# Monitoring and examination of water quality in an urban watershed:

The Waterford River Drainage Basin; Paradise, Mount Pearl, St. John's

# **Prepared By:**

Dan Ficken (B.Sc., ADWQ)

# **Prepared For:**

Northeast Avalon Atlantic Coastal Action Program, Inc.

(NAACAP)

and

Friends and Lobbyists of the Waterford River

(FLOW)

2005

# **Executive Summary**

The Waterford River is the main stem of a river system that flows from the east end of Paradise to its mouth in the west end of the harbour in St. John's. The drainage basin is situated in an almost entirely urban setting, and the quality of the water within the river reflects this. Although the river is not pristine, as seen from the perspective of this report, it does not seem to be excessively stressed by pollutant loadings either. The collection and analysis of water and sediment samples from five sample locations showed a certain degree of anthropogenic input of a wide range of constituents into the Waterford. Urban runoff and sewer overflows were viewed to be possible contributors of some of these unique variables. Many recommendations have been given with respect to the conservation of the Waterford River and the protection of the quality of the water that flows through it.

# **Acknowledgements**

Many people and organisations were helpful in the making of this report. First and foremost, the NGO groups called the Friends and Lobbyists of the Waterford River (FLOW) and Northeast Avalon ACAP (formerly St. John's Harbour ACAP) were the proponents in the study, especially Norm Catto of FLOW, and Diana Baird and Beni Malone of NAACAP. Without these groups, this study would not have occurred. Thanks are also extended to Robert Trenholm at the Fisheries and Marine Institute in St. John's for helping to make it possible to carry out this project. A round of gratitude goes to those in the trace elements lab in the Department of Earth Sciences at Memorial University of Newfoundland, notably Pam King, and also to those who provided equipment and helped out in the labs at the Marine Institute, particularly Judy Perry. An especially big thankyou goes to the Green Team of the Conservation Corps Newfoundland and Labrador (CCNL), who were of invaluable assistance in the field and also in the lab. More thanks go to those at Environment Canada who provided much advice and insight during the sampling and post-sampling periods, notably Glenn Worthman. Last, but not least, a gracious thank-you goes to the financial support of the Government of Canada's Environment Damages Fund and Environment Canada's support of the ACAP program, in addition to the great lab analysis and usage rates offered by MUN Earth Sciences and the Marine Institute.

# **Table of Contents**

Executive Summary	i
·	
Acknowledgements	i
Table of Figures	iv
1.0 Introduction	I
1.1 Scope	1
2.0 Study Area	2
2.0.1 Description of Watershed	
2.0.2 Land Use	
2.1 Site Selection	3
2.1.1 Site 5 Selection	
2.1.1 Site 1	
2.1.3 Site 3	
2.1.5 Site 5	3
3.0 Methodology	5
3.1 Sampling	5
3.2 Field Analysis	6
3.3 Lab Analysis	7
3.3.1 Total Solids	
3.3.2 Total Kjeldahl Nitrogen	
3.3.3 Metals	
3.3.3.1 Hardness	8
3.3.4 E. coli and Non-Fecal Coliforms	
3.3.5 Organic Compounds	
3.4 Determination of Flow	9
4.0 Results and Discussion	0
4.1 Total Solids	
7.1 Total Solids	
4.2 Total Kjeldahl Nitrogen	13
4.3 Metals	14
4.3.1 Aluminum (Al)	
4.3.2 Iron (Fe)	
4.3.3 Selenium (Se)	
4.3.4 Copper (Cu)	19
4 3 5 Zinc (Zn)	21

4.3.6 Lead (Pb)	23
4.3.7 Magnesium (Mg)	25
4.3.8 Manganese (Mn)	26
4.3.9 Cobalt (Co)	
4.3.10 Antimony (Sb)	
4.3.11 Arsenic (As)	
4.3.12 Bismuth (Bi)	
4.3.13 Barium (Ba)	
4.3.14 Cadmium (Cd)	
4.3.15 Chromium (Cr)	
4.3.16 Titanium	
4.3.17 Molybdenum (Mo)	
4.3.18 Tin (Sn)	35
4.4 Hardness	36
4.5 E. coli and Non-Fecal Coliforms	37
4.6 Horiba Probe Measurements	40
4.6.1 pH	40
4.6.2 Dissolved Oxygen	
4.6.3 Specific Conductance	
4.6.4 Turbidity	
4.6.5 Temperature	
4.6.6 Salinity	45
4.7 HACH Kit Analysis Results	46
4.7.1 Alkalinity	46
4.7.2 Ammonia & Nitrite	47
4.7.3 Chloride	49
4.8 Flow	49
5.0 Conclusions	51
6.0 Recommendations	52
7.0 References	53
8.0 Appendix A	54
8.1 Appendix B	
••	
8.2 Appendix C	
8.3 Appendix D	68
8.4 Appendix E	70
8.5 Appendix F	72

# **Table of Figures**

Figure 1: Waterford River study area	3
Figure 2: Mean levels of total suspended solids (TSS)	10
Figure 3: Mean levels of total dissolved solids (TDS)	11
Figure 4: Mean levels of total solids (TS)	
Figure 5: Mean levels of the Volatile Organic Content (VOC)	12
Figure 6: Mean values of Total Kjeldahl Nitrogen (TKN)	13
Figure 7: Mean concentrations of aluminum (Al)	16
Figure 8: Mean concentrations of iron (Fe)	17
Figure 9: Mean concentrations of Selenium (Se)	
Figure 10: Mean concentrations of copper (Cu)	19
Figure 11: Concentrations of copper (Cu) in sediment samples	20
Figure 12: Mean concentrations of zinc (Zn)	21
Figure 13: Concentrations of zinc (Zn) in sediment samples	22
Figure 14: Mean concentrations of lead (Pb)	23
Figure 15: Concentrations of lead (Pb) in sediment samples	24
Figure 16: Mean concentrations of magnesium (Mg)	25
Figure 17: Mean concentrations of manganese (Mn)	26
Figure 18: Mean concentrations of cobalt (Co)	26
Figure 19: Mean concentrations of antimony (Sb)	27
Figure 20: Mean concentrations of arsenic (As)	28
Figure 21: Concentrations of arsenic (As) in sediment samples	29
Figure 22: Mean concentrations of bismuth (Bi)	29
Figure 23: Mean concentrations of barium (Ba)	30
Figure 24: Mean concentrations of cadmium (Cd)	31
Figure 25: Concentrations of cadmium (Cd) in sediment samples	32
Figure 26: Mean concentrations of chromium (Cr)	32
Figure 27: Concentrations of chromium (Cr) in sediment samples	33
Figure 28: Mean concentrations of titanium (Ti)	34
Figure 29: Mean concentrations of molybdenum (Mo)	34
Figure 30: Mean concentrations of tin (Sn)	35
Figure 31: Concentrations of tin (Sn) in sediment samples.	36
Figure 32: Mean levels of hardness	37
Figure 33: Minimum mean counts of non-fecal coliforms	38
Figure 34: Minimum mean counts of E. coli	39
Figure 35: Mean values of pH	40
Figure 36: Mean Dissolved Oxygen (DO) levels	42
Figure 37: Mean conductivity values	43
Figure 38: Mean levels of turbidity	44
Figure 39: Mean values of temperature	45
Figure 40: Mean levels of salinity	46
Figure 41: Mean levels of alkalinity	47
Figure 42: Mean levels of nitrite	48
Figure 43: Mean concentrations of chloride	49
Figure AA. Avanga flow values	50

# 1.0 Introduction

It is a normal occurrence for urban developments to be based near freshwater sources, such as rivers or ponds. Thus, it would come to no surprise that the Waterford River, which is situated in the most developed region of the Northeast Avalon Peninsula, flows visibly through parts of the town of Paradise, the city of Mount Pearl, and the capital city of St. John's, which includes the community of Kilbride. Despite the fact that people are somewhat dependant upon rivers such as the Waterford, they also exert a certain amount of pressure on the delicate riverine ecosystems that go hand in hand with rivers. While it is theoretically and practically impossible for an urbanised area to not have any effect on a river that runs through it, it is possible to minimise any effects that might occur. Thus, the river would have a chance to adapt to any small changes and naturally buffer itself against possible negative urban stresses.

In many cases, however, rivers are used as a place to dispose of industrial and residential waste, or the effects of urban runoff tend to impact them from a less obvious source, such as a commercially operated parking lot. Rivers can also become an obstacle to developers, who might then drastically modify the river's course or general morphology to overcome the problem. The Waterford River is one that has at various times felt these abusive effects, and still does today.

Through the activity and voices of many concerned individuals, groups, and departments, in some regards the Waterford has undergone improvements to its quality and health in more recent times. Much monitoring on the Waterford has taken place over the years, giving rise to the level of awareness associated with any harmful endeavours, which had occurred on the river. Heightened awareness stems from the fact that rivers tend to be the lowest elevated points within a watershed, meaning that pollutants occurring within the watershed may eventually end up in the river. Thus, the health of a river is intimately tied to activity transpiring within the watershed itself. With this in mind, the continued monitoring of the Waterford River will lead to a better understanding on how to protect the overall integrity of this system, and this will lead to active decisions regarding its preservation. The information contained within this report is comprised of the results and their associated interpretations created through the latest comprehensive monitoring activity upon the Waterford to date.

# 1.1 Scope

This study has focused on the continued characterization of the upper half of the Waterford River, mainly in terms of the ambient water quality of five selected sample points and in terms of whether there was any anthropogenic impact on the river. A work plan had to be devised in order to determine the overall health and what, if there were any, parameters that could be contributing to the degradation of the river.

Preliminary research was first conducted to provide an understanding of the watershed; to find out what could be impacting the watershed; to learn about various

contaminants that could affect it; to explore possible methods in field sampling and lab analysis; and to find out what resources were available to accomplish the overall goals of this project. A sampling schedule had to be planned to coincide with the subsequent lab work. Proper sampling and lab techniques also had to be formulated for water and sediment samples to lessen the chances of errors and to make the most efficient use of the time available. A catalogue sheet was developed for efficiently recording data in the field. Additionally, all of the results had to be organised and interpreted in order to make any conclusions and recommendations.

# 2.0 Study Area

## 2.0.1 Description of Watershed

The Waterford River Basin is about 12km long and is located between the east side of Paradise and St. John's. The Waterford River begins at Bremigan's Pond and Brazil Pond in Paradise and flows through Mount Pearl, a part of Kilbride, and St. John's where it discharges into the west end of St. John's Harbour. Along its course, many ponds and brooks flow into the Waterford making it a relatively large system. The river is roughly about 2 to 8m wide at most points, and is about 1.5m at its deepest.

