

# Site Specific Guidelines for Phosphorus in relation to the Water Quality Index Calculations for Prince Edward Island



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## Executive Summary

The Environment (CCME) Water Quality Index (WQI) was developed for communication of water quality data using a simple metric of water quality. Naturally high background levels of some water quality parameters may be the cause of some disparity between WQI scores and local expert opinion on water quality. To account for high background levels, it may be necessary to use site-specific water quality guidelines to obtain representative rankings for the WQI. There is no total phosphorus national guideline for the protection of aquatic life. Under the guidance of the Canadian Environmental Sustainability Indicator program a value of 30 µg/L total phosphorus has been adopted for the purposes of national reporting in the WQI calculation. In the case of Prince Edward Island, levels of total phosphorus often exceed this guideline. The primary purpose of this report was to provide options for the site-specific calculation of the WQI on PEI with regards to total phosphorus. This goal was accomplished by comparing phosphorus levels in less-impacted to more-impacted areas, establishing background levels of phosphorus in groundwater and surface water, and determining the relationship between phosphorus levels in surface water and groundwater.

Evaluation of the water quality dataset for PEI revealed that the data was inadequate, or else not sufficiently consistent at all sites to employ recommended methods for the calculation of site specific guidelines. A new method was developed for the calculation of background levels of total phosphorus using statistical outlier removal. This method was based on the assumption that this would eliminate data points that may have been collected during storm events where total phosphorus would be expected to exceed background levels. The results of this statistical procedure indicated significant variability in background levels of total phosphorus in the streams examined (means from 11 and 69 µg/L). This variability in total background phosphorus was not statistically related to land use within the watersheds examined. This was not taken to imply that land-use activity has no relationship to phosphorus loading as the results only pertain to background phosphorus, not total loadings which may be dominated by storm events. As base-flow in PEI streams is dominated by groundwater, it is presumed that reasons for variability in background total phosphorus on the Island are due to geology, though wetlands also appear to have an influence. While variability in groundwater total phosphorus as measured in wells within the watershed supports this hypothesis, geological information from PEI indicates significant heterogeneity at local scales and reveals no clear reason for the trends.

It was concluded that the best approach for the calculation of the WQI for PEI sites was to incorporate a distinct water quality guideline for total phosphorus at every site. This guideline can be calculated as the mean total phosphorus plus two standard deviations.

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## 1.0 Background

The CCME Water Quality Index (WQI) is a national, public indicator of water quality used by the Canadian Environmental Sustainability Indicator (CESI) program to communicate water quality on a nationwide basis using a single metric. CESI provides guidance in order to provide consistency in the calculation the WQI.

The WQI is based on the Canadian Water Quality Guidelines (WQG) that were intended to protect the designated uses of aquatic ecosystems throughout the country. One of the variables utilized in calculating the WQI for streams in Prince Edward Island is total phosphorus. There is no Canadian Water Quality Guideline for total phosphorus for fresh water aquatic life. Instead a guidance framework for freshwater systems has been developed which indicates that phosphorus should not exceed predetermined “trigger” ranges with specific trophic impact, and not increase more than 50% over background levels. These values have not been determined for PEI. Under CESI guidance a value of 30 µg/L total phosphorus has been adopted for use as a guideline value in the WQI calculation (Government of Canada 2008). This value is an Ontario Water Quality Guideline, advocated by CESI protocols, that is protective of excessive plant growth in streams and rivers.

It has been observed that some of PEI’s less impacted sites are routinely exceeding 30 µg/L of total phosphorus, while some other sites, suspected of having more anthropogenic influences rarely exceed this level. These differences are presumed to be due to high background levels of phosphorus in some areas of the province. As a result WQI scores for some sites do not meet with local water quality experts’ interpretation of actual water quality at these sites, with some sites scoring lower and others higher than expected. To address this issue, the PEI Department of Environment, Energy and Forestry proposes to create site specific guidelines for total phosphorus. These guidelines would utilize background values at various sites around the province and would be used in the WQI calculation for PEI.

This report was prepared to provide scientific and technical guidance on the development of site-specific WQGs using historic data provided for the sites and guidance provided by the CCME on this process. Specifically, this report seeks to:

- Compare phosphorus levels in less-impacted to areas expected to have anthropogenic sources of phosphorus,
- Establish background levels of phosphorus in groundwater and surface water,
- Determine the relationship between phosphorus levels in surface water and groundwater,

- Determine whether background levels of phosphorus are consistent across the province, or whether they are site specific,
- Using CCME guidance, determine Site Specific Guidelines for phosphorus for PEI

## 2.0 Methods

Data were provided for this exercise by the Province of Prince Edward Island both from the Canada/Prince Edward Island Water Quality Agreement database, and from the province’s own water quality data. The surface water data selected for analysis in this report for were from the eleven stations locations that comprise the three Management (Montague/Valleyfield, Wilmot/Dunk, Morell) and three Index (Bear, Mill River, West River) basins on PEI (Figure 1). These stations were selected largely based on the long-term nature of the information which allowed for the examination of temporal trends. Similarly, long-term ground water data chosen for analysis were from within four of the six management and index basins. Supplemental information such as agricultural land use statistics and Water Quality Indices were also obtained from the PEI Department of Environment Energy and Forestry.

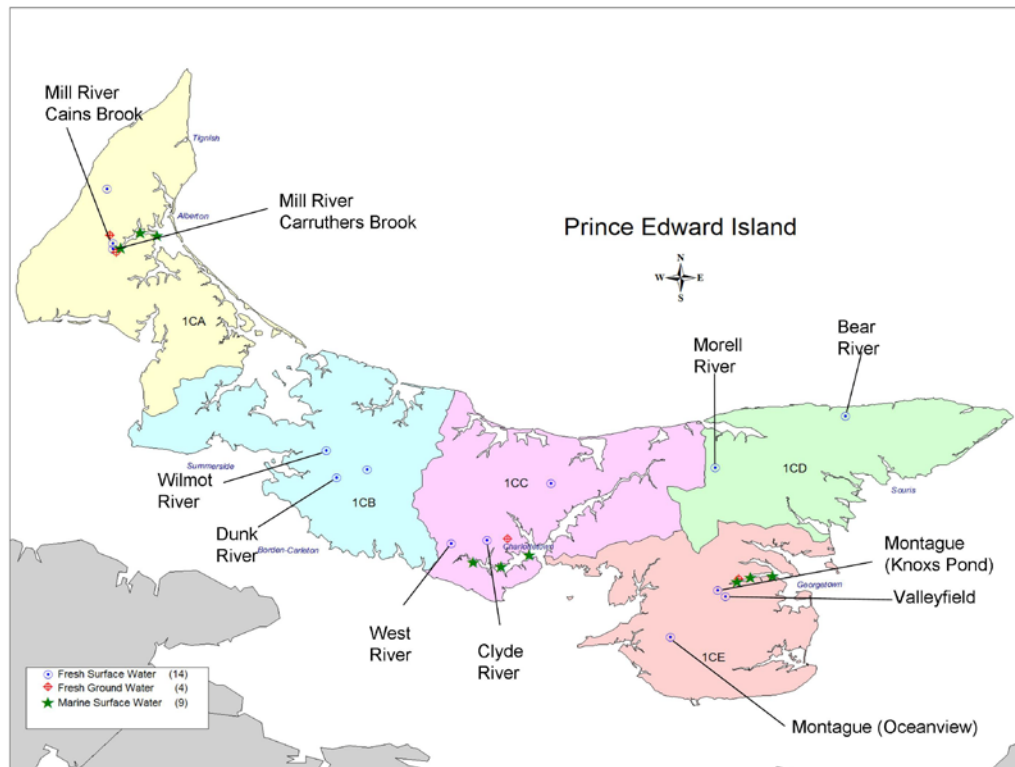


Figure 1. Freshwater surface monitoring stations chosen for total phosphorus data analysis (colours indicate Environment Canada major sub-basin designations).

In a background concentration procedure, the natural background concentrations of a parameter in water are determined and these levels are used to define acceptable water quality conditions at the site under consideration. This approach has been used most commonly, but not exclusively, to define water quality objectives for relatively pristine water bodies. A number of statistical methods have been applied to derive site specific WQGs in terms of the upper limits of 'background' parameter concentrations (CCME 2003). For simplicity of calculation, the method of Dunn (1989) was chosen and given the high sample size, the differences between this approach and the 90th percentile were marginal. This method defines the WQG as the upper limit of background for water quality variables as their mean value plus two standard deviations (SDs). Considerable analysis was conducted by Khan et al. (2005) on the use of mean, median, mean  $\pm$  1 SD, mean  $\pm$  2 SD and 90th percentile for calculating site specific WQG. These analyses found that the use of 2 SD as compared to 90th percentile had only minimal influence on the resultant WQG and subsequently calculated WQI.

Specific procedures have also been developed to generate WQGs where measured parameters vary with the magnitude of stream flow. Total phosphorus is such a parameter as it is generally expected to increase with stream discharge in association with increasing total suspended solids. A rapid assessment approach has been developed to estimate site specific WQGs using either existing flow or turbidity data (Environment Canada, unpublished). Hydrometric stations exist for only five of the eleven sites evaluated and daily mean flows from the online hydrometric database were obtained for those days on which total phosphorus samples were collected. Only weak relationship with flow could be found, and only at some of those sites (Appendix 1). Thus in combination with the lack of flow data at many sites it was unlikely that flow could be used to predict site specific WQGs. Other proposed methods use turbidity in lieu of flow but the use of turbidity data would further have limited the size of the dataset due to the limited instances where both parameters were measured. Because of these data limitations, evaluation of phosphorus-flow or phosphorus turbidity methods for generating WQGs were not pursued further and an alternative method for derivation of background values was utilized.

As no system is pristine, determination of the 'natural background' (pre-human) levels of ubiquitous substances such as are represented by total phosphorus are impossible. However, as total phosphorus from anthropogenic sources is known to travel primarily through surface runoff and will not readily move from surface sources into groundwater, the term background concentration, as it will be used herein, was defined as the levels of phosphorus entering the stream primarily through groundwater. Thus, total phosphorus under conditions of limited surface runoff (when most samples are collected) offered the best surrogate of background concentrations obtainable from existing data. Direct measurement of

groundwater phosphorus is an alternative method, and although this is briefly examined, data does not exist to quantify the groundwater contribution to stream total phosphorus directly.

