

# Assessment of the Effects of Holding Time on Various Water Quality Parameters

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## Table of Contents

ABSTRACT .....	1
1 INTRODUCTION .....	1
2 METHODOLOGY .....	3
2.1 Data Collection .....	3
2.2 Data Analysis .....	4
3 RESULTS AND DISCUSSION .....	5
3.1 Graphs .....	6
3.2 General Linear Method and Dunnett's Comparison .....	8
3.3 Paired t-Test .....	9
4 CONCLUSIONS .....	9
5 RECOMMENDATIONS .....	10
6 REFERENCES .....	11
Appendices .....	I
Appendix I .....	II
NLET Parameter Holding Times .....	II
Appendix II .....	IV
Scatterplots of Parameters versus Holding Time .....	IV
Appendix III .....	X
Boxplots of Parameters versus Holding Time .....	X
Appendix IV .....	XV
GLM Computations by Parameter .....	XV
Appendix V .....	XXVI
Residual Plots by Parameter .....	XXVI
Appendix VI .....	XXXI
Paired t-Test Computations by Parameter .....	XXXI

## List of Tables

Table 1 - Summary of Scatterplot and Boxplot Observations .....	7
Table 2 - Summary of p-values from GLM Analysis and Dunnett's Comparison .....	8
Table 3 - Summary of p-values from Paired t-Test on QVL versus QAQC Data .....	9

# **Assessment of the Effects of Holding Time on Various Water Quality Parameters**

## **ABSTRACT**

The Department of Environment and Conservation in Newfoundland and Labrador has identified that many of the water samples that are shipped to the National Laboratory for Environmental Testing in Burlington, Ontario are exceeding parameter holding times as prescribed by NLET's Schedule of Services. There is concern that the integrity of data is being compromised as a result of holding time exceedences. Ten parameters were identified as consistently failing to meet recommended holding times: total nitrogen, nitrate, total phosphorus, dissolved inorganic carbon, dissolved organic carbon, alkalinity, pH, specific conductivity, turbidity and color. This study was conducted to determine if the length of holding time has a significant effect on the concentration or level of any of the identified parameters. Water samples were collected from three water bodies in the province and the samples were analyzed at five different holding times. The study was conducted in two phases; the first phase of sampling was conducted in March 2009, and the second phase was conducted in October 2009, to observe whether or not seasonality had any effect on parameter concentrations at each holding time. The results of the study indicated that although parameter concentrations varied at different levels of holding time, none of the differences were significant at 0.05. This study is of particular relevance to the province of Newfoundland and Labrador because the results indicate that although recommended holding times cannot always be met, the analysis results for the ten parameters of interest are valid and representative of true water quality. Notwithstanding this conclusion, water samples should always be analyzed as soon as possible after collection.

## **1 INTRODUCTION**

Holding times are the length of time a sample can be stored after collection and prior to analysis without significantly affecting the analytical results. Holding times vary with the analyte, sample matrix, and analytical methodology used to quantify the analytes concentration (Keith, 1991).

Water samples from approximately 79 representative freshwater monitoring stations across Newfoundland and Labrador (NL) are collected seasonally and shipped to the National Laboratory for Environmental Testing (NLET) in Burlington, Ontario as part of a federal-provincial water quality monitoring agreement. Due to the remote locations of some monitoring stations and their distance from a courier service, many water samples submitted for analysis are not meeting the maximum recommended holding times prescribed by NLET. Parameter holding times prescribed by NLET are listed in **Appendix I** at the end of this report. Several commonly tested parameters (total nitrogen, nitrate, total phosphorus, dissolved inorganic carbon, dissolved organic carbon, alkalinity, pH, specific conductivity, turbidity and color) have short holding times of 24 to 48 hours. Samples collected in NL typically take two to five days to arrive at NLET, and even though great effort is made to ensure there are enough ice packs in the coolers to keep sample temperatures below 4°C, the lengthy holding times may be impacting data integrity. The Department of Environment and Conservation (ENVC) in NL must decide if parameter results are valid, despite the fact that holding times are being exceeded, and if other measures need to be explored to ensure the validity of the data.

This study involved the collection of five sets of water samples from each of three water bodies in the province. The samples were shipped to NLET immediately after collection so that analyses could begin within 48 hours. Five holding times were established for analysis: on the first day the samples arrived at the laboratory (T1), and on the 3<sup>rd</sup>, 7<sup>th</sup>, 10<sup>th</sup> and 21<sup>st</sup> days (T2, T3, T4 and T5 respectively) after the samples arrived. Parameter concentrations at T1 represent the control group to which parameter concentrations at all subsequent holding times were compared. One set of samples from each water body was analyzed at each holding time. The purpose of the study was to determine if concentrations and levels of the parameters of interest changed significantly as holding times increased. The study was conducted in two phases; the first phase of sampling was conducted in March 2009, and the second phase was conducted in October 2009, to see if seasonality had any effect on holding time. The results of this study will guide water sampling protocol for ENVC, particularly in determining whether more resources need to be directed toward sample preservation and enabling shorter holding times to be met.

## 2 METHODOLOGY

### 2.1 Data Collection

Five sets of water samples were collected at each of three water bodies in Newfoundland and Labrador on March 2, 2009; Quidi Vidi Lake, a highly developed urban watershed; Corduroy Brook, a moderately developed urban watershed; and Pinchgut Brook, a fairly pristine watershed with low development. A set of water samples consisted of four sample bottles to be analyzed for the following parameters:

<b>Sample Container</b>	<b>Parameters Analyzed</b>
1 x plastic bottle	alkalinity, pH, specific conductance, color, turbidity
1 x glass bottle	nitrates, total nitrogen
1 x glass bottle	DIC/DOC
1 x glass bottle	total phosphorus

The water samples were packed on ice packs in coolers and shipped to NLET immediately after collection. All samples arrived at lab within 48 hours of collection. Sample analysis commenced on the day the samples arrived, which was designated as holding time "day 1." One set of samples from each water body was analyzed according to the following holding time intervals:

- Same day samples arrived at the laboratory(T1)
- 3 days after samples arrived at the laboratory(T2)
- 7 days after samples arrived at the laboratory(T3)
- 10 days after samples arrived at the laboratory(T4)
- 21 days after samples arrived at the laboratory(T5)

All samples were stored in refrigerators and kept below 4°C from the time they arrived at the laboratory until they were analyzed. The study was repeated on October 5, 2009 to determine if seasonality had an effect on parameter concentrations at the various holding times. An extra set of five samples was collected at Quidi Vidi Lake in March and October for quality assurance/ quality control comparison.

## **2.2 Data Analysis**

An examination of the analytical results of each water quality parameter indicated that almost all distributions were positively skewed, and the data included outliers, missing values and less than detection results. Lack of normal distribution along with the presence of outliers, missing values and censored data make parametric statistical analysis unsuitable (Helsel and Hirsch, 2002). The data for each parameter were therefore rank-transformed so that parametric analytical methods could be utilized. The data were analyzed using a three-way ANOVA general linear method (GLM). This method was selected because there were three factors (holding time, location and month) and all factors are categorical. The test statistic is the F-test, testing if the means of the groups formed by values of the independent variables are different enough not to have occurred by chance (Wheater and Cook, 2000). If the group means do not differ significantly, then it is inferred that the independent variables did not have an effect on the dependent variable, or in this case, that holding time, location and month did not have a significant affect on parameter concentration. If the F-test shows a relationship, then a multiple comparison test of significance can be used to examine the impact of each independent variable on the relationship (Garson, 2009). In this study, Dunnett's method compared the means of parameter concentration at each holding time T2, T3, T4 and T5 to the mean of the control holding time T1, relative to location and season. All factors are categorical with holding times represented as T1, T2, T3, T4 and T5; sample locations defined as Quidi Vidi Lake, Corduroy Brook and Pinchgut Brook; and months, March and October. This analysis of variance on the ranks of the data tested the null hypothesis that there was no difference between group means, and the alternative hypothesis that at least one group mean was different. The key ANOVA assumptions were upheld by the distributions of the ranked data, that the groups formed by the independent variables were normality distributed and had relative homogeneity of variance. Minitab 15 software was used to compute the GLM analysis with Dunnett's comparison. A large F-value would indicate a high degree of variability between means, and would generate a small p-value. The decision to reject the null hypothesis was established at p-value < 0.05.

The final phase of analysis for this study involved the comparison of Quidi Vidi Lake data with the duplicate set of data

collected as part of quality assurance/quality control. For this analysis, a paired t-test was selected because each data point is paired with another. The paired t-test compares two paired groups of data to determine if their differences are significantly different from zero (Helsel and Hirsch, 2002). The null hypothesis was set as: there is no difference in parameter concentrations at each holding time interval between the two groups. The level of significance was established at 0.05.

### 3 RESULTS AND DISCUSSION

Data for each parameter were arranged by holding time, location and month as shown in the example below.

#### *Total Nitrogen*

	T1	T2	T3	T4	T5
<b>QVL-M</b>	0.847	0.822	0.800	0.776	0.802
<b>QVL-O</b>	0.715	0.756	0.721	0.696	0.688
<b>QVLQA-M</b>	0.828	0.807	0.813	0.802	0.816
<b>QVLQA-O</b>	0.725	0.796	0.690	0.686	0.683
<b>CB-M</b>	0.901	0.882	0.884	0.862	*
<b>CB-O</b>	0.575	*	0.495	0.475	0.481
<b>PB-M</b>	0.299	0.269	0.291	0.277	0.284
<b>PB-O</b>	0.222	0.229	0.212	0.209	0.196

\* = no data available

- QVL-M            Quidi Vidi Lake-March
- QVL-O            Quidi Vidi Lake-October
- QVLQA-M        Quidi Vidi Lake QAQC-March
- QVLQA-O        Quidi Vidi Lake QAQC-October
- CB-M            Corduroy Brook-March
- CB-O            Corduroy Brook-October
- PL-M            Pinchgut Brook-March
- PL-O            Pinchgut Brook-October

#### **Holding Times:**

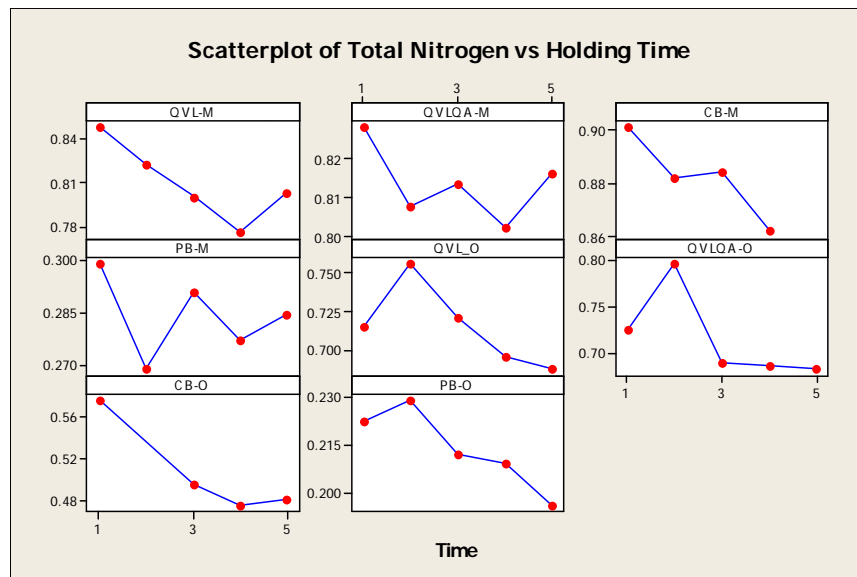
T1 = analysis conducted on the day the samples arrived at the laboratory

T2 = analysis conducted on the 3<sup>rd</sup> day after the samples arrived at the laboratory