#### 2.0.2 Land Use

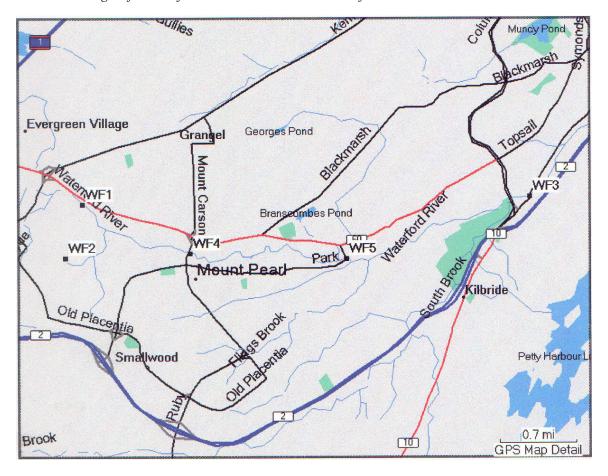
The upper half of the Waterford River, which includes the portion in study from Paradise to the west end of St. John's on Old Bay Bulls Road, flows through wetland, farmland, forest, an industrial zone and an urban zone. The amount of urban development on the river increases downstream as the river flows into St. John's from Mount Pearl. However, before flowing into the more heavily populated portion of its traverse, the Waterford first passes through the Donovan's Industrial Park on the outskirts of Mount Pearl. There are also a few industrial sections in addition to a few agricultural zones between Brookfield Road in Mount Pearl and Old Bay Bulls Road.

In addition to the multitude of heavily used roads and highways near the river, according to The Green Lane (2004) the types of industry occurring at these points include construction and engineering, chemicals, electrical power, materials handling, manufacturing, wholesale and retail industry for food & beverage, recycling, transport and storage, security, and oil and gas. A feed manufacturing plant is also located very near the river's edge on Topsail Road in Mount Pearl and there are two active quarries with on-site asphalt plants in the vicinity as well. On top of all of this activity, due to past city planning and development, the river has undergone many changes with regards to physical alteration and the changing of its original course. Since there is so much activity along the river, it has been observed that portions of it are also quite littered with urban garbage.

# 2.1 Site Selection

The sites to be sampled were selected based on sites picked on a previous study by Powell in 1999. The locations were key points along the Waterford River and would give representative measurements of the quality of the upper portion of the Waterford (*Figure 1*). The first five sites in Powell's report were chosen as the sampling stations for the purposes of this report.

**Figure 1:** Waterford River study area from Donovan's Industrial Park to Waterford Bridge Road area showing all five sites from 1 to 5. Note that site 3 is the furthest downstream.



#### 2.1.1 Site 1

**GPS** Coordinates:

Longitude N 47' 31.701

Latitude W 052' 49.849

Site 1 was located 100m down a recreational trail just east of Corisande Drive. Corisande Drive is located between Donovan's Industrial Park and Topsail Road, which is a major roadway. This section of river is just downstream of the animal feed plant in

Mount Pearl and other industrial activity, and most likely receives runoff from Topsail Road. A submerged concrete culvert was observed sticking out of the sediment, but it was unclear whether it was being used. Fish and ducks were spotted immediately downstream of the sample location. During one sampling occasion, the smell of manure was present in the air, indicating the presence of a nearby farm.

#### 2.1.2 Site 2

**GPS** Coordinates:

Longitude N 47' 31.276

Latitude W 052' 49.650

Site 2 was located at the mouth of Powers Pond in a naturalized park area between the industrial park and a residential subdivision. A heavily used road, called Old Placentia Road is also nearby. In addition to the possibility of runoff and discharge from the nearby industrial activity, it is possible that residents using the area could also potentially contaminate the water while feeding the ducks and geese that gather there. The waterfowl themselves could potentially contaminate the water with bacteria. The sampling site itself, which formed the headwaters of a Waterford River tributary, was very shallow and narrow, and looked like it had been altered as there was concrete set in part of it. It was also observed that the streambed was of bedrock instead of sediment. Powers Pond discharges into the Waterford River less than a kilometre downstream.

The environmental stability of this site is particularly important to understand because while it is not being heavily developed, it seems that measures are being taken by the City of Mount Pearl to keep it in a fairly natural state.

#### 2.1.3 Site 3

GPS Coordinates:

Longitude N 47' 31.762

Latitude W 052' 44.470

Site 3 was located off Mackey Place in the west end of St. John's parallel to Waterford Bridge Road. More specifically, it was just before the bridge that connects Bay Bulls Road and Southside Road to Waterford Bridge Road. This site, while furthest downstream, looked clean and natural despite being surrounded by roads. It should be noted that site 3 was just downstream of where the South Brook tributary convenes with the Waterford just west of the Columbus Drive overpass.

#### 2.1.4 Site 4

GPS Coordinates:

N 47' 31.315

W 052' 48.406

This site was on the upstream side of the Commonwealth Avenue bridge in Mount Pearl. Situated in a valley with high commercial value, this section of the river seemed relatively unpolluted. However, due to the dense development and traffic it was possible that Site 4 was being impacted in some way by runoff directly from the bridge, due to the embankments created extending from its sides, and by runoff from the many parking lots on the inclines of the valley. Otherwise the river appeared healthy, and fish were spotted here.

#### 2.1.5 Site 5

**GPS** Coordinates:

N 47' 31.275

W 052' 46.599

Site 5 was located just east and downstream of the bridge that connects Dunn's Road and Park Avenue next to a motel parking lot in Mount Pearl. The smell of sewage was present at this site and there was quite a bit of debris in the water, including a shopping cart and a bicycle. The water was relatively deep at this point, and the current was fairly strong. It was suspected that this site might not only be impacted by runoff from the road and parking lot, but also by garbage and sewage.

# 3.0 Methodology

In order to characterize the overall quality of the water flowing in the Waterford River, and to establish an idea of what may be polluting the river and, if anything, to what degree, a sampling scheme was devised and appropriate field and lab analyses were researched and conducted. Methods for determining the flow were also generated.

# 3.1 Sampling

Three sampling sweeps were coordinated for the months of July and August approximately two weeks apart from each other. They occurred on July 20<sup>th</sup>, Aug 3<sup>rd</sup>, and August 18<sup>th</sup> respectively. The sampling itself was conducted also with the help of a Green Team, which were hired by the CCNL and contracted by Northeast Avalon ACAP.

The sampling scheme was developed in hopes of contrasting two rain events with two non-rain events, however logistically that did not work according to plan. Instead, there were two non-rain events and one rain event day (sweep 3, August 18<sup>th</sup>), since only three sweeps could be conducted at the time of writing. The purpose was to compare a wet day with a dry day to determine whether runoff from the land would significantly change the water quality of the river system. The total precipitation that fell on the rain event was a two-day total of 8.6 mm, which would have been enough to constitute a possible change in the river due to runoff. It should be noted that on the first sampling sweep, it rained heavily for a short period just before the first sample was taken. The total amount was 1.8 mm. This was not enough rain to constitute a rain event, but it may have been enough water in a short enough amount of time to temporarily affect the river at site 1 at that time, due to a small amount of overland flow that may have occurred.

In order to take samples, certain bottles, properly labeled, relating to particular testing parameters were collected and prepared. Preparation involved the thorough washing of the bottles and also of adding small volumes of specific acids to some of them as preserving agents. Water samples were taken from each of the five sites on every occasion in plastic bottles containing sulphuric acid for solids and nitrogen testing, plastic bottles containing nitric acid for metals, sterilized plastic bottles containing sodium thiosulphate for microbiological analysis, and glass vials for PAH analysis. On one occasion, sediment samples were taken in glass and plastic containers for their appropriate analyses as well.

It should be noted that since river water is always flowing and transporting material away, the water quality readily fluctuates. Thus water samples were taken on every occasion. However, the sediment samples were only collected on one occasion because sediment would be most likely to retain its qualities over a longer period of time. This is understandable given that sediment tends to be an adsorbent surface and, depending on fluctuations in flow, is inclined to remain fairly stationary in one place at the bottom of the river where it was initially deposited (CCME, 2001).

The water samples were taken as grab samples, meaning that the bottles only collected water at the point where they were dipped in. The samples were taken at the median stream width where possible. With the exception of the microbiological bottles, the other bottles were pre-rinsed with river water that was poured slightly downstream from where the samples were taken to avoid any possible contamination from the bottles.

The sediment samples were also taken as grab samples, which involved scooping the material from the streambed directly into the bottles used. The bottles were then capped after decanting the excess water.

# 3.2 Field Analysis

Many tests were performed directly in the field along with the aid of the Green Team. The Marine Institute provided the equipment necessary to perform these tests. A HACH field-testing kit was used to determine four parameters: alkalinity, chloride,

ammonia, and nitrite. A Horiba probe was used as well, and it tested for six parameters: pH, conductivity, turbidity, dissolved oxygen, temperature, and salinity. The procedures for each of these tests were performed following the methods stated in the HACH and Horiba manuals.

These tests were very useful, as they eliminated much of the time and costs associated with being in the lab. However, it meant that more time had to be spent in the field. They were also of great assistance because direct results were obtained for each parameter at each site, meaning no other calculations were needed later.

# 3.3 Lab Analysis

The rest of the tests were to be conducted in the lab, either at the chemistry and microbiological labs at the Marine Institute (MI) or within the trace elements lab at the Department of Earth Sciences at Memorial University of Newfoundland (MUN). These tests will be described in the following subsections.

#### 3.3.1 Total Solids

The total solids, expressed as the mass of the total suspended solids (TSS) plus the mass of the total dissolved solids (TDS), were determined using an oven and a muffle furnace at the chemistry lab at MI. From this the mass of the volatile organic compounds could be determined. The method used was based on a laboratory procedure for the same experiment (Whiteway, 2004). See Appendix D for a description. It involved separating the suspended solids from the dissolved solids with a filter and heating the pre-weighed filters and crucibles containing the separated solids until the water evaporated. From this the crucibles and filters were re-weighed and subtracted from the original weights, giving the TSS and the TDS. Furthermore, the crucibles containing the TDS were superheated until the volatile organic content (VOC) volatilized. Once this occurred, the crucibles could be weighed again and subtracted from the TDS, giving the VOC.

# 3.3.2 Total Kjeldahl Nitrogen

The total Kjeldahl nitrogen was determined using the Kjeldahl method at the chemistry lab at MI. This method was performed as per a laboratory procedure for the same experiment (Whiteway, 2004). See Appendix E for a description. It involved the addition of concentrated sulphuric acid and a catalyst to tubes containing a pre-weighed amount of sample; superheating it so that the samples were effectively digested by the acid; adding de-ionized water and sodium hydroxide; and distilling the freed ammonia into a flask containing boric acid and a colour indicator solution for endpoint determination. This solution was then titrated with hydrochloric acid to determine the total amount of ammonia in the sample. Using the quantified ammonia content, a calculation was then performed to determine the overall nitrogen content using the following formula:

 $\%N = ((A \times B / C) \times 0.014) \times 100$ , - where A is the volume of sample titrant used minus the volume of blank titrant used, B is the normality of the acid used, and C is the weight of the sample

#### **3.3.3 Metals**

A wide range of trace elements was determined using the inductively coupled plasma mass spectrometer (ICP-MS) at the Department of Earth Sciences at MUN. This extremely sensitive piece of equipment works by atomizing, desolvating, and heating the samples at 7,000 – 10,000 degrees Kelvin, creating a plume of argon plasma. The metal analysis is complete when the detection equipment senses the plume. The exact method followed for this procedure was unknown since the samples were analysed by the people working in the trace element lab. The method they used was highly reliable, however, as they were highly trained and experienced individuals. Metals were analysed in the water and sediment samples, and in the case of the sediment the samples were sieved to obtain the fine fraction, as this fraction was more likely to have resulted from the more bioavailable particles settled from the water column.