Evaluation of data indicated that high flow or high total phosphorus were relatively rare events. It was hypothesized that background concentrations at all of the sites should be normally distributed, and thus the removal of statistical extremes and outliers from these data should approximate the current background total phosphorus values. However, if total phosphorus was increasing through time along with elevated anthropogenic inputs into the watersheds it would follow that the values derived are not truly background, but a reflection of increasing phosphorus input into the systems. The time series for the water quality data occurred over the period in the 1990's (in some cases data went back to the 1970's) when significant increases in row crop production occurred in many watersheds, allowing an evaluation of changes in total phosphorus over this period of changing land use as a validation of the methods chosen to determine background phosphorus. Where statistically significant changes over time did occur, the background phosphorus could be adjusted back to the time of the earliest TP measurements. While method detection limits changed over the time period of these datasets, all samples contained detectable TP and thus non-detect values has no bias on these analyses. The mean total phosphorus after outlier removal is henceforth referred to as the background phosphorus level for the purposes of this report.

To summarize, the data evaluation procedure established for surface water was:

- 1) Tabulate total phosphorus and flow data where available (replicate phosphorus numbers were averaged)
- 2) Statistically evaluate phosphorus-flow relationships
- 3) Remove statistical outliers and extremes
- 4) Verify the normal distribution of the data for each site
- 5) Statistically evaluate background phosphorus-time relationships
- 6) Generate a site-specific WQG as being two standard deviations from the mean
- 7) Where phosphorus-time relationships exist, interpolate to the year of earliest data

While total phosphorus is the recommended endpoint under CESI guidance, changes in trophic status generally respond to orthophosphate concentrations as much of the total phosphorus pool is unavailable. Thus the relationship between orthophosphate and total phosphorus was explored. As total phosphorus is the parameter used for the current WQI, there is limited phosphate (or dissolved reactive phosphorus, DRP) data for the systems examined. To supplement the data provided phosphate values for the sites examined were provided from a dataset being collected over the last two years by the Canadian Rivers

Institute at UPEI. Sites were selected where the collection point was either in very close proximity to, or exactly the same as the management and index water quality sites examined. The values are reported as dissolved phosphate, rather than DRP as they were determined by suppressed ion chromatography after filtration through a 0.45 µm syringe filter. Detection limits for the method were 0.001 mg/L and non-detect values were substituted with a value of half the detection limit for statistical calculations.

In order to evaluate the effects of the site specific TP guidelines generated in this exercise, the WQI values for 2007 and 2008 was recalculated using these values. These calculations were performed and provided by Cindy Crane from the PEI Department of Environment, Energy and Forestry.

Ground water total phosphorus concentrations were also examined for a number of wells that were located within the management or index basins in order to examine the hypothesis that ground water total phosphorus can vary regionally or even locally in PEI. Nine wells were chosen representing the Morell River, Mill River, Montague/Valley Field and Dunk/Wilmot watersheds. The analysis procedure for groundwater data was to first examine for temporal trends, followed by analysis of the means, standard deviations and statistical differences between sites.

### **3.0 Data Analysis**

#### **3.1 Surface Water**

Phosphorus, land use, and water quality indices for the management and index basins on PEI are represented in Table 1. Prior to removal of outliers (outside of 99% CI), three of the five sites for which flow data was available had weak statistical relationships (< 80% of the variability explained by the model) between daily mean discharge rate and total phosphorus. Those sites showing relationships between flow and total phosphorus were Carruthers Brook, Dunk River and the Wilmot River. Detailed statistical analyses of the data are provided in Appendix 1.

Evaluation of temporal trends in total phosphorus revealed that only three of the eleven locations (Appendix 1, Table 1) showed significant changes. The West River and Cains Brook demonstrated increasing phosphorus over their respective time series while the Morell River (for which the dataset extends back to 1975) showed a decrease in background phosphorus. The changes over time at these sites were very subtle and the two sites with increasing TP were interpolated back to the time of the earliest measurement.



Table 1. Background phosphorus and watershed data for freshwater sites within the 3 management and 3 index basins on Prince Edward Island.

Site	Data coverage period	Mean Total P (mg/L) (SD, n)	Proposed Guideline ( $\mu\text{g/L}$ )	Mean $\text{PO}_4\text{-P}$ ( $\mu\text{g/L}$ ) (SD, n)	Agriculture (%)	Forest (%)	Wetland (%)	WQI	TP vs. Time	TP vs. Flow
Montague (Oceanview)	1992-2007	0.051 (0.014, 57)	<b>79</b>	NA	9	83	2	59.6	None	NA
Bear River	1992-2007	0.029 (0.007, 106)	<b>43</b>	NA	9	86	4	86.5	None	None
Cains Brook (Bloomfield, Mill River)	1992-2007	0.011 (0.004, 64)	<b>16*</b>	1 (0.5, 7)	24	68	3	88.4	Increasing	NA
Morell River	1974-2007	0.040 (0.009, 214)	<b>58</b>	16 (6, 6)	25	62	8	84.6	Decreasing	NA
Valleyfield River	1992-2007	0.069 (0.012, 74)	<b>93</b>	16 (1.2, 5)	27	65	1	78.7	None	NA
West River	1992-2007	0.060 (0.008, 74)	<b>69*</b>	NA	40	53	1	80.6	Increasing	None
Montague River (Knox's Pond)	1992-2007	0.065 (0.007, 72)	<b>79</b>	16 (8, 7)	50	44	1	80.5	None	NA
Carruthers Brook (Mill River)	1974-2007	0.014 (0.005, 218)	<b>24</b>	3 (3, 3)	57	32	7	75.9	None	Positive
Dunk River	1979-2007	0.041 (0.011, 96)	<b>63</b>	7 (4, 7)	66	26	1	75.9	None	Positive
Clyde River (West River)	1992-2007	0.050 (0.005, 74)	<b>60</b>	NA	71	19	1	65.9	None	NA
Wilmot River	1992-2007	0.046 (0.011, 88)	<b>68</b>	11 (9, 7)	83	11	2	55.2	None	Positive

NA – data not available

\* - interpolated to 1992 levels due to increasing trend in TP with time

Despite some temporal trends, it was believed that the statistical procedure for background total phosphorus determination was relatively robust at both impacted and unimpacted stations. The lack of statistically significant correlation between percent agricultural land-use and the mean background total phosphorus levels derived by this procedure (Figure 2) supports this. There were no significant relationships between background phosphorus concentrations and other land use such as industrial, residential, transportation or forestry. Background phosphorus did decline significantly with increasing area of wetland.

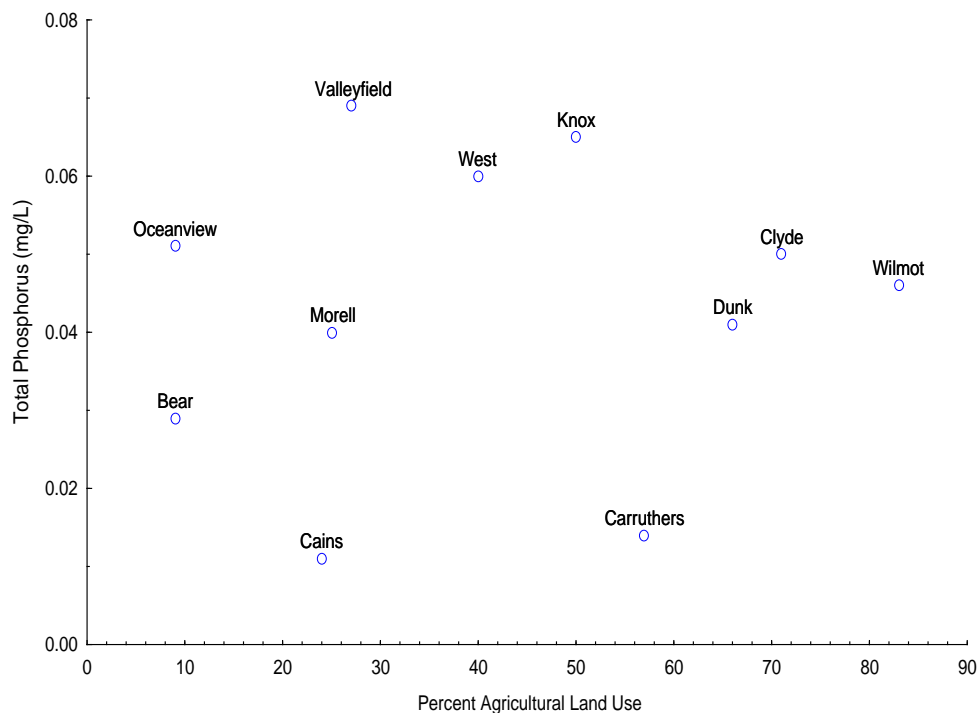


Figure 2. Mean background total phosphorus concentration vs. percent agricultural land use.

Examination of the magnitude of background phosphorus levels on PEI reveals a nearly 7-fold range of concentrations across PEI (Table 1, Figure 3). Differences were apparent across the range of the eleven locations as there were seven statistically distinct groups (Table 2). Mean phosphorus concentrations from nine of the eleven stations exceeds the currently used guidance value of 30  $\mu\text{g/L}$ . The Mill River stations in the western end of the Island had the lowest total phosphorus levels, while two stations in the Montague/Valleyfield watershed in eastern PEI had consistently the highest background phosphorus levels. The mean background phosphorus level for all stations combined was 43.3 (SD=19)  $\mu\text{g/L}$  and thus an island-wide guideline for total phosphorus would be 81.3  $\mu\text{g/L}$ .

Table 2. Statistical differences between background total phosphorus at PEI management and index water quality stations. Asterisks within a column indicate homogeneous groups (alpha=0.05)

Station	Mean TP	
Cains	0.011	*
Mill	0.014	*
Bear	0.029	
Morell	0.040	*
Dunk	0.041	*
Wilmot	0.046	
Clyde	0.050	*
Oceanview	0.051	*
West	0.060	
Knox Pond	0.065	
Valleyfield	0.070	*

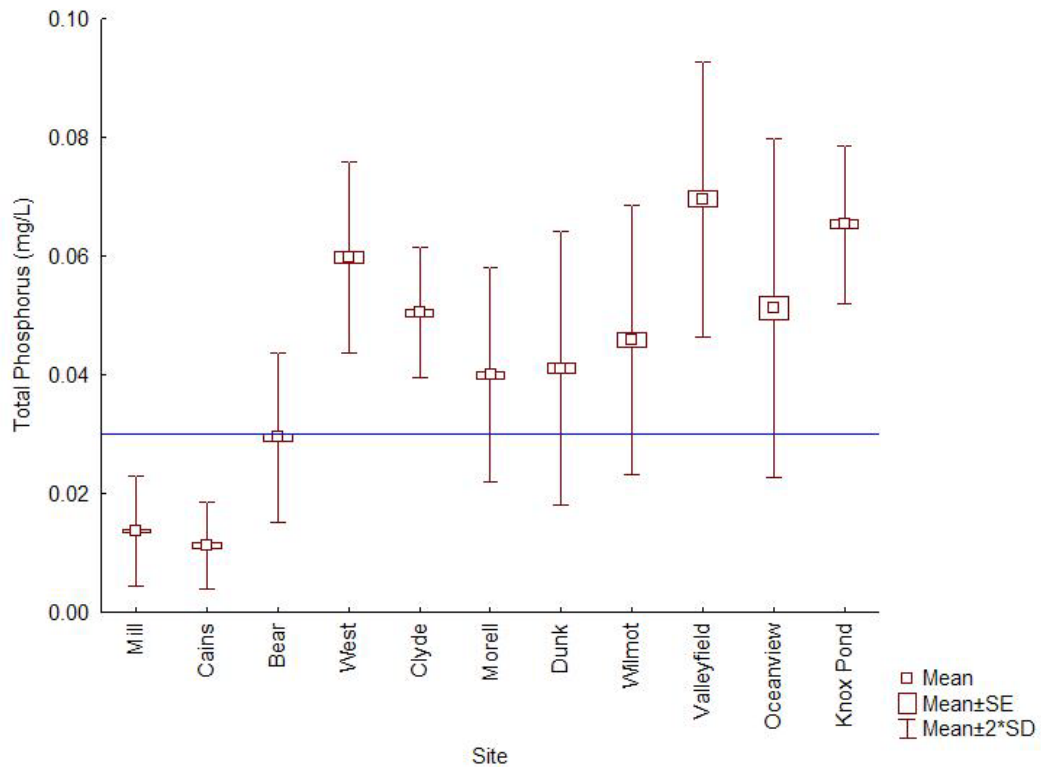


Figure 3. Mean total phosphorus at PEI freshwater management and index sites. The currently used guidance value of 30 µg/L is shown as a horizontal line.

