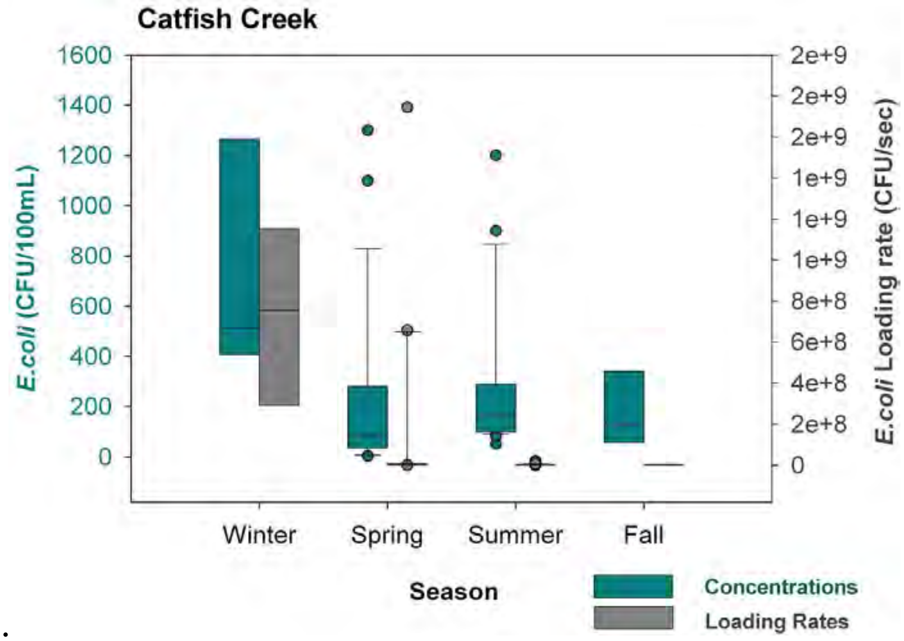
E 16. Bar graphs of the percentage of residual phosphorus and phosphate in total phosphorus values at the mouth of Big Otter Creek according to sample season (winter, spring, summer, fall) between 2007 and 2009. Error bars represent the 25th and 75th percent

Catfish Creek

Box and whisker plots for routine water quality parameters for Catfish Creek.



E 17. Boxplots of all observed chloride concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Catfish Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.



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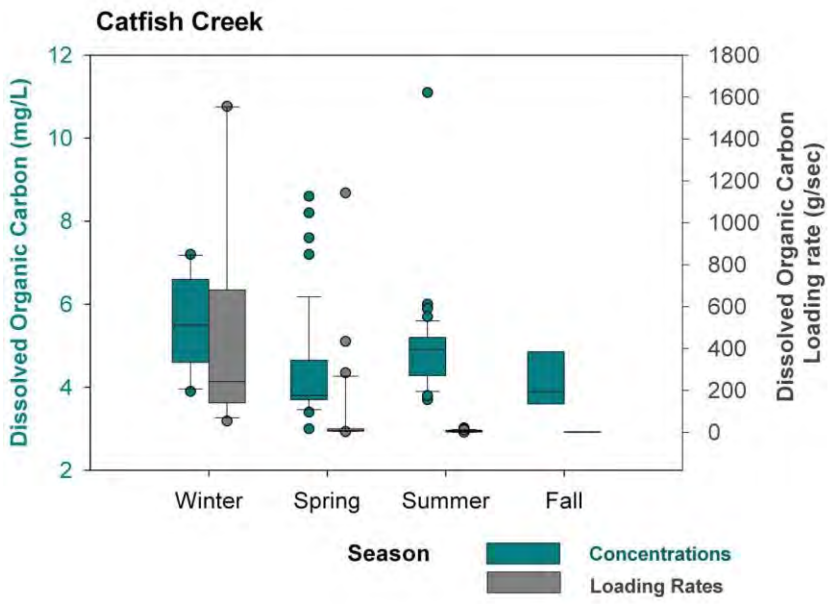
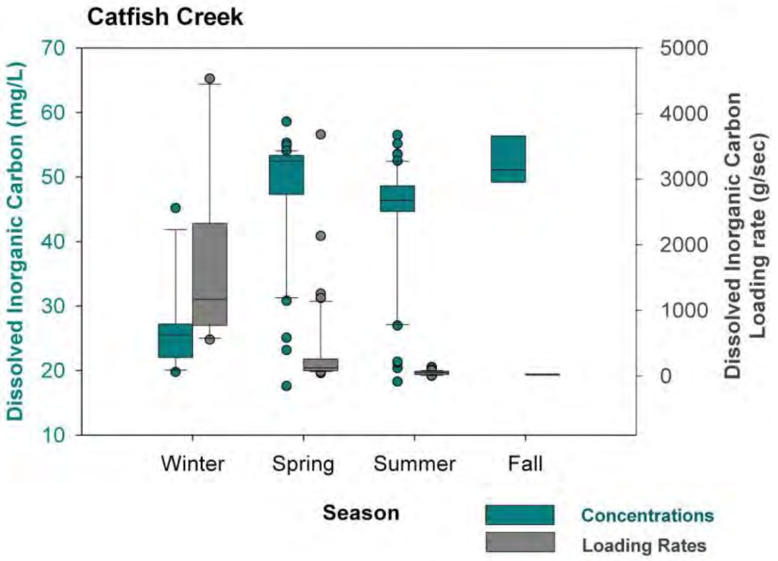
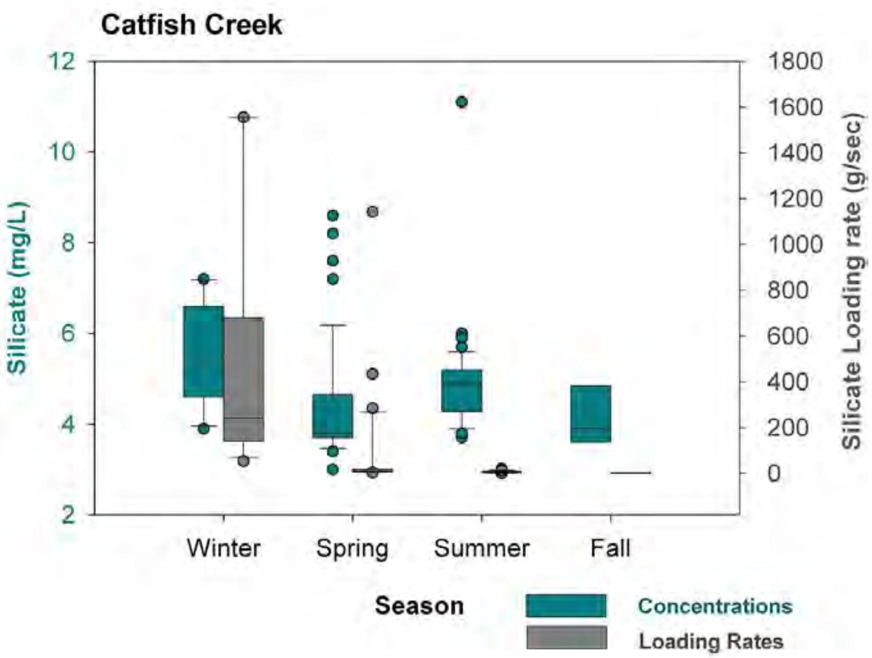
E 18. Boxplots of all observed E. coli concentrations (CFU/100ml; left axis) and loading rates (CFU/100ml/sec; right axis) at the mouth of Catfish Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.