#### 3.3.3.1 Hardness

Using the results obtained in the metals analysis for the concentrations of calcium (Ca), magnesium (Mg), iron (Fe), manganese (Mn), aluminum (Al), strontium (Sr), and barium (Ba), the hardness of the water was calculated using an easily derivable formula, where the sum of the molecular weight of calcium carbonate (CaCO<sub>3</sub>) divided by the molecular weights of each element was multiplied by the concentration of each element respectively. Using this theory, the following formula was derived:

$$CaCO_3$$
  $Hardness\ (ppm) = [(ppm\ Ca\ x\ 2.497) + (ppm\ Mg\ x\ 4.118) + (ppm\ Fe\ x\ 1.792) + (ppm\ Mn\ x\ 1.822) + (ppm\ Al\ x\ 3.709) + (ppm\ Sr\ x\ 1.142) + (ppm\ Ba\ x\ 0.729)]$ 

#### 3.3.4 E. coli and Non-Fecal Coliforms

The determination of *Escherichia coli* coliforms (*E. coli*), and also non-fecal coliforms simultaneously, was achieved using the membrane filtration technique. This method utilized a selective media called M-coli blue, which only allowed the growth of *E. coli* (blue colonies) and non-fecal (red colonies) coliforms at 37.5 degrees Celsius. The technique involved the filtration of the samples and dilutions made of the samples through a micro-porous membrane via special filtration apparatus with the intention of trapping the bacteria in the pores and letting the water pass through. After the M-coli blue was added, the plates were incubated for a day, giving the colonies sufficient time and the right conditions to grow so they could be counted. The method used in this test followed a laboratory procedure for the same experiment (Patel, 2004). See Appendix F for a description.

# 3.3.5 Organic Compounds

It was in the original plan to test for various toxic organic substances, such as polycyclic aromatic hydrocarbons (PAH's), and other petroleum hydrocarbons because these substances were suspected to be present in the river. Due to unforeseen circumstances, this was not entirely possible or successful and the plan had to be discarded. However, the original intention was to prepare and run extractions of the samples through a gas chromatograph (GC) in order to detect any substances.

## 3.4 Determination of Flow

Another important parameter relating to stream characterization is flow. The flow is measured as cubic meters per second ( $m^3/s$ ), or the volume of water moving past a series of certain points, as a line perpendicular to the direction of flow, over a specific time interval. A current meter was borrowed to aid in this. The procedure involved taking depths of the stream at spaced intervals (where possible) and creating a theoretical depth profile ( $Appendix\ C$ ) to obtain an approximate area ( $m^2$ ) of the stream width. Since calculus was not used, and much interpolation and generalization of the streambed had to be surmised, the area determined through this process was an approximate at best, however it was representative.

The next step was to calculate the current. In one of the five sites the flow and the depth were not great enough to utilize the current meter. Placing a floating object, such as a leaf, in the stream and timing its path along the three feet of a yardstick overcame this problem. Once converted, this produced a measure of the current in metres per second (m/s). The current multiplied by the area gave the stream flow (m³/s) at that point on the river. Where the current meter was utilized, it produced a number representing how many times the flowing water turned its propeller over in a controlled amount of time, which was 60 seconds in this case. This number, when expressed in counts per second (cps), could then be plotted on a predetermined graph to give a measure of current in cm/s. Converted to m/s and multiplied by the area determined along the stream width the flow as m³/s was determined for that site.

# 4.0 Results and Discussion

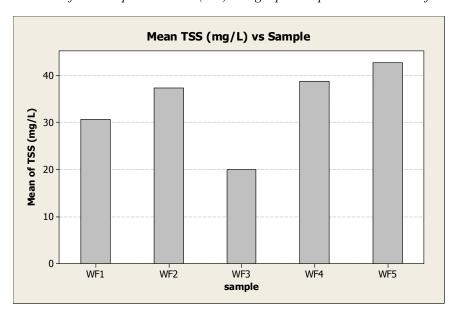
#### 4.1 Total Solids

Various matter occur naturally in rivers and streams as inorganic solids, and also to a lesser extent as organic solids. These solids, which are comprised of either dissolved or suspended material enter the water column directly as a result of eroding streambeds or banks, and can also result from a more distant source during periods of runoff.

Although it is normal for rivers to accommodate some solids, too much can be harmful to aquatic life. In high concentrations these constituents can lower the amount of dissolved oxygen in the river, due to the reduction in the amount of light entering the

stream, resulting in a decrease in photosynthesis. Aerobic microorganisms lower dissolved oxygen even further while decomposing dead plants that are unable to photosynthesise (Murphy, 2002). While increased suspended solids can provide ideal anchor sites for pathogenic microorganisms; damage the benthic environment as it settles; and cause damage to fish gills while lowering the fish's immunity and growth patterns; a difference in the concentration of dissolved solids can also change the density of the water, dangerously altering the flow of water in and out of an organism's cells (CCME, 2003). Additionally, dissolved solids can combine with toxic compounds and heavy metals, and raise the water temperature, also putting aquatic life at risk (Murphy, 2002). Quarrying, construction, industrial waste, and sewage can lead to increased solids in stream water.

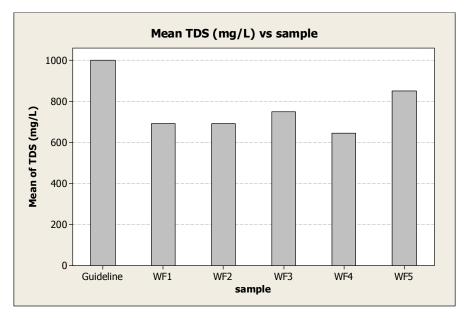
The mean results for the amount of solids (TSS, TDS, TS, and VOC) in each sampling site are tabulated in the following graphs. It should be noted that there are no formal guidelines set with regards to solid constituents in water for the protection of aquatic life, however the Province of British Columbia (BC) (1998) has provided some suggestions that are included on some of the figures in this section. Refer to Appendix A for the raw data associated with these means.



**Figure 2:** *Mean levels of total suspended solids (TSS) in mg/L per sample site in the Waterford River.* 

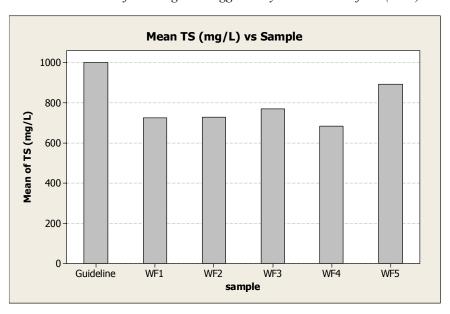
Overall, the Waterford did not show excessively high mean levels of TSS (*Figure* 2). However, the levels did show that there were enough suspended solids present to indicate that the water was not entirely clear. Since the river had a generally healthy flow rate (*Section 4.8*), some of these particles may have been in suspension because they were unable to settle, and they may have been there in the first place due to stream bank erosion or bedload transport. There may have been slight anthropogenic sources as well, since higher individual levels of TSS did not always correlate with higher rates of flow (*Appendix A*).

**Figure 3:** Mean levels of total dissolved solids (TDS) in mg/L per sample site in the Waterford River versus the recommended maximum of 1000 mg/L as suggested by the Province of BC (1998).



Since TDS in this case accounted for nearly all of the solids in the water column, the discussion on total solids (*Figure 4*) will mainly take into account the mean levels shown in Figure 3. It should be noted, however, that none of the mean levels of TDS in the water samples exceeded the guideline of 1000 mg/L (Province of BC, 1998), although site five exceeded the guideline during sweep two at 1150 mg/L (*Appendix A*).

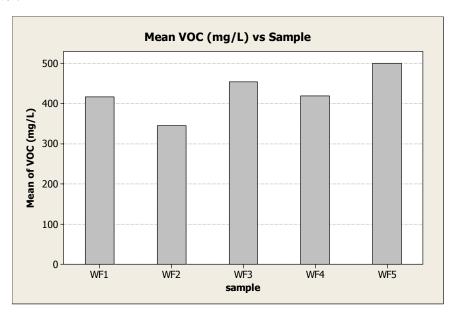
**Figure 4:** Mean levels of total solids (TS) in mg/L per sample site in the Waterford River versus the recommended maximum of 1000 mg/L as suggested by the Province of BC (1998).



The recommended maximum concentration of solids in freshwater is 1000mg/L (Province of BC, 1998), where at this level it can become a threat to aquatic life. This was not so much a problem in the Waterford, since none of the mean values exceeded this recommendation. However, site 5 did generally show concentrations of total solids close to the guidelines at a mean of 892.7 mg/L (*Figure 4*), and in one occasion (sweep 2) site 5 exceeded the guideline at 1206 mg/L while site 3 almost exceeded it during the same sweep with a concentration of 966 mg/L (*Appendix A*).

This particular occasion was not associated with a rain event so the increased dissolved solids did not occur due to overland flow resulting from runoff. Any form of soil disturbance such as road or building construction on or near the river could have contributed to this. Industrial effluent, sewage discharge, or dumping in or near the river could have also contributed to increased loads. Increased dissolution of the streambed and its banks due to warmer summer temperatures could also have caused higher levels of total solids. However, as it will be illustrated in section 4.6.5, the mean water temperatures were actually lower in sweep 2 than for the other sampling periods. In general, summer sampling results would yield higher concentrations of total solids because of the increased dissolution during warmer water temperatures.

**Figure 5:** Mean levels of the Volatile Organic Content (VOC) in mg/L per sample site in the Waterford River.



According to the Province of BC (1998), total organic content (TOC) in natural waters generally ranges up to 30 mg/L, and although VOC is not necessarily the same as TOC, it would make up at least a part of it. Thus, there appeared to be a considerable amount of volatile organic content in the Waterford samples, since the lowest mean value was 345.3 mg/L (*Figure 5*). This organic component could have been due in part to natural organic material in the river, such as decaying plant or animal matter. However, with respect to the urban status of the Waterford River, it was also likely that there may have been airborne and petrogenic constituents entering the river from traffic on nearby

roads, but only alternate testing for specific VOCs could actually verify this. Any sewage present in the river could have also contributed to the mean levels of VOC present.

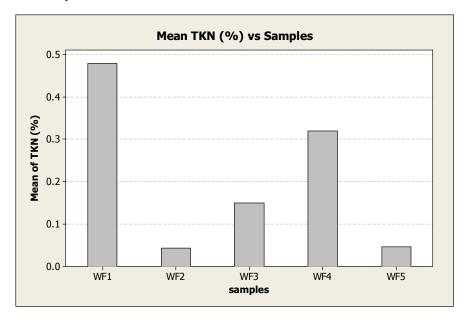
It is of particular note that the individual VOC levels during sweep 2 were much higher than the mean levels for each site. Due to the lack of rain, and thus, lack of runoff during that period, it was quite conceivable that something may have entered the river upstream to cause the VOC levels to increase.