- T3 = analysis conducted on the 7<sup>th</sup> day after the samples arrived at the laboratory
- T4 = analysis conducted on the 10<sup>th</sup> day after the samples arrived at the laboratory
- T5 = analysis conducted on the 21<sup>st</sup> day after the samples arrived at the laboratory

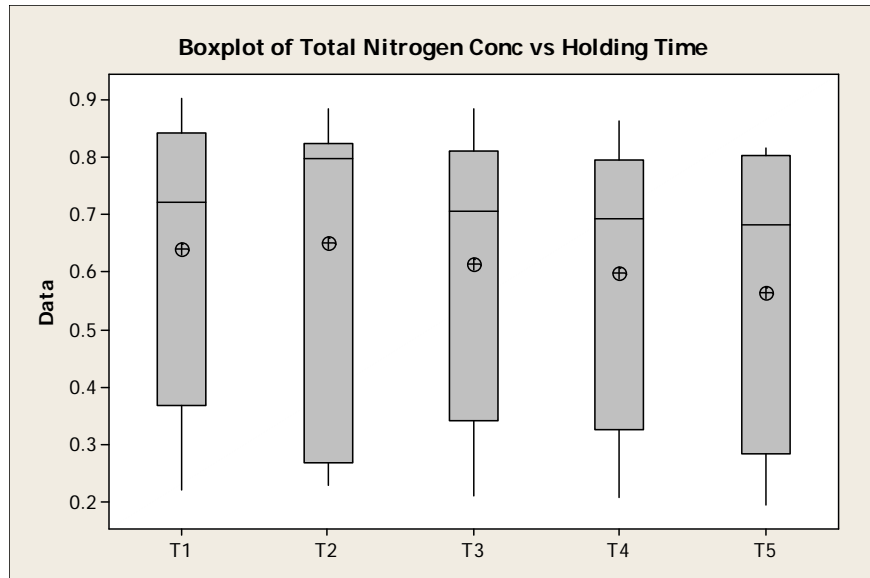
### 3.1 Graphs

The data for each parameter were graphed by scatterplot and boxplot to give an initial observation of the effect of holding time on parameter concentration, as well as an indication of data distribution. A scatterplot and boxplot for total nitrogen concentration at each holding time, location and season is shown in **Figures 1 and 2**:



**Figure 1: Scatterplot of Total Nitrogen Concentrations**

The scatterplots show decreasing total nitrogen concentrations for most data sets.



**Figure 2: Boxplot of Total Nitrogen Concentrations**

The boxplots demonstrate that the means for each holding time are similar in location and show a slight decrease as holding times increase; all distributions are asymmetric.

Scatterplots and boxplots for each parameter are found in **Appendices II and III** respectively. A summary of scatterplot and boxplot observations are found in **Table 1**:

**Table 1: Summary of Scatterplot and Boxplot Observations**

Parameter	Scatterplot Observation	Boxplot Observation
Total Nitrogen	Overall decreasing concentration per increasing holding time	Similar location of means for all groups; slight decrease as holding times increase; asymmetric distributions
Nitrate	Slight increasing concentration per holding time in March; no change in October	Similar location of mean; asymmetric distributions
Total Phosphorus	Small variations in concentration per holding time	Similar location of mean; asymmetric distributions
Dissolved Inorganic Carbon	Concentrations increase per holding time in March, decrease in October	Identical location of mean; asymmetric distributions
Dissolved Organic Carbon	Decreasing concentration at 10 days in March, small variations per holding time in October	Similar location of mean; an outlier value at each holding time; asymmetric distributions

Alkalinity	Small variations per holding time	Small variations in mean between holding times; asymmetric distributions
pH	Decreasing levels at first, then increasing	Decrease in mean at 3 days; asymmetric distributions
Specific Conductance	Small variations in levels per holding time	Similar location of mean; asymmetric distributions
Turbidity	General decreasing concentration between 1- 7 days	Small variation in location of means; outlier at 10 days; asymmetric distributions
Color	Decreasing color per holding time in March; small variations per holding time in October	Slight decrease in mean per holding time; asymmetric distributions

### 3.2 General Linear Method and Dunnett's Comparison

The GLM and Dunnett's comparison, using the F-statistic, generated p-values that would serve as the basis for rejecting the null hypothesis. A p-value < 0.05 was significant evidence to reject the null hypothesis. A summary of p-values generated by the GLM and Dunnett's comparison is shown in **Table 2**:

**Table 2: Summary of p-values from GLM Analysis and Dunnett's Comparison**

Parameter	GLM			Dunnett's			
	Time	Location	Month	T2	T3	T4	T5
Total Nitrogen	0.371	0.000	0.000	0.9992	0.9094	0.5005	0.3739
Nitrate	0.552	0.000	0.000	0.4102	0.8882	0.8191	1.0000
Total Phosphorus	0.393	0.000	0.042	0.3493	0.3282	0.9918	0.8214
DIC	0.814	0.000	0.032	1.0000	0.9997	0.7464	0.9993
DOC	0.670	0.000	0.001	0.9976	0.6420	0.9998	0.9849
Alkalinity	0.859	0.000	0.046	1.0000	0.9963	0.7775	0.9999
pH	0.763	0.000	0.000	0.5996	0.9988	0.9584	1.0000
Specific Conductance	0.710	0.000	0.000	0.8733	0.9215	0.9672	0.9999
Turbidity	0.852	0.000	1.000	0.9942	0.8820	0.9414	0.9848
Color	0.289	0.000	0.005	0.9166	0.8903	0.6545	0.3625

The computations for GLM and Dunnett's comparison for each parameter are found in **Appendix IV**. Residual plots were examined for each parameter to verify that there were no violations of the

assumptions of normality and equal variance. The residual plots for each parameter are found in **Appendix V**.

### 3.3 Paired t-Test

The final statistical analysis was computed on the parameter concentrations of the Quidi Vidi Lake water samples compared to the Quidi Vidi Lake duplicate samples, as part of quality assurance/quality control protocol. A p-value < 0.05 was significant evidence to reject the null hypothesis. A summary of p-values generated by the paired t-test is found in **Table 3**:

**Table 3: Summary of p-Values from Paired t-Test on QVL versus QAQC Data**

Parameter	Mean Difference	P-Value
Total Nitrogen	0.300	0.757
Nitrate	0.111	0.889
Total Phosphorus	0.300	0.690
DIC	2.700	0.002
DOC	0.300	0.886
Alkalinity	0.310	0.797
pH	0.389	0.542
Specific Conductance	0.670	0.572
Turbidity	2.333	0.026
Color	0.110	0.939

The paired t-test computation for each parameter is found in **Appendix VI**.

## 4 CONCLUSIONS

The p-values generated from statistical analysis on the data using the GLM and Dunnett's comparison indicated that there was not enough evidence to reject the null hypothesis for any holding time for any parameter monitored. Even though small variations in concentration were evident in the numerical data, scatterplots and boxplots, they were not significant at  $\alpha = 0.05$ . This study demonstrates that concentrations for the ten parameters identified did not change significantly when analyzed up to 21 days after the samples had arrived at the laboratory.

Parameter concentrations did vary significantly by location, for all parameters at all locations. This is an expected result because Quidi Vidi Lake is the receiving water for a heavily developed urban watershed, while Corduroy Brook is in a moderately developed watershed and Pinchgut Brook is fairly pristine. More importantly, this study concludes that variable parameter concentrations between locations had no impact on holding times in this study.

Seasonality had an impact on turbidity values in this study, as turbidity levels were significantly higher in March than in October. This is reflective of climate conditions at the time of sampling, as rainfall, snowmelt and run-off from road salting operations influenced high turbidity levels in March. The variable turbidity levels had no impact on holding times in this study. No other parameters were significantly influenced by the month of collection, however variability for total phosphorus concentrations and alkalinity levels are approaching significant levels. These seasonal variations do not appear to have any impact on parameter concentrations at each holding time.

The paired t-test on duplicate sets of water samples from Quidi Vidi Lake identified significant differences for two parameters, dissolved inorganic carbon and turbidity. This test, however, holds little power with a very small sample size of two.

In summary, this study concludes that the range of holding times of two to five days that typically elapse between sample collection and laboratory analysis is not affecting data integrity for water samples collected as part of the Canada-Newfoundland and Labrador Water Quality Monitoring Agreement. That being stated, ENVC will continue to strive to reduce holding times to a most practical level, and will continue to follow strict protocols for sample storage and handling.

## **5 RECOMMENDATIONS**

There was no replication in this study. Individual parameters from one sample collected at Quidi Vidi Lake, from one sample collected at Corduroy Brook and from one sample collected at Pinchgut Brook were analyzed at each holding time. The results of this study may have been more reliable if parameters from multiple samples *from each water body* were analyzed at each holding time. Statistical analysis involving replication and interaction could then have been

used to interpret the results. ENVC may conduct a second holding times study in the near future, which will include replication.

## **6 REFERENCES**

Keith, Lawrence H. 1991. Environmental Sampling and Analysis: a practical guide.

Garson, David G. 2009. Univariate GLM, ANOVA, and ANCOVA: Stat notes North Carolina State University  
<http://faculty.chass.ncsu.edu/garson/PA765/anova.htm> Copyright 1998, 2008, 2009 by G. David Garson

Helsel, D.R. and Hirsch, R.M. 2002. Statistical Methods in Water Resources.

Wheater, C.P. and Cook, P.A. 2000. Using Statistics to Understand the Environment.



# Appendices

# **Appendix I**

## **NLET Parameter Holding Times**

## NLET Parameter Holding Times

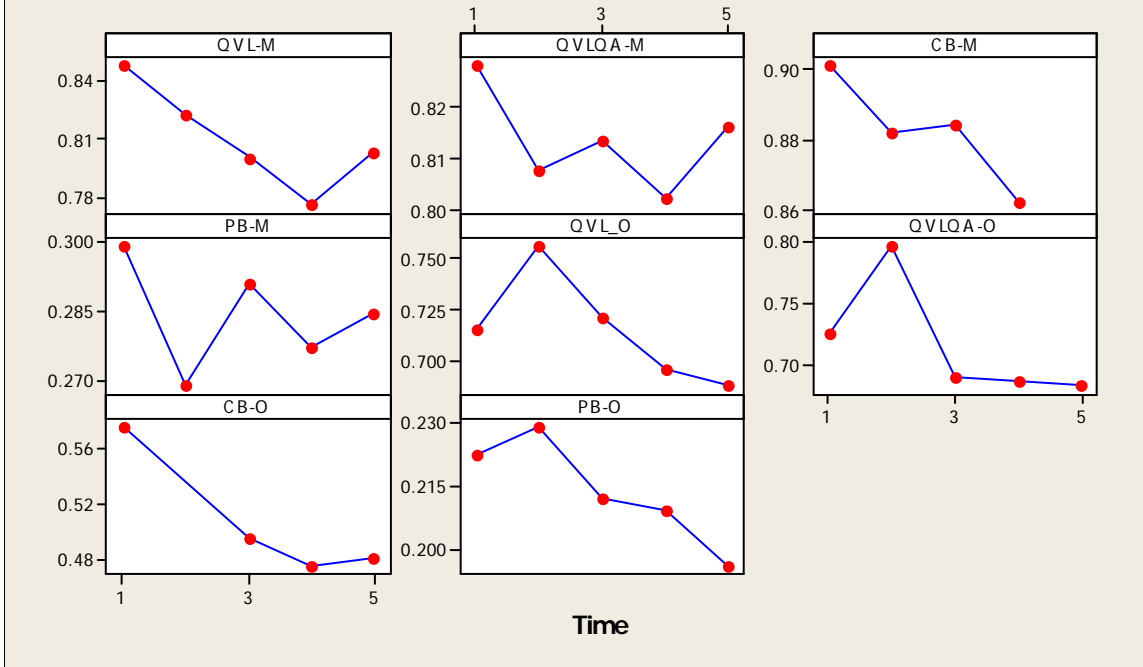
Parameter or Grouping	Bottle Type	Holding Time
<b>Major Ions</b>		
Acidity	500ml polyethylene, round	24 hours
Alkalinity	500ml polyethylene, round	24 hours
Flouride	500ml polyethylene, round	28 days
Chloride	500ml polyethylene, round	28 days
Sulphate	500ml polyethylene, round	28 days
Silica	500ml polyethylene, round	28 days
Calcium	500ml polyethylene, round	8 weeks
Magnesium	500ml polyethylene, round	8 weeks
Sodium	500ml polyethylene, round	8 weeks
Potassium	500ml polyethylene, round	8 weeks
<b>Physicals</b>		
pH	500ml polyethylene, round	24 hours
Conductivity	500ml polyethylene, round	28 days
Colour	500ml polyethylene, round	48 hours
Turbidity	500ml polyethylene, round	24 hours
<b>*Nutrients</b>		
Ammonia	120ml glass, round	24 hours
Nitrate-Nitrite	120ml glass, round	24 hours
Total Kjeldahl Nitrogen	120ml glass, round	24hrs or 7 days if acidified
Total Nitrogen	120ml glass, round	24 hours
Soluble Reactive Phosphorus	120ml glass, round	48 hours
DIC/DOC	120ml glass, round	24 hours
Total Phosphorus	125ml glass, square	1 year
<b>Metals</b>		
Extractable Metals	125ml polyethylene, round	6 months
Total Metals	125ml polyethylene, round	6 months
Total Recoverable Metals	125ml polyethylene, round	6 months
<b>Bacteriological</b>	125ml plastic	24 hours

- For nutrient parameters, the bottle should be filled to the rim to minimize sample degradation.