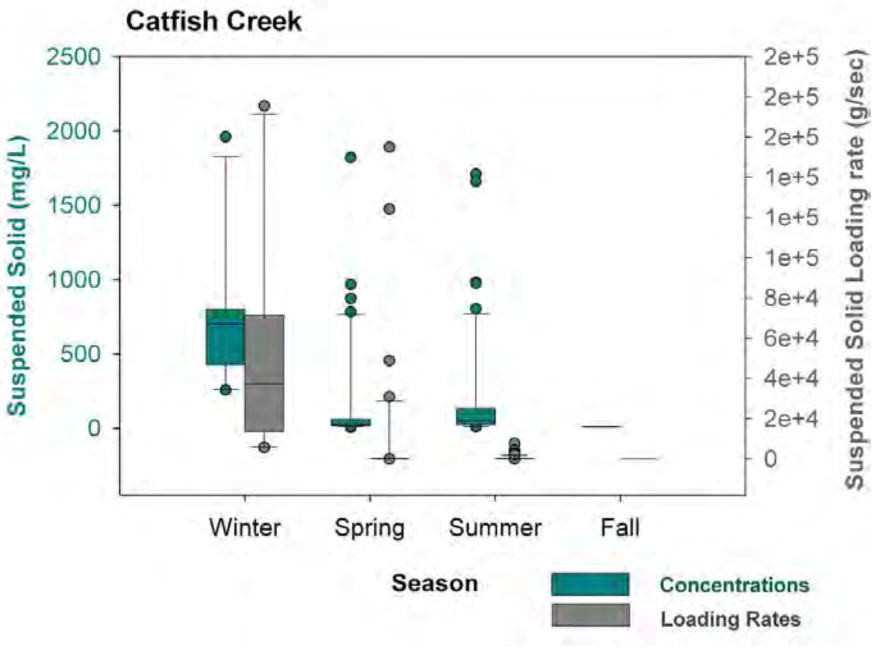
E 19. Boxplots of all observed dissolved organic carbon concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Catfish Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.



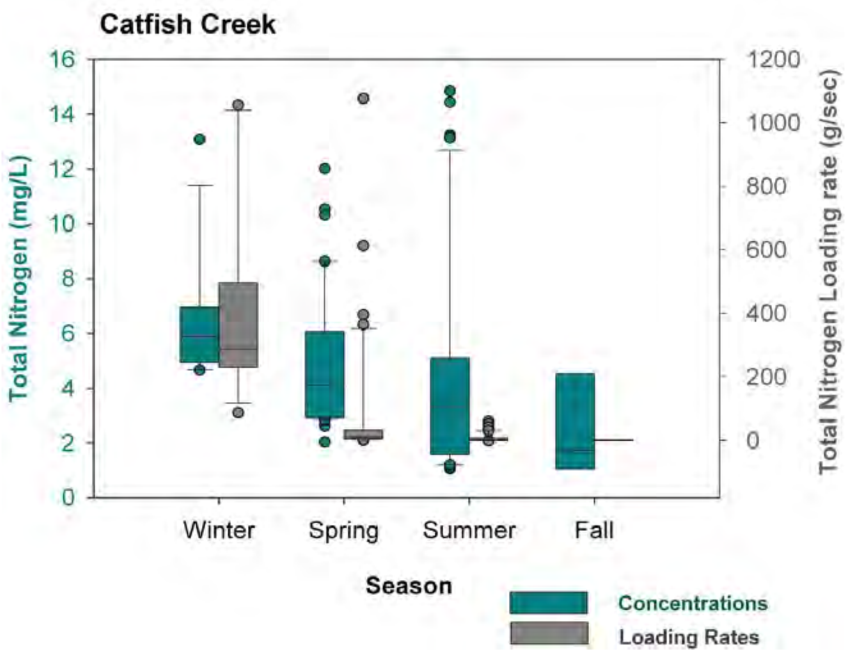
E 20. Boxplots of all observed dissolved inorganic carbon concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Catfish Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.



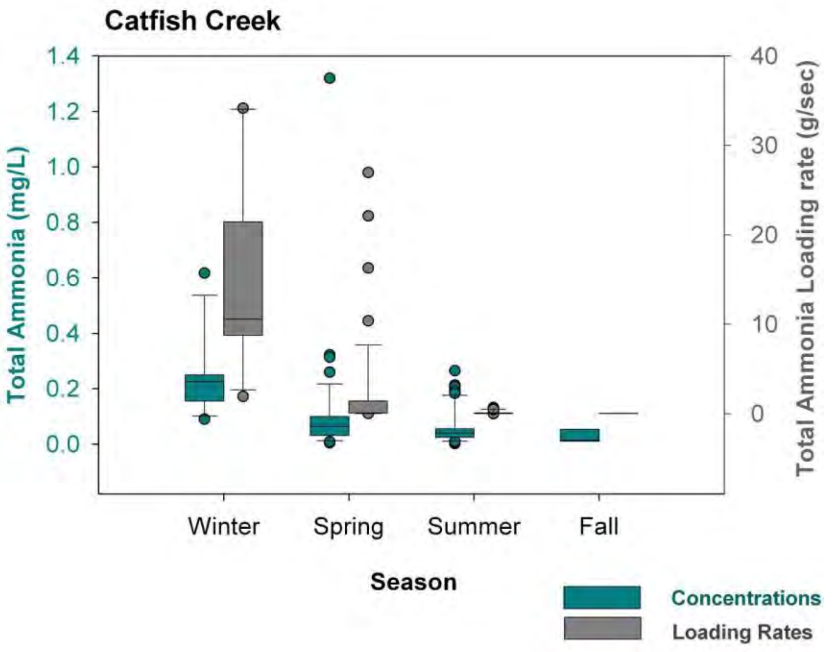
E 21. Boxplots of all observed silicate concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Catfish Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.



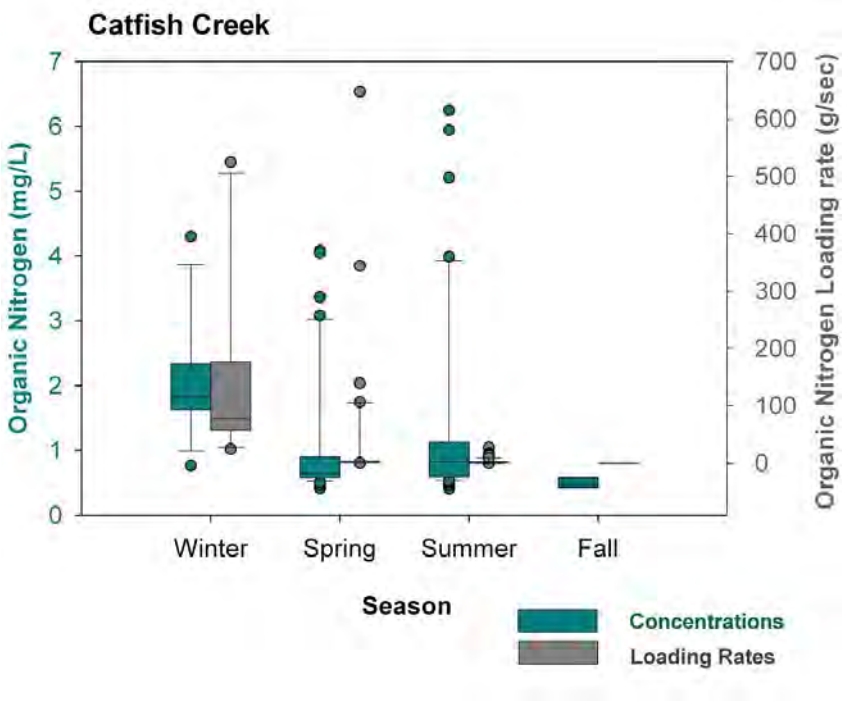
E 22. Boxplots of all observed suspended solids concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Catfish Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.



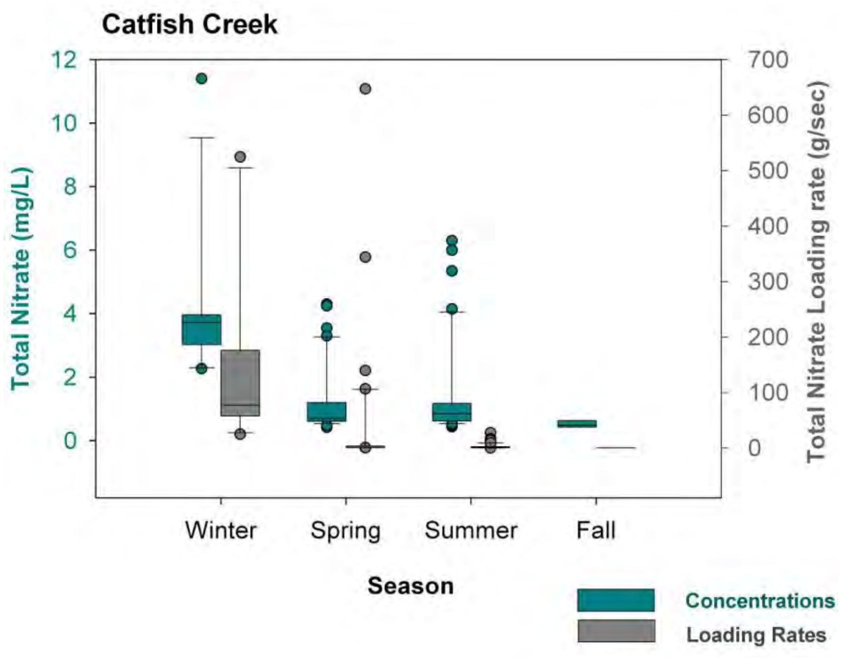
E 23. Boxplots of all observed total nitrogen concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Catfish Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.



