Healthy Lake Huron – Clean Water, Clean Beaches

Southeastern Lake Huron Tributary Water Quality Synthesis and Modelling (October 2010 to September 2016)

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Executive Summary

Nutrient, sediment, and bacterial impacts have increasingly limited both the human uses and the ecological integrity of the near-shore waters of the Great Lakes. A multi-stakeholder program known as the Healthy Lake Huron – Clean Waters, Clean Beaches Initiative is coordinating efforts to ensure that beaches and near-shore areas along the southeast shore have improved water quality. Currently the stakeholders are working locally to support the implementation of watershed management plans through rural best management practices (BMPs) in five key watersheds. As improved water quality is a goal of the Healthy Lake Huron Initiative, this study has provided detailed synthesis for water quality information from October 2010 to September 2016.

Typically concentrations of nutrients (nitrate-N and total phosphorus) in the five priority watersheds exceeded standards established to prevent eutrophication; however, some improvements were identified during the study period. A significant reduction in total phosphorus concentrations was observed in Gully Creek, while nitrate-N concentrations declined significantly in Trick's Creek and Gully Creek. Additionally, sediment concentrations decreased substantially in South Pine River, Garvey Creek/Glenn Drain, and Gully Creek.

Trends in pollutant loads appeared to be largely driven by changes in total flow volume between years. All Lake Huron watersheds in the study revealed moderate to strong relationships between monthly loads and total flow volume. Not surprisingly, the largest percentage of pollutant loads was transported during the spring freshet in March and April, while the lowest percentage of loads occurred during the dry summer months.

Accurate estimates of pollutant loads are required to evaluate trends in water quality. Numerous studies have reported that infrequent sampling and type of load calculation method can yield large uncertainties in the estimation of nutrient and sediment loads. A number of different approaches to calculating pollutant loads were evaluated for their accuracy and precision of the estimate compared to reference ("true") loads. From our analysis, the linear interpolation method in Water Quality Analyser was best suited to calculate loads in the priority watersheds.

Table of Contents

List of Figures

List of Tables

Project Background

The nearshore area of the Great Lakes provides many residents of Ontario with drinking water and recreational opportunities. However, nutrient, sediment, and bacterial impacts have increasingly limited both the human uses and the ecological integrity of these nearshore waters (Smith *et al.* 2015). For example, in 1977, algae were observed as a thin coating at relatively few beaches along the southeast shore of Lake Huron. By 2007, almost all rocky portions of the lake-bed at these same sites were covered by algae (Barton *et al.* 2013). Large and localized accumulations of algae have been washing up on shore and causing odor problems from decaying algal mats.

The Great Lakes Water Quality Agreement (2012) Lakewide Annex states that Canada and the United States will assemble, assess, and report on existing scientific information concerning the state of the waters of each Great Lake including current and future potential threats to water quality. Further, the Canada-Ontario Agreement Respecting the Great Lakes commits agencies to improve the knowledge and understanding of nutrient concentrations and loads in Great Lakes tributary discharges.

A multi-stakeholder program known as the Healthy Lake Huron – Clean Waters, Clean Beaches Initiative is coordinating efforts to ensure that beaches and nearshore areas along the southeast shore are safe and clean. Currently, partners are coordinating actions to implement agricultural best management practices that are aimed at lowering the amount of phosphorus entering Lake Huron in five key watersheds (Figure 1). Monitoring of water quality in the priority watersheds is being coordinated by four conservation authorities (conservation authority name is in parentheses):

- Pine River sub-watershed – South Pine River (Saugeen Valley Conservation Authority);
- North Shore sub-watershed – Garvey Creek/Glenn Drain (Maitland Valley Conservation Authority);
- Bayfield North sub-watershed – Gully Creek (Ausable Bayfield Conservation Authority);
- Main Bayfield watershed – Trick's Creek and Bayfield River (Ausable Bayfield Conservation Authority); and
- Lambton Shores tributaries in Lambton County – Shashawandah Creek (St. Clair Region Conservation Authority).

Report Objectives and Format

This report summarizes the different approaches to evaluating water quality data collected from the priority watersheds along the southeast shore of Lake Huron. The objectives of the project were to:

1) assemble water quality data (total suspended solids, total phosphorus, phosphate-phosphorus, and nitrate-nitrogen concentrations) in each of the five priority watersheds for the period October 2010 to September 2016;
2) analyze data from well-sampled data sets to determine the best method of calculating loads for streams where fewer samples are obtained (*i.e.,* <100 samples per year);
3) calculate seasonal and annual loads for the five priority streams (2010-2016) and the Bayfield River (2014-2016) with the preferred water quality method to spatially and temporally compare loadings; and
4) evaluate the relationship between flow volume and load to see how it impacts our understanding of BMP effectiveness over time.

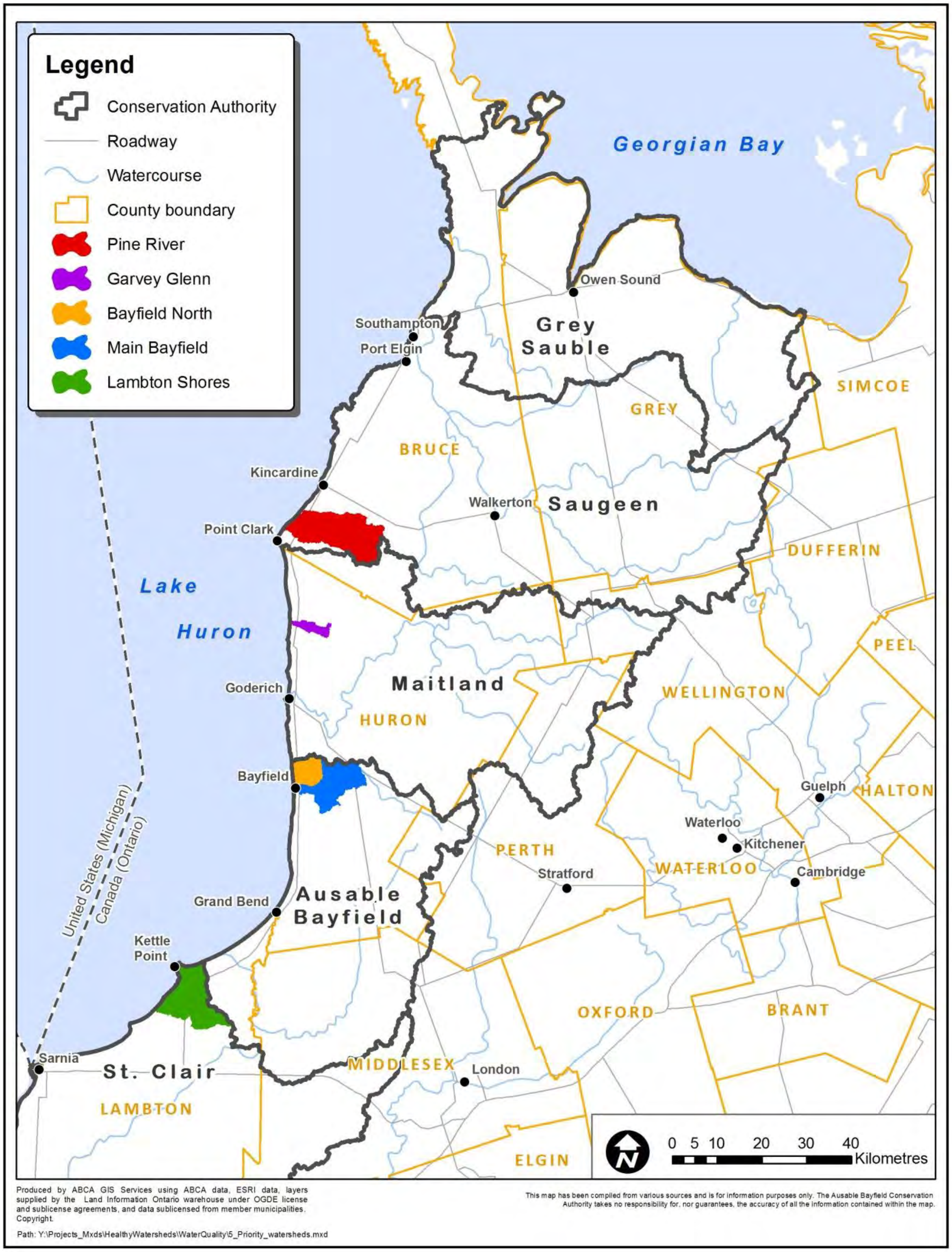

Figure 1: Location of the five priority watersheds in the Healthy Lake Huron – Clean Waters, Clean Beaches Initiative.

To address these project objectives, the remainder of the report is organized into three sections:

1) Methods;
2) Results and Discussion, including:
    a. A comparison of various load estimation algorithms and sampling strategies;
    b. An analysis of spatial and temporal patterns in water quantity and quality indicators; and
3) General conclusions and next steps.

Another report was prepared concurrently and provides output from a process-based hydrologic model for placement and prioritization of agricultural best management practices along the southeastern shore of Lake Huron. The report also identifies other Lake Huron tributaries where water quantity and some water quality data exist.

Methods

Site Selection

The priority Lake Huron watersheds are typically small, except for the Bayfield River watershed, and mostly drain agricultural landscapes (Table 1). A more complete description of the watersheds can be found in other reports (Emmons & Olivier Resources, Inc. *et al.* 2014, LaPorte *et al.* 2012, King *et al.* 2014, Brock *et al.* 2010, Schnaithmann *et al.* 2013, Van Zwol *et al.* 2012). Water quality monitoring stations were selected to be as far downstream as possible in the watershed, but remaining outside of the lake-effect zone. Stations were co-located with reliable flow gauging stations so that water quality results could be combined with stream discharge measurements for the computation of loads (see Appendix A for maps of the study watersheds and sites).

Table 1: Watershed size and land use (based on 2013 cropping year) upstream of sampling location in each study sub-watershed.

Sub-watershed	Size (ha)	Corn (%)	Soya Beans (%)[A]	Winter Wheat (%)	Other Crops (%)[B]	Hay/ Pasture (%)	Natural/ Roughland (%)[C]	Other (%)[D]
South Pine River	2,788	24.1	23.3	13.5	11.6	10.5	14.0	3.0
Garvey Creek/Glenn Drain	1,286	28.0	39.3	10.7	4.7	2.2	11.4	3.7
Gully Creek	1,040	20.7	31.4	19.0	0.0	3.7	20.7	4.4
Trick's Creek	2,116	24.4	21.5	9.5	0.8	7.9	16.9	19.1
Shashawandah Creek	2,681	20.2	31.5	18.9	8.6	4.9	11.9	4.0
Bayfield River	46,305	-	-	-	-	-	-	-

[A] Includes soya and edible beans.

[B] Includes agricultural fields where the crop type was listed as unknown or was another crop including spring cereals, canola, and vegetables.

[C] Includes riparian corridors, ditches, scrub land, woodlands and wetlands.

[D] Includes urban land, roads, pits, farmsteads, farm access roads, and ponds.

- Data not available for this report

Water Quantity Monitoring

Water level (also referred to as water stage) data were collected every five minutes at all stream gauges except for the Varna and Pine River stream gauge, which collected data hourly and every fifteen minutes, respectively. A WaterLOG H-3553 Compact Combo Bubbler System was used to measure water stage, with a twelve-volt, 100-amp-hour valve-regulated lead acid battery and solar panel providing power, and an FTS Axiom H2 Datalogger logging and transmitting data through a Geostationary Operational Environmental Satellite (GOES) antenna. This continuous record of stage was translated to stream discharge by applying a stage-discharge relationship (also called a rating curve). A stage-discharge relationship was developed for each stream gauge by measuring the flow of the stream with a flow meter (Marsh-McBirney Flo-Mate™ Model 2000). For each measurement of discharge there is a corresponding measurement of stage. High and low stages and flows are particularly important for the development of the rating curve; however, it was unsafe to obtain manual measurements of flow in the streams when they were in peak-flow conditions. Instead, a theoretical equation related to the shape, size, slope, and roughness of the channel at the stream gauge was used to iteratively determine the stage-discharge relationship at higher stages and flows. This relationship differs between stream gauging stations and can also change over time at a specific station. More details on the water quantity monitoring methods can be found in Upsdell Wright *et al.* 2015a.

Water Quality Monitoring

Many water quality monitoring programs involve a random sampling strategy, whereby samples are collected on pre-determined days of the month. However, rain, rain-on-snow, and snowmelt events (herein referred to as events) are important because high concentrations of some pollutants, particularly sediment and phosphorus, are transported during these events (Upsdell Wright and Veliz 2013). The monitoring and modelling results in the Watershed Based Best Management Practices Evaluation study found that intermittent channels that form across the land contribute to poor water quality during storm events (Simmons *et al.* 2013). Further, practices to address rural water quality nutrient enrichment issues are undertaken to reduce the formation and/or the effects of these intermittent channels on the landscape. To understand the effectiveness of watershed plans and rural best management practices (BMPs) on water quality, it is imperative to collect *event data* prior to and after the establishment of the watershed plans and BMPs. Therefore, water quality monitoring for this study included sample collection when water was running across the landscape in order to improve the accuracy of pollutant load estimates.

For the purposes of this study, water samples were collected year-round under both low-flow and high-flow conditions. Richards (1998) has shown that the 80th percentile of flow is an appropriate division for separating runoff events from low-flow periods for Lake Erie tributaries in Northwest Ohio. This study used the same approach. Continuous flow data from October 2010 to September 2016 were used to establish the low-flow conditions. A threshold was set at the 80th percentile of the continuous flow record for each of the sites to separate low flow from event flow. Low-flow grab samples were collected monthly between October 1, 2010, and September 30, 2016. High-flow events were sampled with an ISCO® 6712 automated sampler at each of the six stations. The ISCO samplers were set to trigger with a rise in water level and to collect samples throughout the hydrograph, attempting to capture samples at the onset of the event, mid-way up the rising limb of the hydrograph, at the peak, mid-way down the falling limb, and at the end of the event.

Water samples were primarily analyzed for nutrients and suspended solids by the Ministry of the Environment and Climate Change (MOECC) laboratory in Etobicoke; however, on occasion, samples were submitted for analysis to ALS Laboratory in Waterloo. There are different analytical approaches to estimating the bioavailable forms of phosphorus. In this study, phosphate-phosphorus was measured.

Approximately 2300 tributary water quality samples were collected between October 1, 2012, and September 30, 2016. An additional 245 water quality samples were collected in Gully Creek between October 1, 2010, and September 30, 2012.

In the study period (2010 to 2016), all of the watersheds had at least 50 events (Table 2). Gully Creek had 137 events during a six-year period, whereas only 50 events were documented at Bayfield River over three years. Not all events were sampled. Some events were missed due to decisions made *a priori* about the size of the event, equipment malfunctions, and staffing issues (*i.e.,* holidays and other work priorities). A more detailed account of the field methods for monitoring water quality is provided in Upsdell Wright *et al.* 2015a.

Table 2: Number of storm events and water quality samples in Healthy Lake Huron watersheds (October 2010 to September 2016).

Watershed	Water Years	Total Number of Events	Number of Events Sampled	Total Number of Samples
South Pine River[a]	2012 - 2016	66	19	184
Garvey Creek/Glenn Drain[a]	2012 - 2016	59	32	372
Gully Creek	2010 - 2016	137	74	858
Trick's Creek	2012 - 2016	97	60	513
Shashawandah Creek[a]	2012 - 2016	59	31	370
Bayfield River	2013 - 2016	50	21	254

[a] Incomplete flow record for 2013 water year.

Pollutant Load, Mean Concentration, and Export Coefficient Calculation

For this report, both the annual flow-weighted mean concentrations and the loads have been summarized. Dickinson (in Upsdell Wright *et al.* 2015b) suggested that, if the focus of the study is on concentration targets or standards, then concentration values are needed. However, if the focus of the study is on land use management or Great Lakes impacts, then load estimates are needed. Past water quality reports completed by the Ausable Bayfield Conservation Authority have reported findings as concentrations (see http://www.abca.on.ca/publications.php for past reports). However, calculating loads is important for comparing the contributions that are made from the different watersheds to Lake Huron.

Water quality indicator concentrations (nitrate-nitrogen, phosphate-phosphorus, total phosphorus , and total suspended solids) from the grab and ISCO samples collected during the study period were converted to loads (mass per time), flow-weighted mean concentrations (FWMC) (mass per volume), and export coefficients (mass per watershed area). These computations help to remove the variability associated with event discharge and watershed size.

Loads are the product of stream flow (volume per time) and concentration (mass per volume). A mass load (Equation 1) is a calculation of the total mass of a substance, usually expressed in kilograms, that is transported past a particular point on a stream or river over a given time period, often annually (Cooke 2000). In this study, annual loads were calculated (including events and low-flow periods).

Equation 1

Mass Load (kilograms) =$\sum c_i q_i t_i$

Where,

i = 1 to n (number of samples)
c_i = sample concentration (mg/L)
q_i = instantaneous stream flow (L/s)
t_i = time interval (s)

In a flow-proportionate sampling program, an individual water sample does not characterize the event or low-flow period. To estimate the average concentration, each sample must be weighted to represent a particular portion of the hydrograph (Equation 2) (Cooke 2000). Flow-weighted mean concentrations are concentrations that are adjusted for stream flow over a given period – in this study, the length of the water year. This computation allows for comparisons between streams with different flows or the same stream at different times.

Equation 2

Flow-Weighted Mean Concentration (mg/L) = $\frac{Mass\ Load\ (kg)}{Total\ Stream\ Flow\ Volume\ (L)} \times 1000$

The total mass export coefficient or unit-area load (Equation 3) is an estimate of the amount of the constituent that is lost per hectare of watershed for the given time period.

Equation 3

Mass Export (kg/ha) = $\frac{Mass\ Load\ (kg)}{Watershed\ Area\ (ha)}$

Reference Load Calculation

Continuous records of both stream flow and concentrations are needed to calculate loads. Since the concentrations of pollutants are not typically monitored continuously, load-estimation methods are used to calculate loads. Generally, there are five types of load-estimation methods: averaging, numeric integration, ratio, regression, and interpolation (Richards 1998). Averaging techniques determine load based on multiplying the average concentration by the average flow over a period of time. Numeric integration involves multiplying a concentration by the total flow over a period of time and then summing the time intervals (*e.g.*, Equation 1). Ratio estimators determine load by multiplying the mean daily load by a flow ratio (derived by dividing the average flow for the period of interest by the average flow for the days on which water quality samples were collected). A total load is then calculated by multiplying the adjusted load by 365 days. Regression approaches determine load based on fitting a relationship between flow and concentration. Finally, an interpolation approach assumes a linear relationship between consecutive measured concentrations, which are then multiplied together with flow over a period of time.

Water quality data and flow measurements from Gully Creek, Garvey Creek/Glenn Drain, and Trick's Creek were used to calculate a reference load (or "true" load) for each water quality indicator with a numeric integration method (Equation 1). The gauging stations (see Appendix A) were chosen for this analysis because they had reliable flow and exhaustive water quality sampling records, particularly for the 2013 water year (October 1, 2012 to September 30, 2013) and 2014 water year (October 1, 2013 to September 30, 2014). For each study period, we contracted the hydrograph to only those periods with water quality data (*i.e.,* unsampled time periods of the hydrograph were removed) to produce reference loads in which uncertainty of the "true load" was limited. The previous approach involved estimating the reference load for storm events and low-flow periods that were not sampled (see Stuntebeck *et al.* 2008 and Bittman *et al.* 2016).

The contracted datasets included a total of 528 water quality samples that were collected from the three gauging stations (Table 3). Low-flow grab samples and high-flow event samples were collected with an ISCO automated sampler. Water samples were analyzed for nitrate-nitrogen (NO_3-N), phosphate-phosphorus ($P0_4$-P), total phosphorus (TP), and total suspended solids (TSS).

Table 3: Number of water quality samples by watershed for calculating reference loads.