Application of the recommended site-specific TP guidelines to the 2007 and 2008 had the desired effect of improving the WQI at a number of relatively unimpacted sites where the WQI was considered to be less than representative of true water quality. While there was year to year variation, the Valleyfield, Bear, and Morell Rivers in particular showed improvement. The West River saw improvement as well, however this result may be an artifact as this site is problematic in that values between the two years vary substantially.

Table 3. Calculations of the WQI prior to and with proposed site specific guidelines for TP.

	CESI 2007		Proposed		CESI 2008		Proposed	
	WQI	Rating	WQI	Rating	WQI	Rating	WQI	Rating
Mill	76.2	Fair	76.1	Fair	75.9	Fair	75.9	Fair
Cain's	N/A	N/A	N/A	N/A	88.4	Good	87.9	Good
Dunk	58.9	Marginal	62.6	Marginal	68.9	Fair	73.4	Fair
Wilmot	62.7	Marginal	70.9	Fair	55.2	Marginal	60.9	Marginal
Clyde	55.4	Marginal	60.9	Marginal	65.9	Fair	73.2	Fair
West	66.9	Fair	73.1	Fair	80.6	Good	88.3	Good
Morell	83.8	Good	100	Excellent	84.6	Good	88.4	Good
Bear	85.5	Good	100	Excellent	86.5	Good	88.4	Good
Knox Pond	71.1	Fair	76.9	Fair	80.5	Good	88.4	Good
Valleyfield	N/A	N/A	N/A	N/A	78.7	Fair	88.4	Good
Oceanview	N/A	N/A	N/A	N/A	59.6	Marginal	64.6	Marginal

### 3.2 Groundwater

Analysis of total phosphorus in groundwater revealed significant differences between waters both from within and between watersheds (Table 4). There were some similarities to the trends in water in that Mill River water samples were all at the low range of total phosphorus and Morell River samples were within the range of surface water samples. However, three locations from the Dunk/Wilmot spanned a 20-fold range of TP concentrations and the lone Montague well sample was considerably lower than surface water samples from that region. Additional well data may or may not shed more light on the situation as wells within a watershed also appear to vary considerably. Well and casing depth was also not examined and could influence water quality considerably.

Table 4. Analysis of total phosphorus in selected groundwater sampling locations, well construction details are not available. Asterisks within a column indicate homogeneous groups (alpha=0.05).

Well Location	Watershed	Mean TP (SD, n)				
Bloomfield elementary school	Mill River	0.003 (0.002, 55)	*			
Bedeque Senior Citizens	Dunk/Wilmot	0.004 (0.004, 17)	*	*		
Hernewood junior high school	Mill River	0.004 (0.002, 66)	*			
Bloomfield Mall	Mill River	0.009 (0.003, 52)		*		
Montague Senior Citizens Home	Montague	0.013 (0.010, 66)			*	
Summerside Town Well	Dunk/Wilmot	0.020 (0.007, 15)				*
Farm near Bangor	Morell	0.050 (0.017, 16)				*
House near Stanchel	Dunk/Wilmot	0.069 (0.004, 9)				*
Morell Senior Citizens Home	Morell	0.082 (0.014, 66)				*

#### 4.0 Discussion

There is clear evidence from the monitoring database that background levels of phosphorus are above the currently used guidance value of 30 µg/L in many relatively unimpacted systems including the Bear River, and the upper reaches of the Montague. Conversely, moderately impacted systems such as the Mill River have atypically low total phosphorus levels relative to the other stations examined and thus the 30 µg/L guidance level is overly conservative in this case. Supporting the conclusion that background total phosphorus is naturally high in some regions of the island is the general lack of total phosphorus trends over time. This indicates that any land-use changes within these catchments has had relatively little influence on background total phosphorus over the time period encompassed by the data. Exceptions to this were the West River and Cains' Brook where total phosphorus increased significantly between 1992 and 2007.

Increases in total phosphorus could have occurred before the period of record; however, these data span the mid 1990's that saw a substantial increase in potato acreage and changes in agricultural practices. It should be strongly emphasized that these conclusions are specific to *background* phosphorus levels only. There is significant uncertainty as to the proportion of phosphorus loadings that occurs during rainfall events on PEI. Thus, it should not be concluded from these data that agricultural activity has had limited impact on phosphorus loadings. Indeed, quite the contrary may be true as the possibility of increased phosphorus loading due to land use was indirectly indicated by stronger relationships between flow and total phosphorus at the three more impacted sites for which flow data was available. Watersheds with higher proportions of unvegetated earth may be expected to be more susceptible to erosion during rainfall or snow melt events. Increased erosion would likely mean higher phosphorus loading as silt laden run-off flows into streams during some high-flow events. Regular water quality monitoring programs such as

conducted for the collection of these data are not designed for diagnosing/understanding episodic water quality changes related to flow surges. It was also interesting to note that an inverse relationship appears to exist between percentage of wetland coverage and total phosphorus. Wetlands are known to trap phosphorus and thus may make some contribution to the regional phosphorus differences.

A further problem preventing understanding phosphorus loading is the short-term temporal and seasonal differences in the nature of high flow episodes. In general, stream flow-total phosphorus relationships were much weaker than may have been presumed. There are a number of potential reasons for this such as winter or spring thaws which increase flow through groundwater recharge without significant erosion, the sometimes local nature of storm events, and the known hydrological observations that the highest levels of solids occur on the leading edge of storm events - so loading is not necessarily proportional to discharge even within a storm event (Richards 1982).

In freshwater, phosphorus is generally considered to be the limiting element and this would be no different for PEI streams where high nitrate levels often lead to N:P ratios up to 200:1. As the most available form of phosphorus is the orthophosphate ion, total phosphorus is often not the best indicator of the biological availability of phosphorus. The bulk of freshwater systems are thought to have orthophosphate concentrations in the range of 1-10 µg/L (Hudson et al. 2000). Supplemental data indicate that this is often exceeded in many PEI streams, thus orthophosphate is unlikely to be superior to total phosphorus as a water quality monitoring variable in this context. Based on the limited data available for phosphate presented here, it would seem that less than half of the total phosphorus is likely to be available to biota. While organically bound phosphorus can become available to biological systems in a matter of days, inorganic phosphorus complexes are likely biologically inert on a permanent basis due to the insoluble nature of phosphate salts. PEI streams are not typically rich in organic matter. An analysis of the provincial water quality monitoring data for total nitrogen and nitrate indicates that in the Dunk/Wilmot watershed, 100% of nitrogen is in an inorganic form. Similar statistics are 82%, 52%, 82% for the Montague, Morell and Valleyfield Rivers, respectively. While clear regional differences exist, in most cases it could also be expected that total phosphorus is dominated by inorganic forms.

Groundwater total phosphorus proved to be highly variable both within and between watersheds. The wells examined were generally within the lower end of the selected watersheds, meaning that these data give little information relevant to the groundwater sources feeding the streams of interest. The high variability between total phosphorus in groundwater does however suggest that it is feasible, if not likely that groundwater derived phosphorus drives the surface water total phosphorus concentration. Phosphate

salts are sparingly soluble and the source of most available phosphorus is from mineral breakdown. For this reason older groundwater is often found to contain higher levels of phosphorus than rapidly recharged young groundwater.

The regional differences in surface water or groundwater background phosphorus cannot be easily explained by geology or soil types in the various regions. Surface water streams are heavily groundwater driven on PEI, thus the geology is an obvious place to look for reasons for variability in background phosphorus. However, in terms of composition, all of PEI is similarly defined as Permo-Carboniferous redbeds that were thought to be formed as part of an alluvial fan from sources to the west and south (DeGrace 1989). While this creates the perception of geological homogeneity, there can be considerable variation in geology within small spatial scales (within a watershed). PEI sedimentary geology is layered and four distinct sequences (megacyclic sequences I-IV) have been recognized with each sequence being composed of coarse pebble and cobble at the base through to coarse sandstone in the middle and fine sandstone or siltstone at the top with a total thickness of approximately 300 m (van de Pohl, 1983). Those sequences in the central and western regions (I and II) containing Mill River, Dunk Wilmot and West Rivers locations are older and they underlie the more easterly sequences III and IV. Contrary to what one would assume, the Westerly sites have the oldest rock and yet the lowest background phosphorus and thus it is unlikely that the age of the different sequences are related to stream phosphorus levels. However, aquifers feeding PEI streams are generally quite shallow as the sandstone is an effective barrier for vertical water movement. It could be speculated that older, more phosphorus rich groundwater could come through fractures in the sandstone or through permeable cobble/pebble layers. This could be due to very local aquifer conditions, or, the more Westerly sites that span megacyclic sequence I may be less susceptible to sandstone fractures. While the background phosphorus levels are not thought to be strongly influenced by surface runoff, surficial layers in PEI are also very patchy, though they do exhibit a general east to west gradient with more sand and clay phase glacial till to the west, and coarser glacial-fluvial deposits and bedrock to the east (MacDougall et al. 1988). Similar to the complex structure of the underlying geology, multiple and patchy surficial deposits within watersheds and no clear pattern in relation to phosphorus concentrations and make it difficult to draw conclusions on soil type and background phosphorus. While linkages between TP and geology are a likely explanation, only detailed study of the origins of stream water within watersheds could explain the significant variability found in TP within PEI.