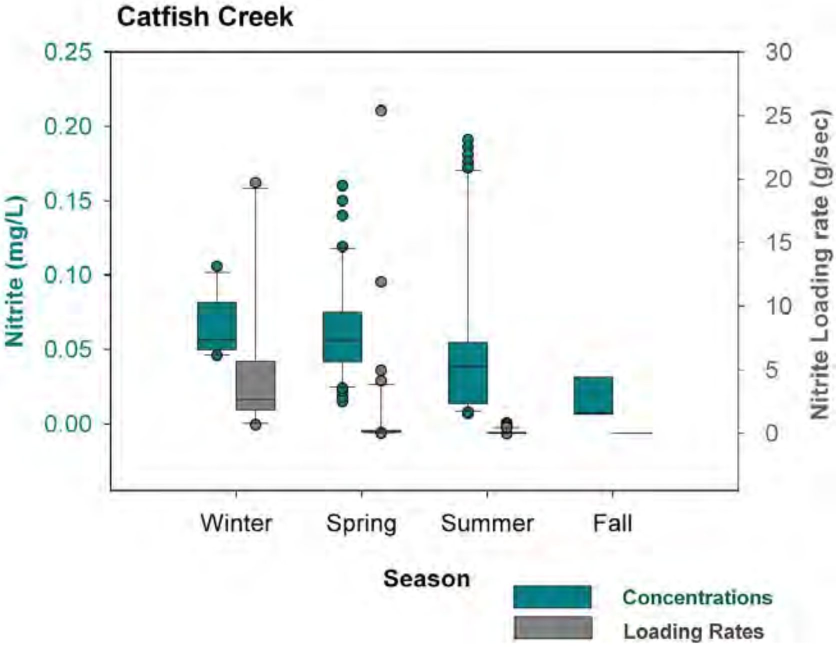
E 24. Boxplots of all observed total ammonia concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Catfish Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.



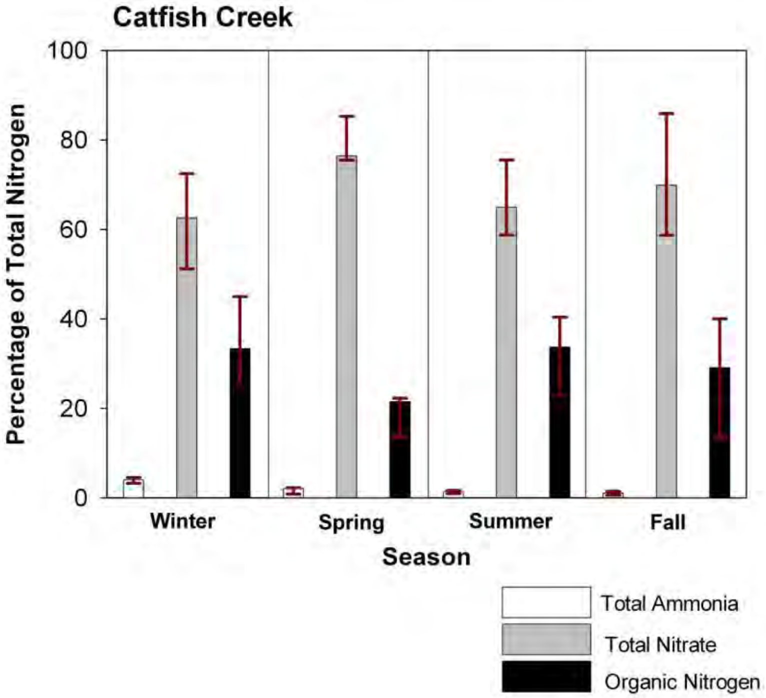
E 25. Boxplots of all observed organic nitrogen concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Catfish Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.



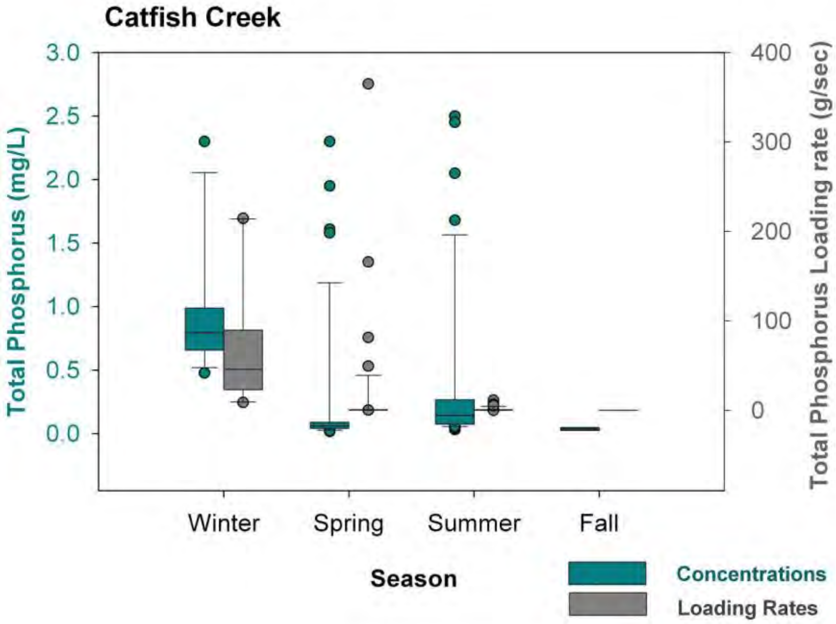
E 26. Boxplots of all observed total nitrate concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Catfish Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.



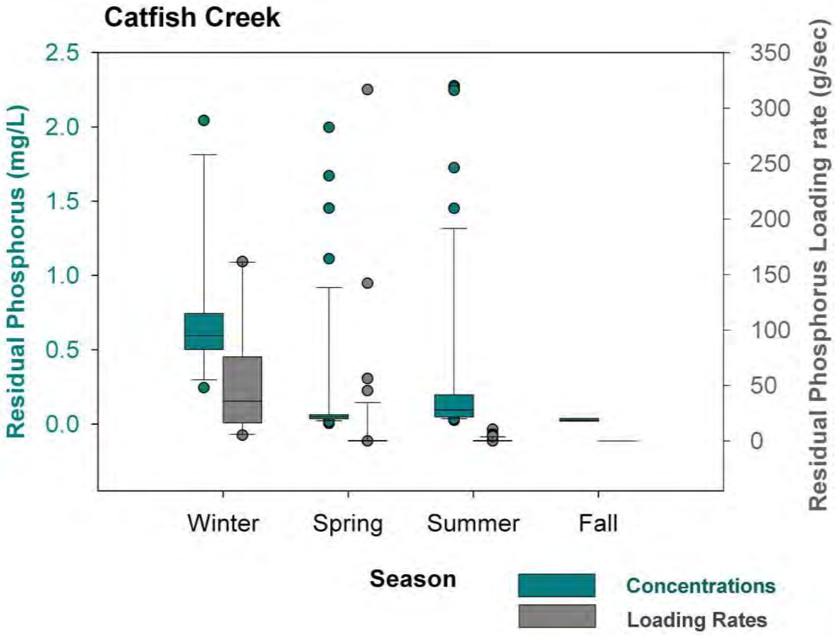
E 27. Boxplots of all observed nitrite concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Catfish Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.