Watershed	Water Year(s)	Total Number of Samples
Garvey Creek/Glenn Drain	2014	112
Gully Creek	2013 - 2014	283
Trick's Creek	2013	133

Load Estimation Algorithms and Sampling Scenarios

This study adapted a Monte Carlo simulation strategy found in Birgand *et al.* (2011) and Williams *et al.* (2015). Monte Carlo simulations are used to help make decisions involving significant uncertainty, such as choosing the best load estimation algorithm from a number of different methods. Without this kind of analysis we might inadvertently choose a load estimation method that is inaccurate and/or imprecise.

In the current study, Monte Carlo simulations were used to sub-sample the reference datasets to assess the effect of sampling frequency and load estimation algorithm on annual load estimates. Fixed period sampling was used to generate a variety of sample collection scenarios. Scenarios were generated by randomly subsampling the reference datasets at fixed intervals, including: one sample per day, one sample every other day, one sample once per week, one sample once every two weeks, and one sample every month. Annual nutrient and suspended sediment loads were then calculated based on the subsampled discharge and water quality concentration data for each iteration of the Monte Carlo simulation. For the analysis, 15 iterations were generated for each stream's dataset (60 iterations in total) and the different sample frequencies. Annual load estimates using six different load estimation algorithms (identified as A1 – A6) from Water Quality Analyser were also compared against the reference datasets and sample frequency. Descriptions for each of the load estimation algorithms are presented in Table 4.

Table 4: Algorithms used to estimate nutrient and suspended sediment loads that were tested in the current study.

Algorithm ID	Algorithm Name	Description
A1	Average Load	Average discharge x average concentration
A2	Beale Ratio Estimator	Mean load of concentration x flow x flow ratio (including bias correction factor)
A3	Linear Interpolation	Linear interpolation of concentrations x continuous flow rates
A4	Continuous Discharge Estimation	Annual flow volume x flow-weighted mean concentration
A5	Flow Stratified	Concentrations are separated into different strata (flow regimes) x flow then sum of all strata
A6	Power Curve	Logarithm power law regression between flow rate and concentrations then sum of concentration x flow

It is important to note that the number of iterations in this study (60) is less than half the suggested 200 iterations required to sufficiently represent the distribution of these values (Birgand *et al.* 2011). Each of the 60 iterations for the different water quality indicators was manually input and calculated in Water Quality Analyser which was very time consuming. In future, use of software, such as R Studio, may be required to effectively meet the requirements above in a timely manner.

Water Quality Analyser

Water Quality Analyser (WQA), developed by eWater Source in Australia, was designed to monitor in-stream water quality and estimate pollutant loads. The software estimates loads and flow-weighted mean concentrations using a variety of averaging, ratio, regression, and interpolation methods (see Appendix B for information on each algorithm). Sample concentration data were matched to the nearest five-minute flow interval in Microsoft Excel and reconciled into WQA. Water Quality Analyser was then given instructions to calculate monthly and annual loads (in kg) and flow-weighted mean concentrations (in mg/L) by six different load estimation algorithms. Software version 2.1.2.4 was used for this report.

Load Uncertainty Analysis

An uncertainty analysis was performed to determine the relative difference between the three station's reference loads for each water quality indicator and the loads estimated by the different sample frequencies and algorithms in WQA. The uncertainty was calculated as the percentage difference between the estimated load and the reference load (Equation 4).

Equation 4

$$Uncertainty\ (\%) = \left(\frac{Estimated\ Load - Reference\ Load}{Reference\ Load}\right) \times 100$$

Following each iteration of the Monte Carlo simulation, the difference between the estimated load and reference load was calculated, which resulted in a distribution of uncertainty values. From this distribution, the minimum and maximum bias of the nutrient load or suspended sediment load was determined. The minimum bias values were used to represent sampling primarily baseflow conditions while maximum bias values were used to represent sampling primarily storm events.

A number of studies (*e.g.,* Guo *et al.* 2002, Haggard *et al.* 2003, Zamyadi *et al.* 2007) have suggested comparing the estimated loads to the reference load (or "true load") using the root mean square error (RMSE in %). The RMSE incorporates an estimation of accuracy (*i.e.,* bias, or the distance between the estimated load and the true load) and precision (*i.e.,* standard deviation, or the spread of the bias about the mean). The value of the RMSE was computed from the distribution of uncertainty values for each sampling frequency and load estimation algorithm. The RMSE (%) was calculated as the standard deviation of the residuals (uncertainty values) to help identify the best overall sampling frequency and load estimation algorithm to use for the Healthy Lake Huron watersheds (Equation 5).

Equation 5

$$RMSE\ (\%) = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(Uncertainty\ (\%))^2}$$

Where,

n = total number of samples in the uncertainty distribution
Uncertainty (%) = result from Equation 4

Spatial and Temporal Patterns

Loads are typically calculated annually and based on a water year (*e.g.*, October 1 to September 30). The United States Geological Survey uses a water year with an October 1 start date, as it is the time of year least likely to have major storm events on either side of that date. Use of this date is thought to avoid inflating or reducing the overall load for that year due to variations in major discharge events. For the purposes of the current study, to better understand baseline water quality conditions in the six watersheds along the southeast shore of Lake Huron, mass load, flow-weighted mean concentration, and mass export values were calculated for the period between October 1, 2010, and September 30, 2016. Water quality was analyzed for nitrate-nitrogen (NO_3-N), phosphate-phosphorus (PO_4-P), total phosphorus (TP), and total suspended solids (TSS).

Annual pollutant transport is typically defined by seasonal changes, in which greater loads occur during large, infrequent storm events (usually during winter and spring) and smaller loads occur during smaller, more frequent storm events and low-flow periods (usually during fall and summer). It is not surprising that 80 to 90 per cent of total loads occur during only 10 to 20 per cent of the time (Richards 1998). For this reason seasonal loads were calculated to evaluate variations in loading throughout the year. Limnological seasons were used in this study and defined as fall (October-November), winter (December-March), spring (April-May), and summer (June to September). Separating the months in this manner effectively groups the seasons into similar climatic conditions based on precipitation and temperature. Additionally, pollutant loads and stream flow volumes were determined for individual months to assess monthly patterns across all streams during the study period.

Trends in Monthly Water Quality Data

Regression analyses were performed to evaluate trends in water quality data for the six watersheds during the current study period. A parametric approach (log-linear trend test) was used to evaluate the trends in monthly log-transformed flow-weighted mean concentrations and loads (*i.e.*, improving trend, no trend, declining trend) for normally distributed datasets. However, if the water quality datasets were non-normally distributed, a non-parametric approach (Mann-Kendall trend test) was used instead. A Shapiro-Wilk test was executed to determine normality of the datasets. A trend was found to be statistically significant when the magnitude of the change is large relative to the variation of the data around the trend line (*i.e.,* $p < 0.05$). Monthly concentrations and loads were used instead of annual concentrations and loads to limit the effect of outliers and to retain inter-annual variability. The average rate of change (%) in monthly flow volumes, flow-weighted mean concentrations, and loads was determined using Equation 6.

Equation 6

$$Monthly\ rate\ of\ change\ (\%) = \left(10^{\beta} - 1\right) \times 100$$

Where,

β = log-linear slope coefficient

In addition, the relationship between flow and pollutant concentrations was also examined in the priority watersheds by comparing patterns in monthly flow volume, flow-weighted mean concentrations, and loads.

Results and Discussion

Load Estimation Algorithms and Sampling Scenarios

Reference loads were compared against five different sampling frequencies and six different load estimation algorithms from Water Quality Analyser (Figure 2). The frequency of sample collection substantially affected the uncertainty in all load estimates (TP, TSS, PO_4-P, and NO_3-N). In general, the precision of nutrient and sediment load estimates decreased with increasing sampling interval, while the bias increased with increasing sampling interval. Estimated annual nitrate-N loads tended to be less biased and more precise than estimated annual TP, TSS, and phosphate-P loads.

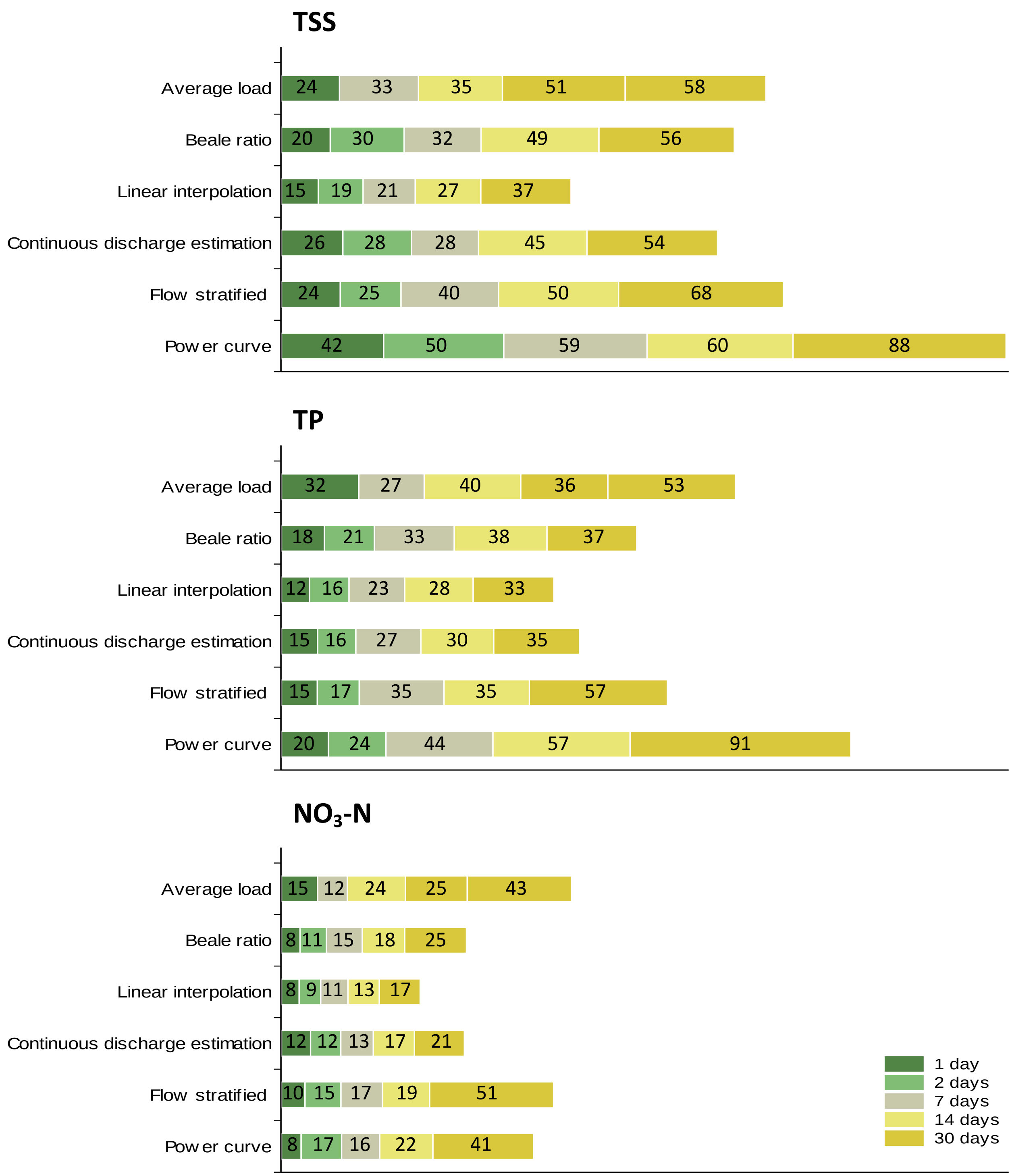

Figure 2: Root mean squared error (%) for six load estimation algorithms over five different sampling frequencies. Values shown are the mean difference between the reference ("true") loads and the estimated loads using water quality data from Gully Creek, Garvey Creek/Glenn Drain, and Trick's Creek.

The algorithms used to compute annual load estimates also had a significant effect on the uncertainty values. Algorithms A2 to A4 resulted in estimates of annual TP loads with mean bias within ±40% of the reference loads. In comparison, algorithms A1, A5, and A6 estimated annual TP loads with mean bias within ±90% of the reference loads.

The regression algorithm (A6) performed poorly across most of the sampling intervals, which is not surprising given that the correlation between concentrations and flow was often weak (typical $r^2 < 0.5$). Walling and Webb (1988) had determined that regression models do not provide accurate load estimates due to seasonal variability, hysteresis, and lag effects which ultimately reduce the strength of the correlation between concentrations and flow. Regression models may predict concentrations reasonably well in one season, but not in other seasons leading to over- or underestimates of annual loads. Additionally, during storm events, the peak of concentrations may precede or follow the hydrograph peaks (*i.e.,* a lack of coincidence between concentration and flow response) which tend to increase uncertainty of the load. Progressive declines or increases in concentrations associated with the sequence of storm events (*i.e.,* supply of concentrations) may also make it difficult to estimate loads with regression algorithms. Current research on regression algorithms by Christopher Wellen (University of Windsor) shows promise in improving load estimates by accounting for seasonal variation and lag effects.

Averaging techniques (A1 and A5), or those that average annual nutrient concentration, also provided poor estimates of annual loads across most of the sampling intervals. Previous studies have shown that averaging methods are only effective when concentration measurements are available for the entire range of flows (e.g., Preston *et al.* 1989, Quilbe *et al.* 2006). With our sampling program, high flows and thus high concentrations are sampled more often than low flows and lower concentrations. The nature of our sampling program, therefore, may increase the uncertainty of annual load estimates when averaging methods are employed.

Of the six algorithms tested, A3 (linear interpolation) and A4 (continuous discharge estimation) resulted in better estimates of annual TP, TSS, phosphate-P, and nitrate-N loads compared to the other methods. Both algorithms maximally underestimated annual TP loads by 30–71%, annual TSS loads by 31–91%, phosphate-P annual loads by 25–73%, and nitrate-N annual loads by 4–32% across the range of sampling intervals. These ranges of values generally represent sampling baseflow conditions more often than event flows. In comparison both algorithms maximally overestimated annual TP loads by 15–65%, annual TSS loads by 22–110%, phosphate-P annual loads by 13–108%, and nitrate-N annual loads by 16–57% across the range of sampling intervals. In general, these ranges of values represent sampling primarily event flows.

Algorithm A3 was more precise on average across all sample frequencies. The RMSE results suggest that in this case A3 performed clearly better than A4 for TSS and slightly better for TP, phosphate-P, and nitrate-N.

Studies conducted in naturally drained and tile-drained landscapes have found both linear interpolation (e.g., Kronvang and Bruhn 1996, Moatar and Meybeck 2005, Tiemeyer *et al.* 2010, Birgand *et al.* 2011, Jiang *et al.* 2014, Williams *et al.* 2015) and continuous discharge estimation (e.g., Walling and Webb 1981, Walling and Webb 1985, Littlewood 1992, Littlewood *et al.* 1998, Moatar and Meybeck 2005, Littlewood and Marsh 2005, Moatar *et al.* 2006, Birgand *et al.* 2010, Birgand *et al.* 2011) to be the preferred algorithm to estimate nutrient loads. Similarly, with our data sets, the Linear Interpolation method (A3) in WQA was best suited to calculate loads for both well-sampled and poorly-sampled stream sites in the priority watersheds and for further analysis in this report.

Spatial and Temporal Patterns

Once the "best" load estimation algorithm was determined, annual mass load, flow-weighted mean concentration, and mass export were calculated for four water quality indicators (nitrate-nitrogen, phosphate-phosphorus, total phosphorus, and total suspended solids) in Water Quality Analyser.

Flow-Weighted Mean Concentrations

In all six watersheds, annual flow-weighted mean TP and nitrate-N concentrations exceeded concentrations that are considered to minimize eutrophication (Figure 3): the Provincial Water Quality Objective for TP (0.03 mg/L; OMOEE 1994) and a concentration identified by the Canadian Council of Ministers of the Environment for nitrate-N (0.9 mg/L; CCME 2012). Mean flow-weighted mean TP concentrations exceeded 0.15 mg/L for all watersheds, excluding Trick's Creek, which had a mean concentration of 0.08 mg/L. Total phosphorus concentrations ranged from 0.14–0.67 mg/L in Gully Creek, 0.16–0.35 mg/L in Pine River, 0.09–0.2 mg/L in Garvey Creek/Glenn Drain, 0.06–0.12 mg/L in Trick's Creek, 0.12–0.21 mg/L in Shashawandah Creek, and 0.09–0.18 mg/L in Bayfield River.

Flow-weighted mean concentrations for nitrate-N exceeded 3.0 mg/L for all watersheds. Nitrate-N concentrations ranged from 3.6–6.2 mg/L in Gully Creek, 3.9–5.9 mg/L in Pine River, 6.3–7.2 mg/L in Garvey Creek/Glenn Drain, 3.1–4.2 mg/L in Trick's Creek, 3.4–7.6 mg/L in Shashawandah Creek, and 4.8–6.0 mg/L in Bayfield River.

Across all watersheds, Gully Creek had the highest flow-weighted mean concentrations for TSS. Total suspended sediment concentrations ranged from 134–614 mg/L in Gully Creek, 53–188 mg/L in Pine River, 28–70 mg/L in Garvey Creek/Glenn Drain, 36–109 mg/L in Trick's Creek, 25–97 mg/L in Shashawandah Creek, and 41–125 mg/L in Bayfield River.

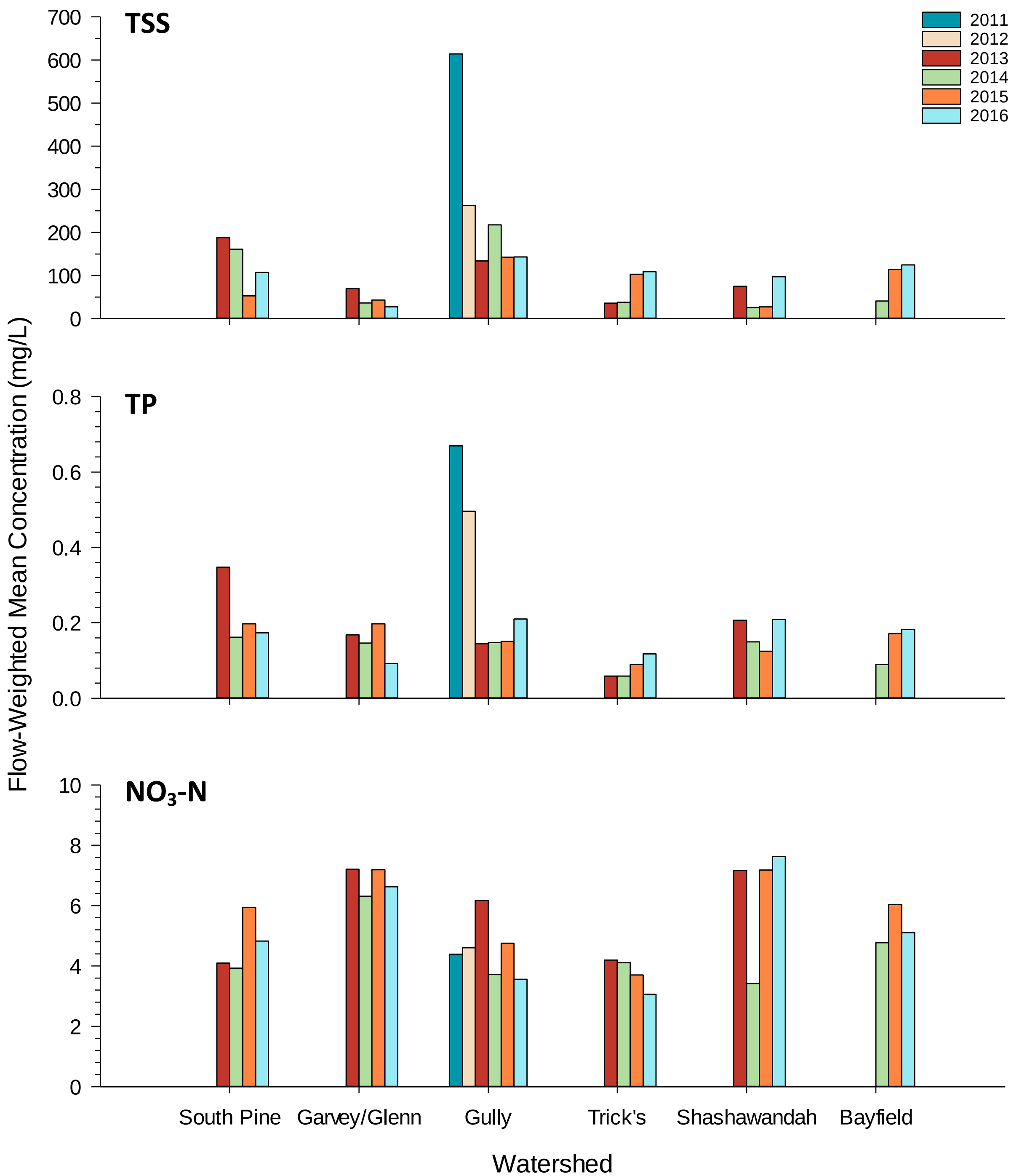

Figure 3: Annual flow-weighted mean concentrations in the Healthy Lake Huron watersheds (October 2010 to September 2016). Notes: 1) GULGUL5 monitoring station data were used to estimate FWMC for the 2012 to 2016 water years. GULGUL2 monitoring station data were used for the 2011 water year. 2) A change of laboratory analysis method for total phosphorus occurred in November 2012 at the Ministry of the Environment and Climate Change.