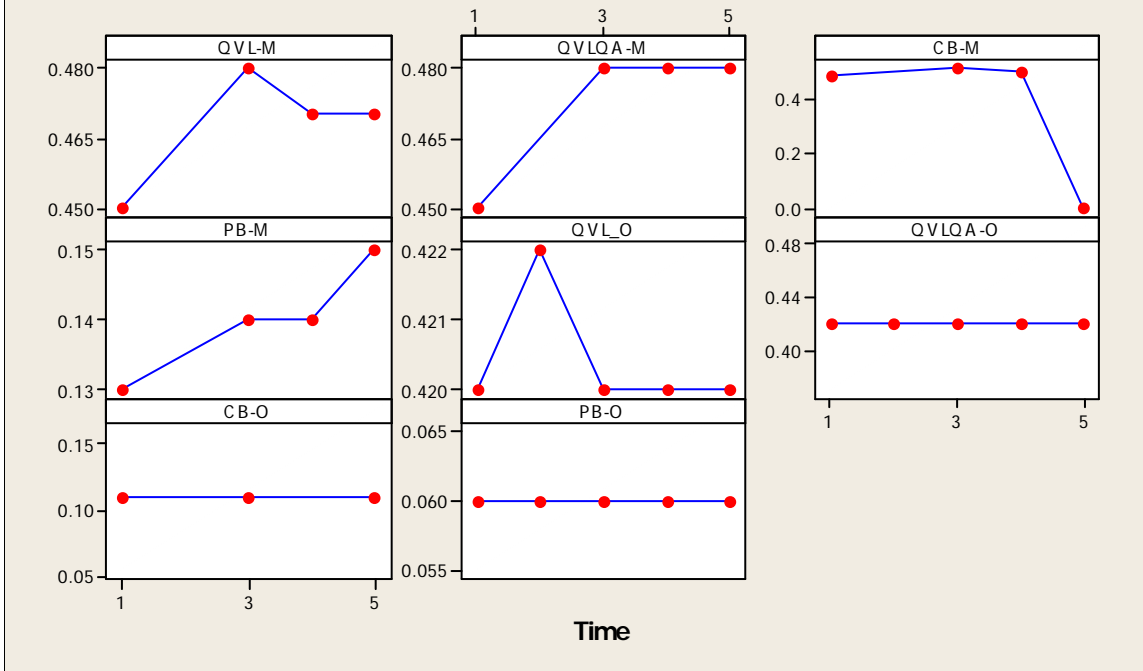
## **Appendix II**

### **Scatterplots of Parameters versus Holding Time**

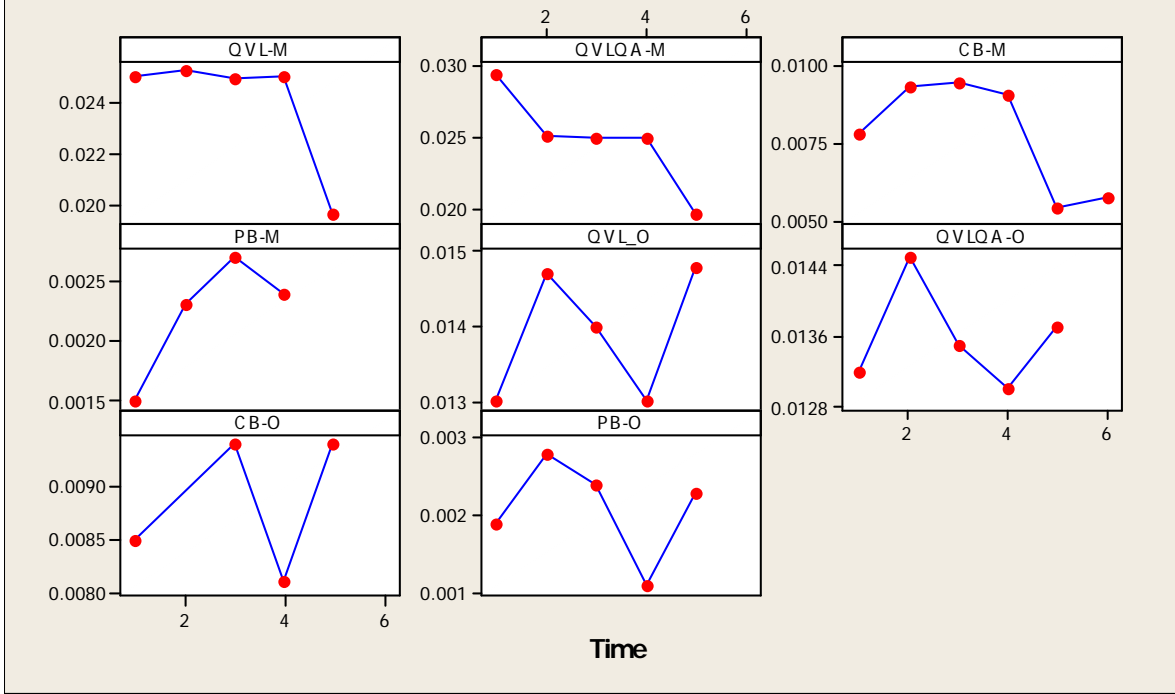
### Scatterplot of Total Nitrogen vs Holding Time



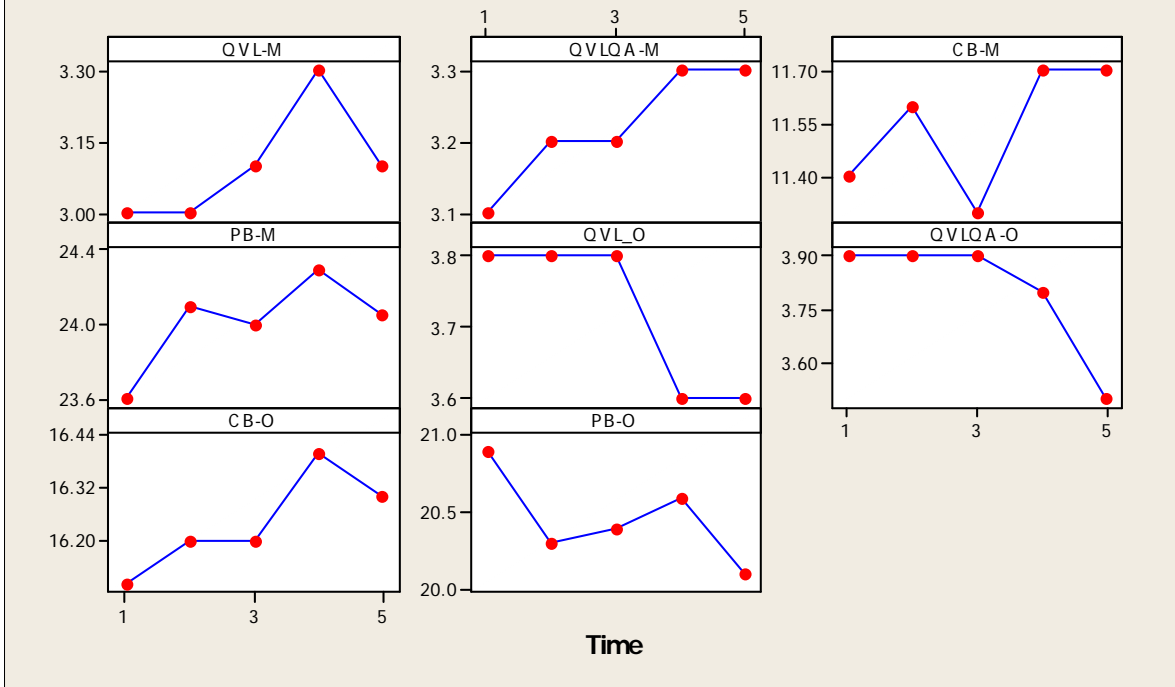
### Scatterplot of Nitrate vs Holding Time



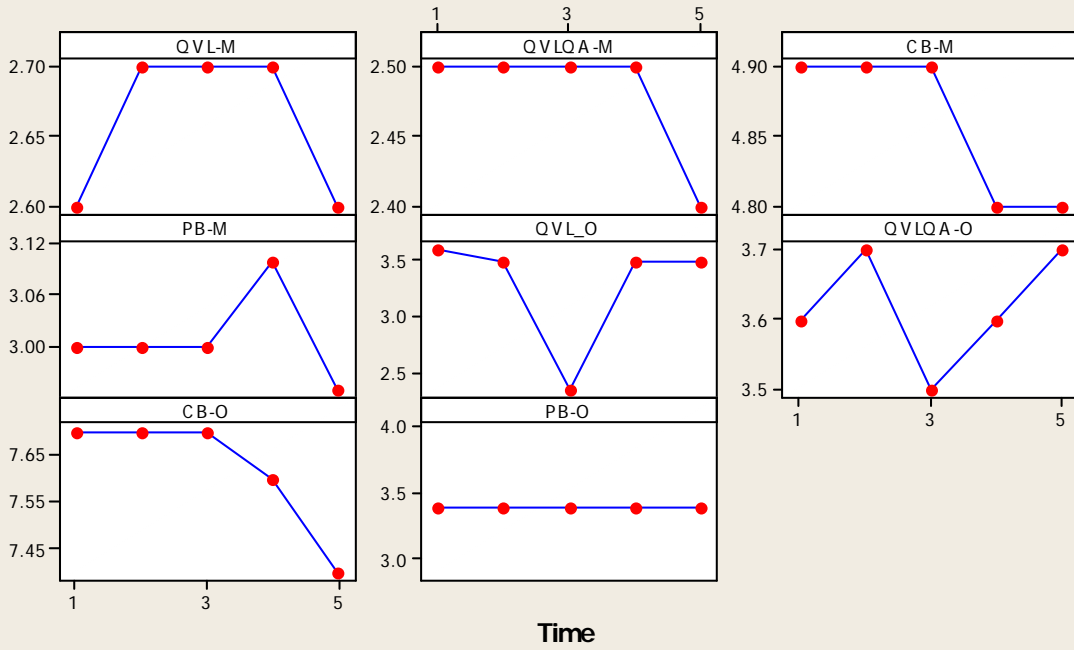
### Scatterplot of Total Phosphorus vs Holding Time