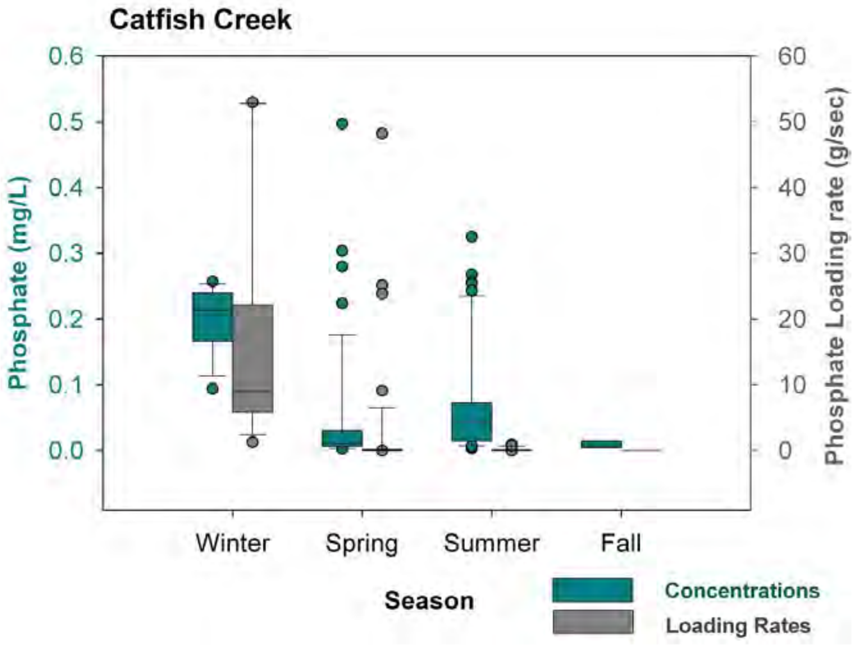
E 28. Bar graphs of the percentage of total ammonia, total nitrate, and organic nitrogen in total nitrogen values at the mouth of Catfish Creek according to sample season (winter, spring, summer, fall) between 2007 and 2009. Error bars represent the 25th and



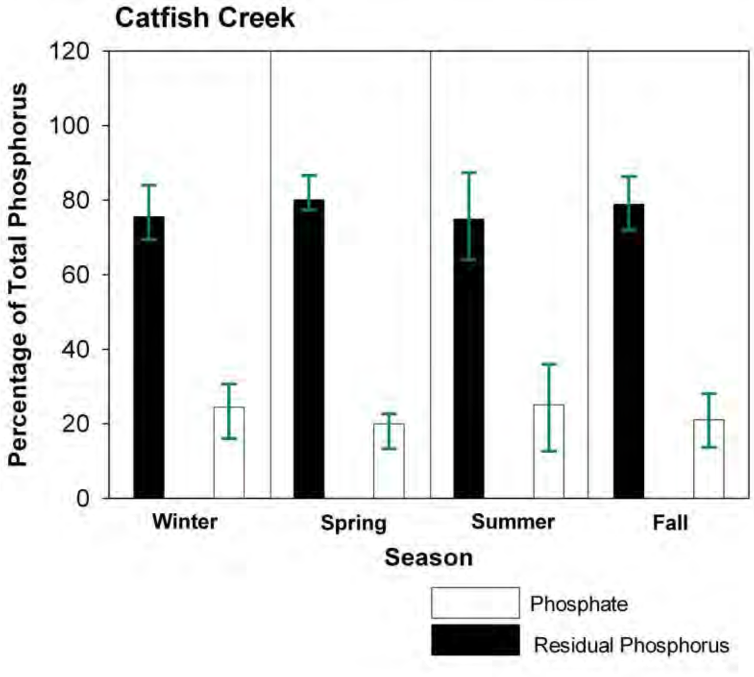
E 29. Boxplots of all observed total phosphorus concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Catfish Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.



E 30. Boxplots of all observed residual phosphorus concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Catfish Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.



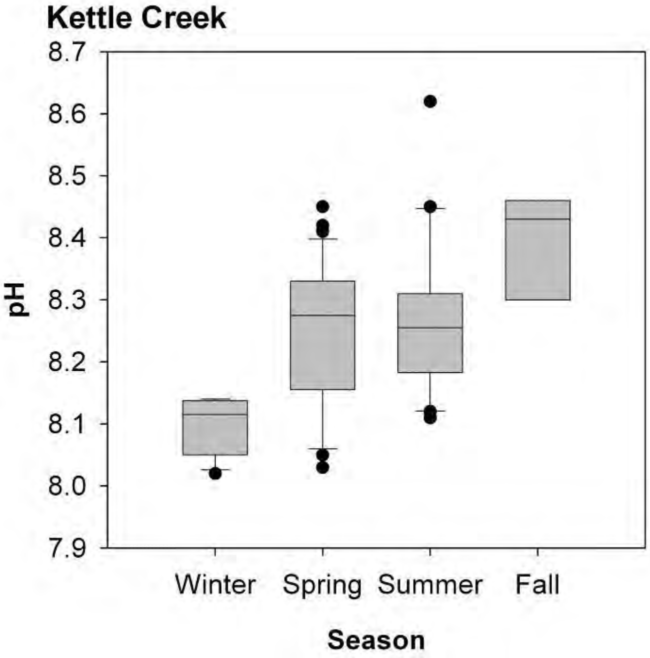
E 31. Boxplots of all observed phosphate concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Catfish Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.



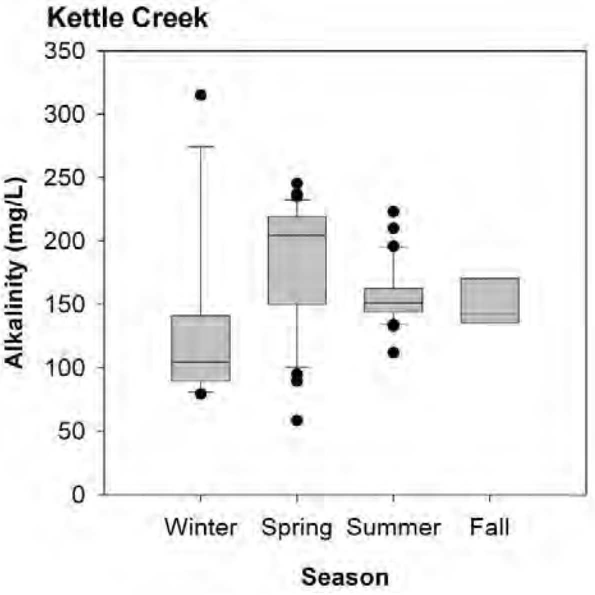
E 32. Bar graphs of the percentage of residual phosphorus and phosphate in total phosphorus values at the mouth of Catfish Creek according to sample season (winter, spring, summer, fall) between 2007 and 2009. Error bars represent the 25th and 75th percentile.

Kettle Creek

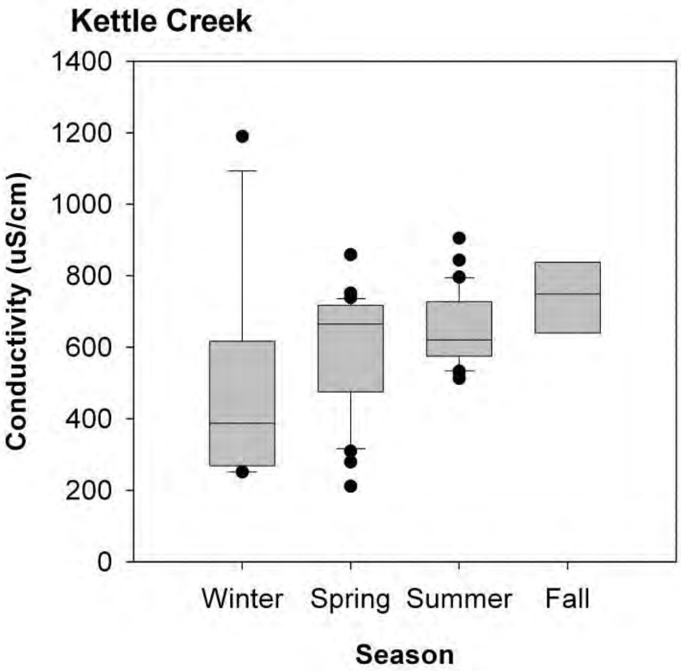
Box and whisker plots for routine water quality parameters for Kettle Creek