Total Annual Loads

Total annual loads in the six watersheds varied noticeably by water quality indicator and monitoring station (Figure 4). Sediment loads were lowest in Garvey Creek/Glenn Drain (222–445 tons) and highest in Bayfield River (16,773–29,526 tons). Four watersheds, including the South Pine River, Gully Creek, Trick's Creek, and Shashawandah Creek had a similar range of annual sediment loads during the study period (307–2,451 tons). Additionally, Bayfield River contributed the greatest loads for total phosphorus (34–43 tons) and nitrate-N (1,203–1,962 tons), while loads for these indicators were comparable among the remaining watersheds (0.7–5.6 tons and 24–125 tons, respectively).

The total TP load to Lake Huron from the priority tributaries, including Bayfield River, ranged from 39.3 to 51 tons per year and averaged 45.1 tons per year between October 2014 and September 2016. In comparison, Dolan and Chapra (2012) reported total phosphorus loads for all Lake Huron tributaries ranging from 1,084 to 3,572 tons per year and averaged 2,140 tons per year between 1994 and 2008. As a result, on average the priority tributaries accounted for approximately 2% of the total annual total phosphorus load to Lake Huron. The proportion of land area represented by the priority watersheds to the total land area of all the Lake Huron tributaries is 0.4% (54,100 ha ÷ 13,410,000 ha).

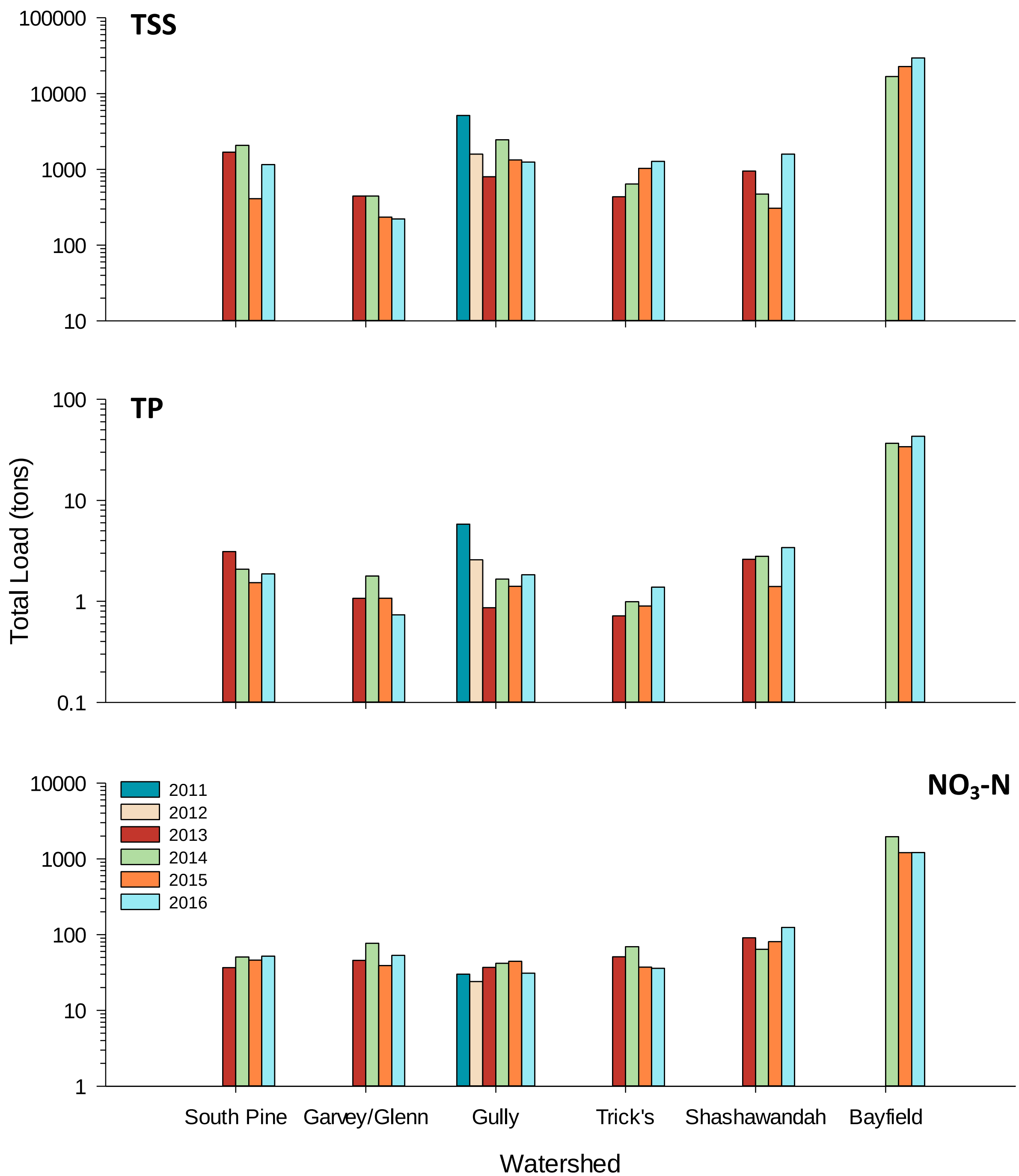

Figure 4: Annual total loads in the Healthy Lake Huron watersheds (October 2010 to September 2016). Notes: 1) GULGUL5 monitoring station data were used to estimate mass export for the 2012 to 2016 water years. GULGUL2 monitoring station data were used for the 2011 water year. 2) A change of laboratory analysis method for total phosphorus occurred in November 2012 at the Ministry of the Environment and Climate Change.

Mass Export Coefficients

Mass export coefficients for total phosphorus in the six watersheds were higher than the range of values found in other streams in Southwestern Ontario (Table 5). The mean TP export coefficient for the six watersheds was 1.09 kg/ha, ranging from 0.34 kg/ha in Trick's Creek during the 2013 water year to 4.41 kg/ha in Gully Creek during the 2011 water year (Figure 5).

Table 5: Summary of annual total phosphorus mass export coefficients in agricultural, urban, and forested tributary catchments in Southwestern Ontario.

Land Use Type	Area	Mean (and Range) of TP Export Coefficient (kg/ha/year)	Reference
Agricultural	Lake Huron Tributaries	1.09 (0.34 to 4.41)	This report
Agricultural	Southwestern Ontario	(0.10 to 1.50)	PLUARG 1978
Agricultural/Urban/Forest	Lake Simcoe Tributaries	0.36 (0.08 to 2.21)	LSRCA 2010
Agricultural	Southwestern Ontario	0.92 (0.20 to 1.89)	OMOE 2012
Agricultural/Urban	Hamilton, Ontario	0.87 (0.14 to 1.40)	Long *et al.* 2015

Sediment mass export coefficients were greatest in Gully Creek (769–4,042 kg/ha). The remaining watersheds had a similar range of annual sediment mass export coefficients during the study period (115–744 kg/ha). Additionally, Garvey Creek/Glenn Drain contributed the greatest loads for nitrate-N (30–60 kg/ha), while nitrate-N mass export loads were comparable in Gully Creek, Shashawanda Creek, and Bayfield River (23–47 kg/ha). The smallest nitrate-N mass export loads occurred in Pine River and Trick's Creek (13–33 kg/ha).

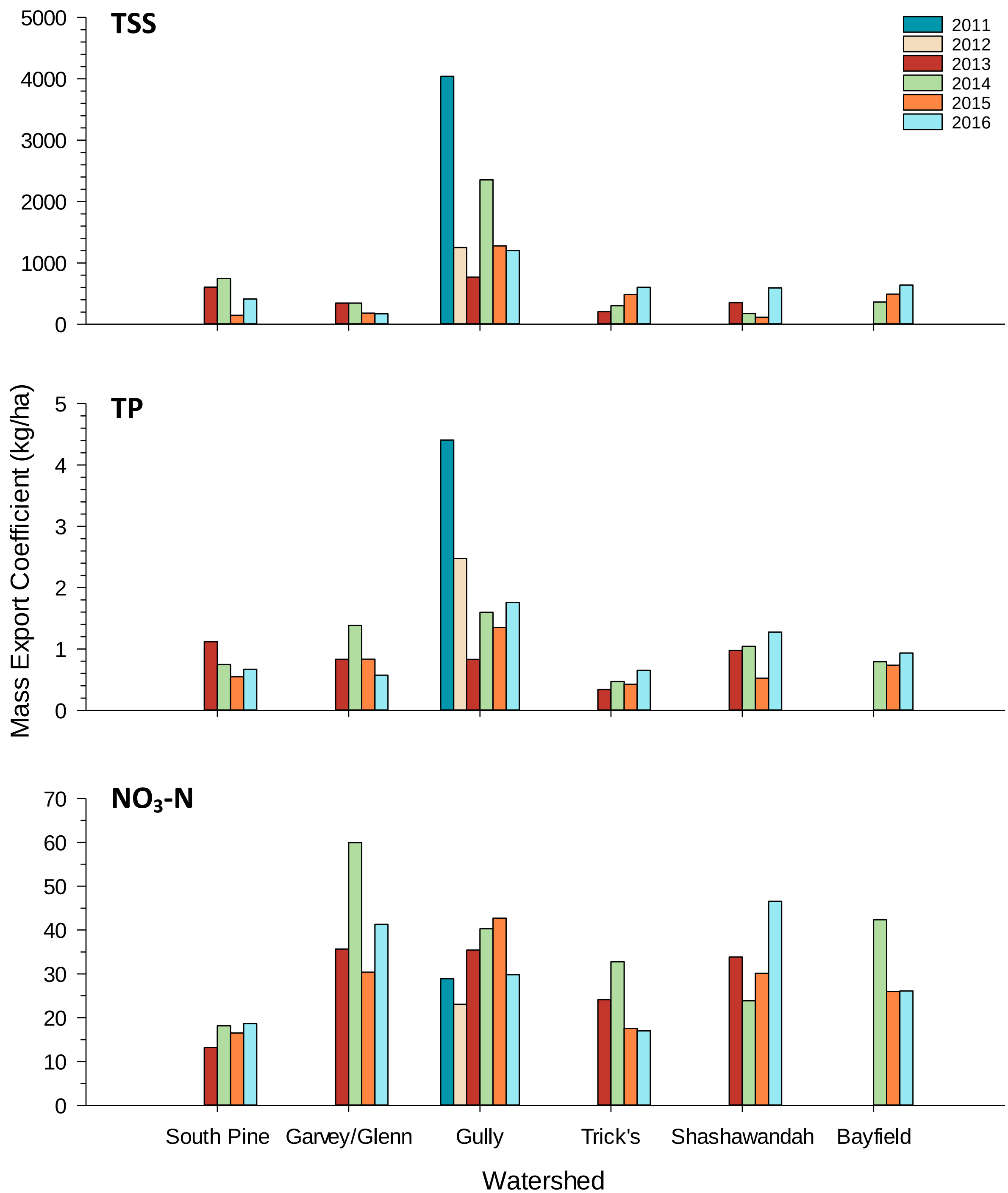

Figure 5: Annual mass export coefficients in the Healthy Lake Huron watersheds (October 2010 to September 2016). Notes: 1) GULGUL5 monitoring station data were used to estimate mass export for the 2012 to 2016 water years. GULGUL2 monitoring station data were used for the 2011 water year. 2) A change of laboratory analysis method for total phosphorus occurred in November 2012 at the Ministry of the Environment and Climate Change.

Trends in Water Quantity and Flow-Weighted Mean Concentrations

Monthly flow volumes and flow-weighted mean concentrations were determined for the priority watersheds over a three- to six-year period with the expectation that patterns in water quality and flow may be detected (Table 6, Figures 6–8). No statistically significant trends in flow were observed, except for the Bayfield River which saw a decrease in flow volume of approximately 108% per year over a three year period. A reduction of this magnitude can be explained by the fact that monitoring began during a very wet year (2013) and subsequent years were much drier.

Total phosphorus concentrations decreased significantly by approximately 19% per year in Gully Creek, even though flow actually increased (albeit non-significantly) during the same period. This finding may provide some evidence that BMPs and land management changes have helped to improve water quality in the watershed. Unfortunately, the opposite trend was observed in Trick's creek. For instance, TP concentrations increased significantly by 26% per year in Trick's Creek, while flow decreased (albeit non-significantly) during the same period. A similar pattern was also observed in Bayfield River; however, we cannot offer an appropriate explanation for why noticeable differences exist between the monitoring locations.

Nitrate-N concentrations decreased significantly by 7 and 14% per year in Gully Creek and Trick's Creek, respectively. A significant reduction in suspended sediments of 21–35% per year was observed at three stations, however, suspended sediments increased significantly by 47 and 57% in Trick's Creek and the Bayfield River, respectively. Again, it was not apparent why concentrations increased in Trick's Creek and Bayfield River while other sites improved. It is important to note that a change of laboratory analysis method for total phosphorus occurred in November 2012 at the MOECC. However, similar patterns were observed for phosphate-P and TSS in Gully Creek, which were not affected by the laboratory method change.

Table 6: Water quantity and quality trends in monthly concentrations for the priority watersheds. Values shown represent annual rates of change (%).

Station	Water Years	Flow	TP	PO_4-P	NO_3-N	TSS
South Pine	2012-2016	12	14	13	6	35
Garvey/Glenn	2012-2016	39	5	0.1	10	29
Gully	2010-2016	13	19	11	7	21
Trick's	2012-2016	10	26	8	14	47
Shashawandah	2012-2016	5	0.7	9	8	16
Bayfield	2013-2016	108	21	14	1	57

Significant positive (degrading) trend ($p < 0.05$)
Significant negative (improving) trend ($p < 0.05$)
x Positive annual rate of change (%)
x Negative annual rate of change (%)

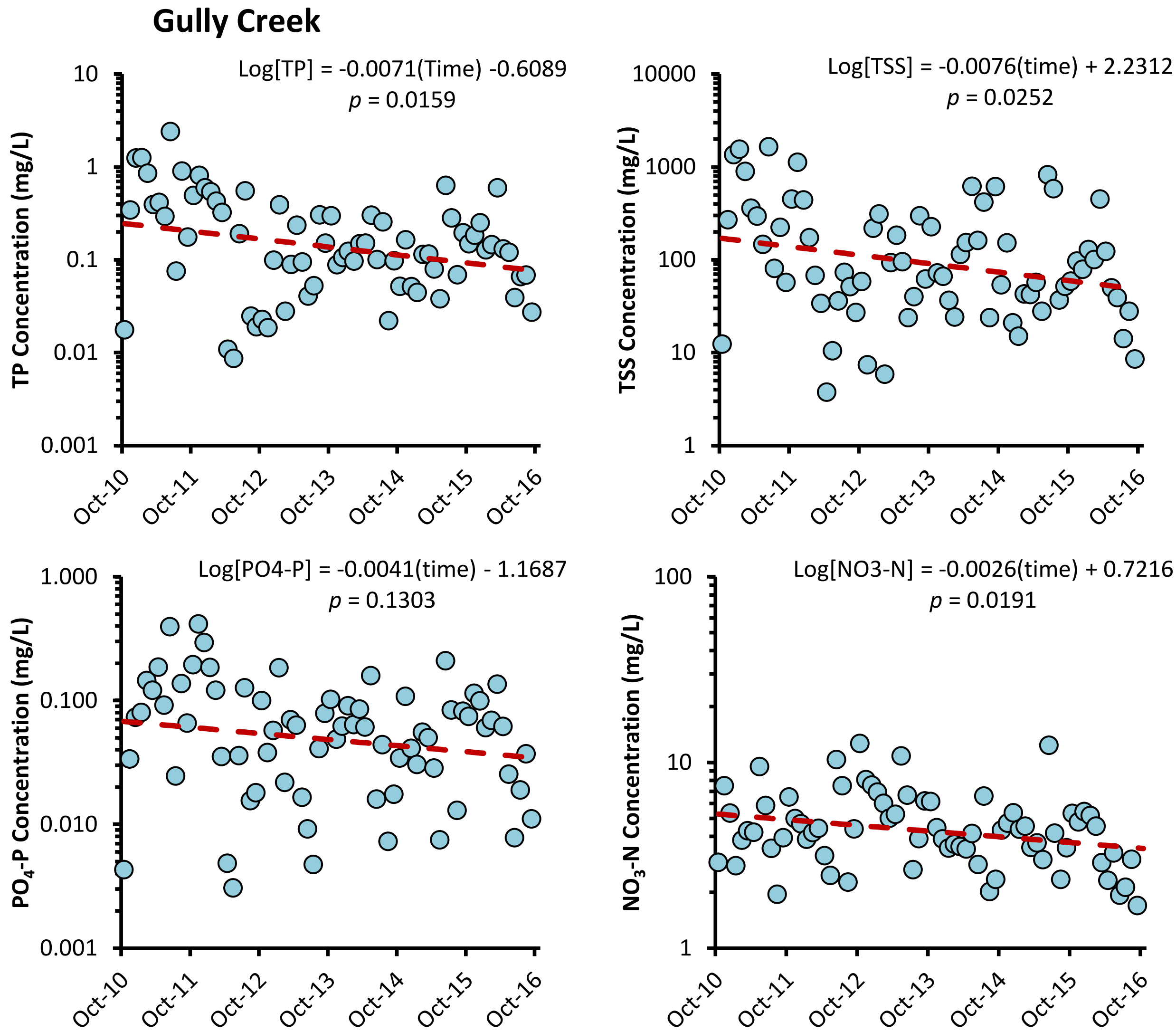

Figure 6: An example of water quality trends in monthly flow-weighted mean concentrations for Gully Creek (October 2010 to September 2016).