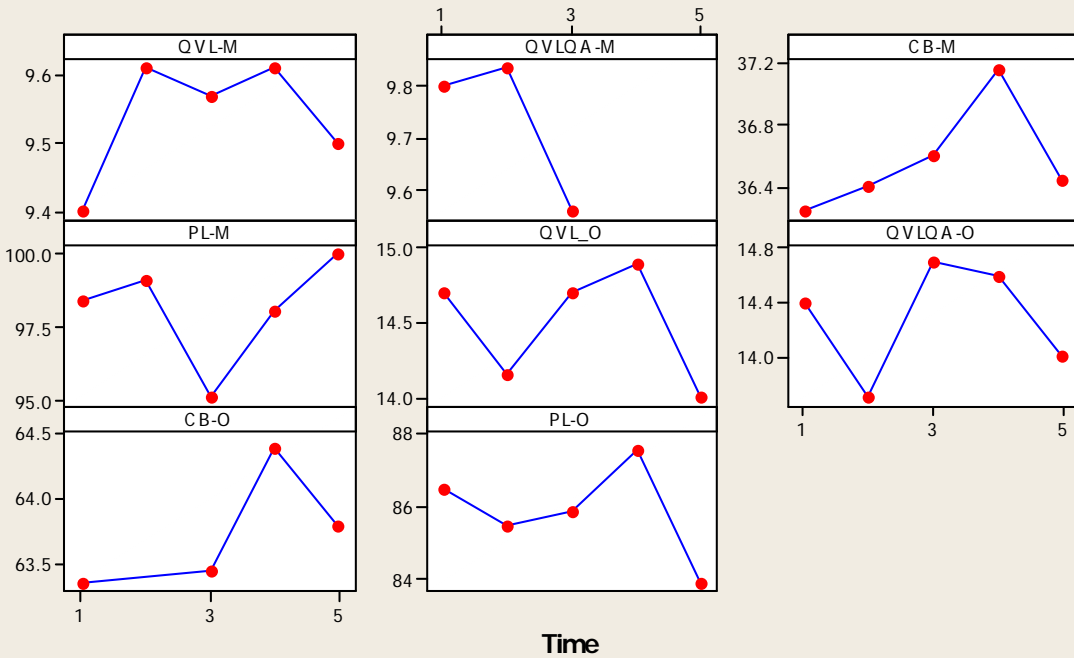
### Scatterplot of DIC vs Holding Time



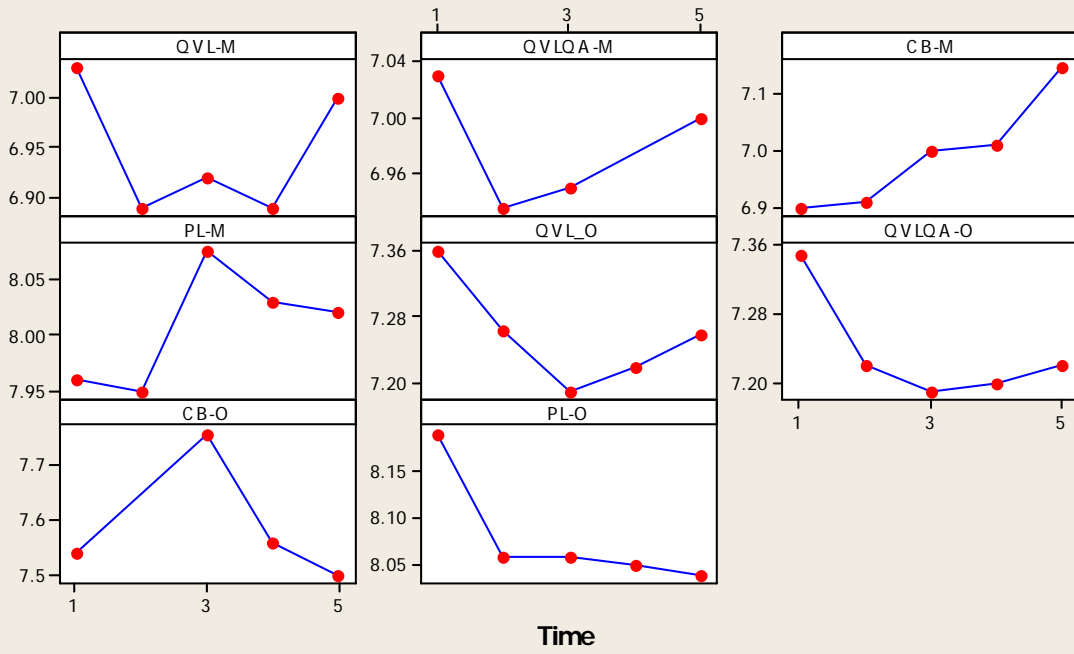
### Scatterplot of DOC vs Holding Time



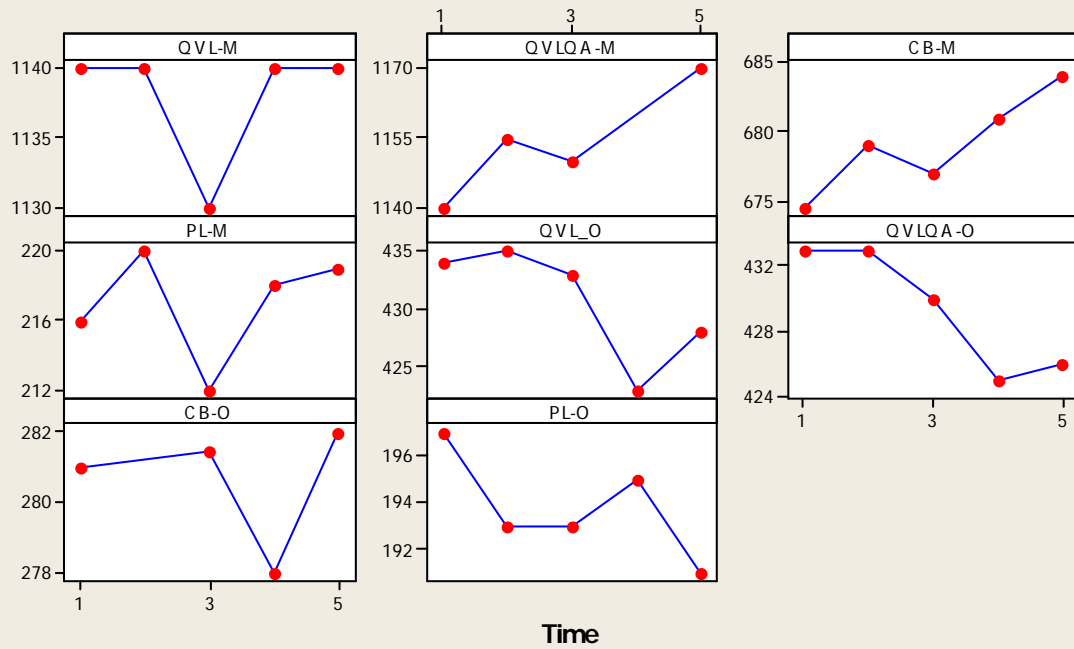
### Scatterplot of Alkalinity vs Holding Time



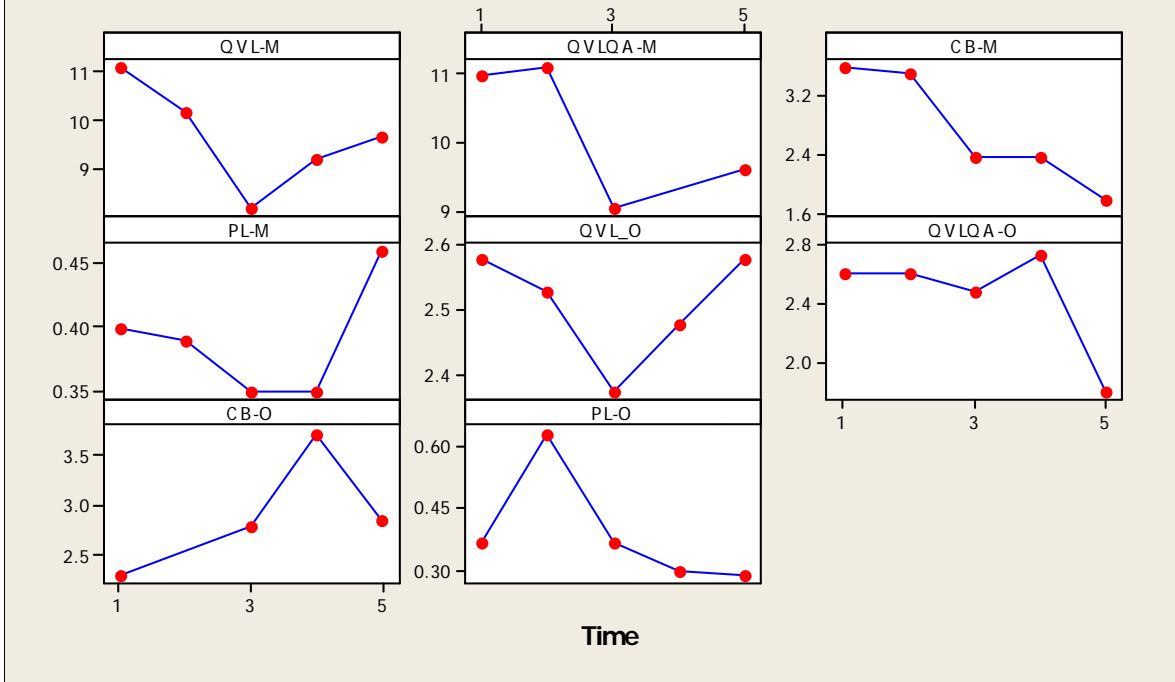
### Scatterplot of pH vs Holding Time



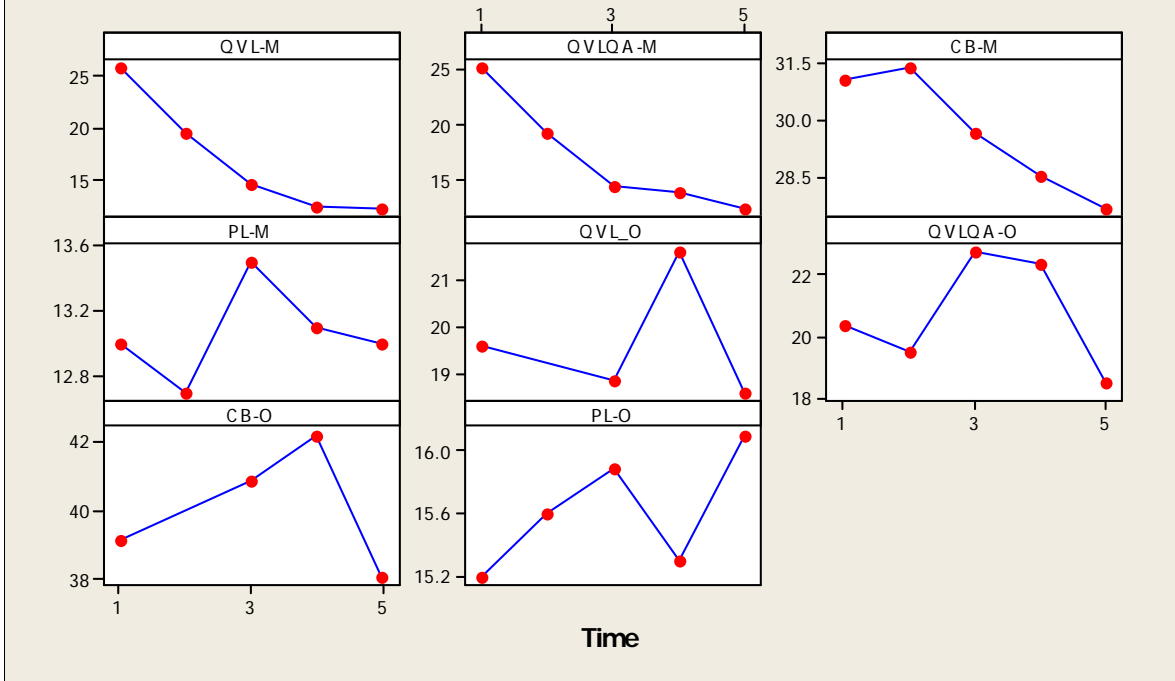
### Scatterplot of Conductance vs Holding Time