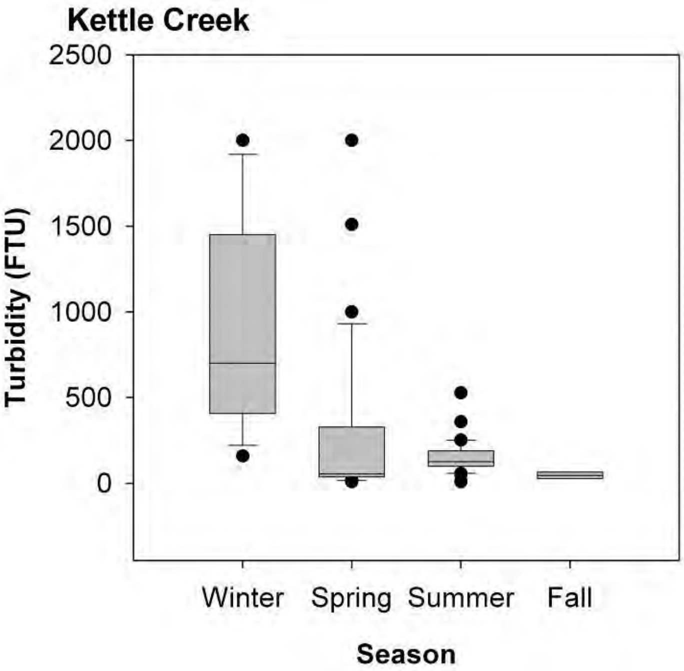
E 33. Boxplots of pH sampled between 2007 and 2009 plotted by season (winter, spring, summer, fall) at the mouth of Kettle Creek.



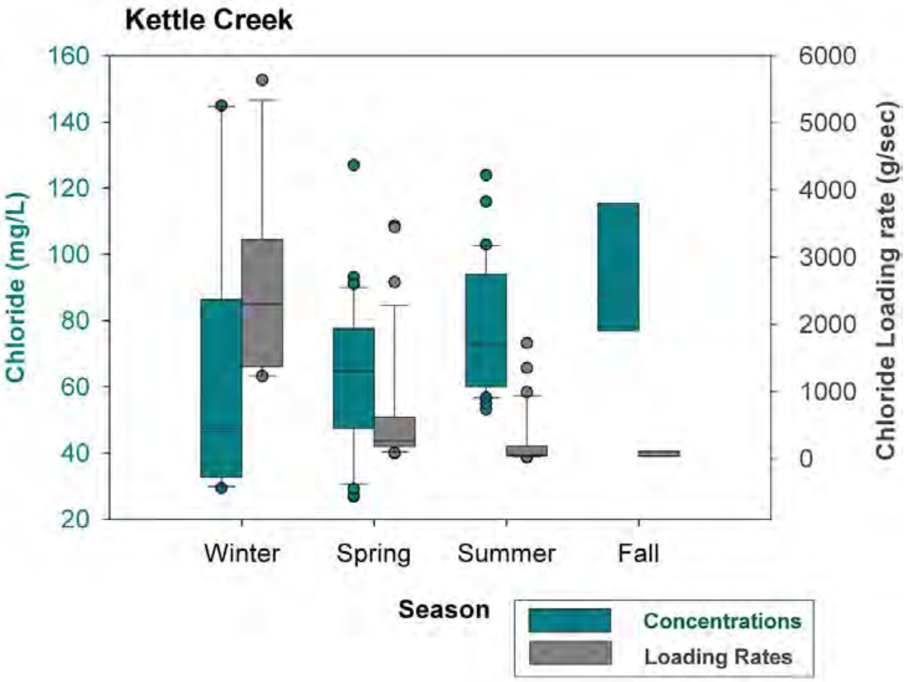
E 34. Boxplots of alkalinity (mg/L) sampled between 2007 and 2009 plotted by season (winter, spring, summer, fall) at the mouth of Kettle Creek.



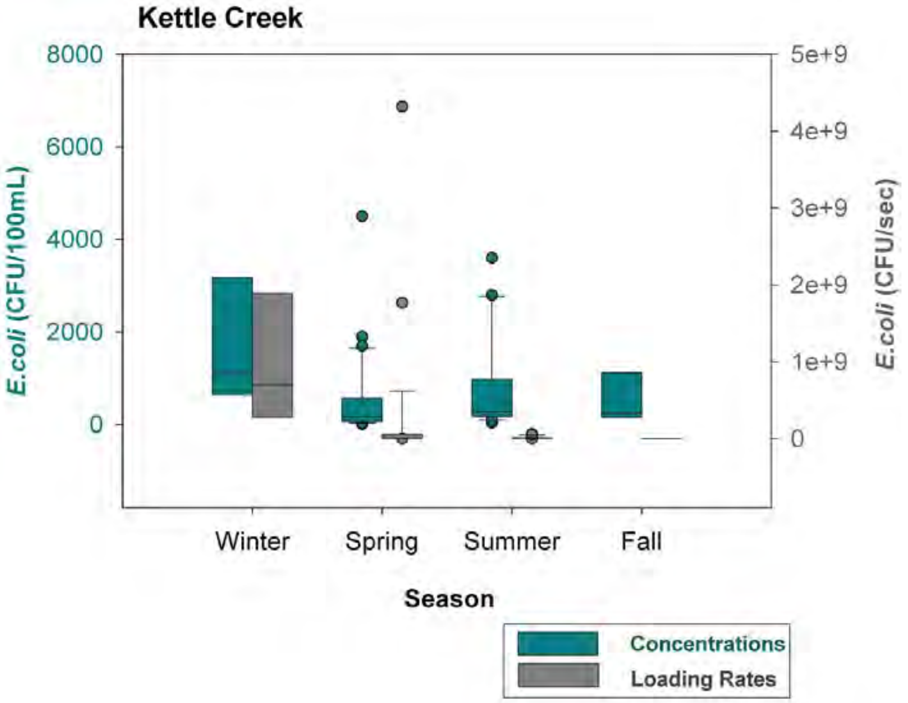
E 35. Boxplots of conductivity (µS/cm) sampled between 2007 and 2009 plotted by season (winter, spring, summer, fall) at the mouth of Kettle Creek.



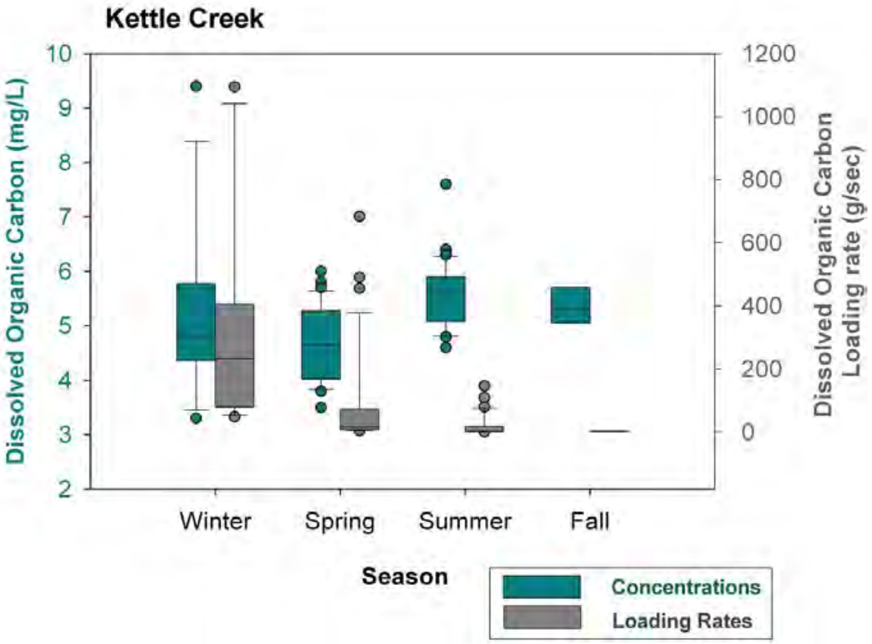
E 36. Boxplots of turbidity (FTU) sampled between 2007 and 2009 plotted by season (winter, spring, summer, fall) at the mouth of Kettle Creek.