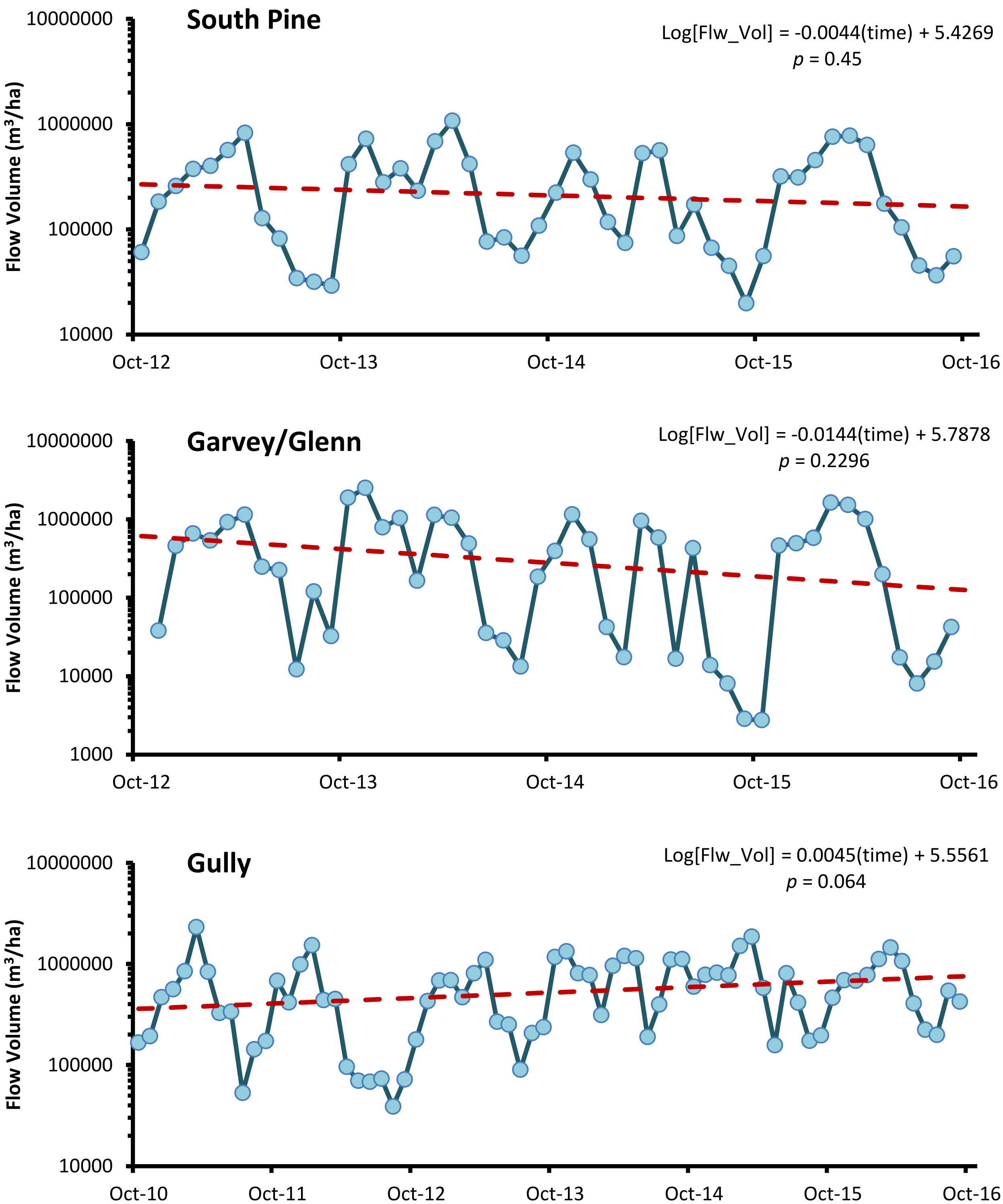

Figure 7: Water quantity trends in monthly flow volume for the priority watersheds (October 2010 to September 2016).

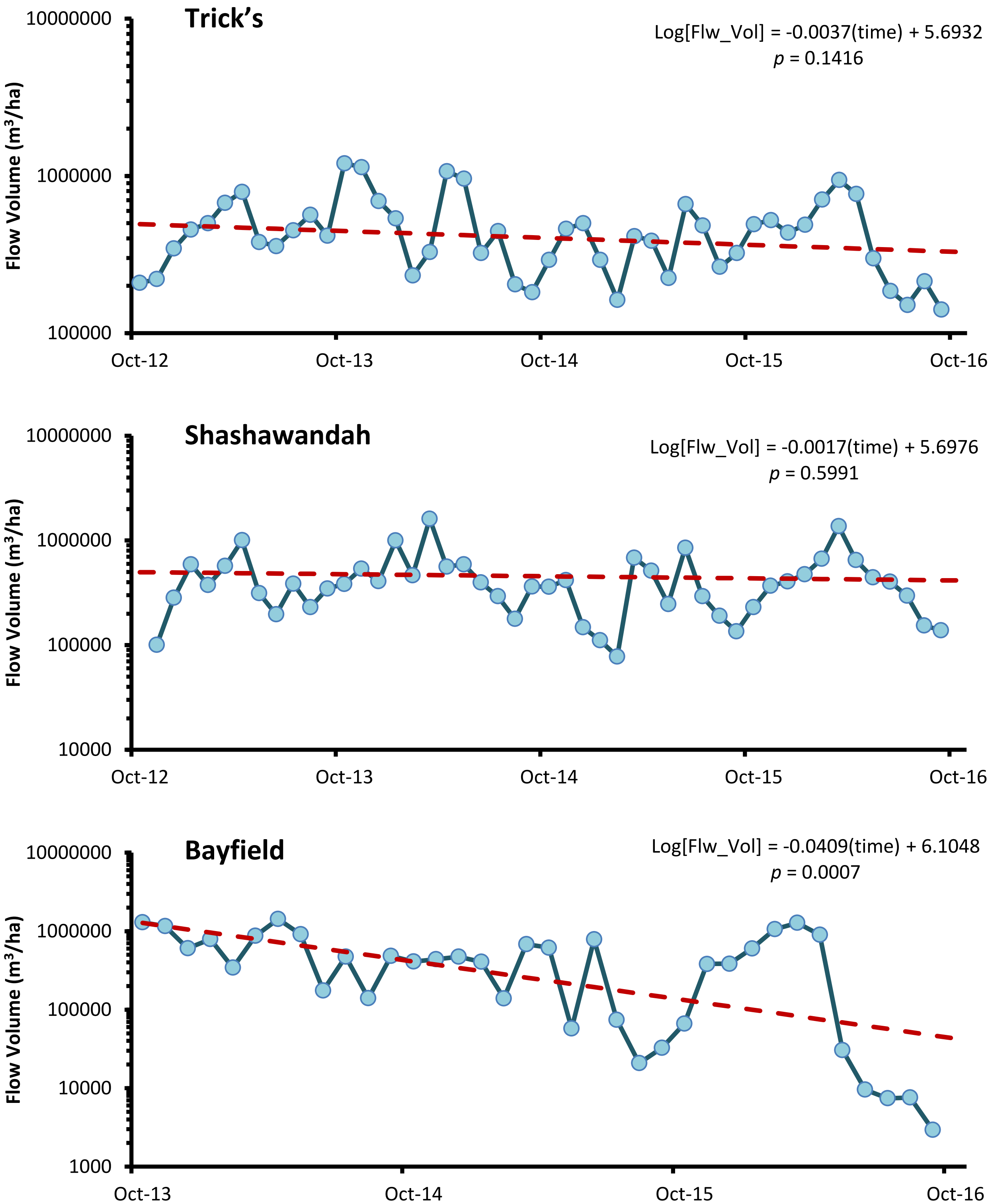

Figure 8: Water quantity trends in monthly flow volume for the priority watersheds (October 2012 to September 2016).

Trends in Water Quantity and Pollutant Loads

Trends in monthly pollutant loads were also determined for the priority watersheds over a three- to six-year period (Table 7, Figure 9). Loads for most water quality indicators were largely influenced by flow volume, except for Gully Creek and Trick's Creek. Some evidence of a decreasing trend in TP loads was observed in Garvey Creek/Glenn Drain (55% per year) and Bayfield River (82% per year) driven by sizeable reductions in flow during the same period.

Sediment loads decreased significantly in Garvey Creek/Glenn Drain (69% per year), while loads increased significantly in Trick's Creek (38% per year), even though flow declined during the same period. Possible evidence of a reduction in TSS loads was observed in South Pine River (48% per year).

Nitrate-N loads decreased significantly in Trick's Creek (28% per year) and Bayfield River (100% per year), while some evidence of a reduction was observed in Garvey Creek/Glenn Drain (45% per year). In addition, phosphate-P loads decreased significantly by 137% per year in Bayfield River, while some evidence of a decline was observed in Garvey Creek/Glenn Drain (53% per year).

Table 7: Water quantity and quality trends in monthly loads for the priority watersheds. Values shown represent annual rates of change (%).

Station	Water Years	Flow	TP	PO4-P	NO3-N	TSS
South Pine	2012-2016	12	27	31	2	48†
Garvey/Glenn	2012-2016	39	55†	53†	45†	69
Gully	2010-2016	13	16	3	3	10
Trick's	2012-2016	10	15	2	28	38
Shashawandah	2012-2016	5	5	14	6	24
Bayfield	2013-2016	108	82†	137	100	39

(red shading) Significant positive (degrading) trend ($p < 0.05$)
(green shading) Significant negative (improving) trend ($p < 0.05$)
x Positive annual rate of change (%)
x (red) Negative annual rate of change (%)
† Not a statistically significant trend, but may have ecological effects ($0.05 < p < 0.1$)

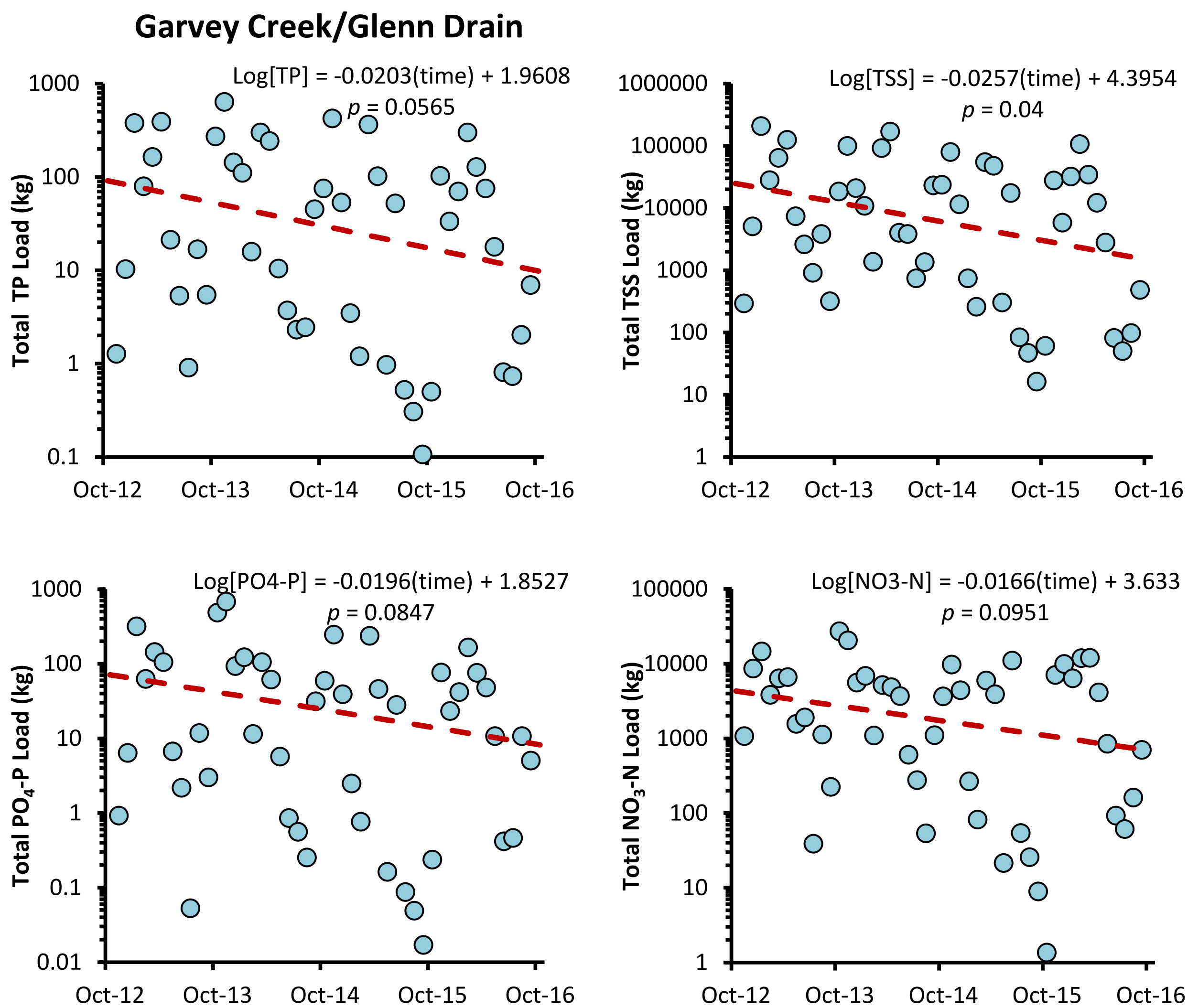

Figure 9: An example of water quality trends in monthly loads for Garvey Creek/Glenn Drain (October 2012 to September 2016).

Seasonal Loading of Pollutants

Flow across all streams in this study was largely seasonally driven (Table 8). For instance, flow was most dominant in winter (45% of total annual flow), while less so in the other seasons, particularly summer (16% of total annual flow). The majority of loads also occurred in the winter, ranging from 43% for nitrate-N to 48% for total phosphorus. Loads in fall, spring, and summer each accounted for less than 25% of the total annual load.

Table 8: Percent of discharge and stream loads delivered by season for the priority watersheds.

Season	Months	Flow	TP	TSS	NO_3-N
Fall	Oct-Nov	19	15	12	20
Winter	Dec-Mar	45	48	45	43
Spring	Apr-May	20	21	20	18
Summer	Jun-Sep	16	16	24	18

Variability in seasonal loads was apparent for water quality indicators between monitoring stations (Figure 10). In fall, TP for all streams ranged from 0.1% of total annual load in both Pine River and Garvey Creek/Glenn Drain to 51% of total annual load in Gully Creek. Total phosphorus loads in the winter made up 22% of total annual loads in Gully Creek and Pine River up to 78% in Bayfield River. The range of TP in spring was 0.1% of total annual loads in Gully Creek up to 41% in Shashawanda Creek and Bayfield River. More seasonal variability in TP within streams was observed during summer. For instance, Gully Creek and Trick's Creek ranged between 2 and 50% of annual loads, Shashawandah Creek and Bayfield River ranged between 1 and 35%, while Garvey Creek/Glenn Drain and Pine River ranged between 1 and 5% of annual loads. This dichotomy of loads was likely due to Garvey Creek/Glenn Drain and Pine River having very low flow during summer, whereas baseflow in the remaining streams was predominant during summer.

The seasonal distribution of TSS loads was similar to TP loads for all streams in fall (0.1 to 51% of total annual loads) and spring (0.1 to 54%). The ranges of TSS, however, were largest in winter (8 to 80% of total annual loads) and summer (0.3 to 72%).

The seasonal variability of nitrate-N for all streams in fall ranged from 0.3% of total annual loads in Pine River up to 62% in Garvey Creek/Glenn Drain. Nitrate-N loads in the winter made up 14% of total annual loads in Shashawandah Creek up to 75% in Garvey Creek/Glenn Drain. The range of nitrate-N values was similar in both spring and summer with 1% of total annual loads occurring in Pine River and Bayfield River up to 59% in Shashawandah Creek.

All indicator loads were greatest in March and April, accounting for 27% of total annual nitrate-N loads, 35% of total annual TSS loads, and 36% of total annual TP loads (Figure 11). Total annual loads for all indicators accounted for less than 10% for July, August, and September combined.

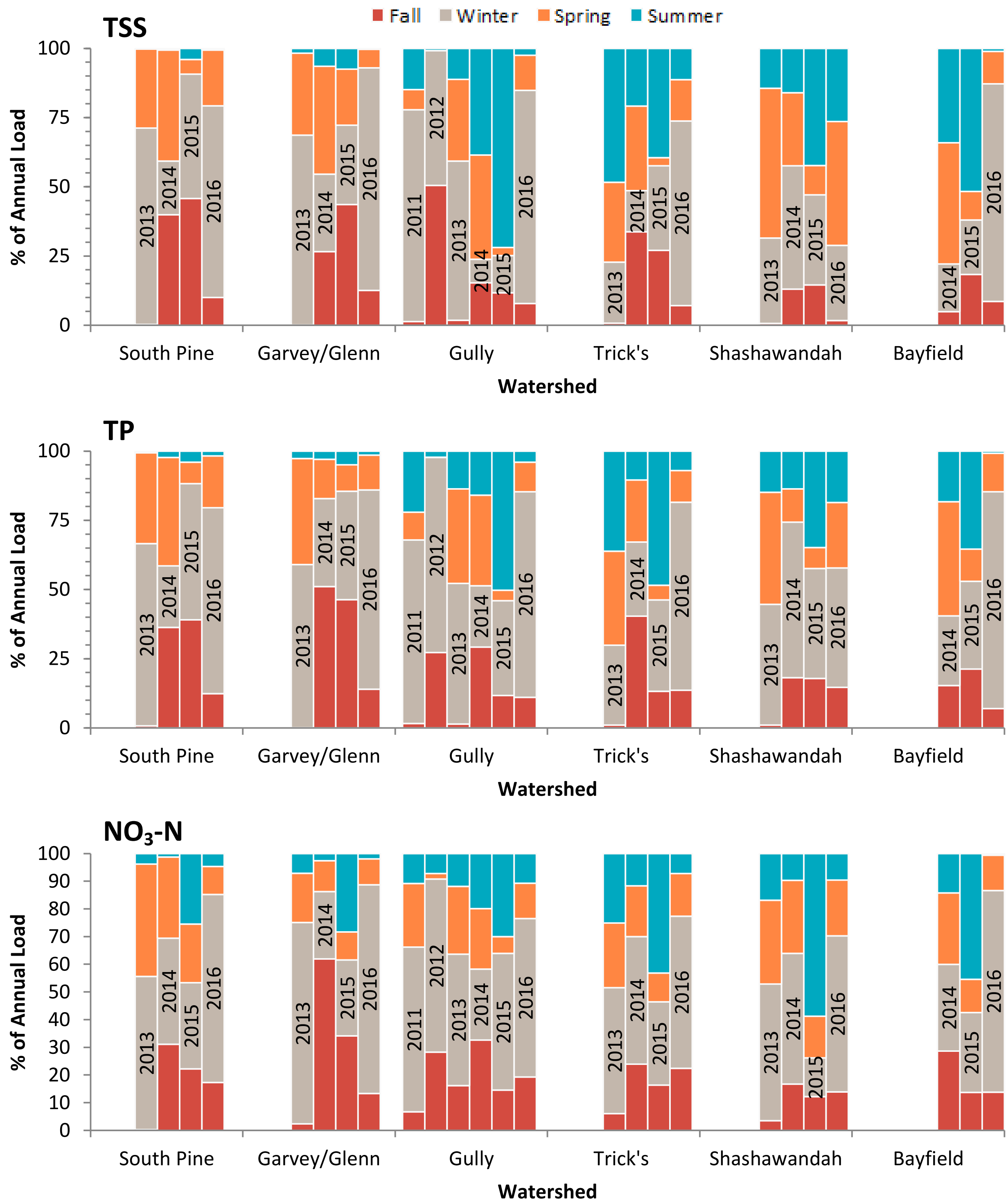

Figure 10: Seasonal loads as a percentage of annual loads for all of the study streams. Water years are shown as vertical labels.