# 4.2 Total Kjeldahl Nitrogen

The sum of the organic nitrogen and ammonia in the sample is measured as total Kjeldahl nitrogen (TKN), and it can indicate an input of organic nutrients into a system. Plants and some aquatic microorganisms need a certain amount of these nutrients to live, and often nitrogen levels in streams are low partly because various organisms are using them. If the levels are too high, the conditions will turn eutrophic, causing some aquatic plants and algae to flourish. Their intense competition within the ecosystem would, however, result in severely diminished levels of dissolved oxygen, harming other forms of life. Certain forms and concentrations of nitrogen can also be directly harmful to fish and other life forms within the aquatic environment (Murphy, 2002).

The mean results for TKN in the water samples of the three sweeps, derived by the formula given in section 3.3.2 are in the following chart. The raw data associated with this graph are listed in Appendix A.

**Figure 6:** Mean values of Total Kjeldahl Nitrogen (TKN) in percent (%) per sample site in the Waterford River water samples.



These results show a very high concentration of TKN in the Waterford with the lowest at 0.04% or 400mg/L, and the highest at 0.48% or 4800mg/L (*Figure 6*). Levels this high would indicate a definite anthropogenic input of nitrogen to the system, such as

raw sewage effluent or fertilisers. It should be noted however that in almost every case, the only times TKN was detected at all was on the first sweep. The only exception being that TKN was detected at a very high concentration at site 1 on the second sweep as well (*Appendix A*).

Given the data, it is probable that sewage and maybe fertiliser enters the system on occasion, but not at all times. It is interesting to note that although site 2 had the lowest TKN values, it was a relatively narrow and shallow section of stream heavily populated by waterfowl. While the birds most likely contributed to the values in this small section, there probably were no significant inputs of sewage or fertilisers here, if at all, due to the small urban influence at this site. To get the high values at the other larger sites, it was likely that there was a much greater anthropogenic discharge to the Waterford itself, due to its urban passage.

Constituents such as organic nitrogen and ammonia (TKN) are fairly unstable and will not remain in water for very long if there is no continuous input. Therefore, it is possible that Kjeldahl nitrogen was not detected in many of the samples for this reason.

#### 4.3 Metals

Metals occur naturally in freshwater due to contact with the grains of the substrate on the riverbed or the sediment in standing water. Metallic constituents can also naturally enter a stream or lake via runoff, when soil is washed into the water during a rain event. Anthropogenic sources are quite possible as well, especially when a river, such as the Waterford, traverses through an urban area. The ground in the watershed can become contaminated with various trace metals when people are using it for industrial, waste, transportation, recreational, or building purposes. This contamination can easily reach a river system when it rains, due to runoff. Metals can also enter a stream as a point source component when contaminants are placed directly into the water, such as what happens when an effluent discharge pipe is positioned on a river.

Metals can occur as particulate matter in the water, such as suspended or settled solids, and they can also be in a dissolved form, which is the more bioavailable form. The toxicity, or bioavailability in this case, of certain trace metals in river water to aquatic life is dependent upon certain factors such as temperature, hardness, and pH, and these characteristics sometimes need to be taken into account when determining the overall toxicity or safety of the water (CCME, 2003). The bioavailability of a trace metal is often linked to its overall solubility and these factors play a big role in determining the extent of the solubility of a metal in the river. For example, a higher temperature is often associated with an increase in solubility, and conversely, a decrease in pH and hardness also often results in a higher solubility (CCME, 2003).

The settling of particulate matter adds additional metallic constituents to the sediment on the riverbed as well. The sediment is essentially a reservoir for metals since these constituents tend to adsorb to the surfaces of the grains in the substrate, which then remain for longer periods of time on the riverbed (CCME, 2003). These trace metals can

then either affect the benthic environment directly, or slowly become released into the water column during periods of changes in various water quality parameters.

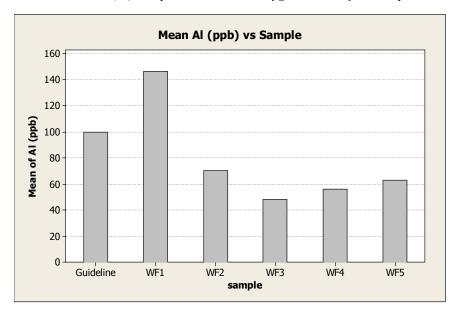
As it will be discussed in a later section, the section of the Waterford River in study would be expected to have a higher occurrence of some trace metals due to its main course through the urban areas. Additionally, the bioavailability of some of these metals might also be increased due to warmer summer water temperatures and relatively low levels of hardness.

The mean concentrations of some of the metals in the water and the sediment samples are displayed in the following graphs. For organisational purposes, discussions of the trace metal analyses for each graph will occur in the following subsections. All of the raw ICP-MS data resulting from the metal analysis of the water and sediment samples are available in Appendix A. For further reading, detailed descriptions of possible trace metal sources in urban waters are available in a report by Powell (1998), which dealt with various constituents entering St. John's Harbour through runoff in the Waterford Basin.

It should be noted that not all of the results were mentioned here because many of them occurred in very low concentrations or were not detected by the ICP-MS method. However, most of the mentioned figures were based on discussions related to the paper by Powell (1998). If they were available, Canadian Council of Ministers of the Environment (CCME) guidelines for the protection of aquatic life (2003) for some of the metals in freshwater and freshwater sediments are also included for comparison, although in some cases the guidelines were site specific and could not always be included in the graphs. These cases will be noted where applicable. With one exception, only sediment that had CCME related guidelines were discussed in the following subsections. The guidelines related to sediment were broken into two levels of guidance by the CCME (2001). The first was the Interim Sediment Quality Guideline (ISQG), which is a level above which there is scientific evidence leaning towards the possibility that there could be adverse environmental effects. The second was the Probable Effect Level (PEL), above which it has been scientifically shown that there would be a great chance of adverse environmental effects. All values obtained from the sediment analysis for all of the metals tested can be found in Appendix B.

# 4.3.1 Aluminum (AI)

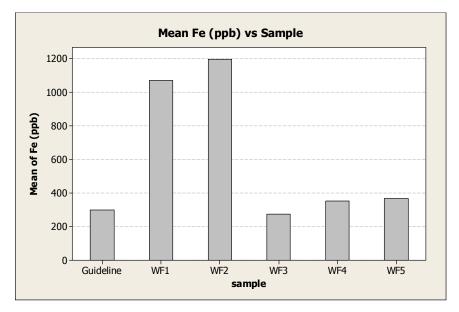
**Figure 7:** Mean concentrations of aluminum (Al) in ppb per sample site in the Waterford River with a maximum CCME guideline (for the protection of aquatic life, 2003) of 100 ppb derived according to the relative calcium (2<sup>+</sup>) ion, pH, and dissolved oxygen content of the samples.



A guideline of 100 ppb has been set by the CCME as a maximum concentration of aluminum allowable for the protection of aquatic life in freshwater, derived according to various parameters, such as pH, dissolved oxygen, and calcium II ions of the water at each site. According to Figure 7, the mean value of site 1 exceeded this guideline at a value of 146.2 ppb. Thus, waters at this site may be unsafe for aquatic life because high concentrations of aluminum in freshwater can have negative effects on various organisms in certain conditions (CCME, 2003). It should also be noted that the highest value by far occurred in site 1 on sweep 1 at 278 ppb (*Appendix A*). As it rained heavily just before the first sample was taken on the first sweep, it is possible that runoff may have contributed to this unusual value.

## 4.3.2 Iron (Fe)

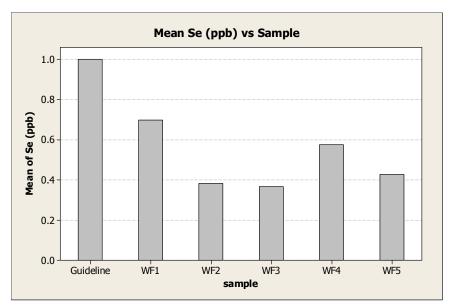
**Figure 8:** Mean concentrations of iron (Fe) in ppb per sample site in the Waterford River with a CCME guideline (for the protection of aquatic life, 2003) of 300 ppb.



The guideline set by the CCME for the protection of aquatic life in freshwater (2003) for Fe is 300 ppb. All of the sites, with the exception of site 3, exceeded this guideline. While the mean value for site 3 was close to exceedance at 274 ppb, the mean values of sites 1 and 2 greatly exceeded this guideline at 1073.2 ppb and 1198 ppb respectively (*Figure 8*). It should be noted that the highest value overall was 1941 ppb at site 1 on sweep 1 (*Appendix A*), and may have possibly occurred because of the suspected overland flow due to the short rain period at that time. Although iron is a relatively common element naturally found in waters on the Avalon Peninsula, the much higher values upstream suggest an additional input from an anthropogenic source.

## 4.3.3 Selenium (Se)

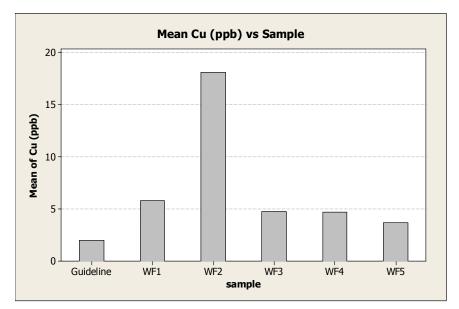
**Figure 9:** Mean concentrations of Selenium (Se) in ppb per sample site in the Waterford River with a CCME guideline (for the protection of aquatic life, 2003) of 1.0 ppb.



It was difficult to quantify the trace amount of selenium in the Waterford because all of the values fell below the detection limits of the ICP-MS. In a statistical sense, it is sometimes appropriate to divide the detection limit values in half to get a general but usable result (M. Pippy, personal communication, October  $19^{th}$ , 2005), and this is the reason why a graph could be created. However, in this case, all of the values fell below the detection limits, thus the only accurate interpretation that could be made was that all the values of selenium were less than the highest values (detection limits) given in the raw data (*Appendix A*).

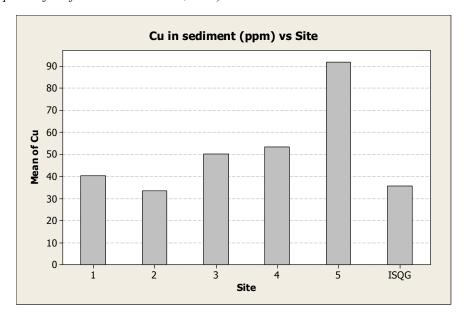
## 4.3.4 Copper (Cu)

**Figure 10:** Mean concentrations of copper (Cu) in ppb per sample site in the Waterford River with a maximum CCME guideline (for the protection of aquatic life in freshwater, 2003) of 2.0 ppb derived according to the relative hardness of the samples.