The evaluation conducted here has verified the existing observation that the application of the CESI guidance value for phosphorus as it currently stands to PEI surface waters is not generally representative

of true water quality due to *both* unusually high and low natural levels of total phosphorus. There are a number of possible options that could be adopted to remedy this problem. While one could adopt the derived global value of 81.3 µg/L for Prince Edward Island, this approach would not provide an accurate representation for the majority of stations should water quality deteriorate due to phosphorus inputs, and would not adequately reduce scores in streams where background phosphorous is atypically high and as such would defeat the purpose of the index.

The preferred option is to adopt a phosphorus guideline value specific to each station being examined. This would prevent WQI exceedences due to high natural background levels of total phosphorus at particular sites, but equally important, it will mean that the index is far more responsive to increased TP at sites where TP is substantially lower than 30µg/L. Evaluation of the site specific water quality guidelines for TP was conducted by recalculating the 2007 and 2008 WQI values with these proposed values. This exercise verified that there were improvements in the WQI for some of the sites that were being influenced by naturally high TP. However, these changes are somewhat obscured by the very high year-to-year variability in the index. This variability is a reflection of the calculation of the index with a relatively low number of water quality variables (five). In this situation, one or more failures in a particular parameter are magnified to have substantial effects on the overall calculation.



## 5.0 Conclusions

- Background phosphorus levels in PEI streams are not driven by agricultural or any other land-use but are inversely proportional to wetland coverage.
- Insufficient data exists to determine if phosphorus loading differs between sites of varying agricultural impact.
- Background levels in phosphorus across PEI vary dramatically with averages ranging from 11 to 69 µg/L.
- Phosphorus levels in surface water on PEI are likely driven by groundwater input but more evidence would be required to make firm conclusions.
- Site-specific guidelines for total phosphorus at individual stations on PEI would range between 18 and 92 µg/L and provide the best option for the WQI to accurately reflect stream quality.
- The proposed site-specific guidelines had the anticipated effects on those sites thought to be overtly influenced by high TP.
- The WQI on PEI is disproportionately biased by occasional failures of a parameter due to the nature of the calculation when using a low number of water quality variables.

## 6.0 Recommendations

- The most appropriate approach for the calculation of the Canadian WQI as applied on PEI is to use a WQG for total phosphorus that is specific to each individual station examined. This prevents those sites with high background TP from failing this parameter but will also make the WQI more useful for examining long-term trends in those sites where TP is very low.
- Further attention should be directed at estimating phosphorus loading in the study basins. While this is not part of the WQI, it may be an important indicator of surface water quality. This would involve detailed analyses of storm events at gauged sites and the derivation of loading models based on stream-flow. Permanent gauging stations at all sites would assist in this regard.
- In future water quality analyses, DRP or phosphate (as P) should be evaluated in addition to total phosphorus.
- In order to test what drives surface water phosphorus concentrations, TP and DRP and/or groundwater age should be measured from significant spring at the headwaters of the streams of interest.
- The WQI calculation should be adjusted so as not to magnify the influence of relatively low numbers of parameter failures.

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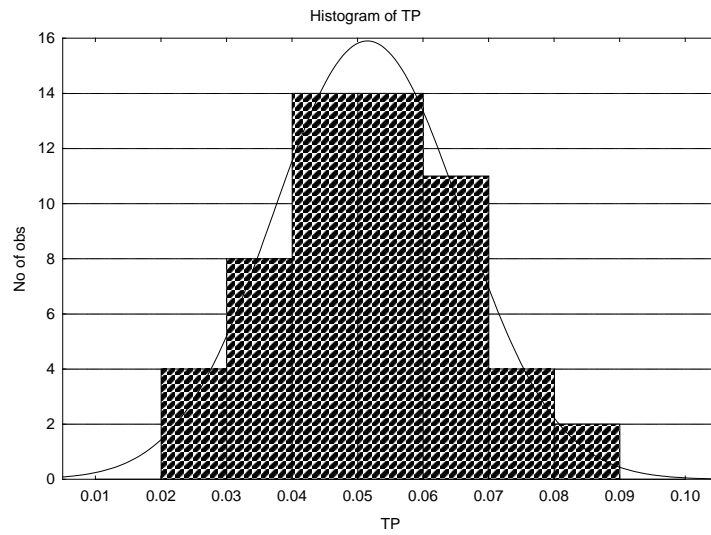
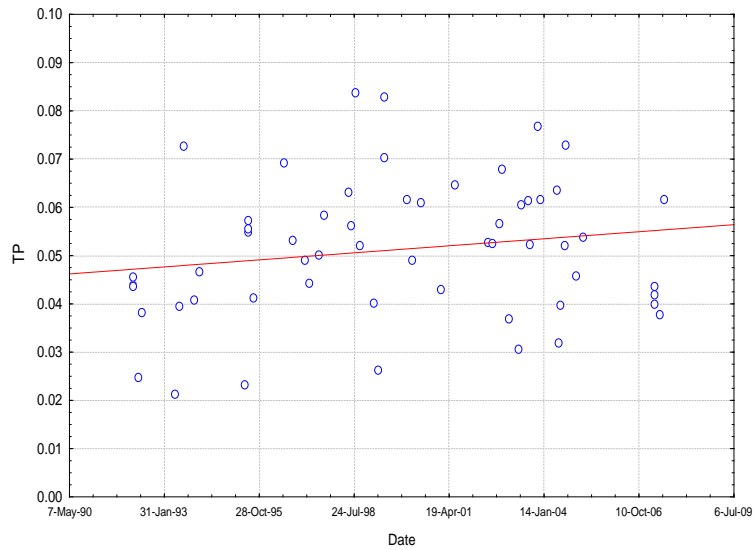
## **Appendix 1**

### **Statistical Summary**

## Montague (Oceanview)

Relationship with time after outlier removal  $r^2=0.012$

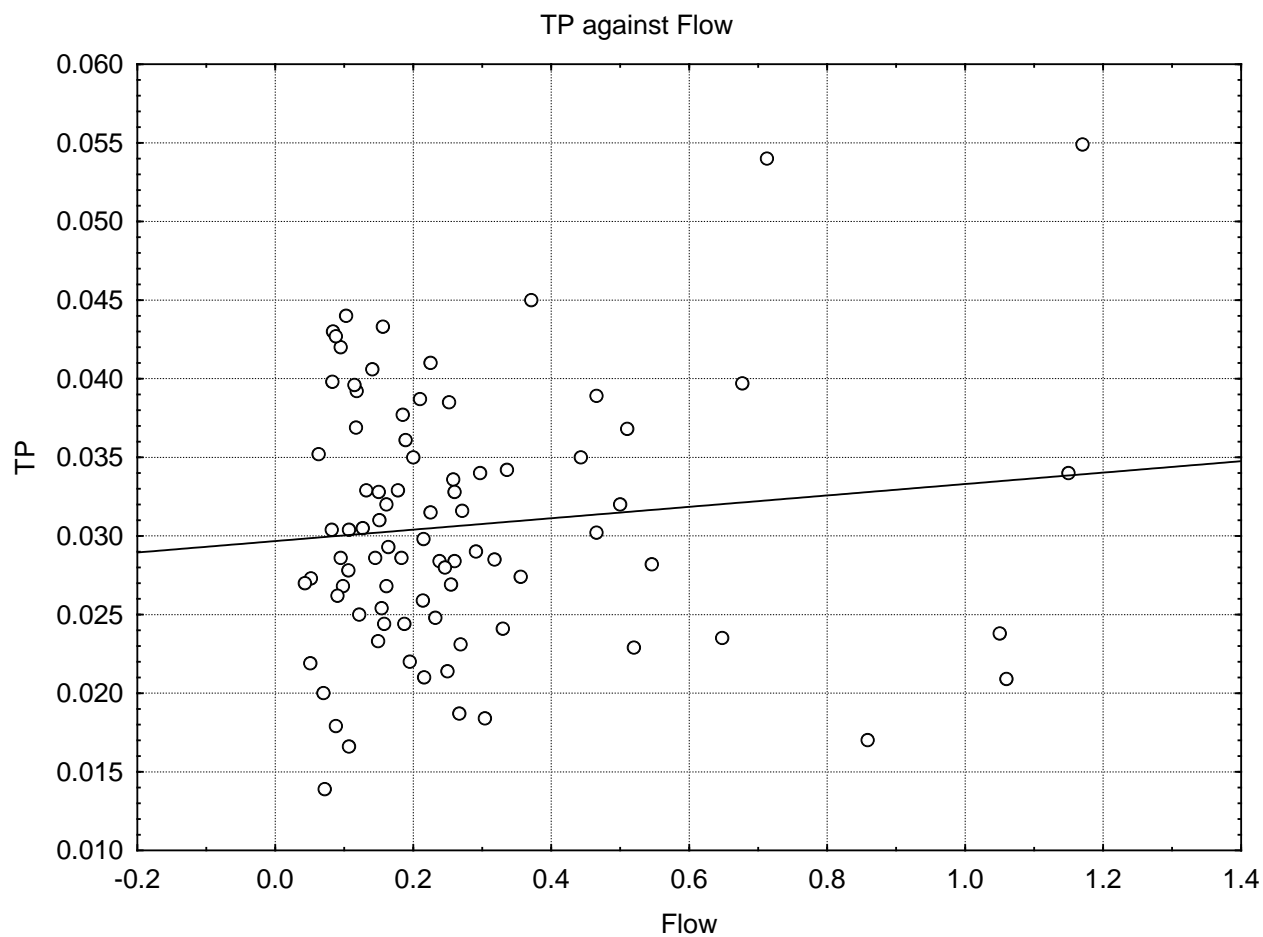
Univariate Tests of Significance for TP (Spreadsheet2 in Workbook1) Sigma-restricted parameterization Effective hypothesis decomposition					
	SS	Degr. of - Freedom	MS	F	p
<b>Intercept</b>	0.000000	1	0.000000	0.002186	0.962878
<b>Date</b>	0.000339	1	0.000339	1.678771	0.200499
<b>Error</b>	0.011113	55	0.000202		