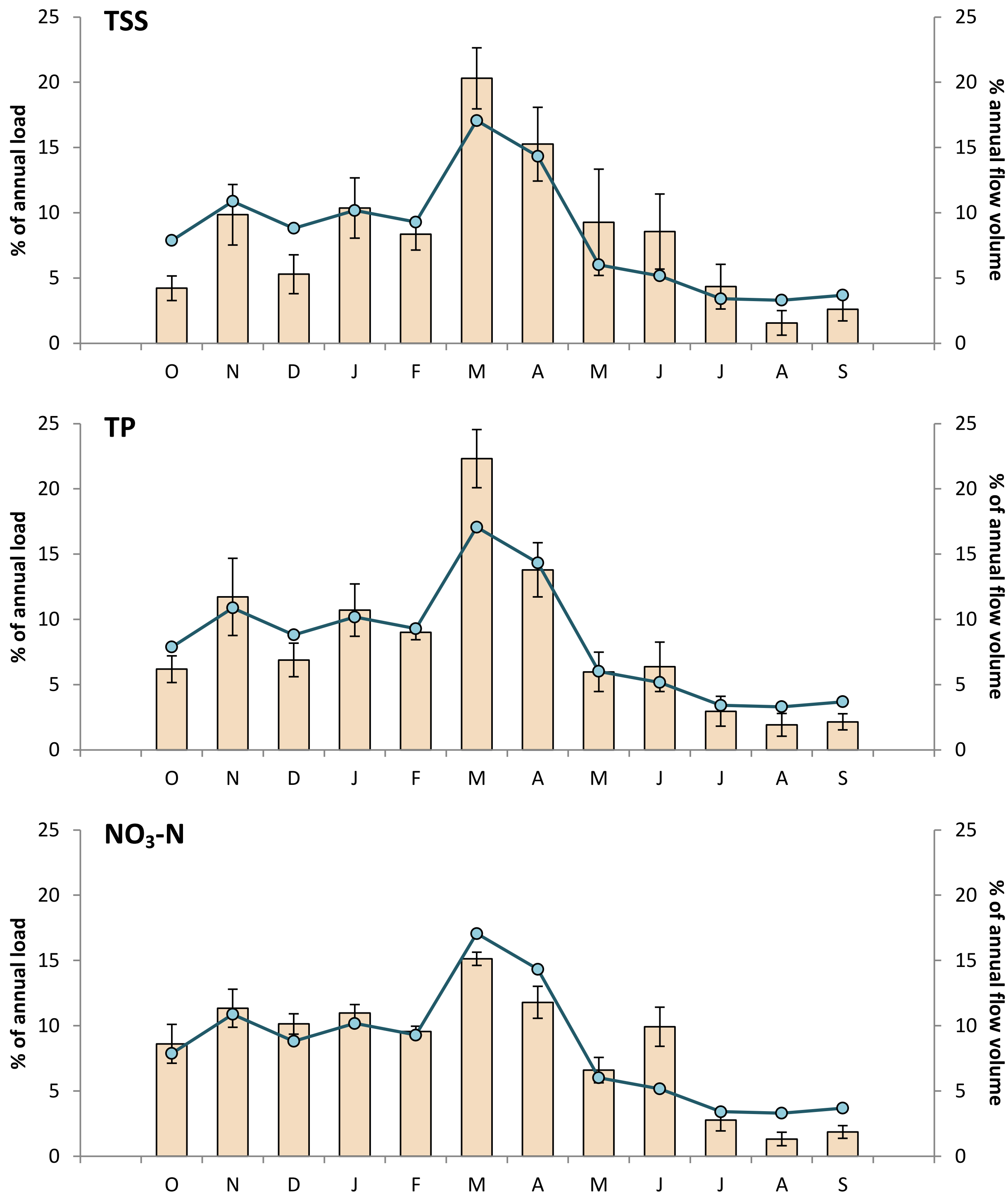

Figure 11: Percent annual load (pale bars, left axis) and percent annual flow volume (blue line, right axis) averaged across all of the study streams. Error bars are standard error of the mean, representing variability in annual loads among streams.

Relationship Between Pollutant Loads and Flow Volume

Monthly water quality loads across all streams did not correlate well to total monthly flow volume for all water quality indicators (Table 9). This finding is in agreement with the seasonal concentration-flow relationships reported in Bittman *et al.* (2016), which showed weak overall correlations (typical $r^2 < 0.5$). Weak concentration-flow relationships generally occur due to seasonal variability, hysteresis (*i.e.,* lack of coincidence in timing between concentrations and flow) and lag (*i.e.,* progressive exhaustion of concentration supply) effects during storm events (*e.g.,* Walling and Webb 1988).

When considering each site individually; however, monthly water quality loads were highly correlated to total monthly flow volume for all water quality indicators in Pine River and Garvey Creek/Glenn Drain, while most of the indicators were highly correlated to flow volume in Bayfield River. In general, the majority of water quality indicators were moderately correlated to flow volume in the remaining watersheds. These findings indicate that pollutant loads respond differently to a range of flow conditions in each priority watershed, but in general, larger flow volumes likely generate larger loads. In addition, these results offer an alternative approach to estimating loads based on measured flow volumes.

Table 9: Pearson's correlation coefficients for monthly flow volume and pollutant loads in the priority watersheds.

Station	TP Load vs Flow Volume	PO_4-P Load vs Flow Volume	NO_3-N Load vs Flow Volume	TSS Load vs Flow Volume
South Pine	0.84	0.86	0.7	0.78
Garvey/Glenn	0.91	0.86	0.92	0.86
Gully	0.57	0.69	0.82	0.53
Trick's	0.53	0.63	0.62	0.32
Shashawandah	0.58	0.67	0.48	0.47
Bayfield	0.82	0.89	0.93	0.64
All streams	**0.51**	**0.55**	**0.48**	**0.51**

Weakly correlated ($r^2 < 0.5$)
Moderately correlated ($0.5 < r^2 < 0.7$)
Highly correlated ($r^2 > 0.7$)

Conclusions

This report has provided technical staff from the Healthy Lake Huron program with the opportunity to summarize the water quantity and quality data that has been collected in the priority watersheds along the south east shores of Lake Huron. Monitoring has been undertaken since June 2010 for Gully Creek, the fall of 2012 for four other watersheds, and the fall of 2013 for Bayfield River. It is important to note that prior to the establishment of these priority areas, water samples were not collected with corresponding flow information and were not typically collected during runoff events. To evaluate the effectiveness of land-based BMPs, a water sampling program that reflects the times when water is running across the landscape must be used to obtain accurate estimates of pollutant loads. Furthermore, as pollutant concentrations are related to discharge condition, calculating the loads of various pollutants is necessary for evaluation. The requirements of sampling runoff events and the use of flow data in combination with water quality data represent a considerable change in human resources for monitoring programs that have been established by the technical staff in the Healthy Lake Huron.

As there are different approaches to combining discharge and concentration data to determine load, considerable effort was spent to evaluate different approaches. We chose to focus our evaluation on the data set collected for Gully Creek, Trick's Creek, and Garvey Creek/Glenn Drain as they had the most robust water quality sampling effort for 2013 and 2014 water years. Evaluation of the different approaches to produce load values included the accuracy and precision of the estimate compared to reference ("true") loads that were calculated with numeric integration. Results from the uncertainty analysis indicate that infrequent sampling can yield large uncertainties in the estimation of nutrient and sediment loads. The results also show that the algorithm used to compute loads has a dramatic effect on the uncertainty bias and precision. From our analysis, with well-sampled and poorly-sampled data sets, a linear interpolation method in WQA was best suited to calculate loads in the priority watersheds. The uncertainty analysis should be further developed to determine the optimal number of samples required for each priority watershed to estimate loads within a limited amount of error of the "true" load (*e.g.,* ±10%). This approach may assist in reducing staff time and sampling costs.

Typically concentrations of nutrients (nitrate-N and TP) in the six Lake Huron watersheds exceeded standards established to prevent eutrophication; however, some improvements were detected during the study period. For instance, a significant reduction in total phosphorus concentrations was observed in Gully Creek, while nitrate-N concentrations declined significantly in Trick's Creek and Gully Creek. Additionally, sediment concentrations decreased substantially in South Pine River, Garvey Creek/Glenn Drain, and Gully Creek. Although these results are encouraging, we also found significant increases in concentrations of TP and sediments in Trick's Creek. All Lake Huron watersheds revealed moderate to strong relationships between monthly loads and total flow volume. This finding indicates that in many cases monthly flow volumes can predict total loads reasonably well. As loads are largely influenced by flow volumes, this approach alone may not be helpful in evaluating the effectiveness of BMPs unless we observe significant reductions in runoff across the landscape. Instead, the relationship between flow and concentration should further be evaluated to see how it may impact our understanding of BMP effectiveness over time. This method requires adjusting or removing the flow portion of each observed concentration to determine the impact that flow has on pollutant transport or to see what level of impact land management changes have on pollutant loading.

We have found that monitoring data alone are inadequate to explain variability in nutrient concentrations and loads. If data collection and analysis are to explain causal changes, the building of scenarios may be necessary. Hydrologic models can help to synthesize observations, analyze interactions amongst different processes and fill gaps in information. To date, a Soil and Water Assessment Tool (SWAT) and Rural Stormwater Management Model (RSWMM) have been developed for the Gully Creek watershed to evaluate the relationship between land management practices and hydrologic conditions. This information is useful if we want to get an idea of the amount of nutrients and sediment that can be reduced under different scenarios at the watershed scale; however, it is not yet known how well the modelled results simulate monitored data for evaluating BMPs.

At this point, technical staff from the Healthy Lake Huron project has only been able to use the output from the SWAT model that was developed for the period 2002 to 2011. Due to the complexity of running SWAT for years that extended beyond the Watershed Based BMP Evaluation project time frame, 2012 to 2015, we continue to collaborate with researchers at the University of Guelph to support ongoing SWAT development. However, ongoing efforts to support watershed management agencies to collaborate with researchers will develop the potential for these models to help to explain changes in water quality with changes in land use and climate.

Next Steps

In summary, further analysis of these data sets, as well as other data collected from tributaries on the south east shores of Lake Huron, would provide water managers with better approaches to understand water quality conditions. As discussed above, more analysis is required to:

1) Evaluate changes in water quality over time without the influence of streamflow using flow-adjusted concentrations. In doing so, we may be able to differentiate times when load is influenced by changes in flow or when anthropogenic impacts (e.g., land use changes, land management practices, etc.) affect loads;

2) Evaluate optimal trigger levels (*e.g.,* 90^{th} percentile of flow/stage) for ISCO automatic samplers in the priority watersheds to improve workload efficiencies;

3) Optimize the number of samples required in the priority watersheds to reliably estimate loads (*e.g.,* within ±10% of the “true” load) while maintaining low sampling costs;

4) Evaluate how the streams respond to precipitation events by looking at peak precipitation and peak flow rates. From previous edge-of-field research, we have observed not only pollutant reductions through BMP implementation, but also reductions in peak runoff – can we see similar responses at the watershed scale?;

5) Use hydrologic process models (e.g., SWAT) to explain water quality changes over time. For instance, hydrologic models may help us examine in more detail the increasing phosphorus and sediment concentrations in Trick’s Creek, as well as low nitrate-N mass export coefficients in South Pine River; and

6) Enhance understanding and context of our work to other environmental agencies and groups through workshops and training opportunities, as well as invite a more technical audience to review our work and provide insight and direction for future projects.

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Appendix A: Monitoring Stations

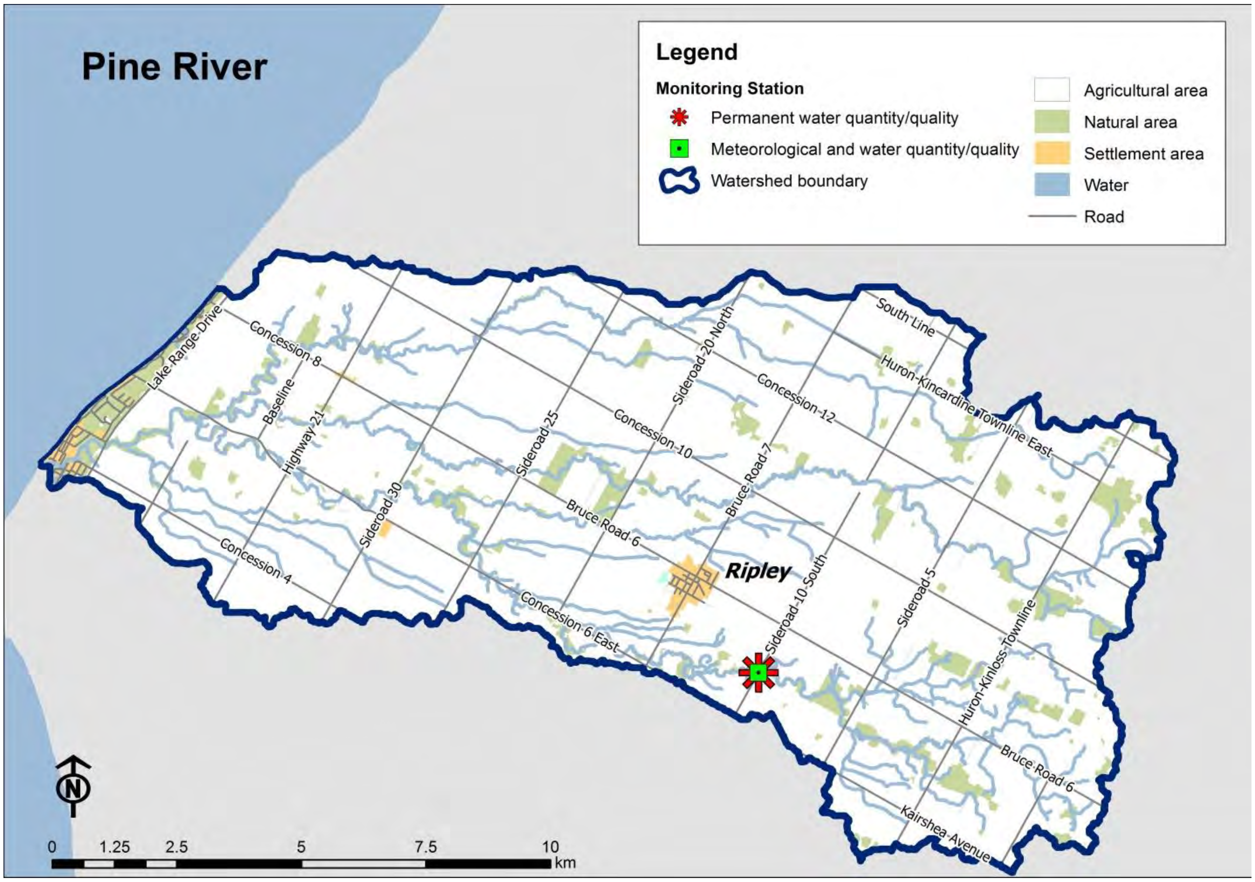

Figure A-1: Location of the water quantity/quality monitoring station (red) in South Pine River.

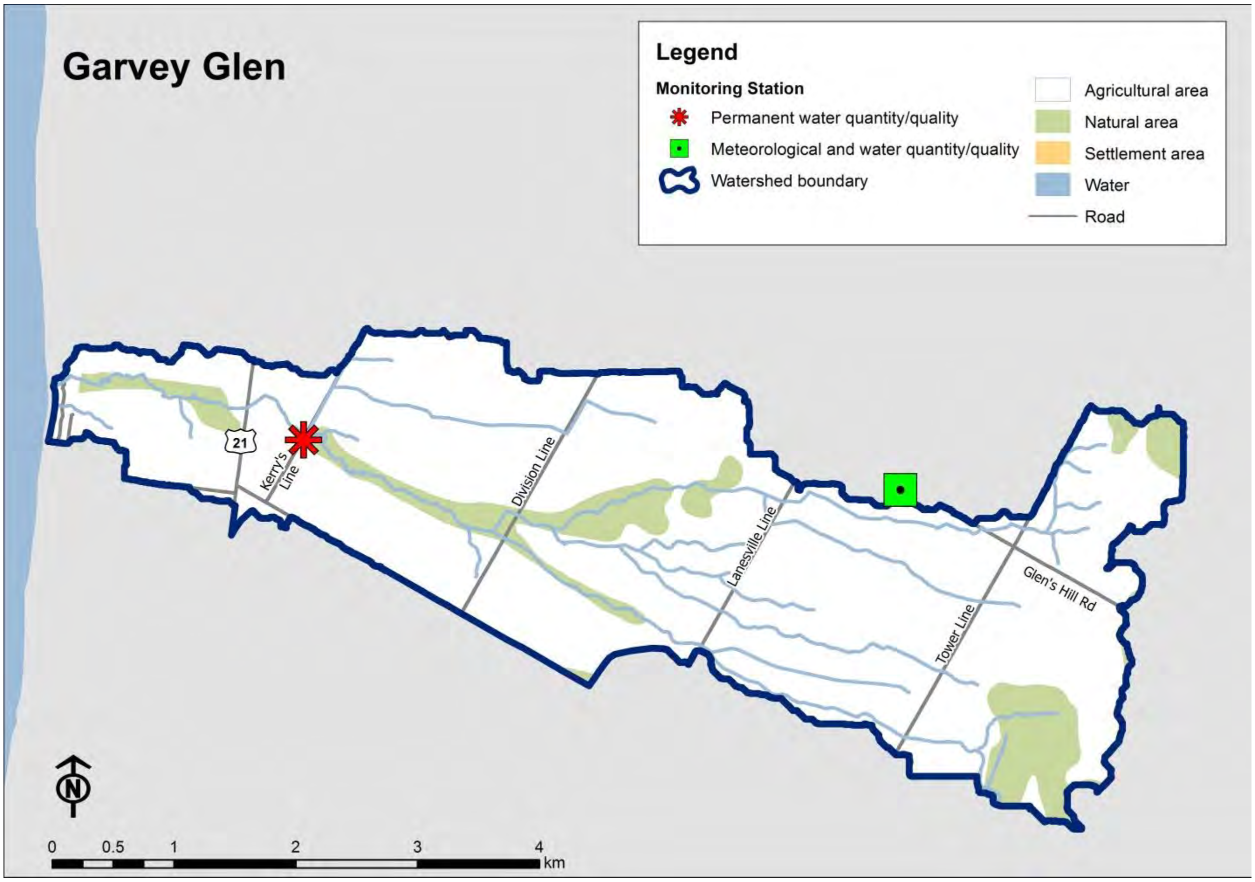

Figure A-2: Location of the water quantity/quality monitoring station (red) in Garvey Creek/Glenn Drain.

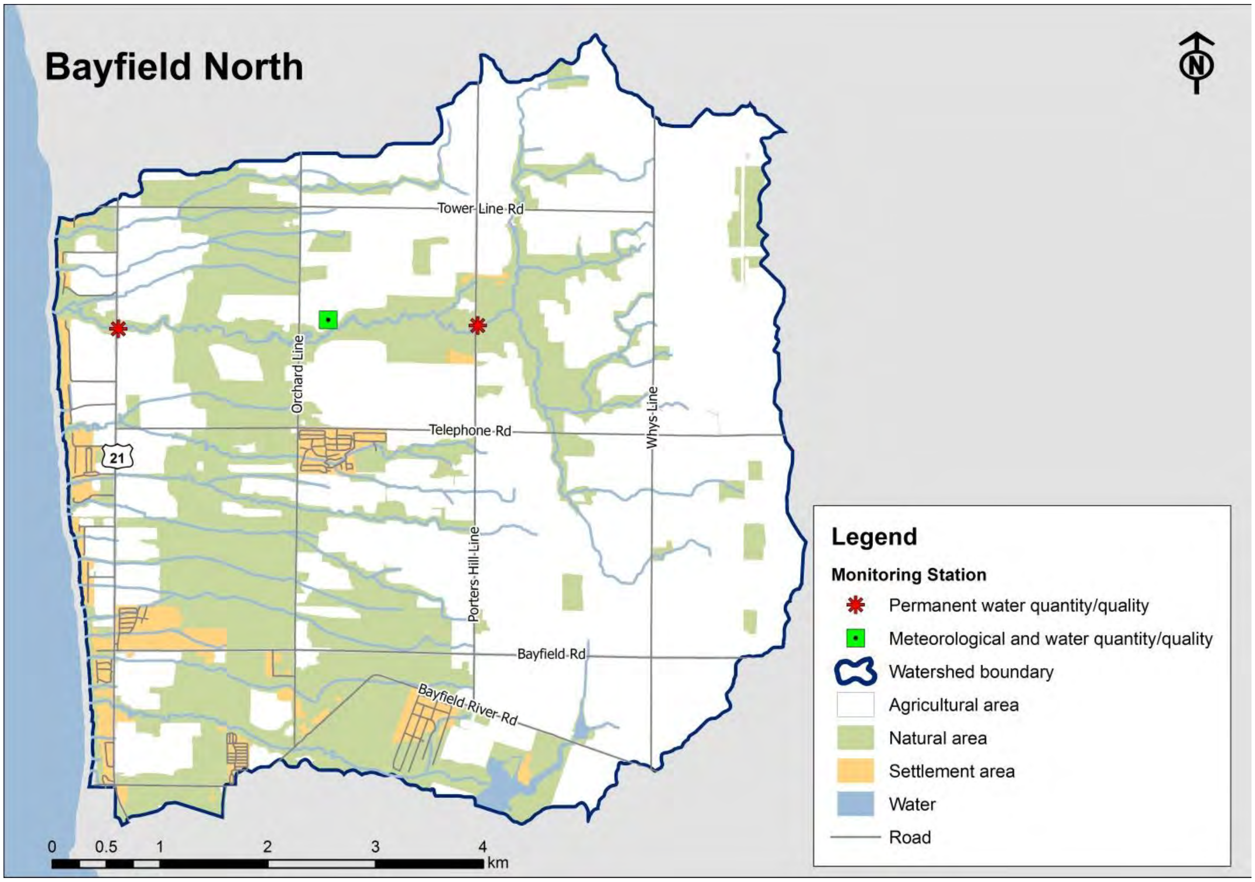

Figure A-3: Location of the water quantity/quality monitoring stations (red) in Gully Creek.