The guideline set by the CCME for the protection of aquatic life in freshwater (2003) with regards to copper, which was derived specifically according to the relative hardness of each sample, is 2 ppb. Figure 10 shows that all mean values of copper in the Waterford have exceeded this guideline. It can also be seen in the appendix that all of the raw data values of Cu have also exceeded the guideline. Site 2 showed exceptionally high values, and was by far the site with the highest concentration with a mean value of 18.1 ppb. The next highest was site 1, especially during the first sweep with a value of 9.64 ppb, which again may have been due to the short rainfall at that time. In very small quantities copper is an essential element to life. However, it can be quite toxic in higher concentrations, given certain hardness conditions of the water (CCME, 2003). In this case copper seems to be problematic in the Waterford, given the 100% exceedance rate.

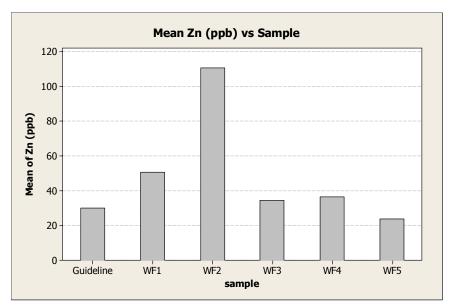
**Figure 11:** Concentrations of copper (Cu) in ppm per sample site in the Waterford River sediment samples, with a CCME Interim Sediment Quality Guideline (ISQG) of 35.7 ppm (for the protection of aquatic life in freshwater sediments, 2003).



The CCME interim guideline for copper in freshwater sediment for the protection of aquatic life (2003) is 35.7 ppm. Except for site 2 at an average value of 33.3 ppm, all of the other sites exceeded the ISQG for Cu in the Waterford. Site 5 greatly exceeded it with an average concentration of 91.9 ppm (*Figure 11*). The PEL for copper is 197.0 ppm, but it will be disregarded here since none of the samples were close to it. It is interesting to note that high values of copper in the sediment reflect a correlative lower concentration of copper in the water at the same site, and vice versa.

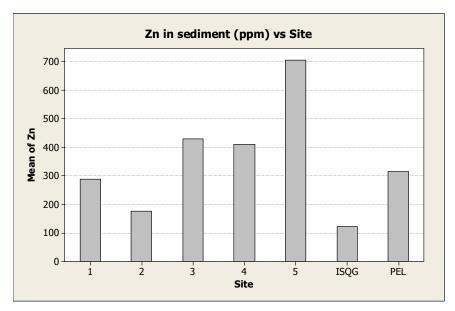
## 4.3.5 Zinc (Zn)

**Figure 12:** Mean concentrations of zinc (Zn) in ppb per sample site in the Waterford River with a CCME guideline (for the protection of aquatic life, 2003) of 30 ppb.



According to Figure 12, all sites with the exception of site 5 exceeded the CCME guideline for the protection of aquatic life in freshwater (2003) of 30 ppb Zn. Site 2 greatly exceeded this guideline with a mean value of 110.8 ppb, and again site 1 had a relatively high value of 111.2 ppb on the first sweep as well (*Appendix A*). It should be noted that accurate values of zinc were more difficult to determine since all of the results from sweep 3 fell below the detection limits. However, according to statistical advice received (M. Pippy, personal communication, October 19<sup>th</sup>, 2005), dividing these results in half gave an appropriate estimate because the detection limits at that time were set at higher levels, giving values similar to other lower and detectable values during the other sweeps.

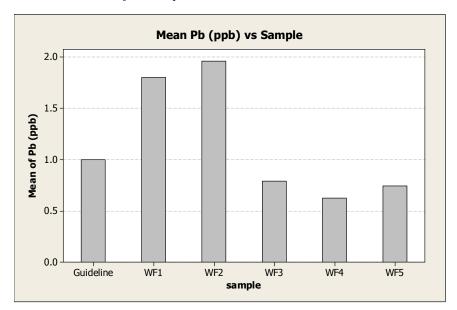
**Figure 13:** Concentrations of zinc (Zn) in ppm per sample site in the Waterford River sediment samples, with a CCME Interim Sediment Quality Guideline (ISQG) of 123.0 ppm and a Probable Effect Level (PEL) of 315.0 ppm (for the protection of aquatic life in freshwater sediments, 2003).



The CCME interim guideline for zinc in freshwater sediment for the protection of aquatic life (2003) is 123.0 ppm, and the PEL is 315.0 ppm. All of the sites exceeded the ISQG for zinc in the Waterford, and sites 3, 4, and 5 exceeded the PEL as well (*Figure 13*). Site 5 greatly exceeded the PEL at a concentration of 704.8 ppm. In a similar fashion to the copper results in sediment, there was an inverse correlation to the levels of zinc in the sediment samples and to the concentrations found in the water samples.

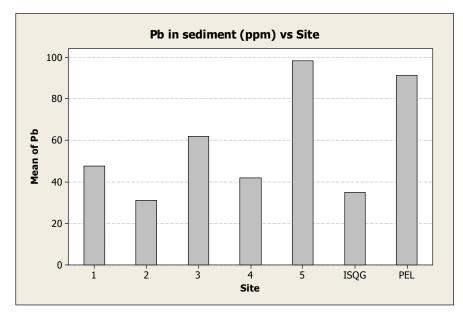
# 4.3.6 Lead (Pb)

**Figure 14:** Mean concentrations of lead (Pb) in ppb per sample site in the Waterford River with a maximum CCME guideline (for the protection of aquatic life, 2003) of 1.0 ppb derived according to the relative hardness of the samples.



According to the relative hardness of the samples, a CCME guideline for the protection of aquatic life in freshwater for lead of 1.0 ppb was derived. Sites 1 and 2 exceeded this limit (*Figure 14*), with site 2 having the highest mean value of 1.96 ppb. The raw data also show that site 2 always exceeded the guideline, and sites 3 and 5 had values that nearly exceeded it. Again, it will be noted that the highest value of 4.1 ppb occurred during sweep 1 at site 1 (*Appendix A*). Lead is toxic to life given certain levels of hardness (CCME, 2003), thus it should be pointed out that site 2 was rather problematic with regards to lead concentrations.

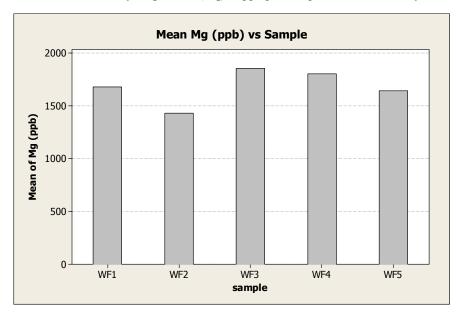
**Figure 15:** Concentrations of lead (Pb) in ppm per sample site in the Waterford River sediment samples, with a CCME Interim Sediment Quality Guideline (ISQG) of 35.0 ppm and a Probable Effect Level (PEL) of 91.3 ppm (for the protection of aquatic life in freshwater sediments, 2003).



The CCME interim guideline for lead in freshwater sediment for the protection of aquatic life (2003) is 35.0 ppm, and the PEL is 91.3 ppm. According to Figure 15 all but site 2 exceeded the ISQG and site 5 exceeded the PEL at 98.3 ppm as well. Site 2 came close to exceeding the ISQG at 31.0 ppm. For the most part, the above-mentioned trend also applies to concentrations of lead in the sediment and water samples of the same site being inversely correlated to each other.

# 4.3.7 Magnesium (Mg)

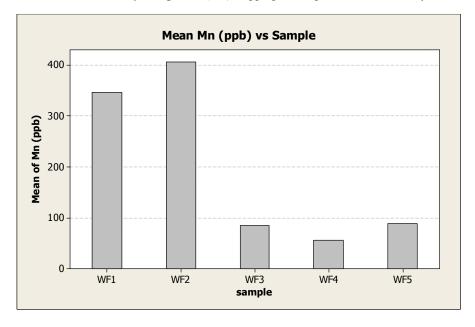
Figure 16: Mean concentrations of magnesium (Mg) in ppb per sample site in the Waterford River.



There is no CCME guideline set for Mg for the protection of aquatic life in freshwater. However, as magnesium is found naturally in abundance in the region it will be mentioned that all of the values are above 1200 ppb, and there does not appear to be much variance from site to site, although it can be noted that sites 3 and 4 exhibit the highest mean concentrations of 1858.6 ppb and 1804.7 ppb respectively. In this case, site 1 did not show an increased value during the first sweep (*Appendix A*). It is not suspected that human sources were contributing greatly to magnesium in the Waterford River.

# 4.3.8 Manganese (Mn)

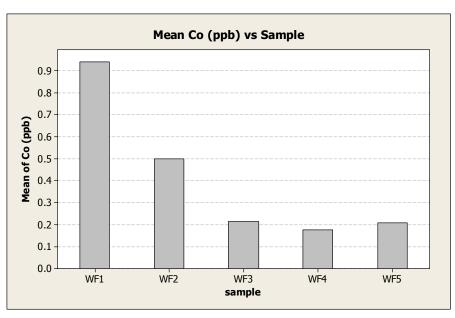
Figure 17: Mean concentrations of manganese (Mn) in ppb per sample site in the Waterford River.



There is no CCME guideline set for Mn for the protection of aquatic life in freshwater. However, it was mentioned due to the higher values found at sites 1 and 2, with site 2 having the highest mean value of 405.8 ppb (*Figure 17*). Again, the highest value of 588.3 ppb was obtained at site 1 on the first sweep (*Appendix A*).

# 4.3.9 Cobalt (Co)

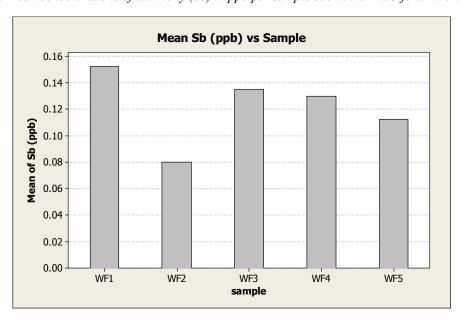
Figure 18: Mean concentrations of cobalt (Co) in ppb per sample site in the Waterford River.



There is no CCME guideline set for Co for the protection of aquatic life in freshwater, but it can be said that site 1 had the highest mean concentration of 0.94 ppb (*Figure 18*), and the highest value of 2.01 ppb during the first sweep (*Appendix A*). Site 2 also had a higher mean level of cobalt (0.5 ppb) than sites 3, 4 and 5.

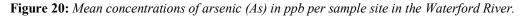
## 4.3.10 Antimony (Sb)

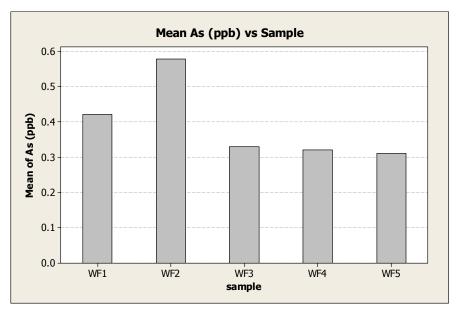
**Figure 19:** Mean concentrations of antimony (Sb) in ppb per sample site in the Waterford River.



There is no CCME guideline set for Sb for the protection of aquatic life in freshwater, but it can be said that again, site 1 had the highest mean concentration of 0.15 ppb (*Figure 19*), and the highest value of 0.21 ppb during the first sweep (*Appendix A*). Although in this case site 2 had the lowest mean concentration of antimony at 0.08 ppb, it can be said that there was not a lot of noticeable variance between the samples, except for sites 1 and 2.