### Bear River

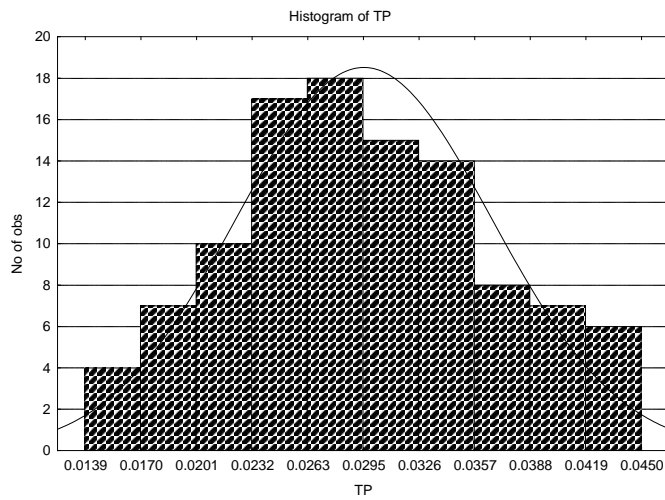
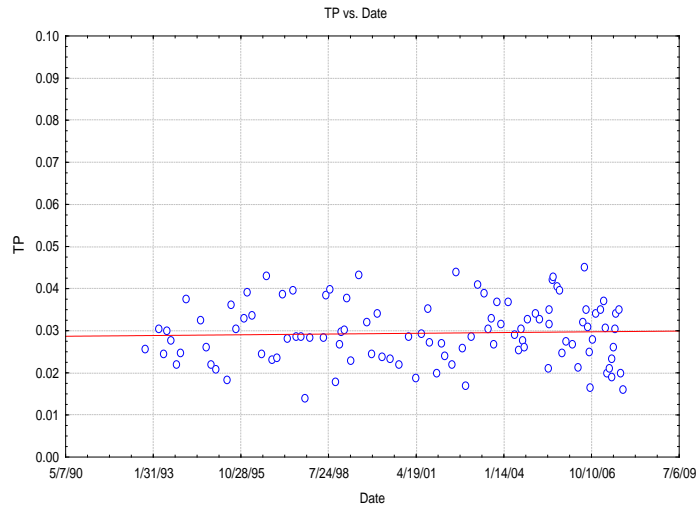
Total phosphorus vs. flow,  $r^2=0.0002$

Univariate Tests of Significance for TP4 (Spreadsheet3 in Bear) Sigma-restricted parameterization Effective hypothesis decomposition					
	SS	Degr. of - Freedom	MS	F	p
<b>Intercept</b>	0.032910	1	0.032910	503.7252	0.000000
<b>Flow</b>	0.000067	1	0.000067	1.0228	0.314829
<b>Error</b>	0.005357	82	0.000065		



Bear River  
 Relationship with time after outlier removal,  $r^2 < 0.0001$

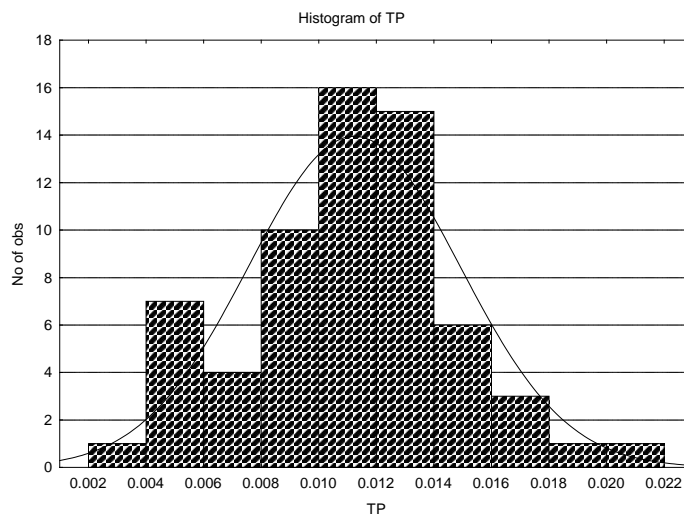
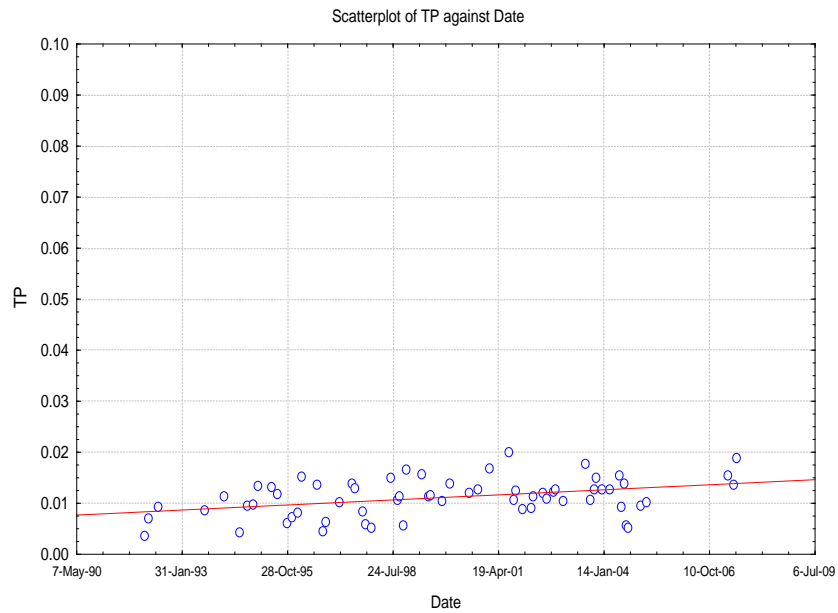
Univariate Tests of Significance for TP4 (Spreadsheet3 in Bear wo outliers.stw) Sigma-restricted parameterization Effective hypothesis decomposition					
	SS	Degr. of Freedom	MS	F	p
Intercept	0.000110	1	0.000110	2.155339	0.145093
Date	0.000009	1	0.000009	0.175643	0.676009
Error	0.005285	104	0.000051		



## Cain's Brook

Relationship with time after outlier removal,  $r^2=0.14$

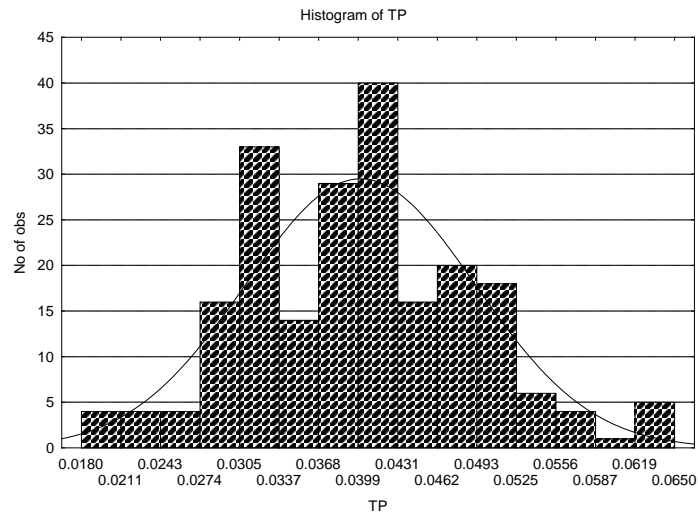
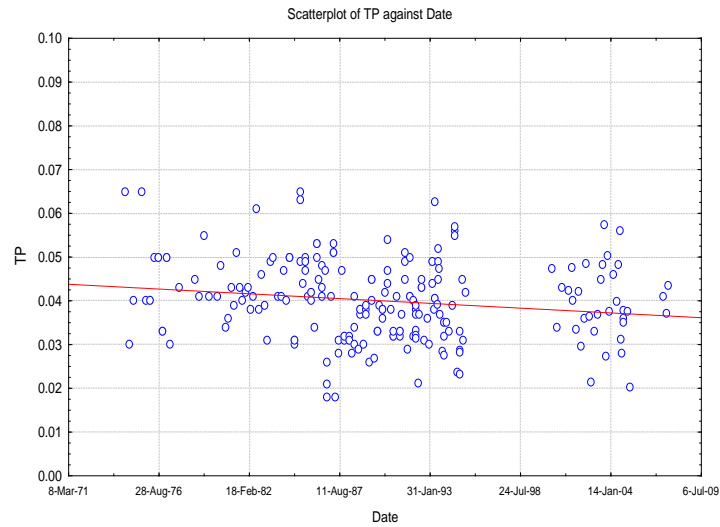
Univariate Tests of Significance for TP (Spreadsheet31 in Workbook2) Sigma-restricted parameterization Effective hypothesis decomposition					
	SS	Degr. of - Freedom	MS	F	p
<b>Intercept</b>	0.000063	1	0.000063	5.45494	0.022763
<b>Date</b>	0.000132	1	0.000132	11.46153	<b>0.001237</b>
<b>Error</b>	0.000712	62	0.000011		



## Morell River

Relationship with time after outlier removal  $r^2=0.02$

Univariate Tests of Significance for TP (Spreadsheet11 in Workbook1) Sigma-restricted parameterization Effective hypothesis decomposition					
	SS	Degr. of - Freedom	MS	F	p
<b>Intercept</b>	0.005242	1	0.005242	65.36078	0.000000
<b>Date</b>	0.000508	1	0.000508	6.33519	0.012577
<b>Error</b>	0.017004	212	0.000080		



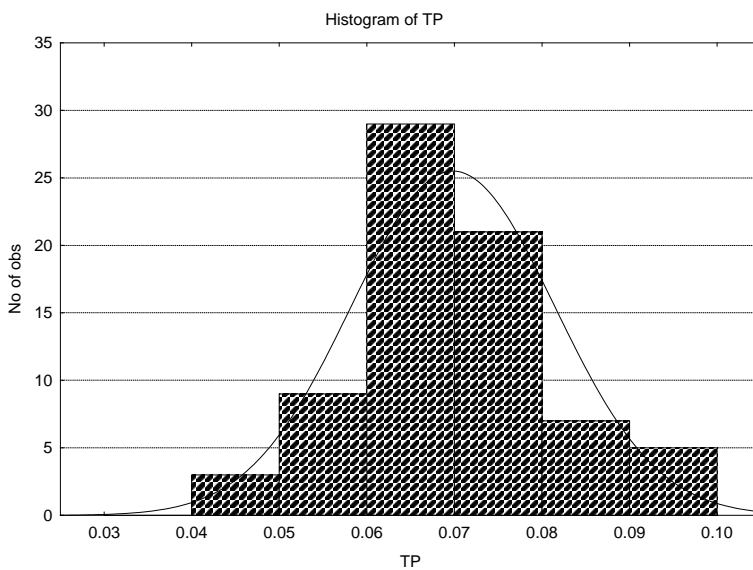
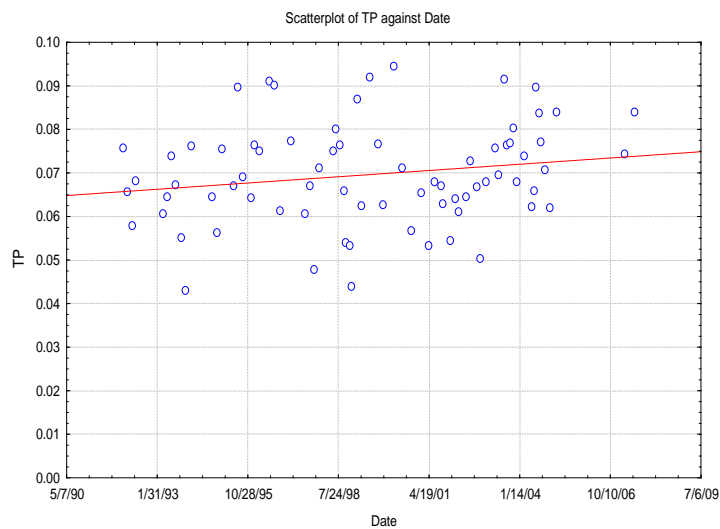