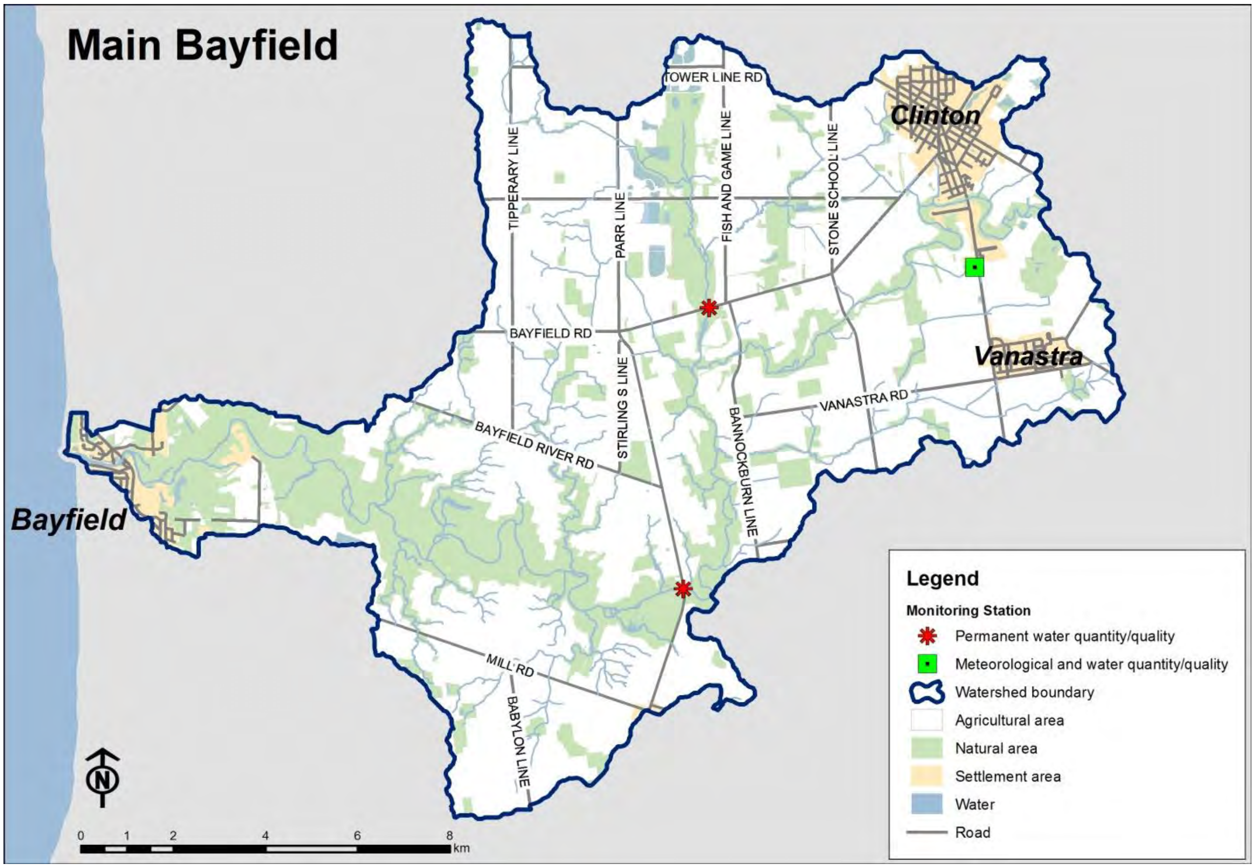

Figure A-4: Location of the water quantity/quality monitoring station (red) in Bayfield River and Trick's Creek.

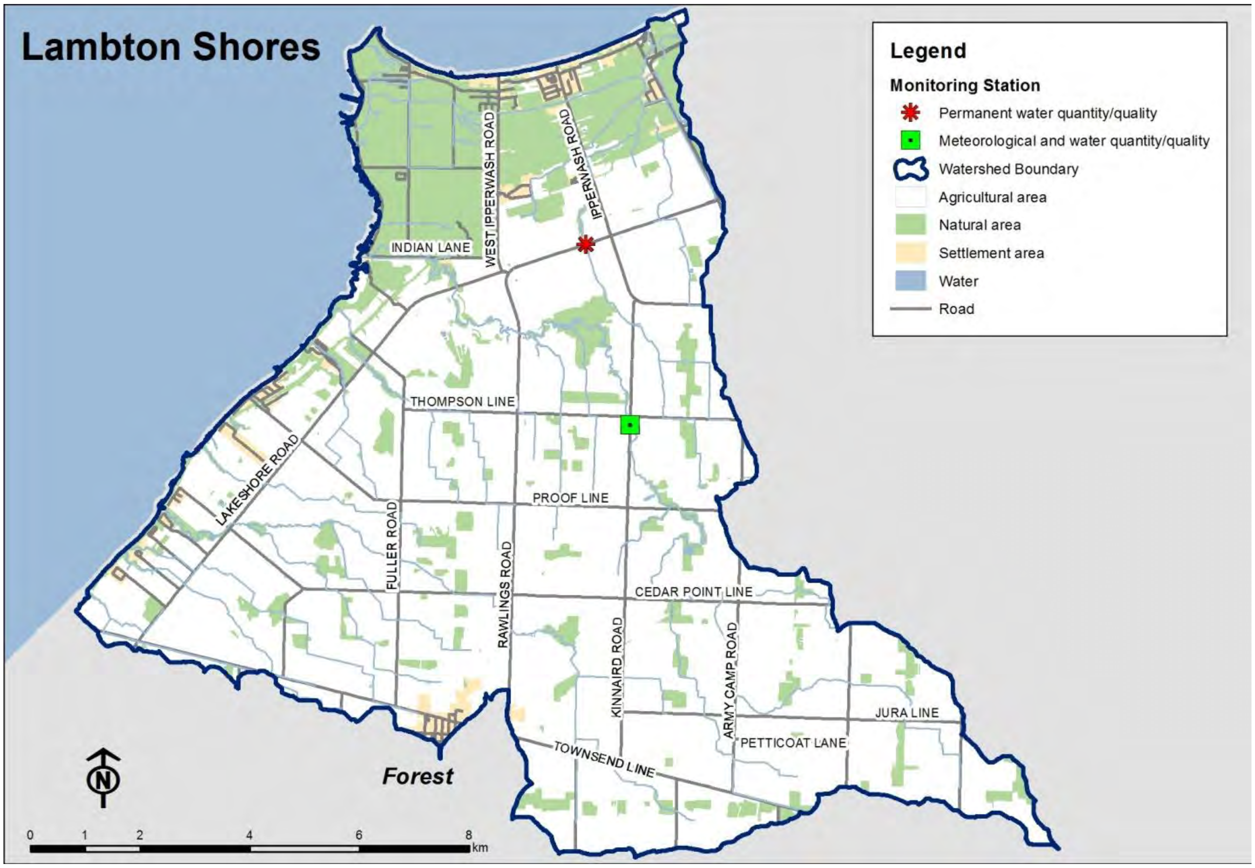

Figure A-5: Location of the water quantity/quality monitoring station (red) in Shashawandah Creek.

Appendix B: Water Quality Analyser Load Estimation Equations

A1: Average Load Estimation Method

$$Load = k \sum_{i=1}^{n} \frac{q_i c_i}{n}$$

Where,

k = number of time intervals in period (*e.g.*, k=365)
n = total number of samples
i = number of a particular sample
q_i = flow rate measured at the day and time of the ith sample
c_i = concentration measured at the day and time of the ith sample

A2: Beale Ratio Estimator Method

$$Q\left(\frac{\bar{l}}{\bar{q}}\right)\left\{\frac{1 + \frac{1}{N}\frac{\rho \sigma_L \sigma_Q}{\bar{l}_{\bar{q}}}}{1 + \frac{1}{N}\frac{\sigma_Q^2}{\bar{q}^2}}\right\}$$

Where,

Q = total discharge for period
$\bar{l}$ = average load for sample
$\bar{q}$ = average of N discharge measurements
$\boldsymbol{\sigma}_L$ = standard error of observed load
$\boldsymbol{\sigma}_Q$ = standard error of total discharge for period
$\boldsymbol{\rho}$ = coefficient correlation for load and discharge

The term in curly brackets is the bias correction term. *N* is the expected population size (this is included in the calculation, to compensate for the effects of correlation between discharge and load).

A3: Linear Interpolation of Concentration Data Method

$$\sum_{i=1}^{n} \frac{c_i + c_{int}}{2} q_j$$

Where,

n = total number of samples
i = number of a particular sample
c_i = concentration measured at the day and time of the ith sample
q_j = inter-sample mean flow
c_{int} = linearly interpolated concentration value between samples

A4: Continuous Discharge Estimation Method

$$V\frac{\sum_{i=1}^{n} q_i c_i}{\sum_{i=1}^{n} q_i}$$

Where,

V = annual cumulative flow volume (continuous data)
q_i = flow rate measured at the day and time of the *i*th sample
c_i = concentration measured at the day and time of the *i*th sample
n = total number of samples

A5: Flow Stratified Sampling Method

$$\sum_{j=1}^{n_s}\frac{N_j}{n_j}\left[\sum_{i=1}^{n_j} q_i c_i\right]$$

Where,

N_j = number of measured flow days for each strata (flow regime)
n_j = number of sampled concentration days for each strata (flow regime)
n_s = total number of strata (flow regimes) in a year
q_i = flow rate measured at the day and time of the *i*th sample
c_i = concentration measured at the day and time of the *i*th sample

A6: Concentration Power Curve Method

$$c = aq^b$$

Where,

c = constituent concentration
a = a model coefficient
q = flow rate
b = a power coefficient

Appendix C: Phosphate-Phosphorus Load Uncertainty

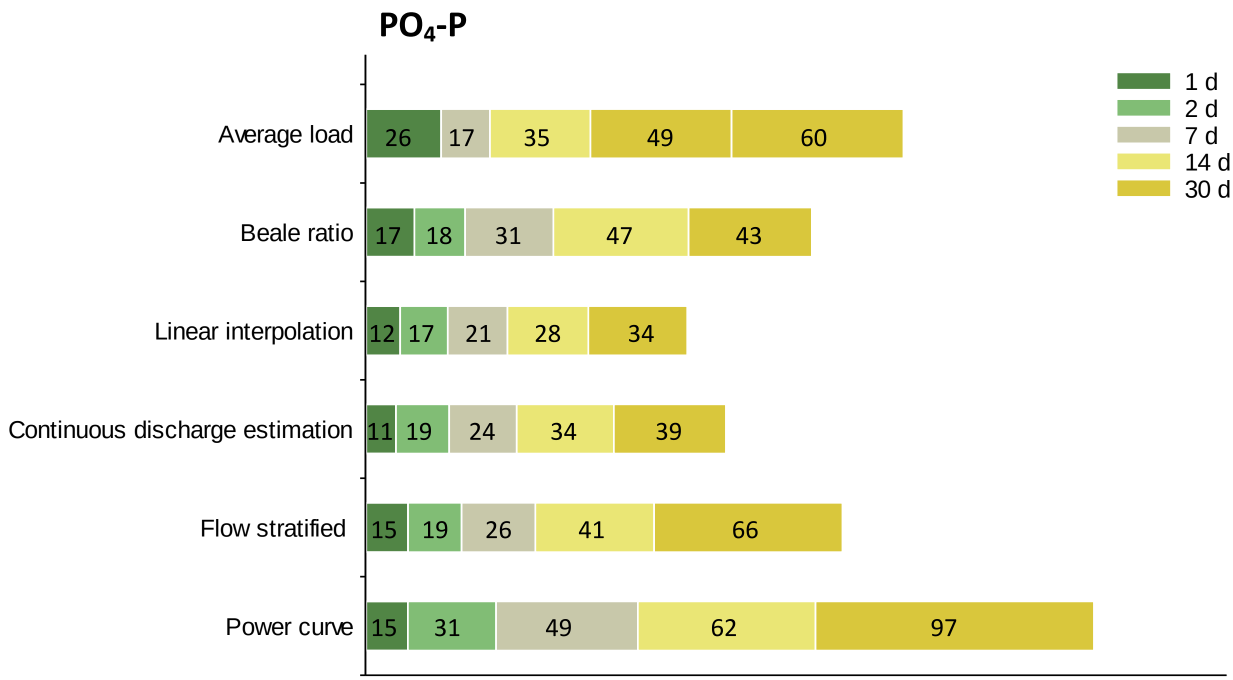

Figure C-1: Root mean squared error (%) for six load estimation algorithms over five different sampling frequencies. Values shown are the mean difference between the reference ("true") loads and the estimated loads using water quality data from Gully Creek, Garvey Creek/Glenn Drain, and Trick's Creek.

Appendix D: Phosphate-Phosphorus Flow-Weighted Mean Concentrations

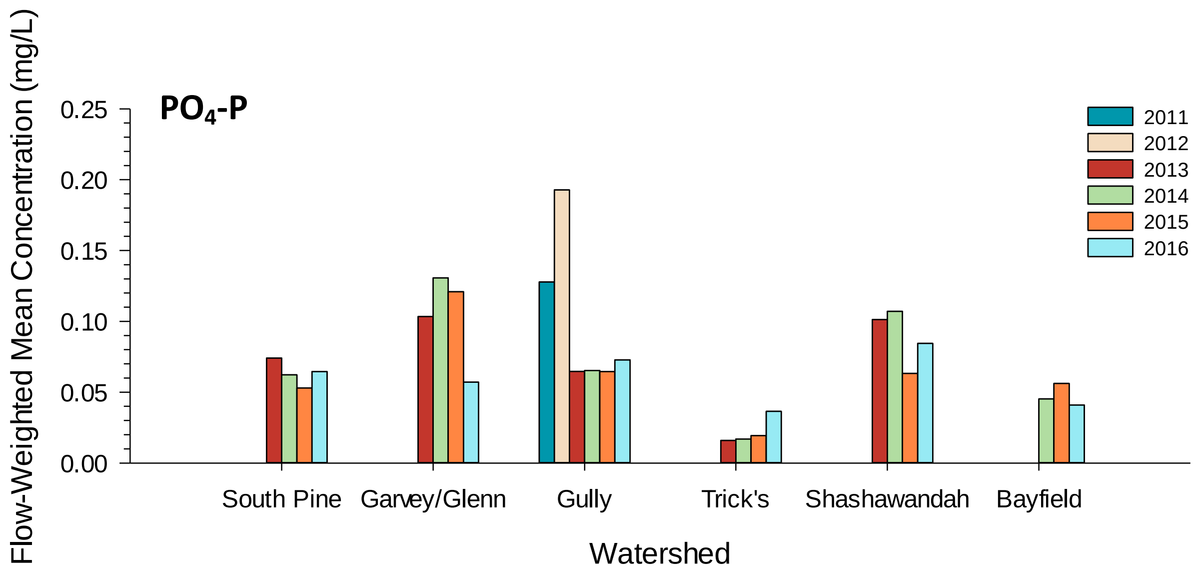

Figure D-1: Annual phosphate-phosphorus flow-weighted mean concentrations in the Healthy Lake Huron watersheds (October 2010 to September 2016). Notes: GULGUL5 monitoring station data were used to estimate FWMC for the 2012 to 2016 water years. GULGUL2 monitoring station data were used for the 2011 water year.

Appendix E: Phosphate-Phosphorus Total Loads

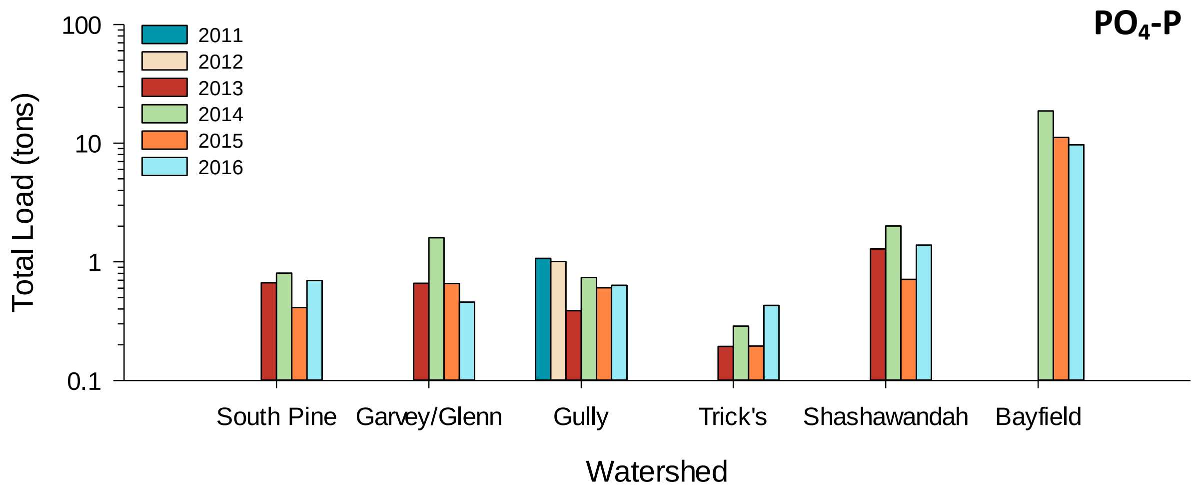

Figure E-1: Annual phosphate-phosphorus loads in the Healthy Lake Huron watersheds (October 2010 to September 2016). Notes: GULGUL5 monitoring station data were used to estimate FWMC for the 2012 to 2016 water years. GULGUL2 monitoring station data were used for the 2011 water year.

Appendix F: Phosphate-Phosphorus Mass Export Coefficients

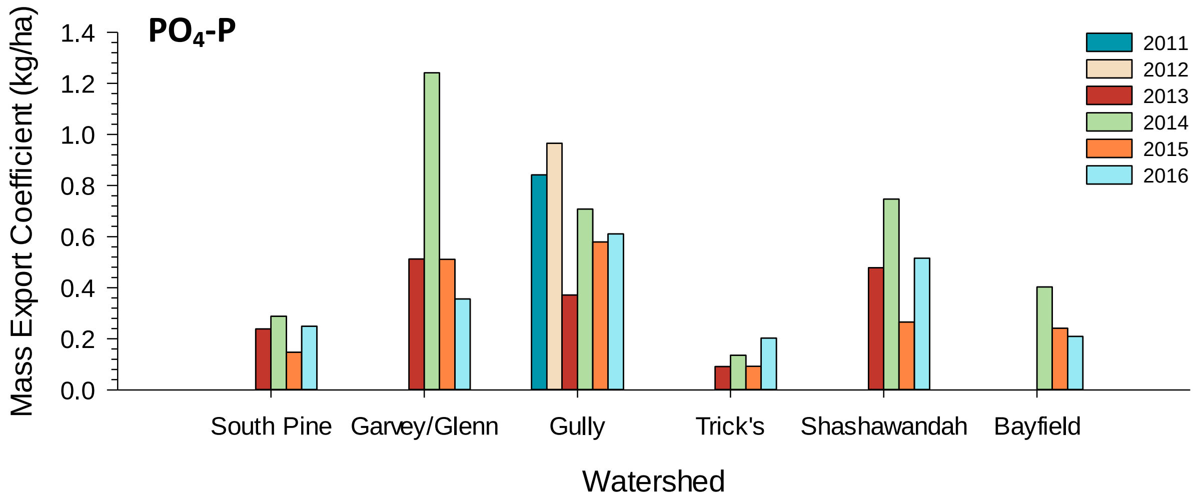

Figure F-1: Annual phosphate-phosphorus mass export coefficients in the Healthy Lake Huron watersheds (October 2010 to September 2016). Notes: GULGUL5 monitoring station data were used to estimate FWMC for the 2012 to 2016 water years. GULGUL2 monitoring station data were used for the 2011 water year.