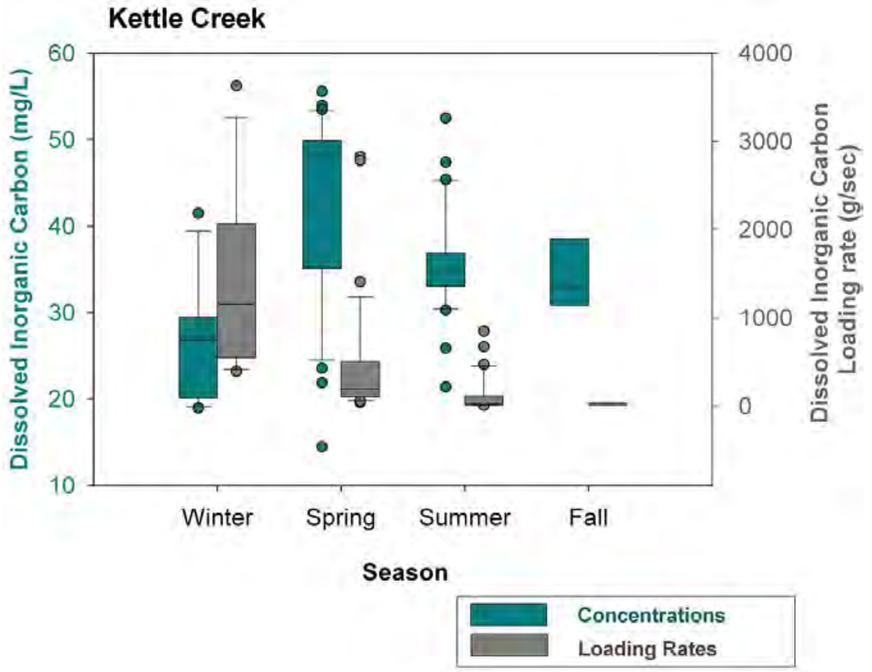
E 37. Boxplots of all observed chloride concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Kettle Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.



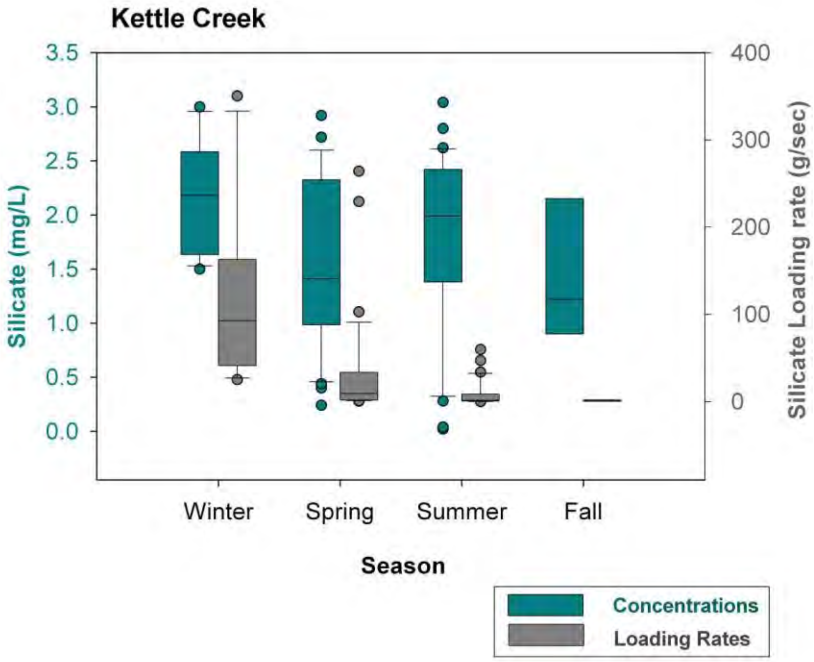
E 38. Boxplots of all observed E. coli (CFU/100ml) concentrations (CFU/100ml; left axis) and loading rates (CFU/100ml/sec; right axis) at the mouth of Kettle Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.



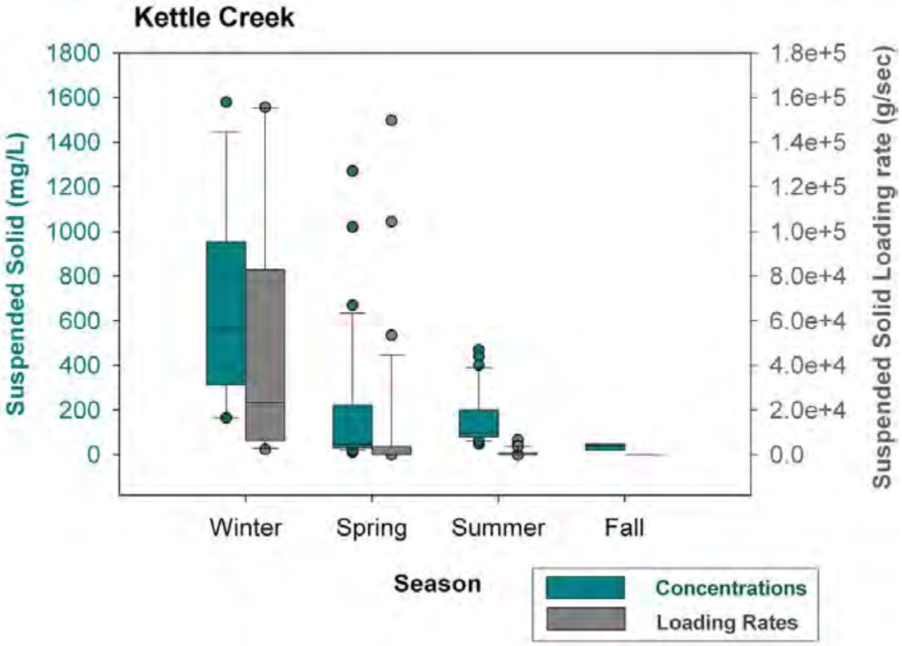
E 39. Boxplots of all observed dissolved organic carbon concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Kettle Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.



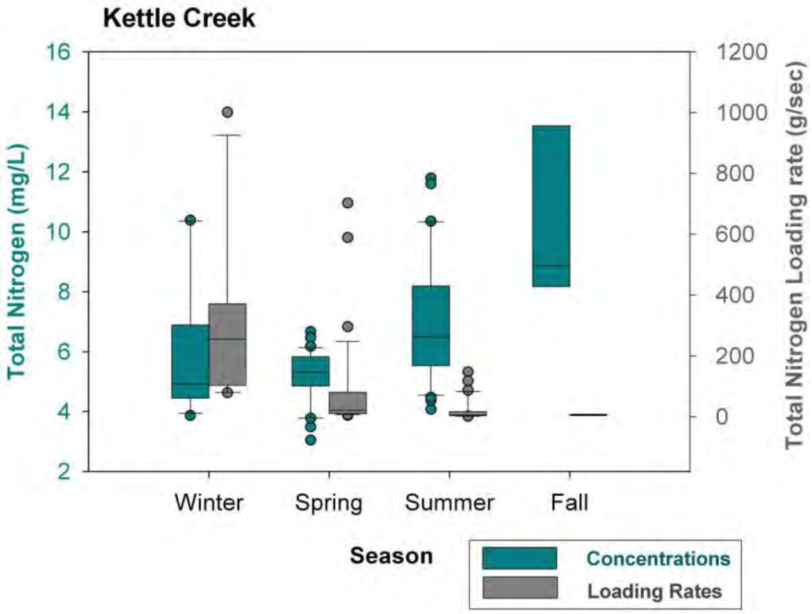
E 40. Boxplots of all observed dissolved inorganic carbon concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Kettle Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.