## Valleyfield River

Relationship with time after outlier removal,  $r^2=0.02$

Univariate Tests of Significance for TP (Spreadsheet3 in Valleyfield) Sigma-restricted parameterization Effective hypothesis decomposition

	SS	Degr. of - Freedom	MS	F	p
<b>Intercept</b>	0.000037	1	0.000037	0.284929	0.595133
<b>Date</b>	0.000336	1	0.000336	2.559897	0.113985
<b>Error</b>	0.009441	72	0.000131		

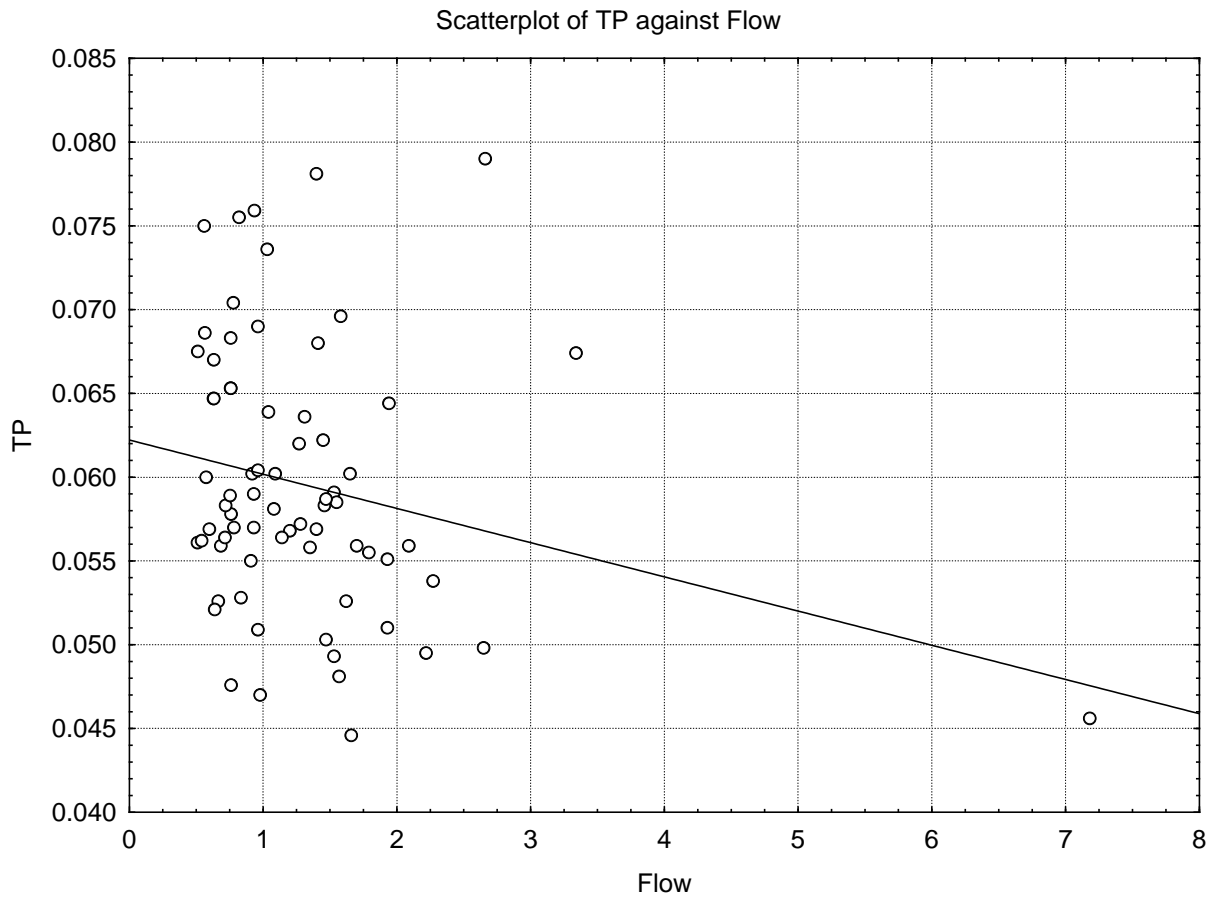


### West River

Total phosphorus vs. flow,  $r^2=0.01$

Univariate Tests of Significance for TP (Spreadsheet19 in West River) Sigma-restricted parameterization  
Effective hypothesis decomposition

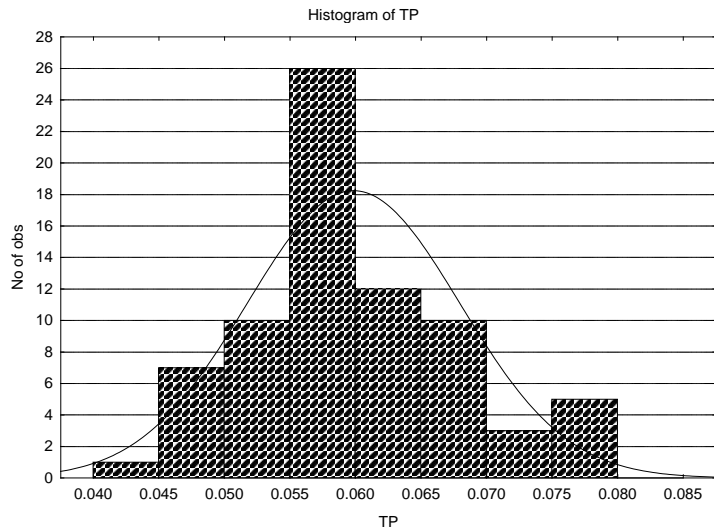
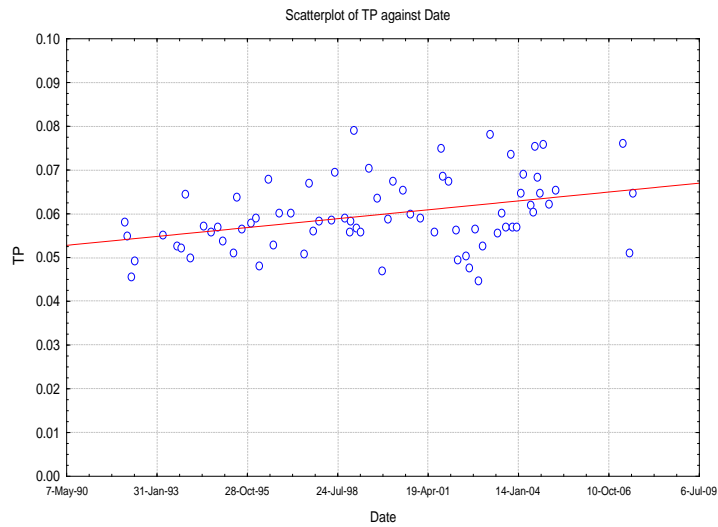
	SS	Degr. of - Freedom	MS	F	p
<b>Intercept</b>	0.210815	1	0.210815	750.2288	0.000000
<b>Flow</b>	0.000567	1	0.000567	2.0176	0.159578
<b>Error</b>	0.021356	76	0.000281		



West River  
 Relationship with time after outlier removal,  $r^2=0.13$

Univariate Tests of Significance for TP (Spreadsheet19 in West River) Sigma-restricted parameterization  
 Effective hypothesis decomposition

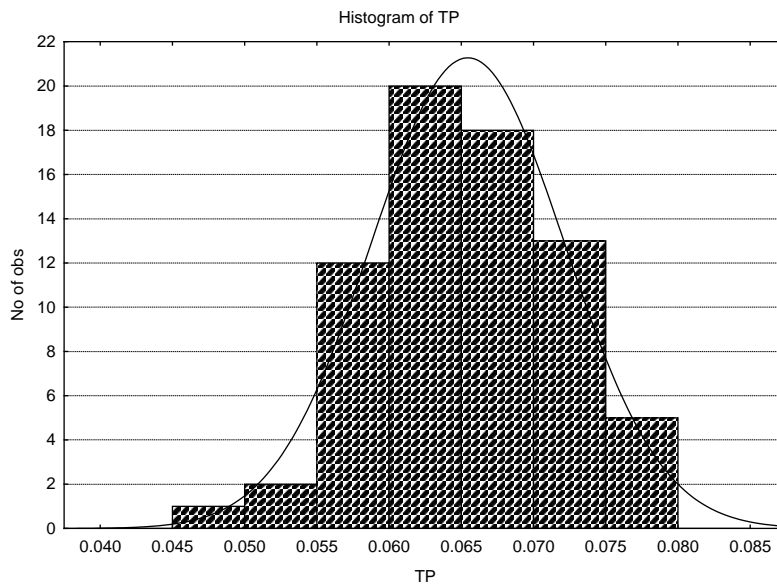
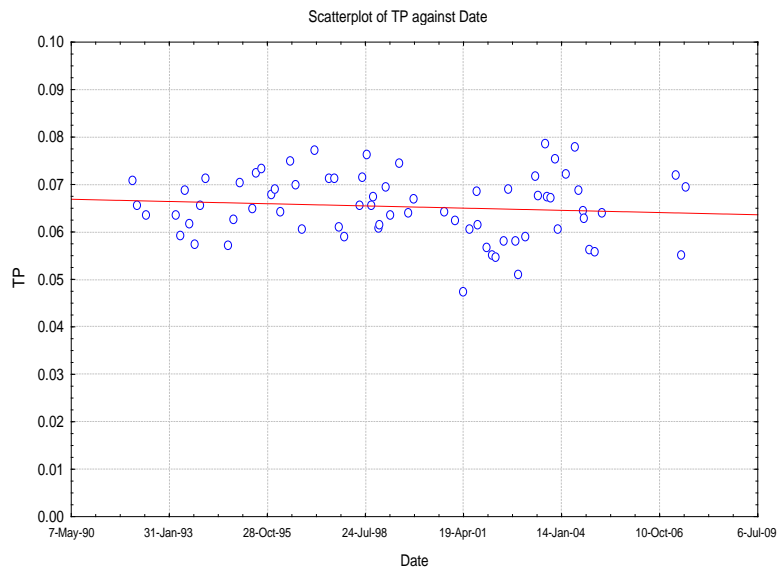
	SS	Degr. of - Freedom	MS	F	p
<b>Intercept</b>	0.000025	1	0.000025	0.44241	0.508087
<b>Date</b>	0.000685	1	0.000685	12.04036	<b>0.000883</b>
<b>Error</b>	0.004095	72	0.000057		