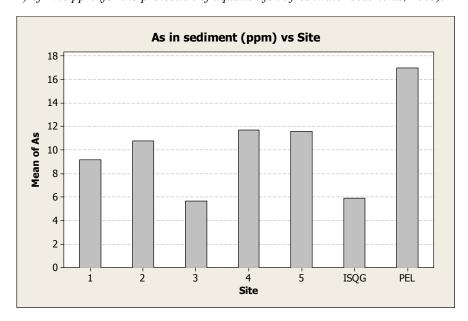
## 4.3.11 Arsenic (As)





Although the CCME guideline for arsenic for the protection of aquatic life in freshwater is set at 5.0 ppb (2003), the mean values of arsenic as shown in Figure 20 were so low, the guideline was excluded from the graph. Sites 2 and 1 had the highest mean concentrations of 0.58 ppb and 0.42 ppb respectively (*Figure 20*), however, site 1 again had a high relative value of 0.63 ppb during the first sweep (*Appendix A*). The third sweep in all cases showed that the detection limit was set higher than the other two times because none of the values were detected (*Appendix A*). As before, for statistical purposes these values were divided in half to give a representative concentration of arsenic during sweep 3 in the Waterford.

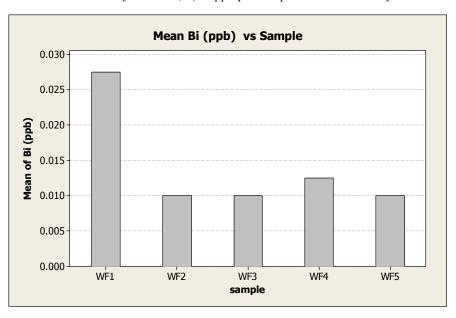
**Figure 21:** Concentrations of arsenic (As) in ppm per sample site in the Waterford River sediment samples, with a CCME Interim Sediment Quality Guideline (ISQG) of 5.9 ppm and a Probable Effect Level (PEL) of 17.0 ppm (for the protection of aquatic life in freshwater sediments, 2003).



The CCME interim guideline for arsenic in freshwater sediment for the protection of aquatic life (2003) is 5.9 ppm, and the PEL is 17.0 ppm. Site 3 was the only site to not exceed the ISQG with a concentration of 5.6 ppm, although it was very close. Although sites 4 and 5 greatly exceeded the ISQG at levels of 11.7 ppm and 11.3 ppm respectively, no sites exceeded the PEL for arsenic in the Waterford River sediment (*Figure 21*).

## 4.3.12 Bismuth (Bi)

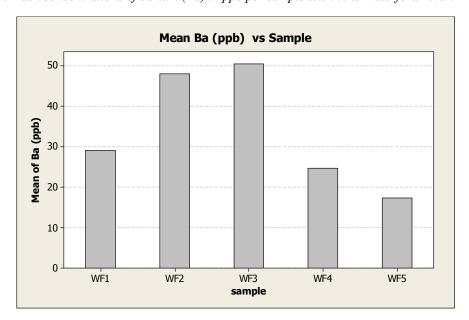
Figure 22: Mean concentrations of bismuth (Bi) in ppb per sample site in the Waterford River.



The values of bismuth in the Waterford River were quite low and an accurate quantification of this trace element was difficult because many of the values fell below the detection limits. However, it should be pointed out that site 1 continued to follow its normal trend by having the highest value of 0.04 ppb during the first sweep (*Appendix A*).

### 4.3.13 Barium (Ba)

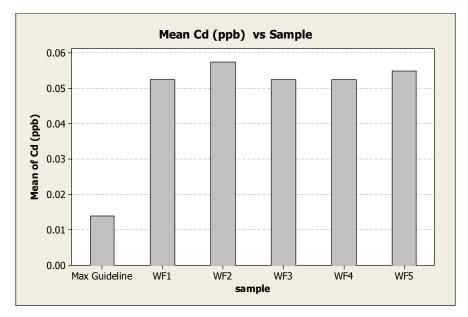
**Figure 23:** *Mean concentrations of barium (Ba) in ppb per sample site in the Waterford River.* 



Although there was no CCME guideline for Ba for the protection of aquatic life in freshwater, there was a difference between some of the sites with respect to mean concentrations, with sites 3 and 2 being the highest of 50.4 ppb and 48.0 ppb respectively (*Figure 23*). According to the raw data results site 1 had its highest value of 33.5 ppb recorded during sweep one. However, site 3 had the highest value overall of 124.7 ppb (*Appendix A*).

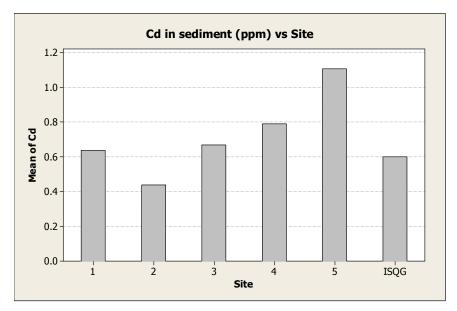
## 4.3.14 Cadmium (Cd)

**Figure 24:** Mean concentrations of cadmium (Cd) in ppb per sample site in the Waterford River with a maximum average CCME guideline (for the protection of aquatic life, 2003) of 0.014 ppb derived according to the relative hardness of the samples.



Although a CCME guideline for the protection of aquatic life in freshwater (2003) of 0.014 ppb for cadmium was derived from the formula  $10^{\{8.6[\log{(hardness)}]-3.2\}}$ , it was impossible to determine whether all of the mean values (*Figure 24*) actually exceeded this guideline due to the fact that all of the raw values for Cd fell below the detection limits (*Appendix A*). Despite the fact that in this case all of the maximum possible values (the detection limits) were divided in half, (for statistical purposes stated above) there were no actual values recorded to gauge whether the information given in Figure 24 was correct.

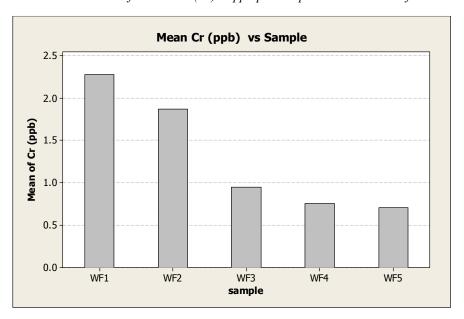
**Figure 25:** Concentrations of cadmium (Cd) in ppm per sample site in the Waterford River sediment samples, with a CCME Interim Sediment Quality Guideline (ISQG) of 0.6 ppm and a Probable Effect Level (PEL) of 3.5 ppm (for the protection of aquatic life in freshwater sediments, 2003).



The CCME interim guideline for cadmium in freshwater sediment for the protection of aquatic life (2003) is 0.6 ppm, although site 2 at 0.4 ppm was the only site in the study area to not exceed this guideline (*Figure 25*). Site 5 had the highest concentration of Cd at 1.1 ppm. The PEL is 3.5ppm, but no sites exceeded this limit.

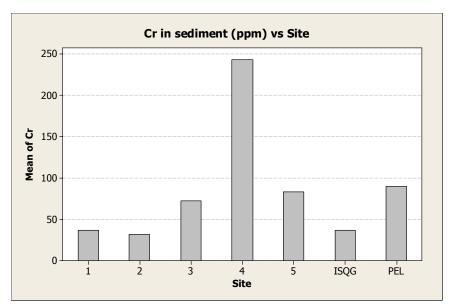
## **4.3.15 Chromium (Cr)**

**Figure 26:** Mean concentrations of chromium (Cr) in ppb per sample site in the Waterford River.



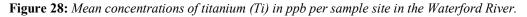
There are guidelines for Cr set by the CCME for the protection of aquatic life in freshwater (2003) but they are specifically for trivalent (III) and hexavalent (VI) chromium, and in this case total chromium was obtained so there was uncertainty regarding the quantities of chromium at each valence state. Hence, the guidelines were disregarded here. According to Figure 26 the highest mean concentrations of Cr were found at sites 1 and 2 at 2.28 ppb and 1.87 ppb respectively. Depending upon the concentrations at each valence state, this may have been significant. The highest recorded value of 4.39 ppb again occurred at site 1 during sweep 1 (*Appendix A*).

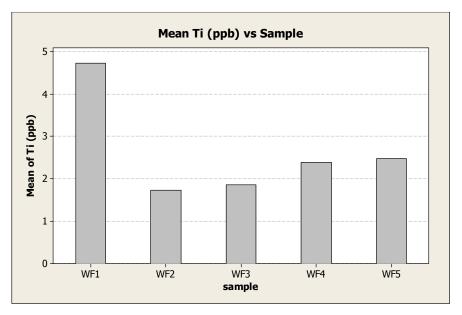
**Figure 27:** Concentrations of chromium (Cr) in ppm per sample site in the Waterford River sediment samples, with a CCME Interim Sediment Quality Guideline (ISQG) of 37.3 ppm and a Probable Effect Level (PEL) of 90.0 ppm (for the protection of aquatic life in freshwater sediments, 2003).



The CCME interim guideline for cadmium in freshwater sediment for the protection of aquatic life (2003) is 37.3 ppm, and the PEL is 90.0 ppm. Sites 1 and 2 did not exceed the ISQG with respective values of 37.2 ppm and 32.2 ppm, however site 4 greatly exceeded it as well as the PEL at 242.7 ppm. No other sites exceeded the PEL, however site 5 came close with a concentration of 83.3 ppm (*Figure 27*). With the exception of site 4, the concentrations of chromium in the sediment samples were inversely correlative with the concentrations found in the water samples of the same sites.

### 4.3.16 Titanium

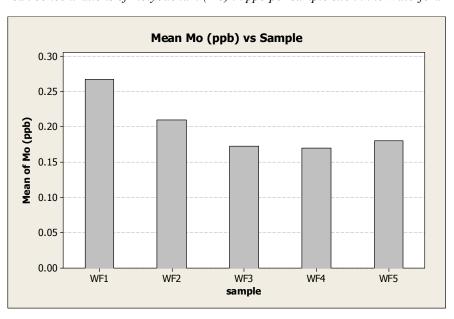




There was no guideline set by the CCME for the protection of aquatic life in freshwater regarding titanium, but it was mentioned due to the significantly higher mean concentration of 4.74 ppb noted at site 1 (*Figure 28*) as compared with the means of the other sites, which were all less than 2.50 ppb. The highest value of 6.34 ppb was again recorded at site 1 during the first sweep (*Appendix A*).

### 4.3.17 Molybdenum (Mo)

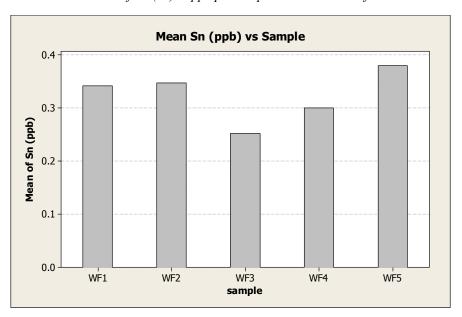
Figure 29: Mean concentrations of molybdenum (Mo) in ppb per sample site in the Waterford River.