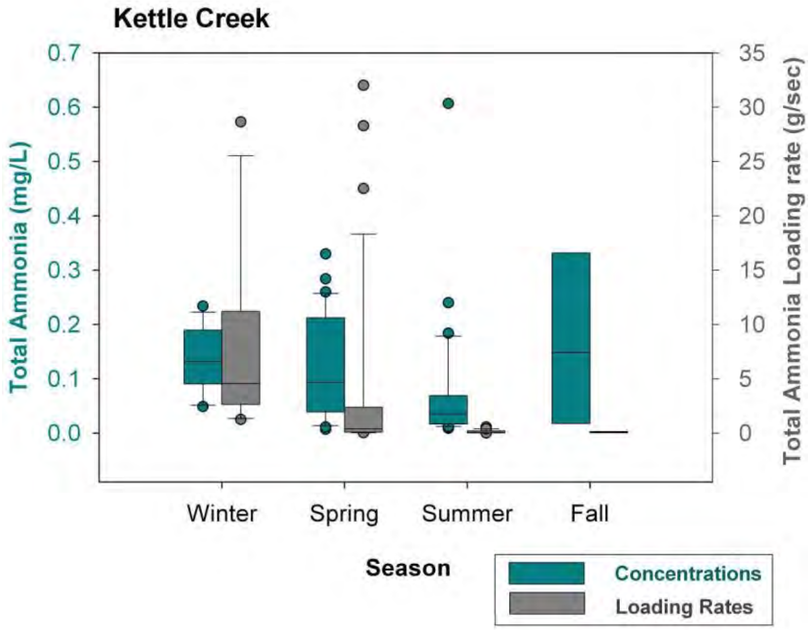
E 41. Boxplots of all observed silicate concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Kettle Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.



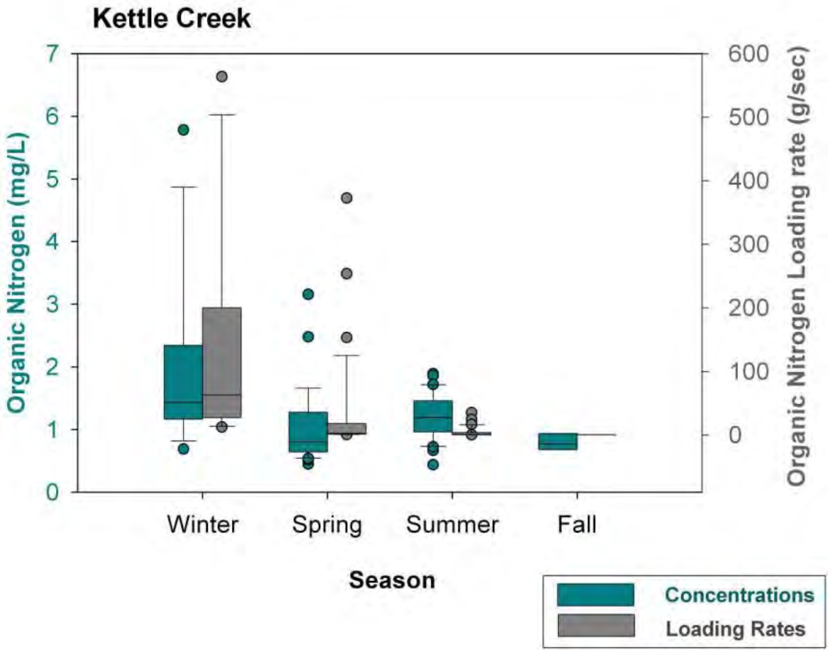
E 42. Boxplots of all observed suspended solids concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Kettle Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.



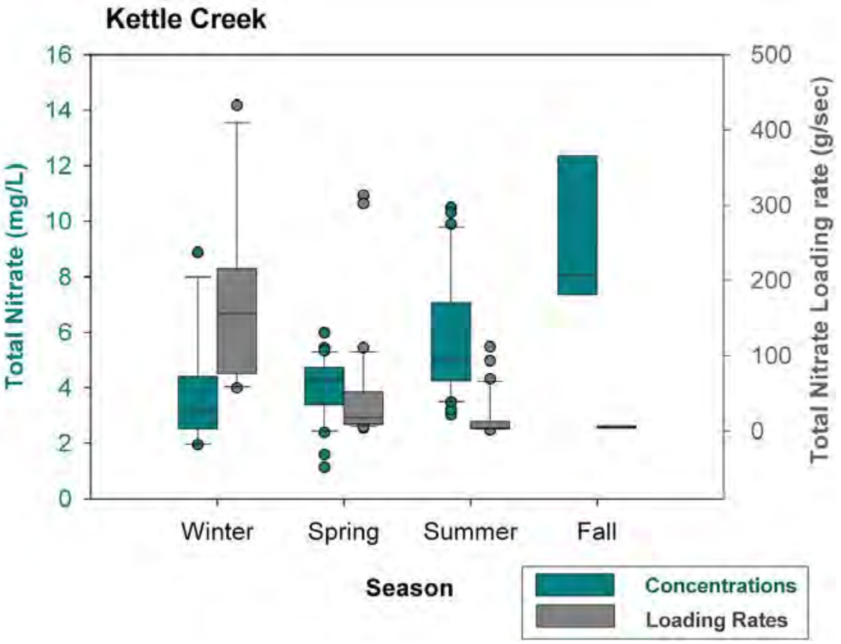
E 43. Boxplots of all observed total nitrogen concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Kettle Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.



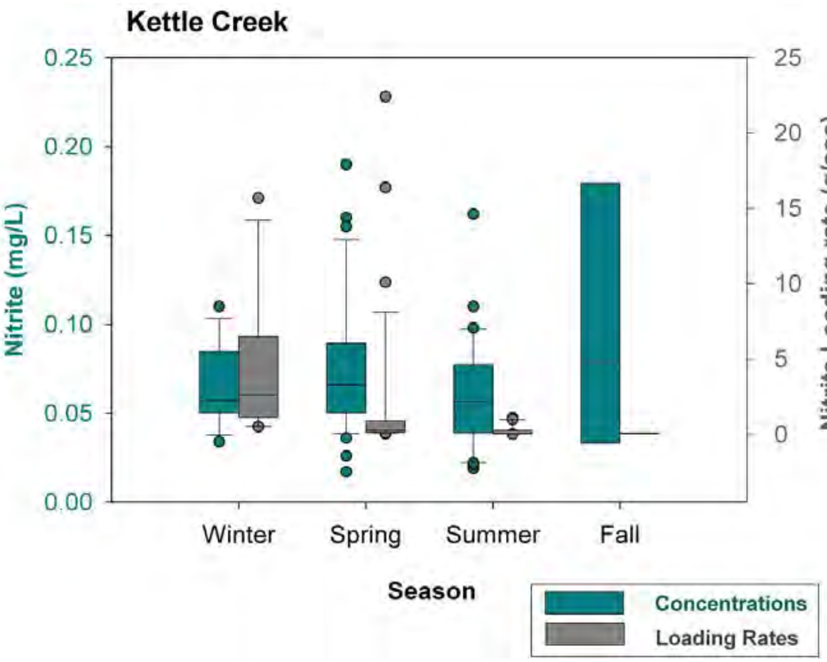
E 44. Boxplots of all observed total ammonia concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Kettle Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.



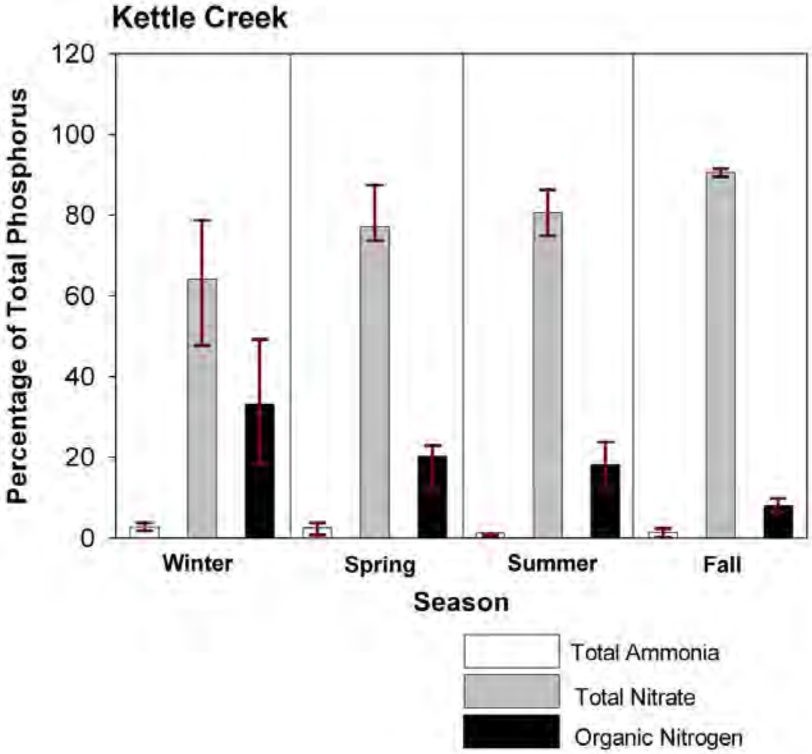
E 45. Boxplots of all observed organic nitrogen concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Kettle Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.