## Montague River at Knox Pond

Relationship with time after outlier removal,  $r^2=0.003$

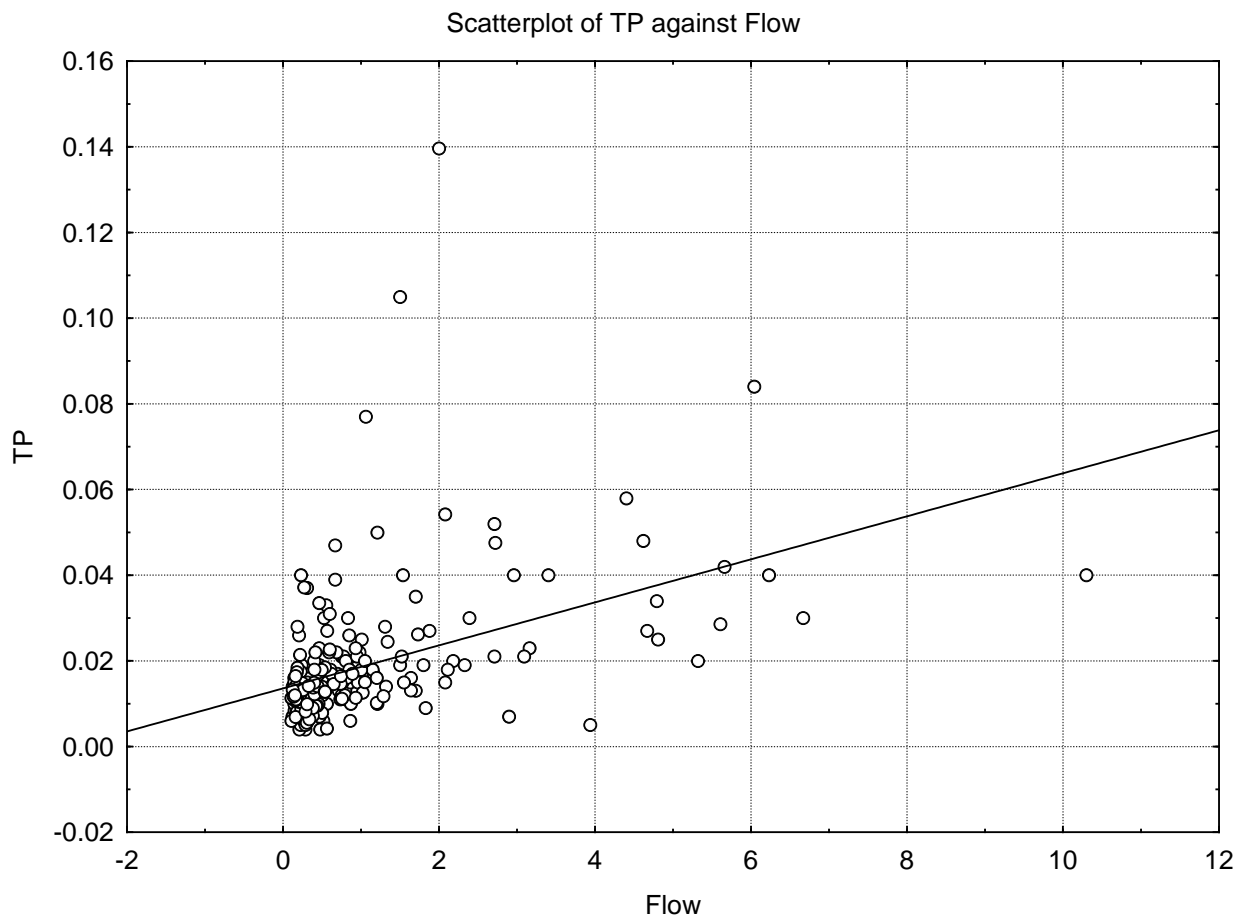
Univariate Tests of Significance for TP (Spreadsheet34 in Workbook3) Sigma-restricted parameterization Effective hypothesis decomposition					
	SS	Degr. of - Freedom	MS	F	p
<b>Intercept</b>	0.000820	1	0.000820	18.44974	0.000056
<b>Date</b>	0.000035	1	0.000035	0.78434	0.378892
<b>Error</b>	0.003066	69	0.000044		



### Mill River, Carruthers Brook

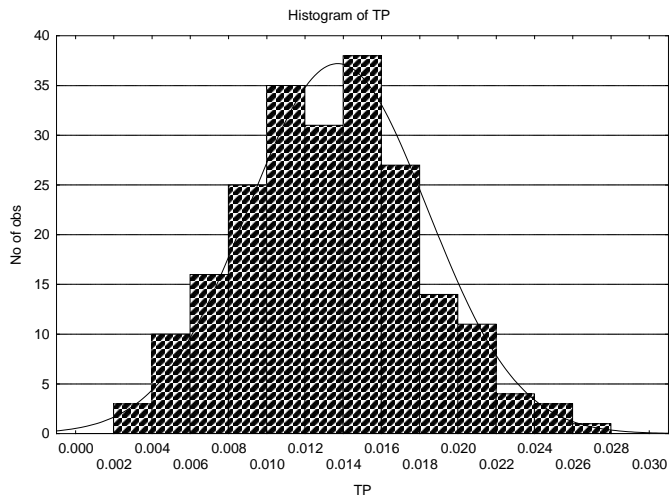
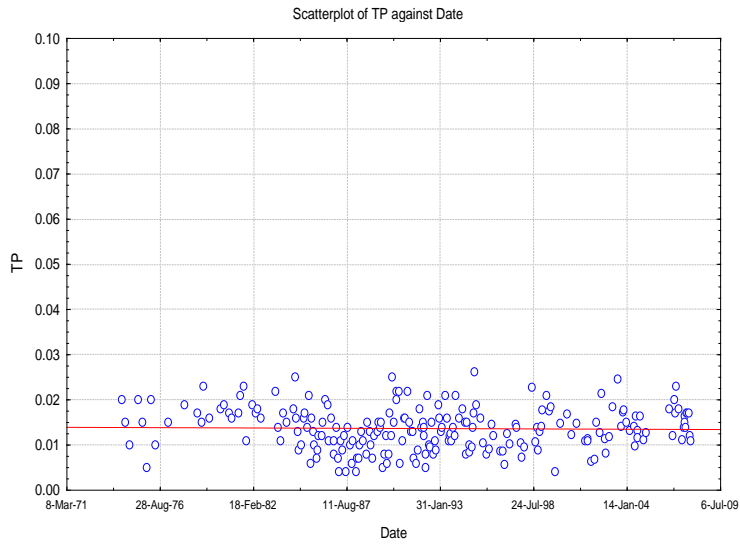
Total phosphorus vs. flow,  $r^2=0.199$

Univariate Tests of Significance for TP (Spreadsheet11 in Mill outliers) Sigma-restricted parameterization Effective hypothesis decomposition					
	SS	Degr. of - Freedom	MS	F	p
<b>Intercept</b>	0.030117	1	0.030117	170.9474	0.000000
<b>Flow</b>	0.010857	1	0.010857	61.6279	0.000000
<b>Error</b>	0.042811	243	0.000176		



Mill River, Carruthers Brook  
 Relationship with time after outlier removal,  $r^2=0.004$

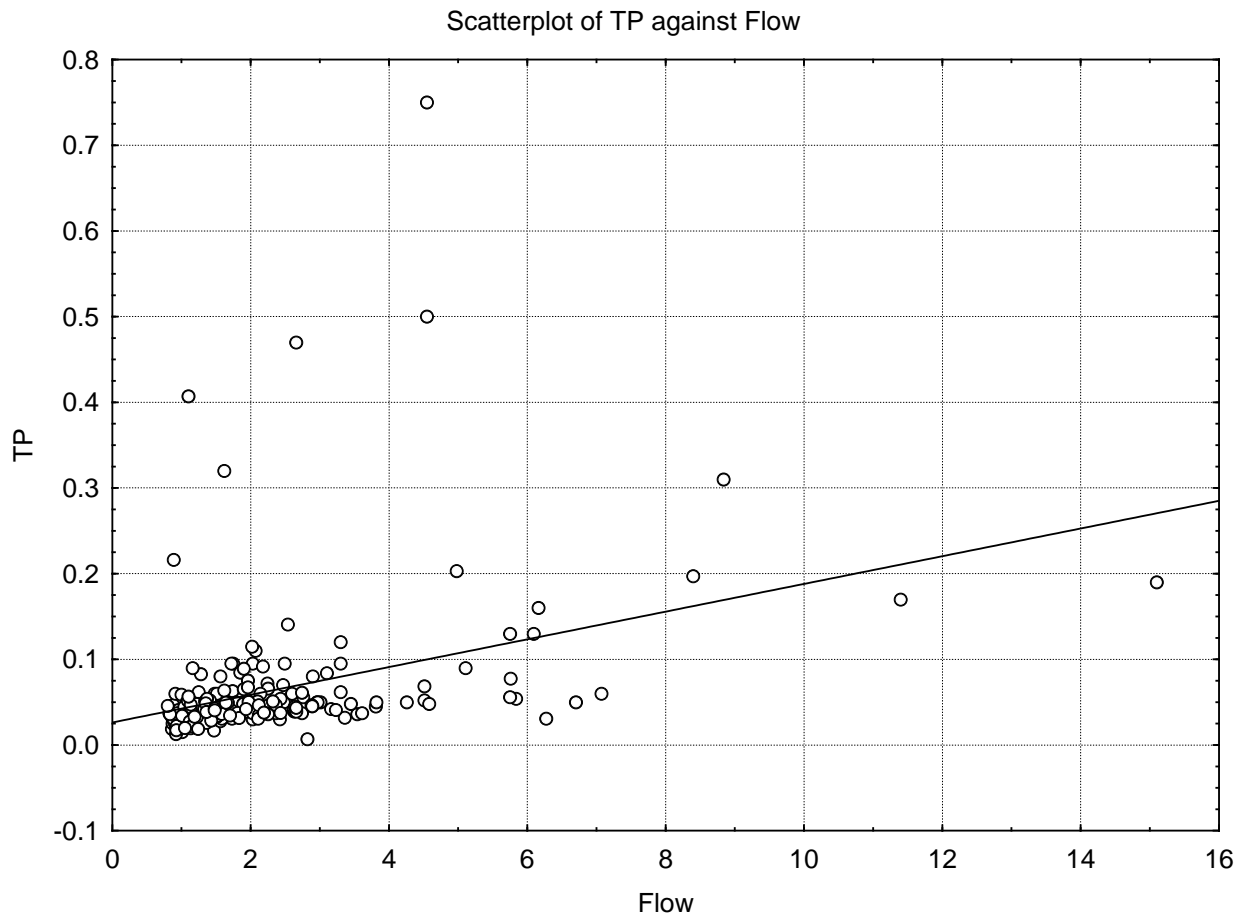
Univariate Tests of Significance for TP (Spreadsheet11 in Mill no outliers) Sigma-restricted parameterization Effective hypothesis decomposition					
	SS	Degr. of Freedom	MS	F	p
<b>Intercept</b>	0.000378	1	0.000378	17.24376	0.000047
<b>Date</b>	0.000002	1	0.000002	0.10949	0.741052
<b>Error</b>	0.004741	216	0.000022		