### Scatterplot of Turbidity vs Holding Time

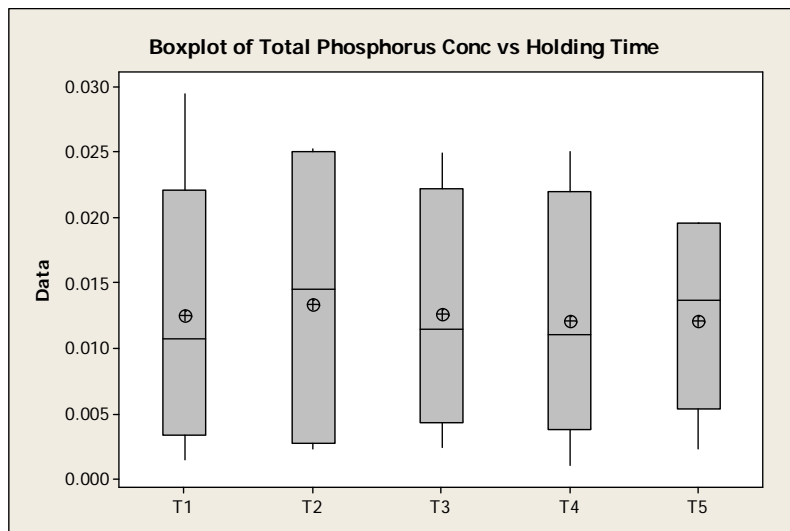
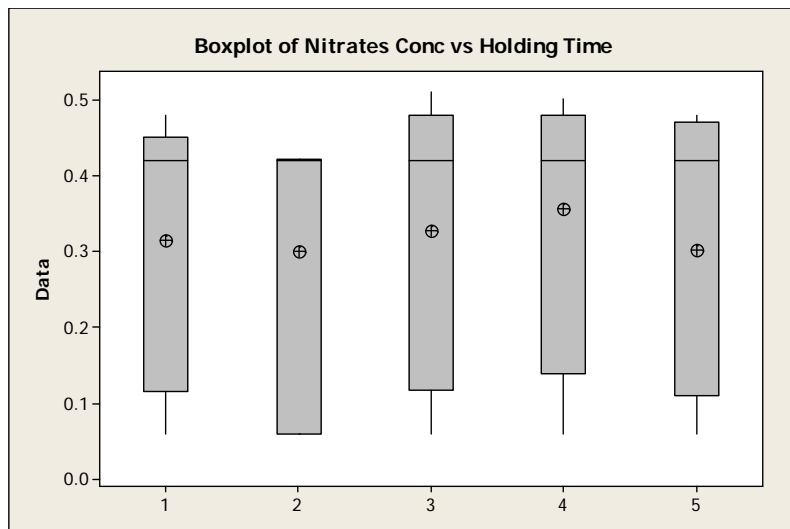
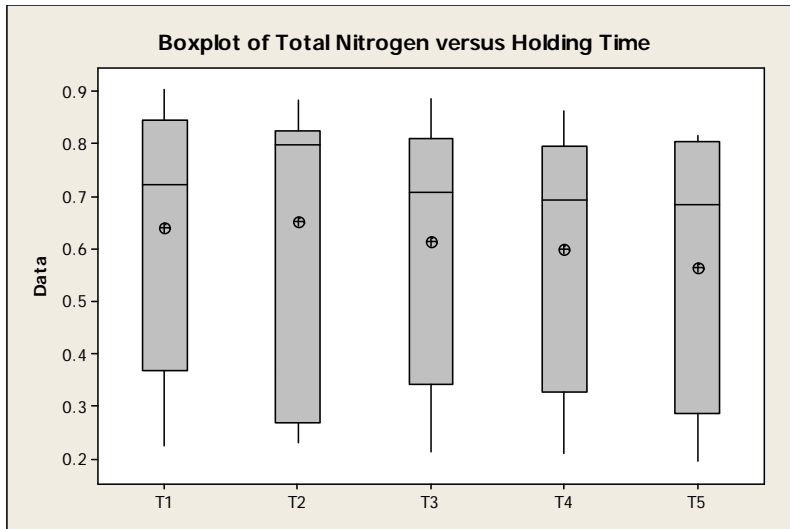


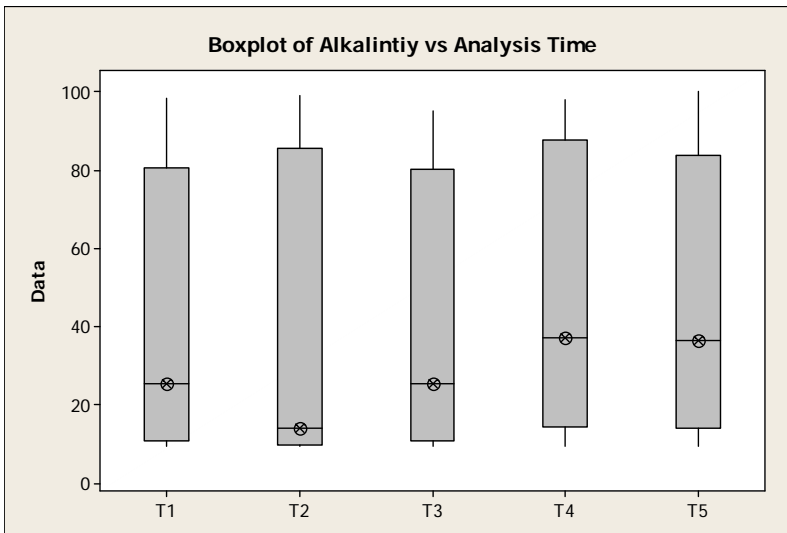
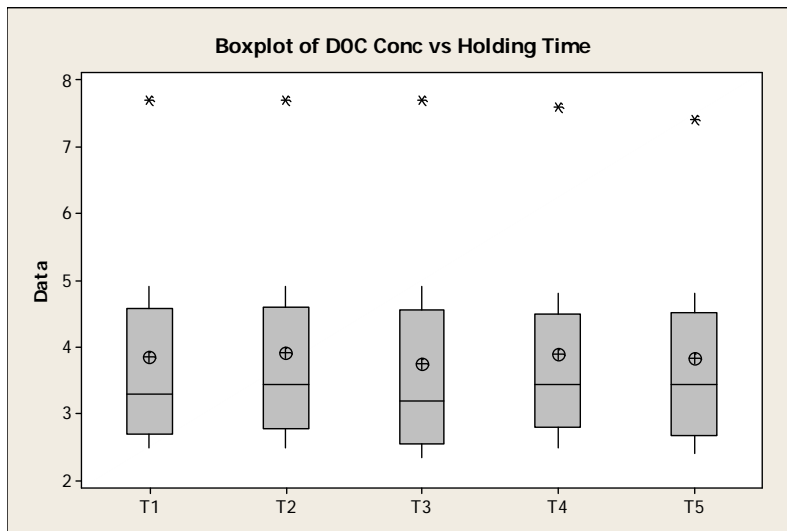
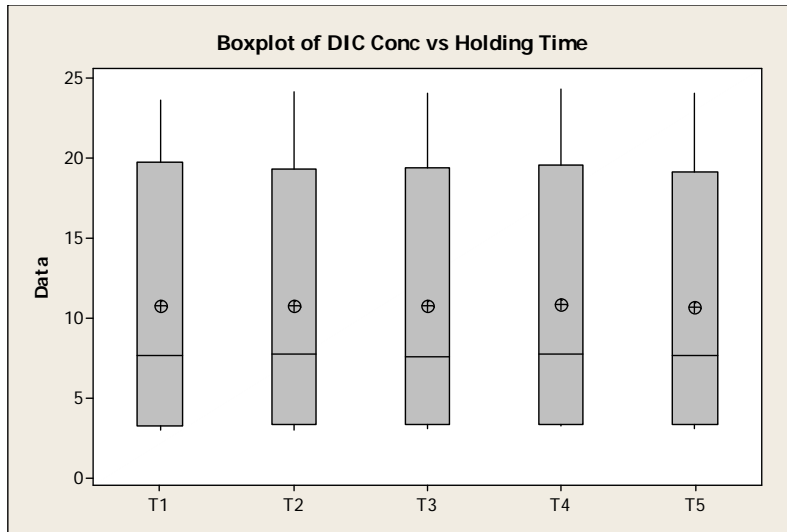
### Scatterplot of Color vs Holding Time

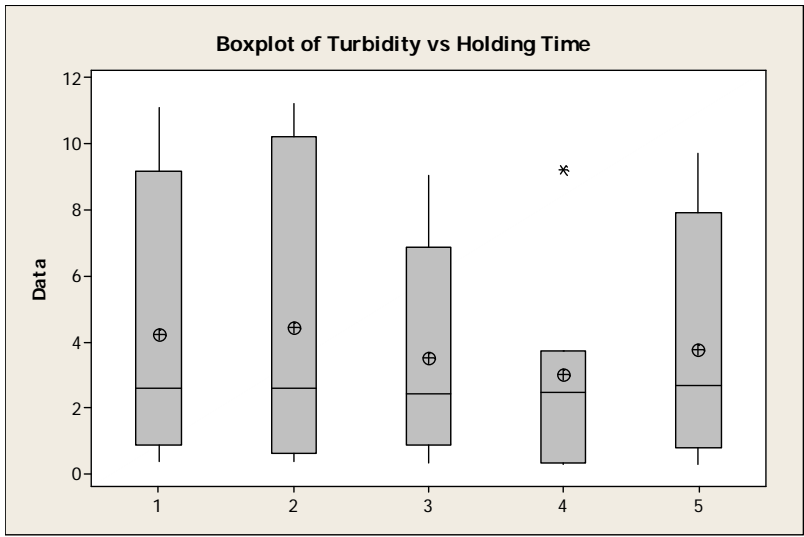
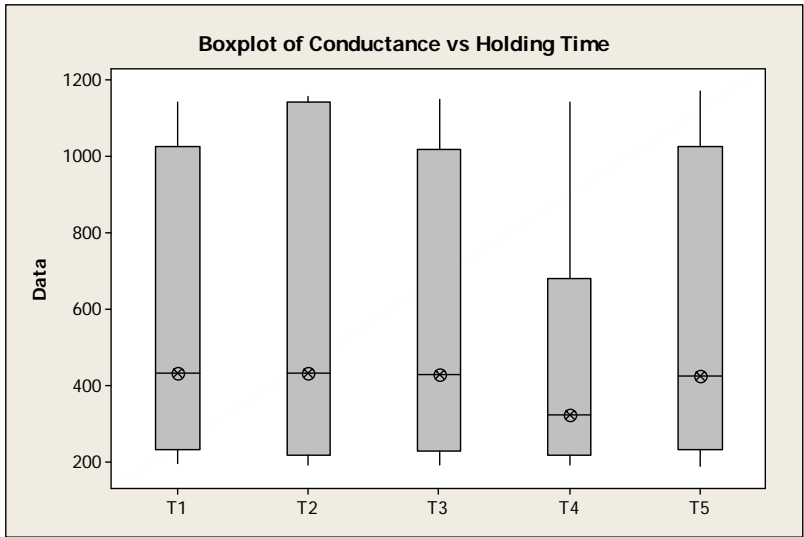
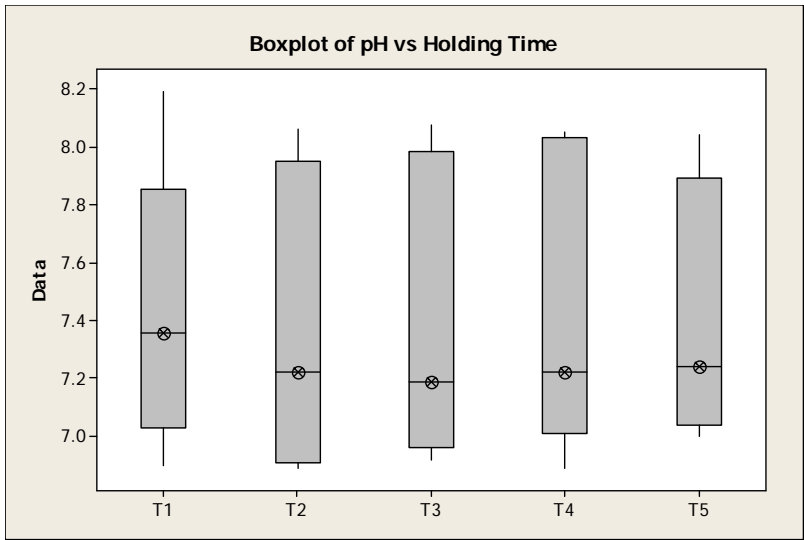