Appendix G: Trends in Monthly Flow-Weighted Mean Concentrations

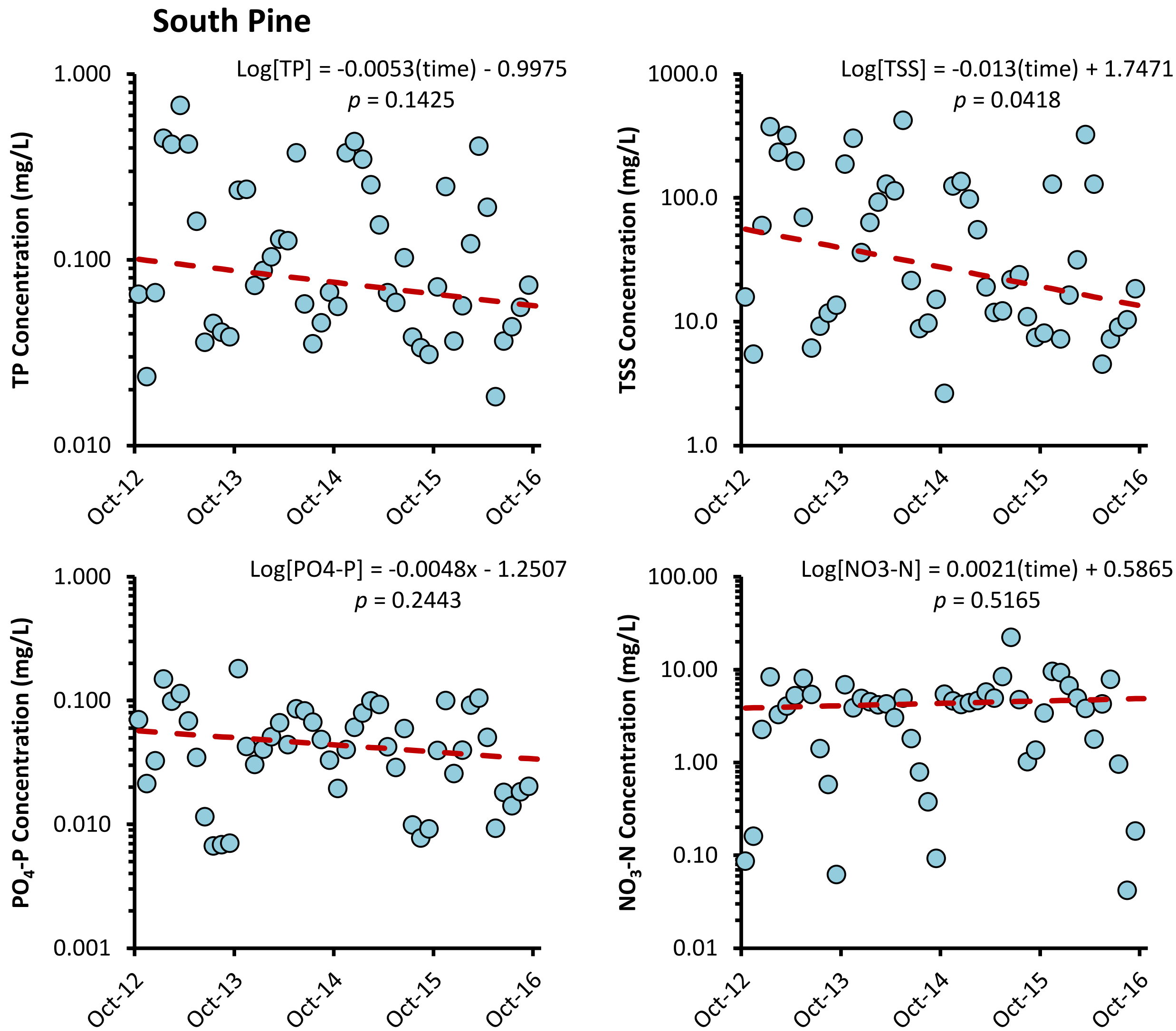

Figure G-1: Water quality trends in monthly flow-weighted mean concentrations for South Pine River (October 2012 to September 2016).

Garvey/Glenn

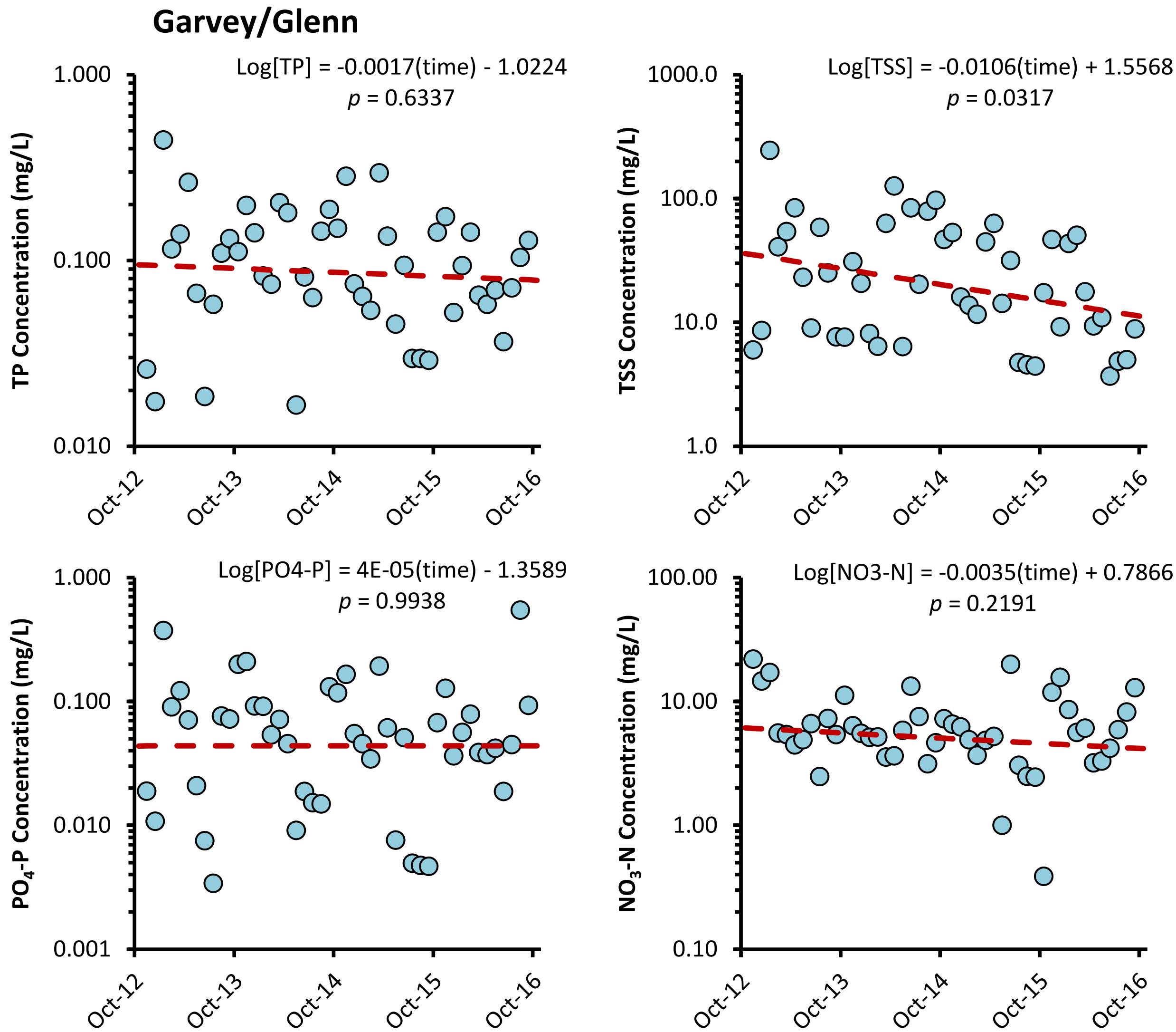

Figure G-2: Water quality trends in monthly flow-weighted mean concentrations for Garvey Creek/Glenn Drain (October 2012 to September 2016).

Trick's

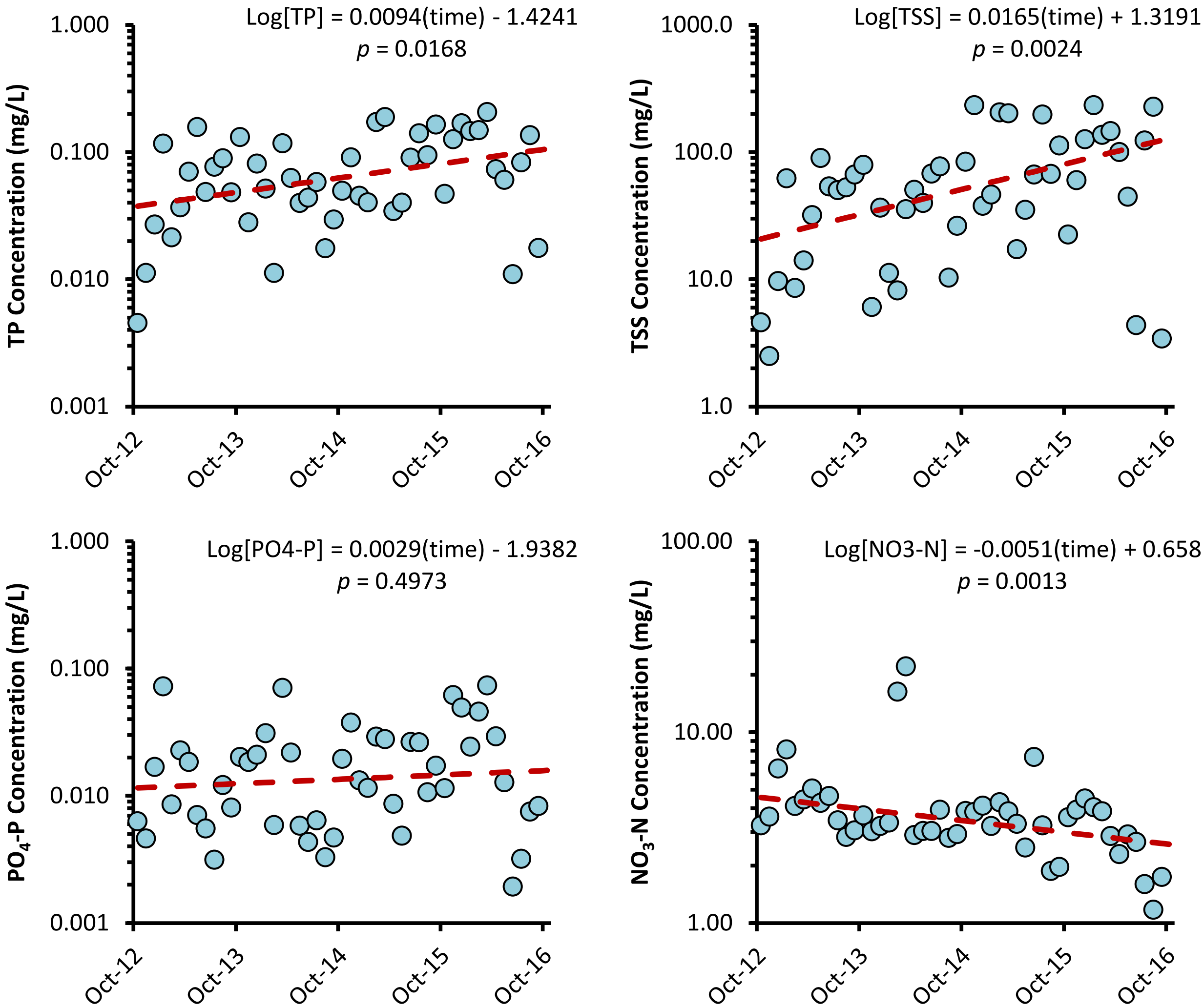

Figure G-3: Water quality trends in monthly flow-weighted mean concentrations for Trick's Creek (October 2012 to September 2016).

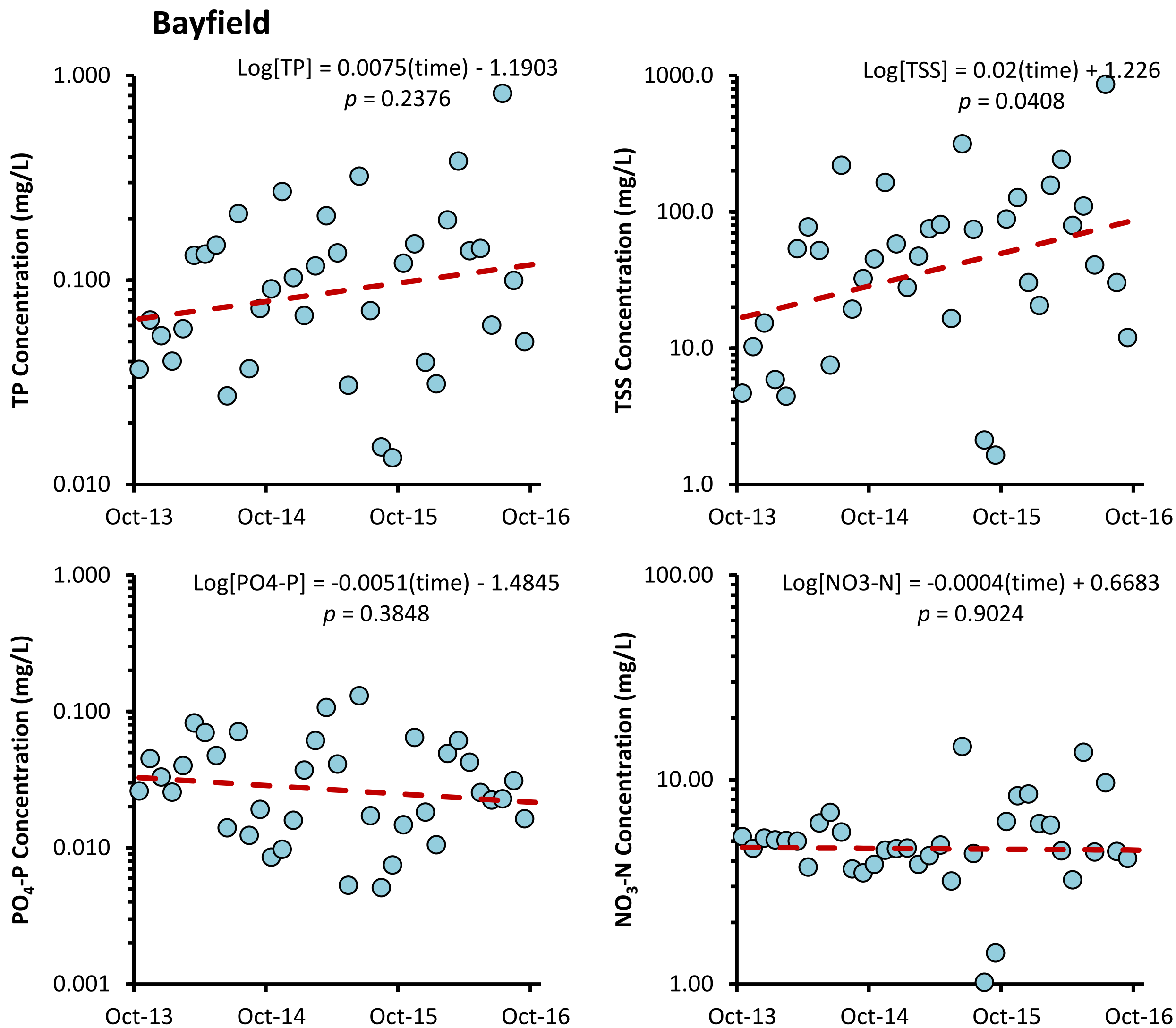

Figure G-4: Water quality trends in monthly flow-weighted mean concentrations for Bayfield River (October 2013 to September 2016).

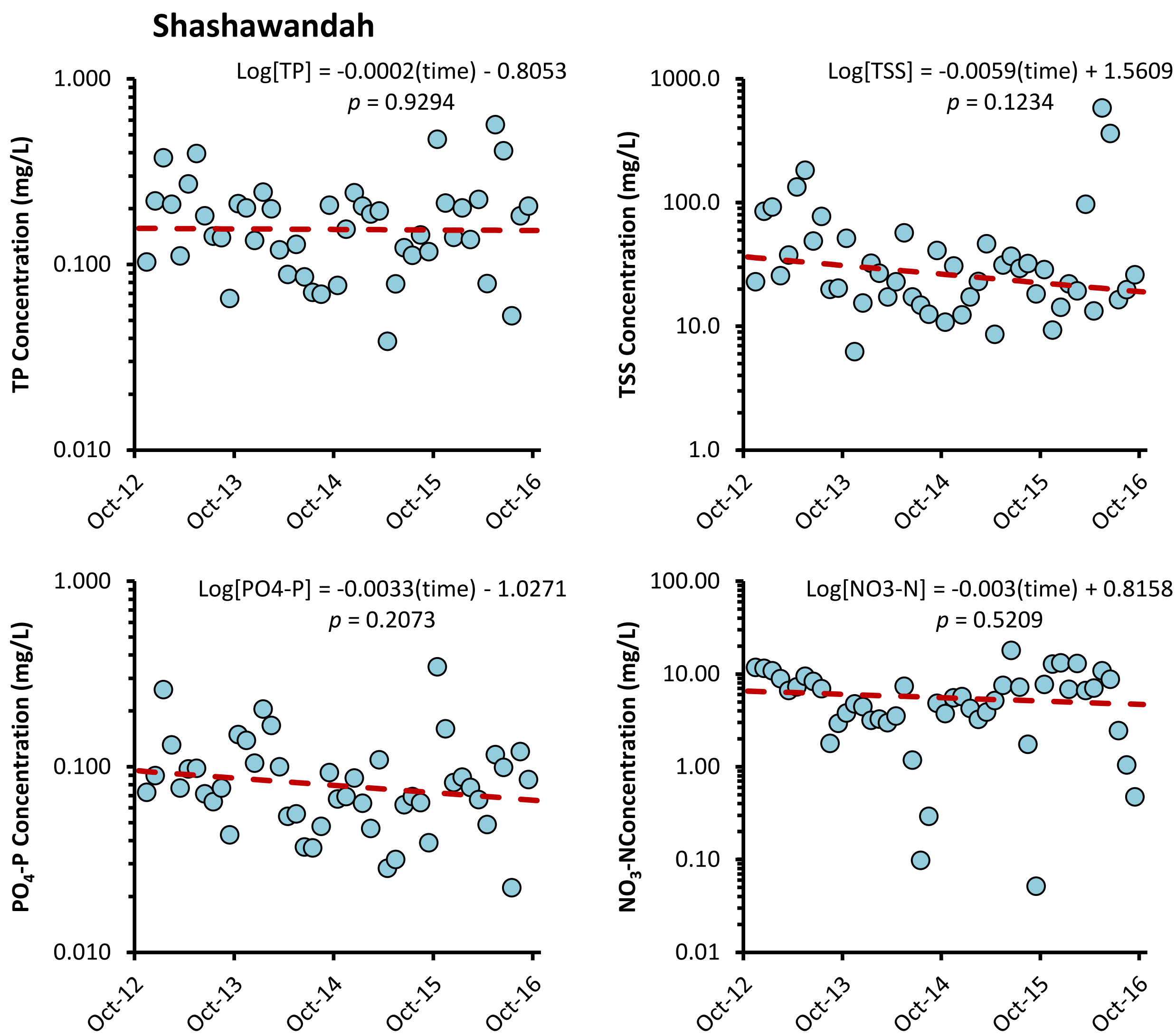

Figure G-5: Water quality trends in monthly flow-weighted mean concentrations for Shashawandah Creek (October 2012 to September 2016).