### Dunk River

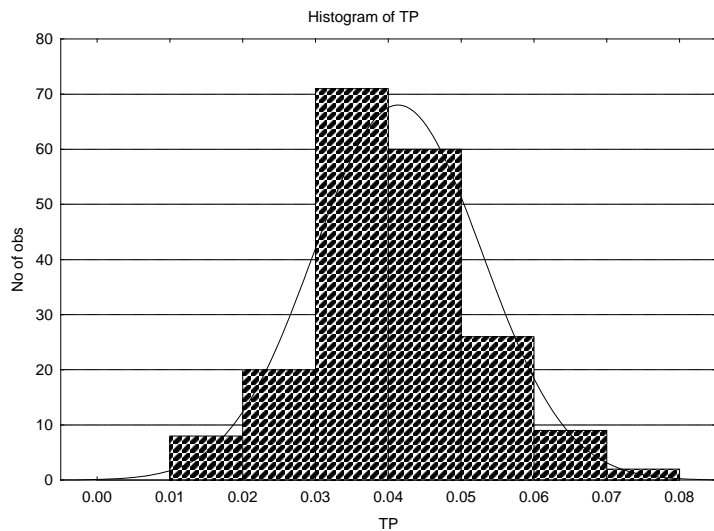
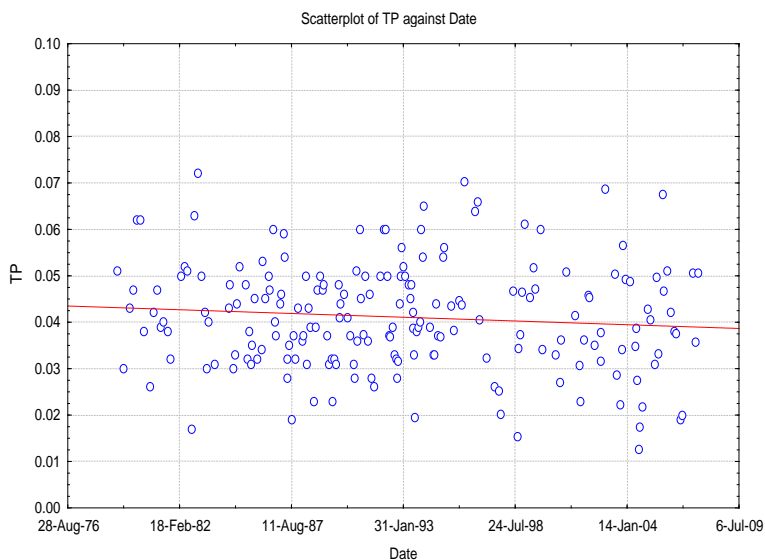
Total phosphorus vs. flow,  $r^2=0.177$

Univariate Tests of Significance for TP (Spreadsheet44 in Dunk) Sigma-restricted parameterization Effective hypothesis decomposition					
	SS	Degr. of - Freedom	MS	F	p
<b>Intercept</b>	0.061351	1	0.061351	12.06198	0.000617
<b>Flow</b>	0.177117	1	0.177117	34.82219	0.000000
<b>Error</b>	1.149511	226	0.005086		



Dunk River  
 Relationship with time after outlier removal,  $r^2=0.004$

Univariate Tests of Significance for TP (Spreadsheet44 in Dunk) Sigma-restricted parameterization Effective hypothesis decomposition					
	SS	Degr. of - Freedom	MS	F	p
<b>Intercept</b>	0.003885	1	0.003885	29.54461	0.000000
<b>Date</b>	0.000244	1	0.000244	1.85847	0.174381
<b>Error</b>	0.025512	194	0.000132		

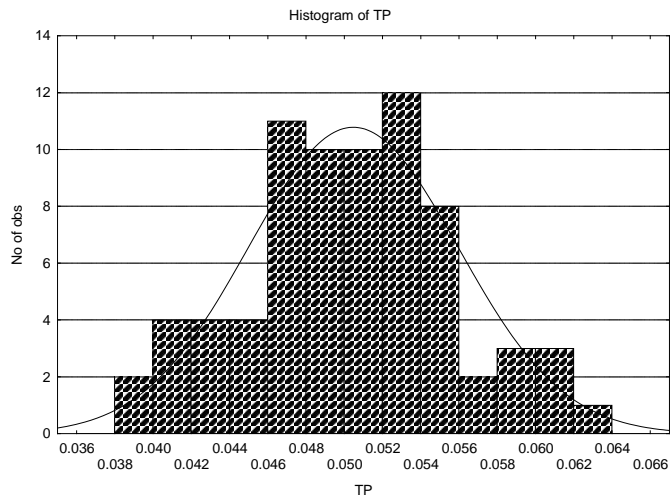
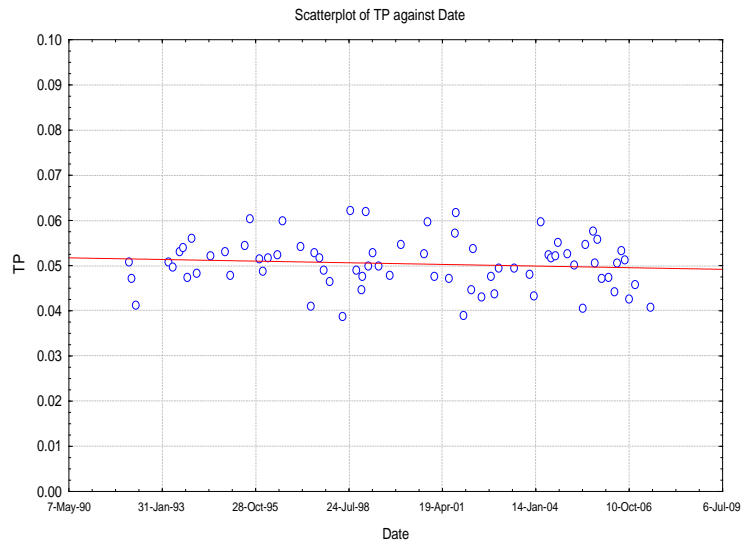




## Clyde River

Relationship with time after outlier removal,  $r^2=0.002$

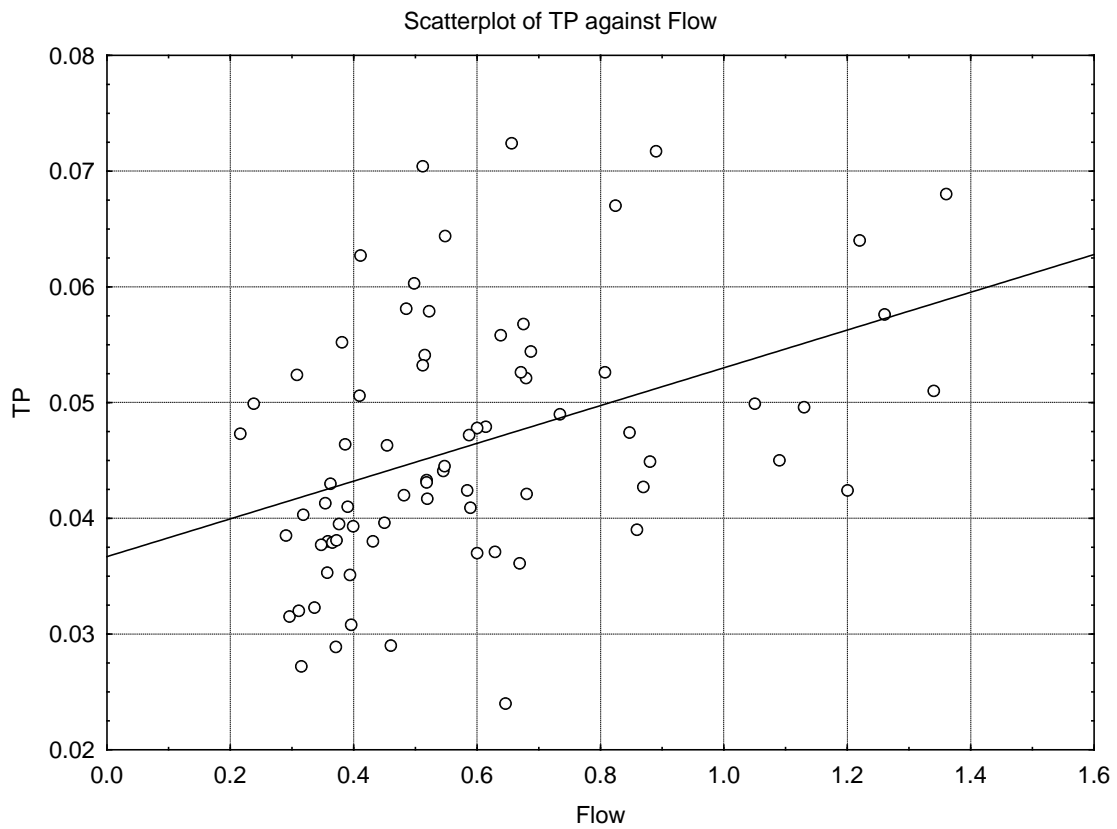
Univariate Tests of Significance for TP (Spreadsheet39 in Clyde) Sigma-restricted parameterization Effective hypothesis decomposition					
	SS	Degr. of - Freedom	MS	F	p
<b>Intercept</b>	0.000600	1	0.000600	19.99256	0.000028
<b>Date</b>	0.000026	1	0.000026	0.87333	0.353158
<b>Error</b>	0.002161	72	0.000030		



## Wilmot River

Total phosphorus vs. flow,  $r^2=0.164$

Univariate Tests of Significance for TP (Spreadsheet2 in Wilmot) Sigma-restricted parameterization Effective hypothesis decomposition					
	SS	Degr. of - Freedom	MS	F	p
Intercept	0.106352	1	0.106352	27.36795	0.000001
Flow	0.068895	1	0.068895	17.72914	0.000064
Error	0.326423	84	0.003886		



Wilmot River

Relationship with time after outlier removal,  $r^2=0.01$

Univariate Tests of Significance for TP (Spreadsheet2 in Wilmot) Sigma-restricted parameterization Effective hypothesis decomposition					
	SS	Degr. of - Freedom	MS	F	p
<b>Intercept</b>	0.000535	1	0.000535	4.093222	0.046161
<b>Date</b>	0.000011	1	0.000011	0.081562	0.775878
<b>Error</b>	0.011238	86	0.000131		