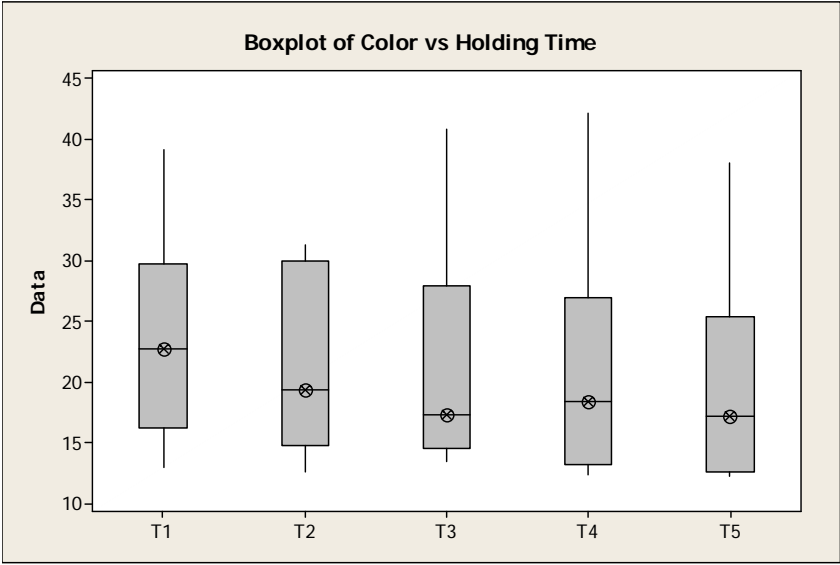
## **Appendix III**

### **Boxplots of Parameters versus Holding Time**









# **Appendix IV**

## **GLM Computations by Parameter**

## General Linear Model: TN versus TIME, LOCATION, MONTH

Factor	Type	Levels	Values
TIME	fixed	5	1, 2, 3, 4, 5
LOCATION	fixed	3	1, 2, 3
MONTH	fixed	2	M, O

Analysis of Variance for TN, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
TIME	4	186.46	102.61	25.65	1.13	0.371
LOCATION	2	2287.73	2287.73	1143.86	50.34	0.000
MONTH	1	895.36	895.36	895.36	39.40	0.000
Error	20	454.48	454.48	22.72		
Total	27	3824.03				

S = 4.76698 R-Sq = 88.12% R-Sq(adj) = 83.96%

Dunnett 95.0% Simultaneous Confidence Intervals

Response Variable TN

Comparisons with Control Level

TIME = 1 subtracted from:

TIME	Lower	Center	Upper
2	-7.19	0.535	8.257
3	-9.15	-1.833	5.483
4	-10.98	-3.667	3.650
5	-12.21	-4.487	3.235

-12.0      -6.0      0.0      6.0

Dunnett Simultaneous Tests

Response Variable TN

Comparisons with Control Level

TIME = 1 subtracted from:

TIME	Difference of Means	SE of Difference	T-Value	Adjusted P-Value
2	0.535	2.905	0.184	0.9992
3	-1.833	2.752	-0.666	0.9094
4	-3.667	2.752	-1.332	0.5005
5	-4.487	2.905	-1.545	0.3739

**General Linear Model: Nitrates versus TIME, LOCATION, SEASON**

Factor	Type	Levels	Values
TIME	fixed	5	1, 2, 3, 4, 5
LOCATION	fixed	3	C, P, Q
SEASON	fixed	2	M, O

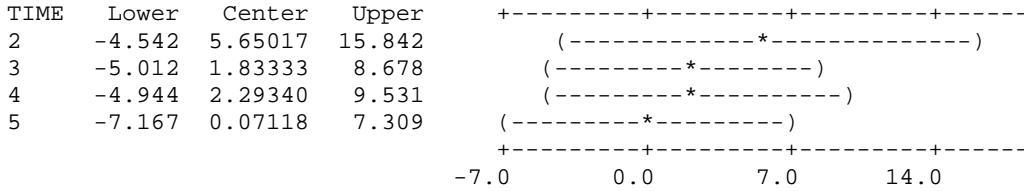
Analysis of Variance for Nitrates, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
TIME	4	82.51	58.94	14.74	0.78	0.552
LOCATION	2	1146.85	1146.85	573.43	30.50	0.000
SEASON	1	828.82	828.82	828.82	44.08	0.000
Error	16	300.82	300.82	18.80		
Total	23	2358.99				

S = 4.33601 R-Sq = 87.25% R-Sq(adj) = 81.67%

Dunnett 95.0% Simultaneous Confidence Intervals

Response Variable Nitrates  
 Comparisons with Control Level  
 TIME = 1 subtracted from:



Dunnett Simultaneous Tests  
 Response Variable Nitrates  
 Comparisons with Control Level  
 TIME = 1 subtracted from:

TIME	Difference of Means	SE of Difference	T-Value	Adjusted P-Value
2	5.65017	3.727	1.51582	0.4102
3	1.83333	2.503	0.73234	0.8882
4	2.29340	2.647	0.86640	0.8191
5	0.07118	2.647	0.02689	1.0000

**General Linear Model: TP versus TIME, LOCATION, SEASON**

Factor	Type	Levels	Values
TIME	fixed	5	1, 2, 3, 4, 5
LOCATION	fixed	3	C, P, Q
SEASON	fixed	2	M, O

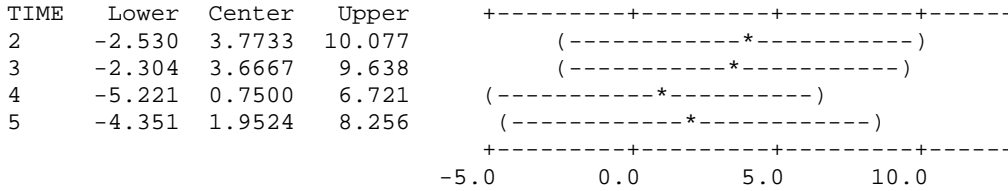
Analysis of Variance for TP, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
TIME	4	92.35	65.36	16.34	1.08	0.393
LOCATION	2	2764.99	2725.69	1362.85	90.10	0.000
SEASON	1	71.50	71.50	71.50	4.73	0.042
Error	20	302.51	302.51	15.13		
Total	27	3231.36				

S = 3.88918    R-Sq = 90.64%    R-Sq(adj) = 87.36%

Dunnett 95.0% Simultaneous Confidence Intervals

Response Variable TP  
 Comparisons with Control Level  
 TIME = 1 subtracted from:



Dunnett Simultaneous Tests

Response Variable TP  
 Comparisons with Control Level  
 TIME = 1 subtracted from:

TIME	Difference of Means	SE of Difference	T-Value	Adjusted P-Value
2	3.7733	2.371	1.5917	0.3493
3	3.6667	2.245	1.6330	0.3282
4	0.7500	2.245	0.3340	0.9918
5	1.9524	2.371	0.8236	0.8314



## General Linear Model: DOC versus TIME, LOCATION, SEASON

Factor	Type	Levels	Values
TIME	fixed	5	1, 2, 3, 4, 5
LOCATION	fixed	3	C, P, Q
SEASON	fixed	2	M, O

Analysis of Variance for DOC, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
TIME	4	55.38	55.38	13.85	0.60	0.670
LOCATION	2	2709.82	2709.82	1354.91	58.25	0.000
SEASON	1	323.41	323.41	323.41	13.90	0.001
Error	22	511.73	511.73	23.26		
Total	29	3600.34				

S = 4.82293 R-Sq = 85.79% R-Sq(adj) = 81.26%

Unusual Observations for DOC

Obs	DOC	Fit	SE Fit	Residual	St Resid
2	27.0000	18.2667	2.4905	8.7333	2.11 R
14	1.0000	15.1833	2.4905	-14.1833	-3.43 R

R denotes an observation with a large standardized residual.

Dunnett 95.0% Simultaneous Confidence Intervals

Response Variable DOC

Comparisons with Control Level

TIME = 1 subtracted from:

TIME	Lower	Center	Upper	
2	-6.66	0.667	7.992	(-----*-----)
3	-10.41	-3.083	4.242	(-----*-----)
4	-6.99	0.333	7.659	(-----*-----)
5	-8.41	-1.083	6.242	(-----*-----)

-10.0      -5.0      0.0      5.0

Dunnett Simultaneous Tests

Response Variable DOC

Comparisons with Control Level

TIME = 1 subtracted from:

TIME	Difference of Means	SE of Difference	T-Value	Adjusted P-Value
2	0.667	2.785	0.239	0.9976
3	-3.083	2.785	-1.107	0.6420
4	0.333	2.785	0.120	0.9998
5	-1.083	2.785	-0.389	0.9849



## General Linear Model: ph versus TIME, LOCATION, SEASON

Factor	Type	Levels	Values
TIME	fixed	5	1, 2, 3, 4, 5
LOCATION	fixed	3	C, P, Q
SEASON	fixed	2	M, O

Analysis of Variance for ph, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
TIME	4	53.83	45.74	11.44	0.46	0.763
LOCATION	2	2411.94	2346.27	1173.13	47.30	0.000
SEASON	1	966.33	966.33	966.33	38.96	0.000
Error	21	520.84	520.84	24.80		
Total	28	3952.95				

S = 4.98017 R-Sq = 86.82% R-Sq(adj) = 82.43%

Unusual Observations for ph

Obs	ph	Fit	SE Fit	Residual	St Resid
3	3.0000	12.0530	2.5790	-9.0530	-2.12 R
17	37.0000	28.2606	2.6008	8.7394	2.06 R

R denotes an observation with a large standardized residual.