Appendix H: Trends in Monthly Loads

South Pine

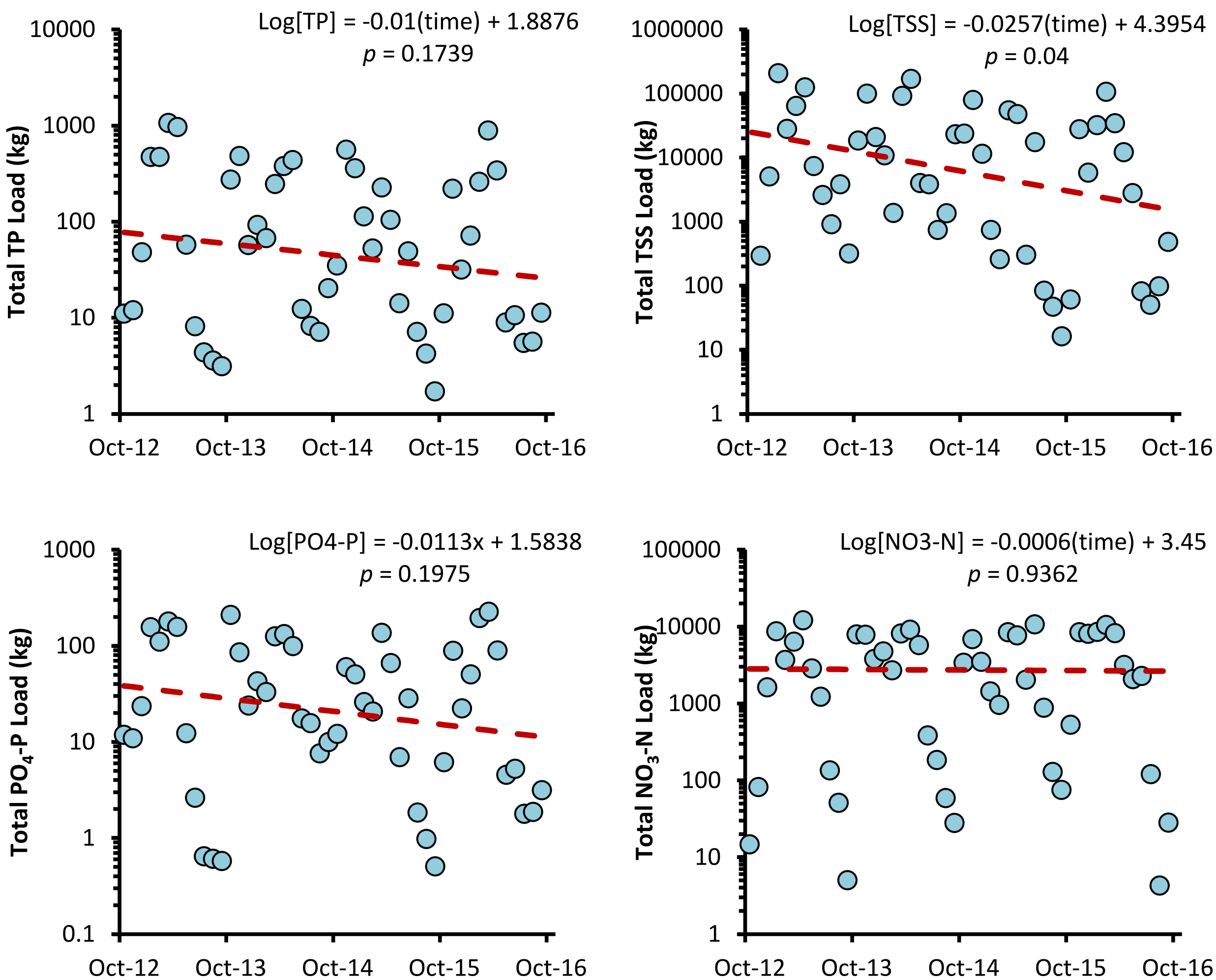

Figure H-1: Water quality trends in monthly loads for South Pine River (October 2012 to September 2016).

Gully

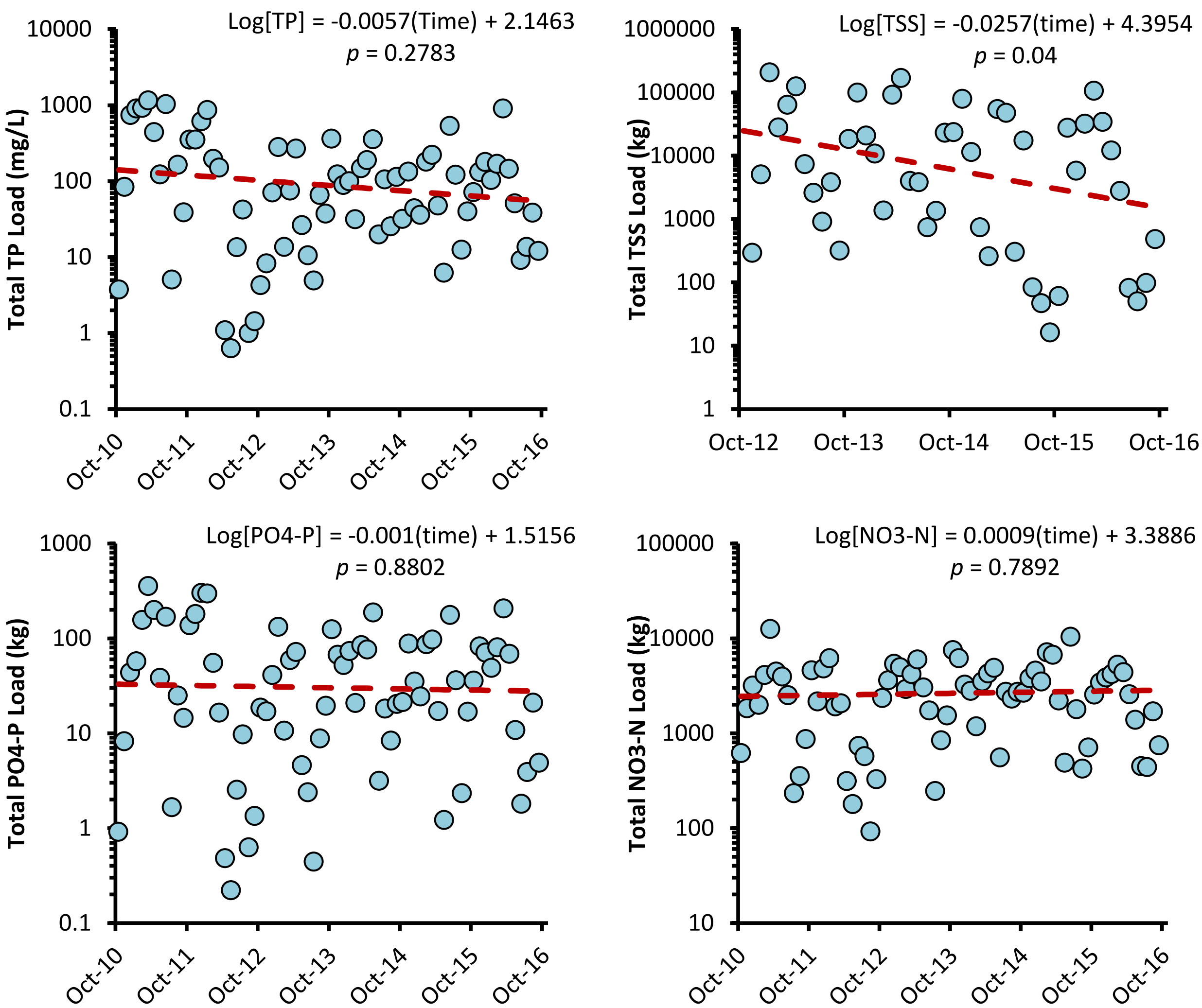

Figure H-2: Water quality trends in monthly loads for Gully Creek (October 2010 to September 2016).

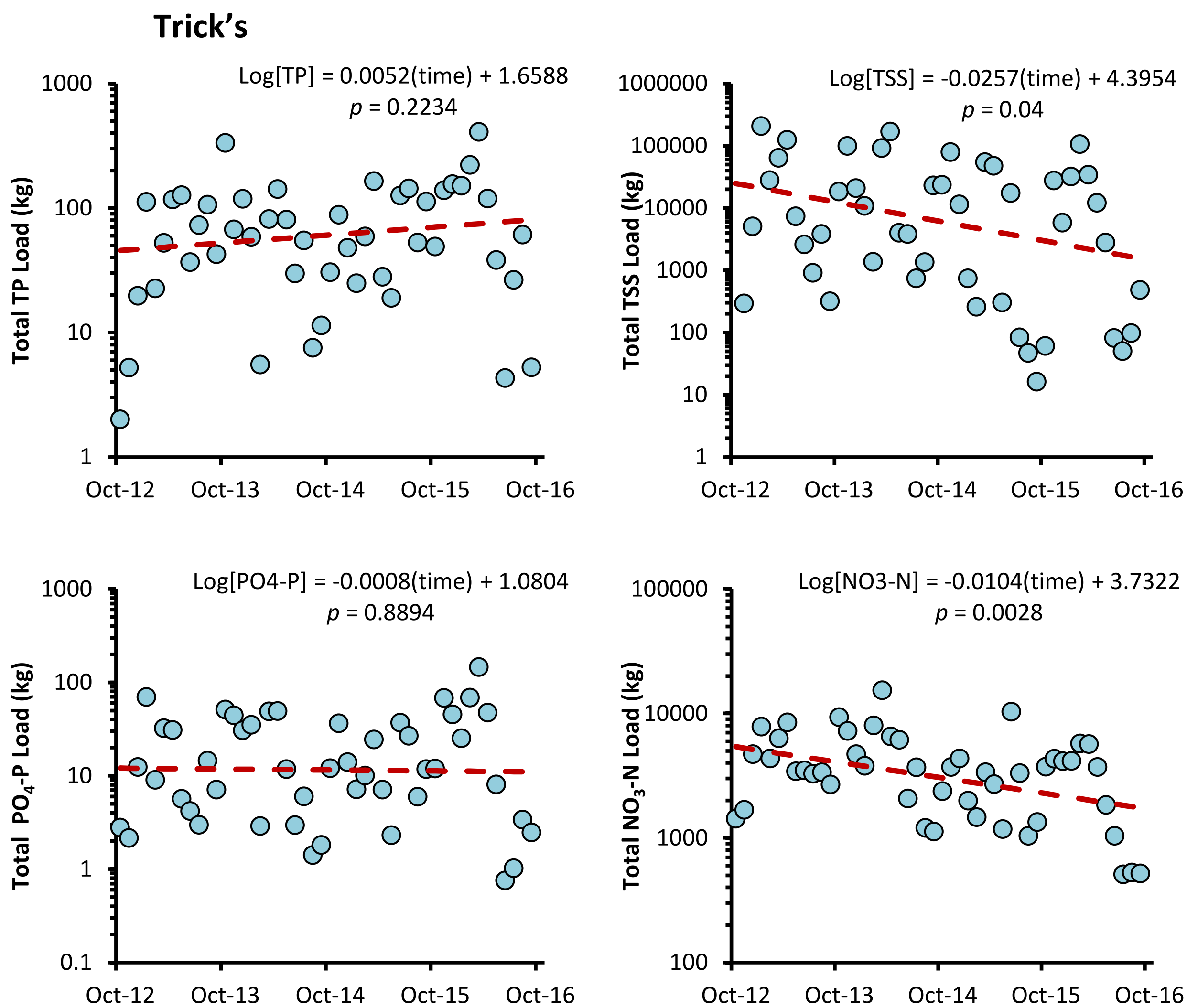

Figure H-3: Water quality trends in monthly loads for Trick's Creek (October 2012 to September 2016).

Bayfield

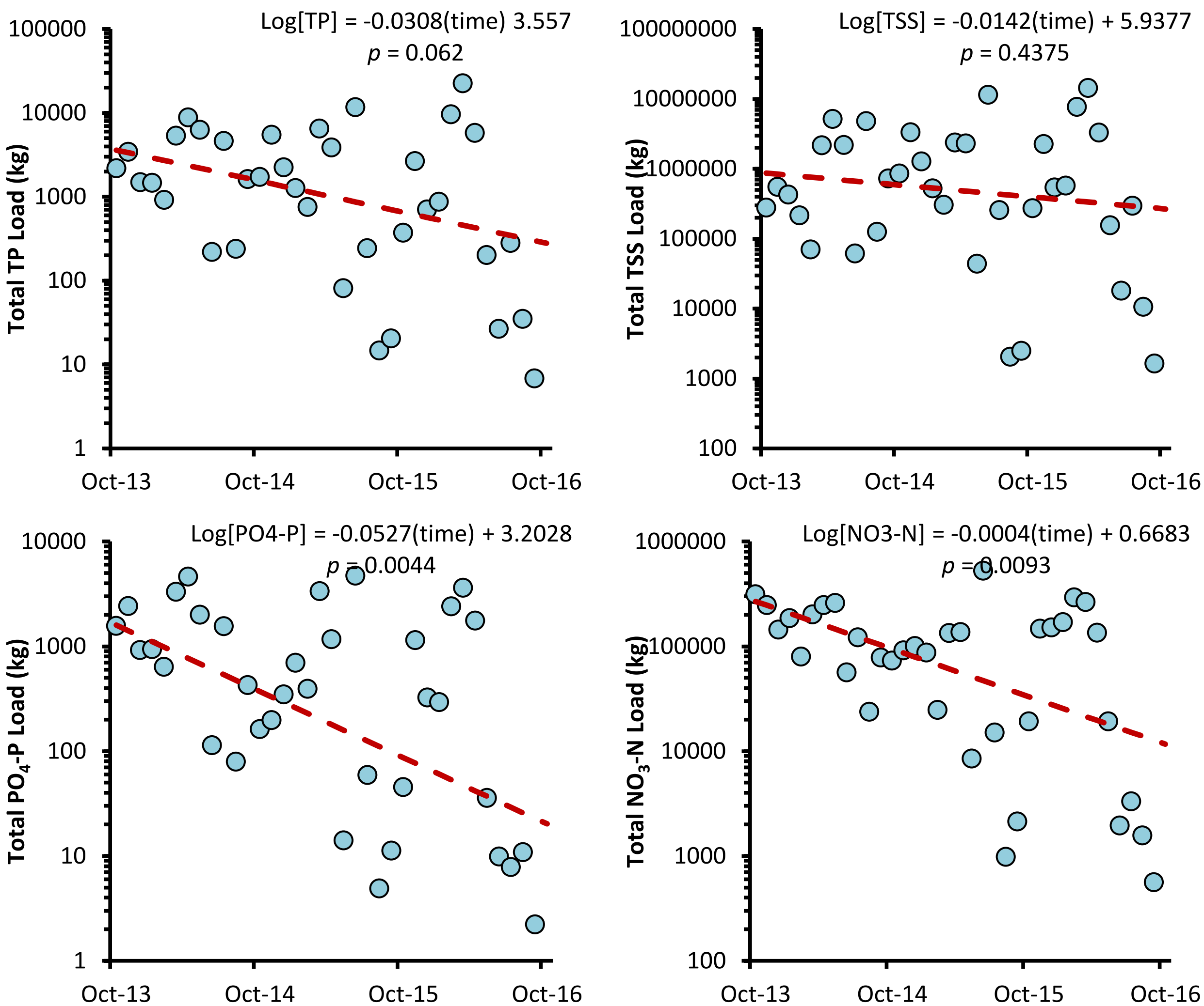

Figure H-4: Water quality trends in monthly loads for Bayfield River (October 2013 to September 2016).

Appendix I: Seasonal Phosphate-Phosphorus Loads by Monitoring Station

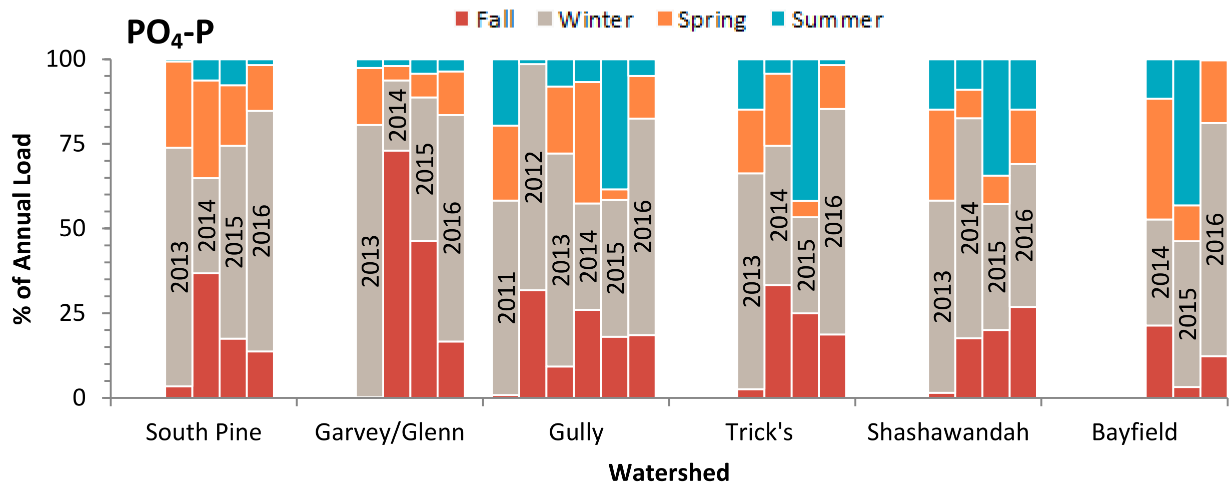

Figure I-1: Seasonal phosphate-phosphorus loads as a percentage of annual loads for all of the study streams. Water years are shown as vertical labels.

Appendix J: Seasonal Phosphate-Phosphorus Loads Averaged Across All Monitoring Stations

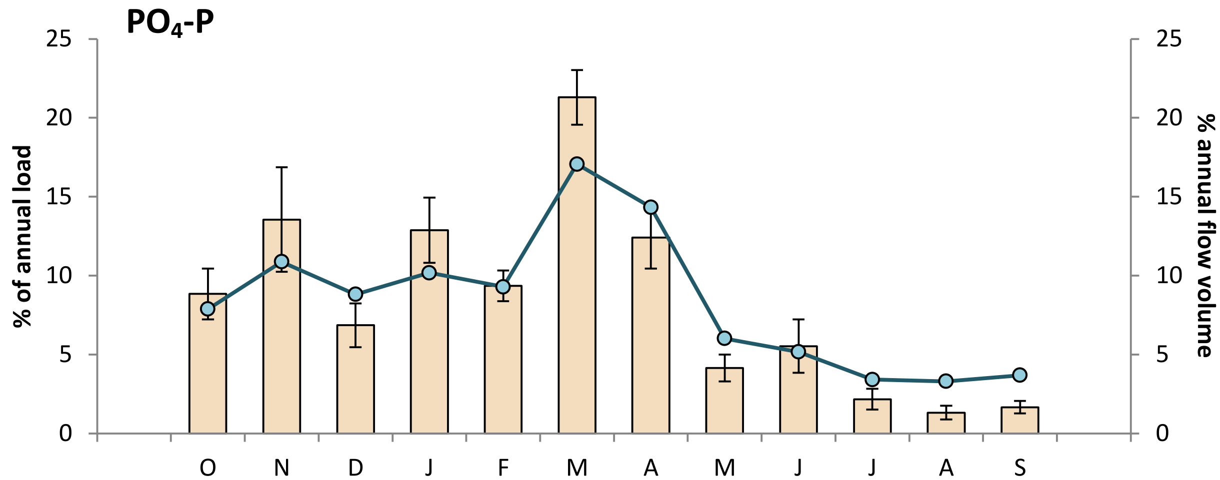

Figure J-1: Percent annual load (pale bars, left axis) and percent annual flow volume (blue line, right axis) averaged across all of the study streams. Error bars are standard error of the mean, representing variability in annual loads among streams.