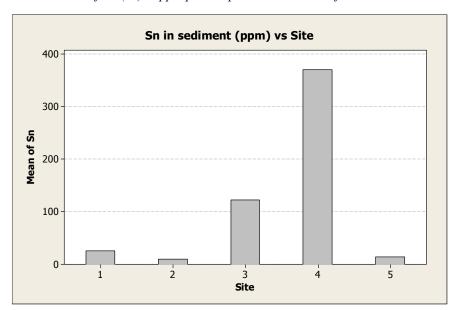
A guideline of 73 ppb for molybdenum had been set by the CCME for the protection of aquatic life in freshwater (2003), however the mean concentrations were so low in the Waterford that this guideline was disregarded. The highest mean concentration of 0.27 ppb was at site 1, but there was not much variation between the mean values at any of the sites with the lowest being sites 3 and 4 with equal means of 0.17 ppb (*Figure 29*). It can be noted that in this case, the highest concentrations of Mo at each site were recorded during sweep 3, the day of the actual rain event. This is one of the few cases where the event made any significant difference to the results.

## 4.3.18 Tin (Sn)

**Figure 30:** Mean concentrations of tin (Sn) in ppb per sample site in the Waterford River.



There was no CCME guideline for tin regarding the protection of aquatic life in freshwater. Tin occurred in a similar fashion to molybdenum in that there was not much difference in the mean concentrations with the highest being site 5 at 0.38 ppb and the lowest being site 3 at 0.25 ppb (*Figure 30*), and that the rain event on sweep 3 caused an overall increase in raw values in all of the samples (*Appendix A*).



**Figure 31:** Concentrations of tin (Sn) in ppm per sample site in the Waterford River sediment samples.

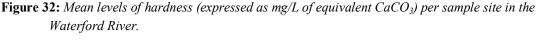
Although no CCME guidelines for the protection of aquatic life in freshwater sediments were available for tin, it was of interest to note that like many of the other examples, there was an inverse correlation between the amount of tin recorded in the sediment samples and the concentrations recorded in the water samples of the same sites.

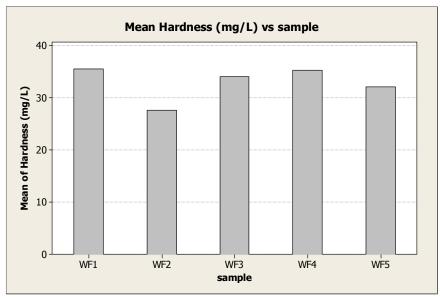
### 4.4 Hardness

The hardness of the water, expressed as equivalent mg/L CaCO<sub>3 (EQ.)</sub>, could be summed up using one easily derived formula (*see section 3.3.3.1*). Results from the ICP-MS testing were used to fit the variables in the equation. The collective concentrations of calcium and magnesium make up the bulk of the constituents contributing to hardness, but the presence of iron, manganese, aluminum, strontium, and barium also contribute to a smaller degree (CCME, 2003). To obtain the most representative values for hardness, all of these elements were taken into account when performing the calculations.

Hardness, which is closely related to pH and alkalinity, has the ability to lower toxicity levels in water in some cases. This is particularly due to the fact that metals, for example, tend to form carbonates with calcium and become un-ionized, thus non-bioavailable. However, this toxicity is also directly dependant on the alkalinity and pH of the system (CCME, 2003).

The calculated mean values for hardness for each sample site in the Waterford River are located in the following table. The raw values of hardness for each site on each sweep are located in Appendix A.





Hardness is often categorised in varying degrees from soft to hard. Soft water generally has a value of 20mg/L or less, while hard water is usually classified as being greater than 120mg/L CaCO<sub>3 (EQ.)</sub>. The mean values shown in Figure 32 signified that all of the sample sites had a slight hardness in the range between 20 and 60mg/L CaCO<sub>3 (EQ.)</sub>, with the lowest being site 2 at 27.6 mg/L CaCO<sub>3 (EQ.)</sub> and the highest being site 1 at 35.6 mg/L CaCO<sub>3 (EQ.)</sub>. It would seem, at least from this, that the Waterford River was fairly well buffered, meaning that its hardness did not really change significantly from site to site along its path. It was understandable that site 2 had a slightly lower mean value for hardness because it came from a different source with fewer urban influences. However, with respect to the relatively soft conditions of the natural water systems common in the Northeast Avalon region, there had not been a great degree of urban contribution to hardness along the Waterford in this case.

The low mean levels of hardness in the river are also one major factor that led to the outcome of many of the site-specific CCME guideline derivations, and account in part for the reason why some of these guidelines were fairly low. This meant that the toxicity of certain metals could be increased in the Waterford due to the low ion-binding capacity of the water within it. Although, in many cases the pH, temperature, alkalinity, and other such factors could also play a role in the overall toxic nature of some of the trace elements.

### 4.5 E. coli and Non-Fecal Coliforms

Coliform bacteria are a large group of microorganisms that exist naturally in soil, sediment, and bodies of water. A certain enteric group of fecal coliforms, known as *Escherichia coli*, do not exist naturally outside the gastrointestinal tracts of warmblooded animals. Hence, finding this particular type of bacteria in the environment would

signal the presence of fecal matter at the sampling location (Patel, 2004). Although not all types are pathogenic or disease causing, some strains of *E. coli* can be especially deadly. Additionally, since fecal matter must be present for *E. coli* to show up in tests, then the presence of this microorganism would indicate the possibility of other pathogenic enteric bacteria and viruses (Patel, 2004). The Waterford River has a high recreational value, thus if high levels of *E. coli* show up in the testing then there could potentially be fecal matter and deadly pathogens where people use the river.

The mean results of the triplicate M-coli blue testing for *E. coli* and non-fecal coliforms for every site are displayed in the following graphs. It should be noted that dilutions were not performed for any of the tests on the first sweep, as it was unexpected that some of the colony-forming unit (CFU) levels would be as high as they were. Thus averages were derived of results obtained from the second and third sweeps and are considered to be minimum mean CFU counts. The raw data associated with the microbiological testing are located in the appendix.

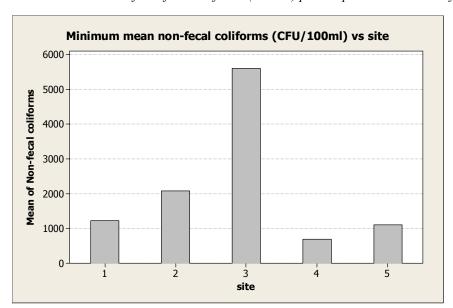
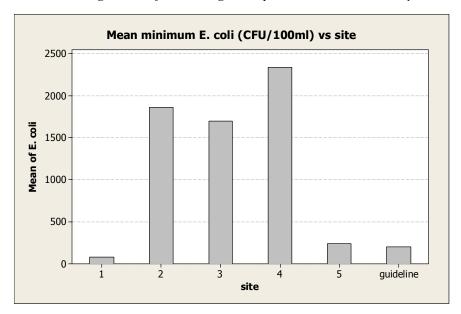


Figure 33: Minimum mean counts of non-fecal coliforms (in CFU) per sample site in the Waterford River.

Non-fecal coliforms are obtained simultaneously with *E. coli* when using the M-coli blue test. These organisms are not necessarily harmful, but represent a count of the bacteria that would be living naturally in the river. In most cases, non-fecal coliforms would be expected to appear in far greater numbers than *E. coli* because water would be one of their natural habitats. With 5607.5 mean CFU, site 3 showed an elevated presence of non-fecal coliforms over the other sites (*Figure 33*), and it should be noted that on the third sweep even after a dilution, there were too many colonies to count at site 3. It was estimated that, at that time, the maximum number of coliforms that could be accurately counted in a 1/10 dilution would be about 7000, which was the number picked to create Figure 33, so this number is most likely a minimum CFU for that sample site.

**Figure 34:** Minimum mean counts of E. coli (in CFU) per sample site in the Waterford River with a US EPA recommended guideline of 200 average CFU per 100 ml in recreationally used waters.



The US Environmental Protection Agency (EPA) has recommended that the maximum average count of *E. coli* in water used for recreational purposes is 200 CFU per 100ml. *E. coli* was detected at every site along the Waterford, indicating the presence of fecal matter in the river. All sites, with exception to site 1 at 80.5 mean CFU, exceeded this guideline. Site 5 barely exceeded with a count of 239.1 CFU, but sites 2, 3, and 4 greatly exceeded this value with counts of 1860 CFU, 1697.5 CFU, and 2340.8 CFU respectively (Figure 34). It should be noted that since these are all minimum mean counts, the CFU at all sites would be expected to be higher, making these exceedances more extraordinary.

Also of note, site 4 had a much higher mean count of E. coli than non-fecal coliforms, and this mainly occurred on the third sweep because a count of 6600 CFU of E. coli was recorded then (Appendix A). This is an unusual occurrence, since non-fecal coliforms would be expected to be in much higher numbers. The rain event that occurred on sweep 3 could have possibly caused a nearby sewer overflow adding sewage to the river at that point. There may have been a sewer outfall near site 4 to cause this high count because there was not much correlation between the rain event and the other sites, although sites 1 and 5 showed an increased number of E. coli during the event as well (Appendix A). In general, since it was determined that there was fecal matter at all of the sites then it could be assumed that sewage might have been entering the river at certain points in varying amounts, although site 2 was most likely contaminated by the high numbers of birds that resided on the water there. The results of the total Kjeldahl nitrogen in section 4.2 help to back these points up. A paper prepared for the provincial (NL) and federal governments in 1992 also states that the Waterford River does receive storm water from all sewer outfalls in the area due to possible cross connections between the sanitary and storm sewers, in addition to the fact that there are some improperly operated septic tanks and private cesspools along its path (*Ullah W. et al*).

Where *E. coli* was present in high numbers at some of the sites, it would be recommended that further testing be carried out in the future, and that testing for other pathogens, such as Salmonella or *Giardia lamblia*, be carried out if possible. Additionally, testing for the highly lethal *E. coli* O157:H7 should also be performed because this strain can also be transmitted through human waste (Patel, 2004). If sewage is presently entering the Waterford, then it could be harmful to the health of the people using the river, thus it is important to know the *E. coli* counts on a more regular basis.

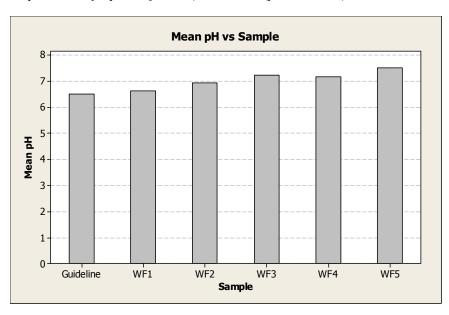
### 4.6 Horiba Probe Measurements

In determining the useful water quality parameters of pH, specific conductivity, dissolved oxygen, turbidity, temperature, and salinity, a Horiba probe was used, which is an *in situ* device that can detect all of these variables at once. A description of each is listed in the following subsections in addition to the mean results found for each parameter at every site. A discussion of the results will also be included in the subsections. The raw data obtained from the *in situ* testing is found in Appendix A.