Dunnett 95.0% Simultaneous Confidence Intervals

Response Variable ph

Comparisons with Control Level

TIME = 1 subtracted from:

TIME	Lower	Center	Upper	
2	-11.59	-3.568	4.455	(-----*-----)
3	-8.19	-0.583	7.020	(-----*-----)
4	-9.10	-1.500	6.103	(-----*-----)
5	-7.69	-0.083	7.520	(-----*-----)

-----+-----+-----+-----  
-6.0 0.0 6.0

Dunnett Simultaneous Tests

Response Variable ph

Comparisons with Control Level

TIME = 1 subtracted from:

TIME	Difference of Means	SE of Difference	T-Value	Adjusted P-Value
2	-3.568	3.034	-1.176	0.5996
3	-0.583	2.875	-0.203	0.9988
4	-1.500	2.875	-0.522	0.9584
5	-0.083	2.875	-0.029	1.0000

## General Linear Model: SpC versus TIME, LOCATION, SEASON

Factor	Type	Levels	Values
TIME	fixed	5	1, 2, 3, 4, 5
LOCATION	fixed	3	C, P, Q
SEASON	fixed	2	M, O

Analysis of Variance for SpC, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
TIME	4	27.15	18.88	4.72	0.54	0.710
LOCATION	2	2329.49	2291.97	1145.98	130.33	0.000
SEASON	1	751.04	751.04	751.04	85.41	0.000
Error	21	184.65	184.65	8.79		
Total	28	3292.33				

S = 2.96527 R-Sq = 94.39% R-Sq(adj) = 92.52%

Dunnett 95.0% Simultaneous Confidence Intervals

Response Variable SpC

Comparisons with Control Level

TIME = 1 subtracted from:

TIME	Lower	Center	Upper	
2	-3.440	1.337	6.114	(-----+-----+-----+-----+)
3	-5.610	-1.083	3.444	(-----+-----*-----)
4	-5.360	-0.833	3.694	(-----+-----*-----)
5	-4.694	-0.167	4.360	(-----+-----*-----)

-----+-----+-----+-----+  
-3.5            0.0            3.5            7.0

Dunnett Simultaneous Tests

Response Variable SpC

Comparisons with Control Level

TIME = 1 subtracted from:

TIME	Difference of Means	SE of Difference	T-Value	Adjusted P-Value
2	1.337	1.807	0.7401	0.8733
3	-1.083	1.712	-0.6328	0.9215
4	-0.833	1.712	-0.4868	0.9672
5	-0.167	1.712	-0.0974	0.9999

**General Linear Model: TURBIDITY versus TIME, LOCATION, SEASON**

Factor	Type	Levels	Values
TIME	fixed	5	1, 2, 3, 4, 5
LOCATION	fixed	3	C, P, Q
SEASON	fixed	2	M, O

Analysis of Variance for TURBIDITY, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
TIME	4	60.57	65.17	16.29	0.33	0.852
LOCATION	2	2193.33	2174.22	1087.11	22.24	0.000
SEASON	1	144.30	144.30	144.30	2.95	0.100
Error	21	1026.50	1026.50	48.88		
Total	28	3424.69				

S = 6.99148 R-Sq = 70.03% R-Sq(adj) = 60.04%

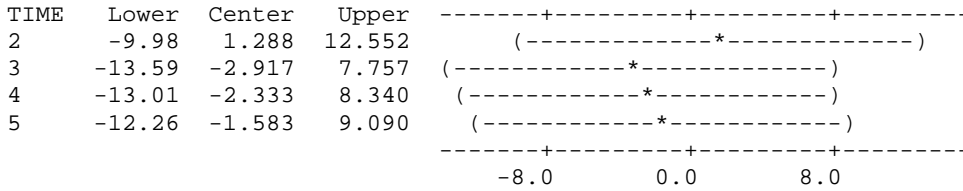
Unusual Observations for TURBIDITY

Obs	TURBIDITY	Fit	SE Fit	Residual	St Resid
22	29.0000	17.1061	3.7015	11.8939	2.01 R

R denotes an observation with a large standardized residual.

Dunnett 95.0% Simultaneous Confidence Intervals

Response Variable TURBIDITY  
 Comparisons with Control Level  
 TIME = 1 subtracted from:



Dunnett Simultaneous Tests  
 Response Variable TURBIDITY  
 Comparisons with Control Level  
 TIME = 1 subtracted from:

TIME	Difference of Means	SE of Difference	T-Value	Adjusted P-Value
2	1.288	4.260	0.3023	0.9942
3	-2.917	4.037	-0.7226	0.8820
4	-2.333	4.037	-0.5781	0.9414
5	-1.583	4.037	-0.3923	0.9848

**General Linear Model: COLOR versus TIME, LOCATION, SEASON**

Factor	Type	Levels	Values
TIME	fixed	5	1, 2, 3, 4, 5
LOCATION	fixed	3	C, P, Q
SEASON	fixed	2	M, O

Analysis of Variance for COLOR, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
TIME	4	94.33	186.52	46.63	1.34	0.289
LOCATION	2	2811.67	2916.42	1458.21	41.98	0.000
SEASON	1	338.84	338.84	338.84	9.76	0.005
Error	20	694.66	694.66	34.73		
Total	27	3939.50				

S = 5.89348 R-Sq = 82.37% R-Sq(adj) = 76.20%

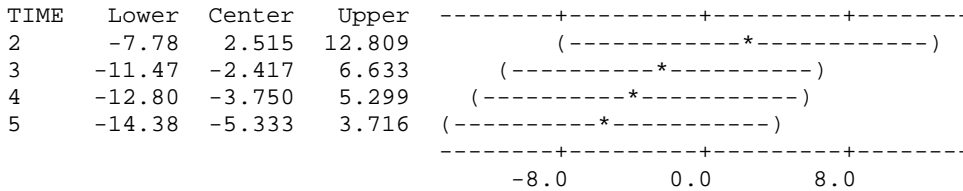
Unusual Observations for COLOR

Obs	COLOR	Fit	SE Fit	Residual	St Resid
1	28.0000	16.4513	3.0805	11.5487	2.30 R
7	31.0000	18.9660	3.4948	12.0340	2.54 R
19	2.0000	12.7013	3.0805	-10.7013	-2.13 R
25	1.0000	11.1180	3.0805	-10.1180	-2.01 R

R denotes an observation with a large standardized residual.

Dunnett 95.0% Simultaneous Confidence Intervals

Response Variable COLOR  
 Comparisons with Control Level  
 TIME = 1 subtracted from:



Dunnett Simultaneous Tests

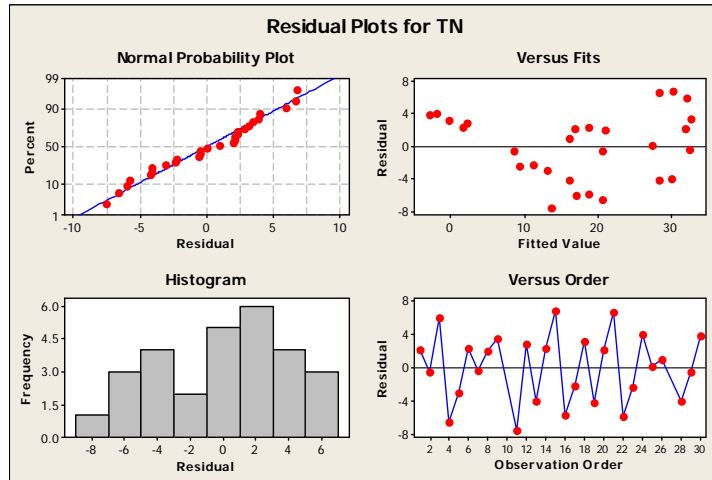
Response Variable COLOR  
 Comparisons with Control Level  
 TIME = 1 subtracted from:

TIME	Difference of Means	SE of Difference	T-Value	Adjusted P-Value
2	2.515	3.871	0.650	0.9166
3	-2.417	3.403	-0.710	0.8903
4	-3.750	3.403	-1.102	0.6545
5	-5.333	3.403	-1.567	0.3625