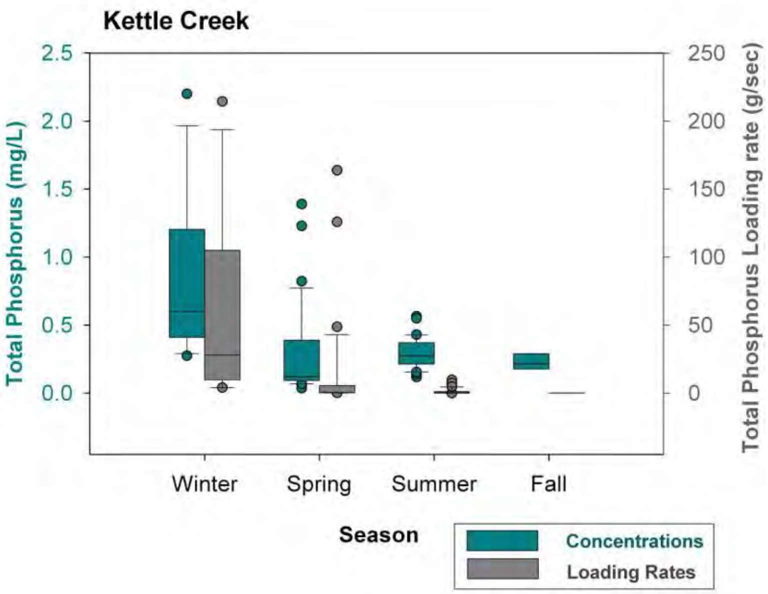
E 46. Boxplots of all observed total nitrate concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Kettle Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.



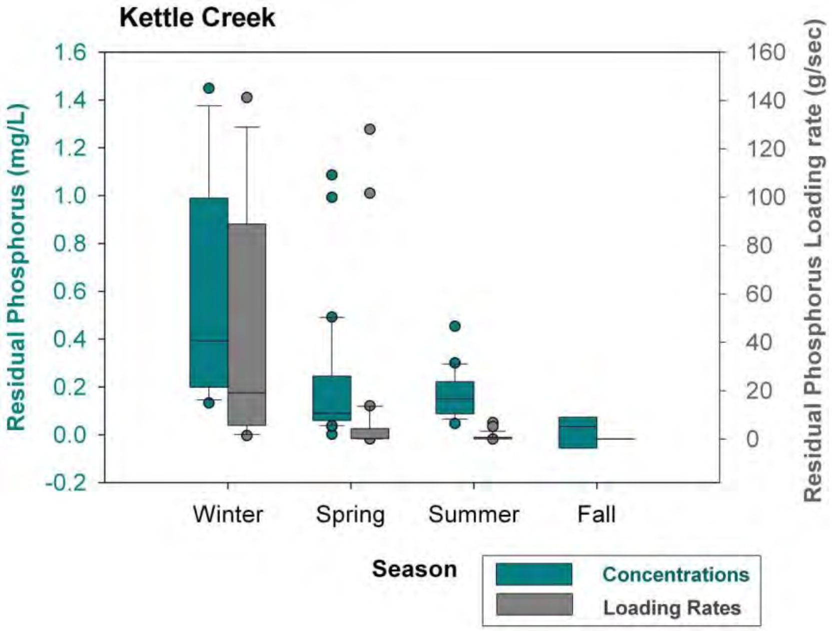
E 47. Boxplots of all observed nitrite concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Kettle Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.



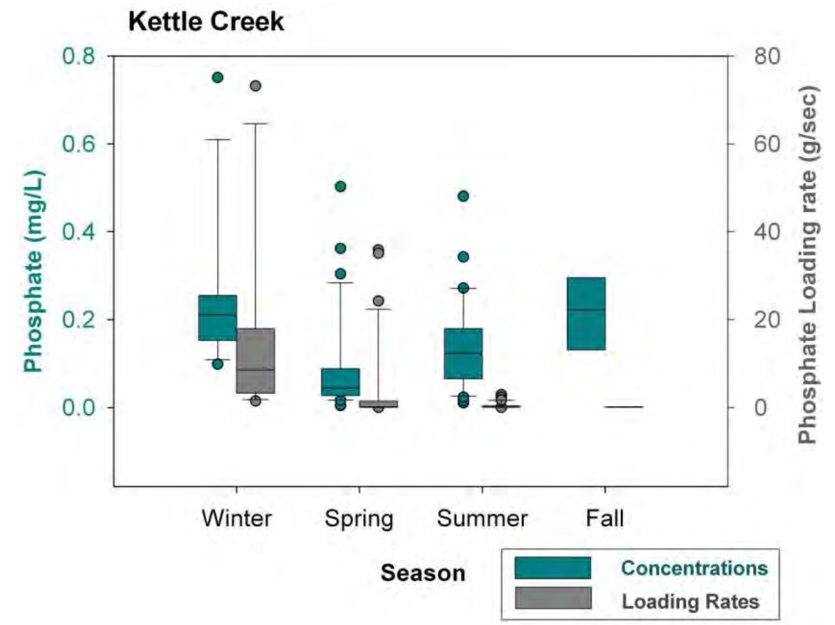
E 48. Bar graphs of the percentage of total ammonia, total nitrate, and organic nitrogen in total nitrogen values at the mouth of Kettle Creek according to sample season (winter, spring, summer, fall) between 2007 and 2009. Error bars represent the 25th and



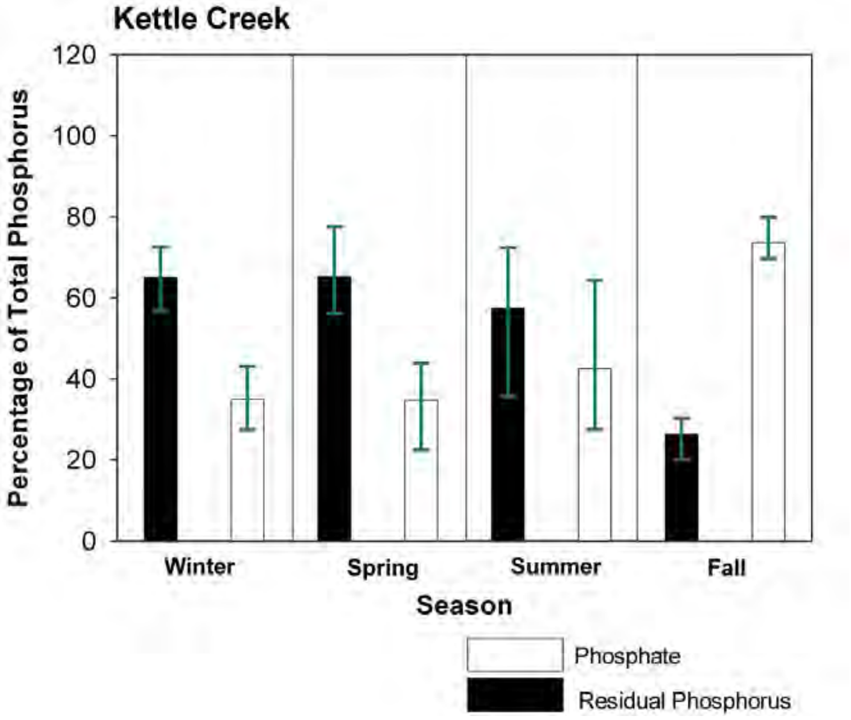
E 49. Boxplots of all observed total phosphorus concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Kettle Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.



E 50. Boxplots of all observed residual phosphorus concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Kettle Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.



E 51. Boxplots of all observed phosphate concentrations (mg/L; left axis) and loading rates (g/sec; right axis) at the mouth of Kettle Creek plotted by season (winter, spring, summer, fall) between 2007 and 2009.



E 52. Bar graphs of the percentage of residual phosphorus and phosphate in total phosphorus values at the mouth of Kettle Creek according to sample season (winter, spring, summer, fall) between 2007 and 2009. Error bars represent the 25th and 75th percentile.