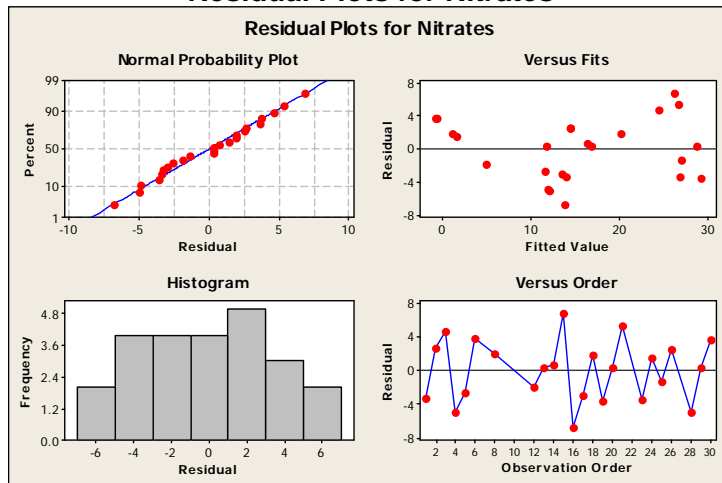
# **Appendix V**

## **Residual Plots by Parameter**

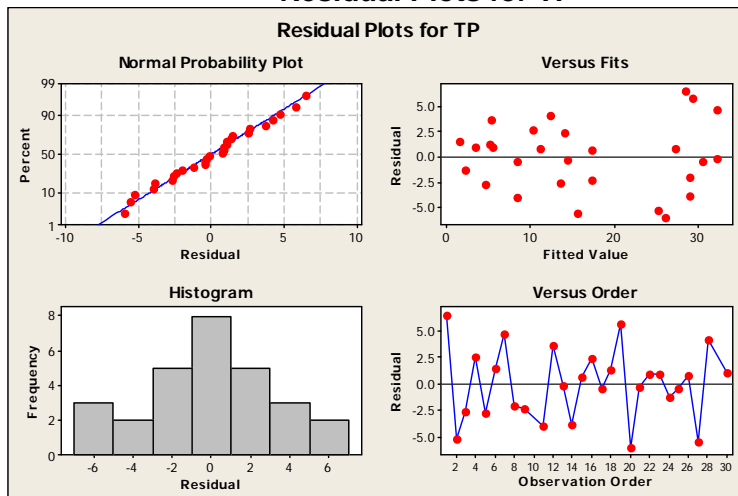
### Residual Plots for TN



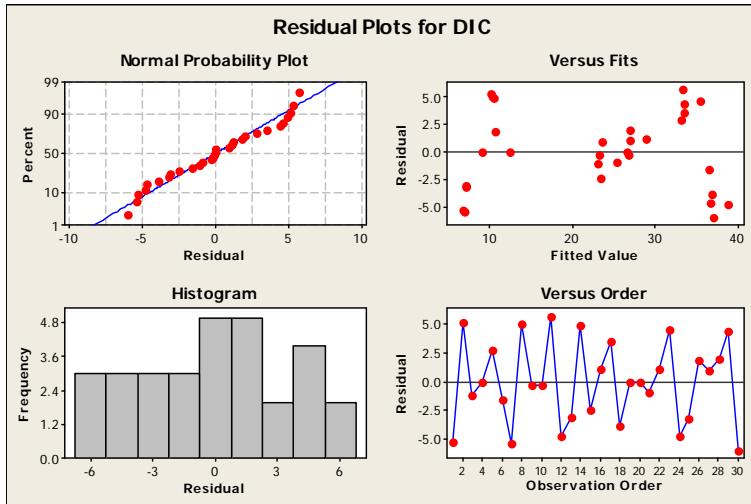
### Residual Plots for Nitrates



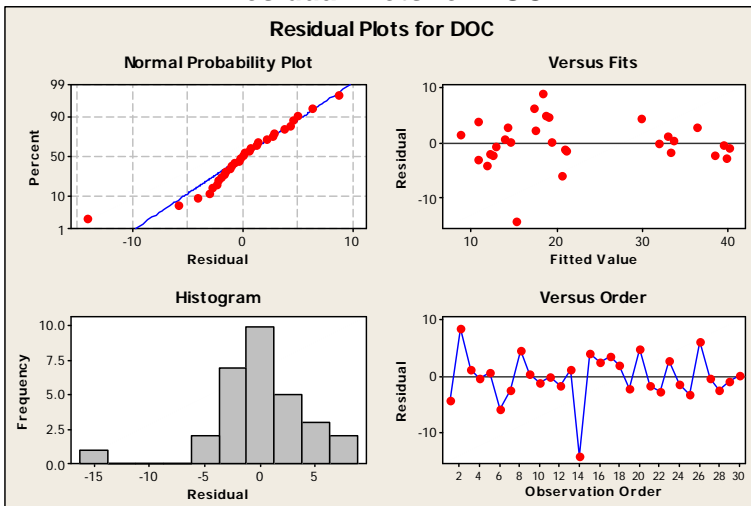
### Residual Plots for TP



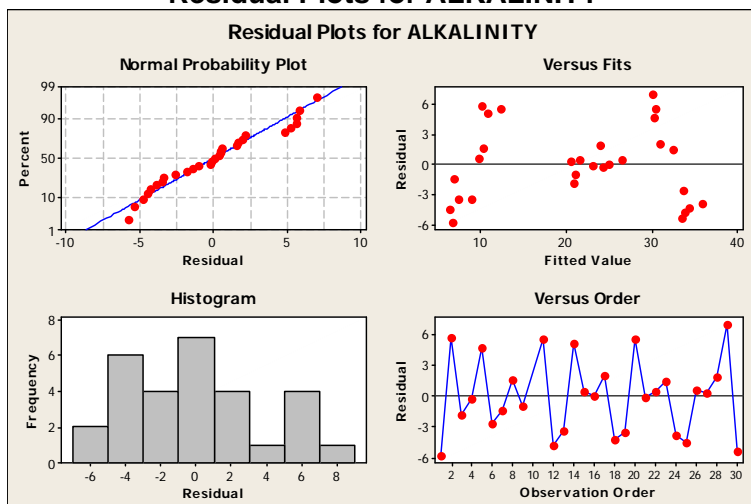
## Residual Plots for DIC



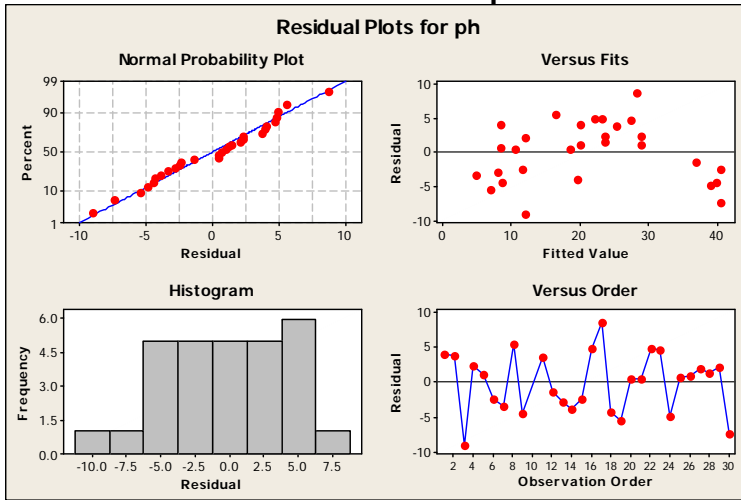
## Residual Plots for DOC



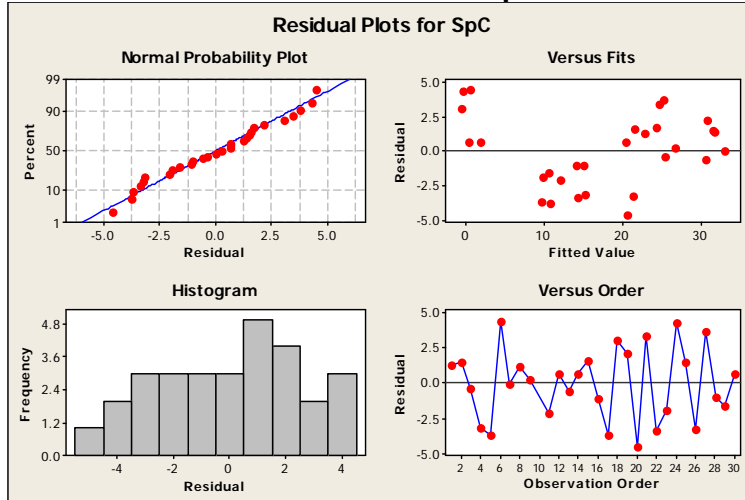
## Residual Plots for ALKALINITY



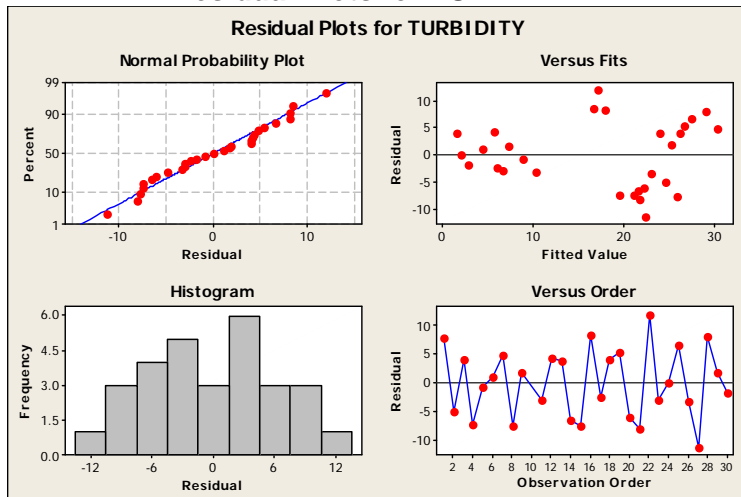
## Residual Plots for ph



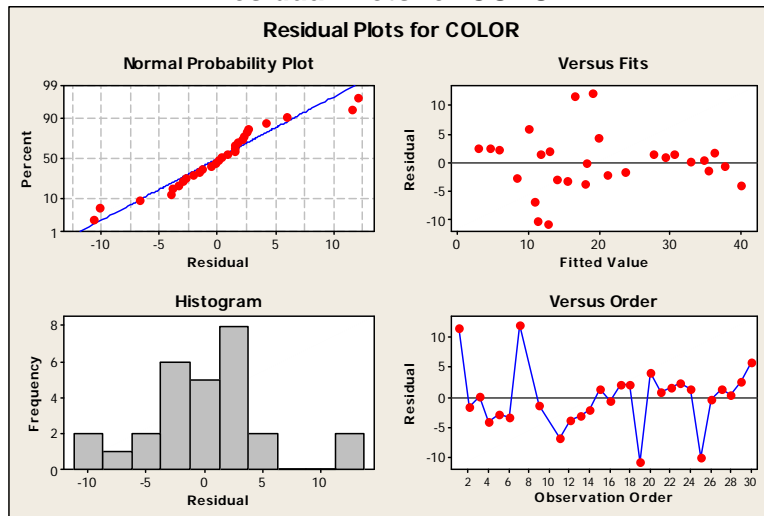
## Residual Plots for SpC



## Residual Plots for TURBIDITY



# Residual Plots for COLOR



## **Appendix VI**

### **Paired t-Test Computations by Parameter**

### Paired t-Test and CI: QVL-TN, QVLQA-TN

Paired T for QVL-TN - QVLQA-TN

	N	Mean	StDev	SE Mean
QVL-TN	10	10.35	5.57	1.76
QVLQA-TN	10	10.65	6.54	2.07
Difference	10	-0.300	2.974	0.940

95% CI for mean difference: (-2.427, 1.827)

T-Test of mean difference = 0 (vs not = 0): T-Value = -0.32 P-Value = 0.757

### Paired t-Test and CI: QVL-NO3, QVLQA-NO3

Paired T for QVL-NO3 - QVLQA-NO3

	N	Mean	StDev	SE Mean
QVL-NO3	9	9.44	4.56	1.52
QVLQA-NO3	9	9.56	5.61	1.87
Difference	9	-0.111	2.315	0.772

95% CI for mean difference: (-1.891, 1.669)

T-Test of mean difference = 0 (vs not = 0): T-Value = -0.14 P-Value = 0.889

### Paired t-Test and CI: QVL-TP, QVLQA-TP

Paired T for QVL-TP - QVLQA-TP

	N	Mean	StDev	SE Mean
QVL-TP	10	10.35	6.11	1.93
QVLQA-TP	10	10.65	5.95	1.88
Difference	10	-0.300	2.300	0.727

95% CI for mean difference: (-1.945, 1.345)

T-Test of mean difference = 0 (vs not = 0): T-Value = -0.41 P-Value = 0.690

### Paired t-Test and CI: QVL-DIC, QVLQA-DIC

Paired T for QVL-DIC - QVLQA-DIC

	N	Mean	StDev	SE Mean
QVL-DIC	10	9.15	5.90	1.87
QVLQA-DIC	10	11.85	5.80	1.83
Difference	10	-2.700	2.044	0.646

95% CI for mean difference: (-4.162, -1.238)

T-Test of mean difference = 0 (vs not = 0): T-Value = -4.18 P-Value = 0.002

### Paired t-Test and CI: QVL-DOC, QVLQA-DOC

Paired T for QVL-DOC - QVLQA-DOC

	N	Mean	StDev	SE Mean
QVL-DOC	10	10.35	4.45	1.41
QVLQA-DOC	10	10.65	7.24	2.29
Difference	10	-0.30	6.41	2.03

95% CI for mean difference: (-4.88, 4.28)

T-Test of mean difference = 0 (vs not = 0): T-Value = -0.15 P-Value = 0.886

### Paired t-Test and CI: QVL-ALK, QVLQA-ALK

Paired T for QVL-ALK - QVLQA-ALK

	N	Mean	StDev	SE Mean
QVL-DOC	8	10.38	6.28	2.22
QVLQA-DOC	8	10.06	4.21	1.49
Difference	8	0.31	3.31	1.17

95% CI for mean difference: (-2.45, 3.08)

T-Test of mean difference = 0 (vs not = 0): T-Value = 0.27 P-Value = 0.797

### Paired t-Test and CI: QVL-ph, QVLQA-pH

Paired T for QVL-ph - QVLQA-pH

	N	Mean	StDev	SE Mean
QVL-ph	9	10.67	6.26	2.09
QVLQA-pH	9	10.28	4.68	1.56
Difference	9	0.389	1.833	0.611

95% CI for mean difference: (-1.020, 1.798)

T-Test of mean difference = 0 (vs not = 0): T-Value = 0.64 P-Value = 0.542

### Paired t-Test and CI: QVL-SpC, QVLQA-SpC

Paired T for QVL-SpC - QVLQA-SpC

	N	Mean	StDev	SE Mean
QVL-SpC	9	9.44	4.42	1.47
QVLQA-SpC	9	10.11	6.92	2.31
Difference	9	-0.67	3.39	1.13

95% CI for mean difference: (-3.27, 1.94)

T-Test of mean difference = 0 (vs not = 0): T-Value = -0.59 P-Value = 0.572

### Paired t-Test and CI: QVL-TURB, QVLQA-TURB

Paired T for QVL-TURB - QVLQA-TURB

	N	Mean	StDev	SE Mean
QVL-TURB	9	8.67	6.44	2.15
QVLQA-TURB	9	11.00	5.04	1.68
Difference	9	-2.333	2.562	0.854

95% CI for mean difference: (-4.302, -0.364)

T-Test of mean difference = 0 (vs not = 0): T-Value = -2.73 P-Value = 0.026

### Paired t-Test and CI: QVL-COLOR, QVLQA-COLOR

Paired T for QVL-COLOR - QVLQA-COLOR

	N	Mean	StDev	SE Mean
QVL-COLOR	9	9.89	6.43	2.14
QVLQA-COLOR	9	10.00	5.45	1.82
Difference	9	-0.11	4.23	1.41

95% CI for mean difference: (-3.36, 3.14)

T-Test of mean difference = 0 (vs not = 0): T-Value = -0.08 P-Value = 0.939