### 4.6.1 pH

The pH scale determines, logarithmically, the level of how acidic or basic a water sample is based on the amount of hydrogen ions present in the sample. Since different levels of pH can partially and directly determine the toxicity of certain substances, there is a certain range of pH required for a healthy aquatic ecosystem. For example, pH can determine the extent of the solubility of certain metals and ammonia. The higher the solubility of these constituents, the more bioavailable they would be to aquatic life (CCME, 2003). Depending on the toxicity of a substance at a certain pH, this would mean that a higher bioavailability could be more damaging. Industrial inputs of various trace elements and acids could contribute to changes in pH of a river system. The mean results of pH per sample site are displayed in the following graph.

**Figure 35:** Mean values of pH per sample site in the Waterford River, with a minimum CCME guideline (for the protection of aquatic life, 2003) to meet 6.5 (pH = 9.0 max).

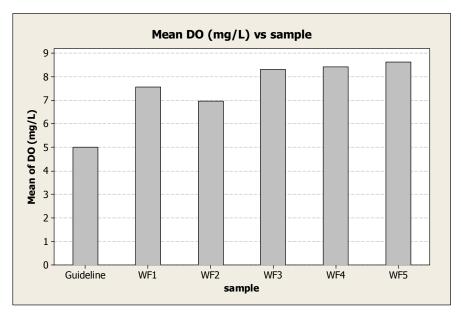


According to the CCME guidelines (for the protection of aquatic life, 2003), the recommended range of pH in rivers in general is between 6.5 and 9.0 (note: pH has no specific units of measure). Streams in the Northeast Avalon region can often be naturally below this range due to the natural acids that tend to form in the boggy headwaters, however the Waterford River seemed to fall within the healthy limit of the guideline regardless (Figure 35). The river also seemed somewhat buffered, since pH fluctuations were fairly minimal and the water fell close to the neutral mark in most of the cases, although it should be noted that site 1 had a slightly lower mean pH than the others with a value of 6.62, and could have been due to the somewhat higher levels of various trace minerals found in the water at that site.

## 4.6.2 Dissolved Oxygen

Oxygen dissolved between molecules of water is used by and directly supports aquatic life. The amount of dissolved oxygen (DO) in a sample is dependent on the amount of activity occurring at that site. The more biological respiration occurring by aquatic flora and fauna, the more oxygen will be used up from the water. For example, if the amount of bacteria at a site suddenly increases, the DO will most likely decrease due to the increased use of oxygen. Areas where aquatic biological production is too high to sustain itself will have low levels of DO. Conversely, DO will tend to increase with increasing flow in the system and decrease with stagnation. Other factors that can decrease DO are increased organic matter, increased temperature, and decreased photosynthesis. If there is an increase in the amount of salts at a site in the form of TDS and TSS, turbidity will increase, effectively decreasing the amount of light entering the system, thus affecting the level of photosynthesis (Murphy, 2002). The mean results of dissolved oxygen per sample site are displayed in the following graph.

**Figure 36:** Mean Dissolved Oxygen (DO) levels per sample site in mg/L in the Waterford River, with a CCME guideline (for the protection of aquatic life, 2003) of 5.0 mg/L derived according to site-specific criteria (CCME, 2003).



Dissolved oxygen (DO) is one of the most important factors affecting aquatic life with 4mg/L being the minimum amount for invertebrates and 5mg/L being the minimum for other forms of life such as coldwater fish (but not including the highly sensitive embryo stages) [Province of BC, 1998]. For the purposes of this report and based on guidelines derived by the CCME (for the protection of aquatic life, 2003) and the Government of British Columbia (1998), DO values lower than 5mg/L would have been flagged as being dangerously unacceptable or depending on how much lower, completely unacceptable conditions for supporting aquatic life. It should be noted that 7 – 11 mg/L DO is a more acceptable range for freshwater organisms.

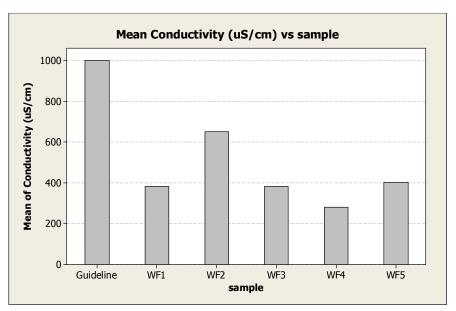
The results displayed in Figure 36 show that the mean DO levels in the Waterford River fall within the specified range that is healthy for aquatic life. This was to be expected since the river has a healthy flow, and there did not seem to be a problem with algae or aquatic plants choking the system. Also, due to the highly sandy or pebbly composition of the substrate, there did not appear to be much settled organic matter in the river to lower DO levels either. Site 2 had the lowest mean measure of 6.97 mg/L (*Figure 36*), which is on the borderline of the optimal DO range. Its lower mean level was most likely due to the increased organic matter at this site from the feeding birds, relative to its smaller volume and flow. With the exception of the unique conditions at site 2, it was of note that site 1 had lower DO levels than the other sites at 7.57 mg/L.

### 4.6.3 Specific Conductance

Specific conductance, or conductivity, is a measure of how well water can carry an electric charge, depending on what constituents are in it. Closely related to TDS, the

influence of conductivity is based on concentrations of certain substances dissolved in it, including chloride, nitrate, sulphate, phosphate, sodium, magnesium, calcium, and iron (Murphy, 2002). Thus, higher values of conductivity would indirectly infer higher concentrations of these ions, and would also mean that the water would have more saline properties. The mean results obtained for conductivity per sample site are displayed in the following graph.

**Figure 37:** Mean conductivity values in  $\mu$ S/cm per sample site in the Waterford River, with a non-specific guideline of 1000  $\mu$ S/cm.

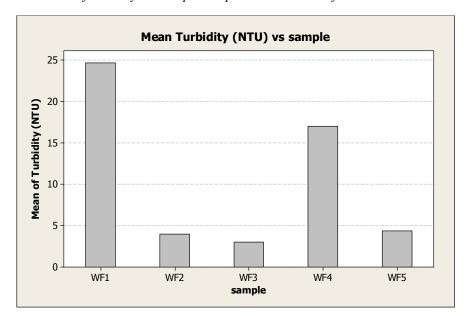


No official guideline for conductivity in freshwater currently exists, however water would typically tend to have more saline properties at a conductivity of more than  $1000~\mu\text{S/cm}$ , which is why a non-specific guideline was derived to help define freshwater quality. None of the sites exceeded this guideline, and none of the mean values of conductivity even came close, with the highest value being  $650~\mu\text{S/cm}$  at site 2 and the lowest being  $280.3~\mu\text{S/cm}$  at site 4 (*Figure 37*). Although these values do reflect the fact that the water is not pure, and that there are more constituents contributing to conductivity in site 2 specifically, the results still reflect a healthy water system. It should be noted, however, that on the first sweep site 2 had a specific conductance value of 930  $\mu\text{S/cm}$ , which nearly exceeded the guideline (*Appendix A*). The higher values observed in site 2 most likely reflect the high activity of the waterfowl in that section with respect to the small amount of space that the water has to travel through.

## 4.6.4 Turbidity

Turbidity is a measure of the amount of light that can pass through water based on the amount of matter present in it. This matter would mainly consist of suspended solids, but could also be due to high numbers of microorganisms. Anything that could cause the water to become cloudy would lead to an increase in turbidity (Murphy, 2002). Since

turbidity will impede light within the water sample, plant photosynthesis will subsequently decrease. And as turbidity is mainly suspended solids, particles associated with increased turbidity can house more bacteria and can also choke aquatic life (Province of BC, 1998). The mean results obtained for turbidity per sample site are displayed in the following graph.

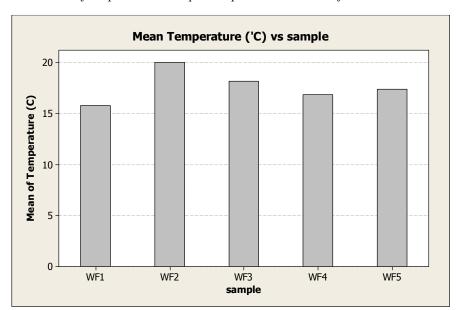


**Figure 38:** *Mean levels of turbidity in NTU per sample site in the Waterford River.* 

The only guidelines that really exist for turbidity are related to the amount of turbidity in a sample relative to the amount measured in a reference site. Since there was no reference site in this study, a guideline could not be established. For perspective, pure water would have zero turbidity. However, a river is not pure therefore it would be expected to have some level of turbidity. Water that appears clear and colourless would normally have a low value of turbidity, such as is the case of sites 2, 3, and 5, which all had values below 5 NTU, as shown by Figure 38. Site 1 was noted in the field to not always be as clear as the other sites; hence its mean measure of turbidity was higher at 24.7 NTU (*Figure 38*). The first sweep was noted to exhibit higher individual levels of turbidity overall for all of the sites (*Appendix A*).

### 4.6.5 Temperature

The intensity of stored heat in a body of water is measured as the temperature, and this parameter can influence the solubility of certain substances, making them more or less bioavailable. Depending on the toxicity of the substance, a temperature increase could cause harmful effects in the aquatic ecosystem (CCME, 2003). It also directly affects the solubility of dissolved oxygen, where an increase in temperature results in a decrease of DO (Province of BC, 1998). Temperature can also influence the biological activity of aquatic flora, fauna, and bacteria (Murphy, 2002). The mean results obtained for temperature per sample site are displayed in the following graph.

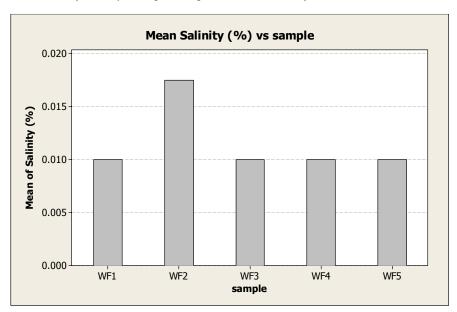


**Figure 39:** *Mean values of temperature in °C per sample site in the Waterford River.* 

The recorded mean temperatures are about what they would be expected to be in the Waterford during the summer, between the range of 15°C and 20°C (*Figure 39*). The lowest mean temperature occurred at site 1 at 15.8°C, and this was probably due to the fact that this site was more shaded and sheltered from the sun than all of the other sites. Site 1 was also relatively deep, which may have contributed to its slightly lower mean temperature. Site 2 had the highest mean temperature at 20°C, and this was most likely due to the fact that it had a much smaller stream channel, making it easier to heat by the sun. There was a lot of biological activity occurring there as well, generated from the residing birds.

# 4.6.6 Salinity

Salinity is related to conductivity because it measures the concentration of salts in the water. Freshwater typically has a very low salt concentration relative to seawater. A higher salinity would indicate the input of salts to the system. The results of salinity per sample site are displayed in the following graph.



**Figure 40:** *Mean levels of salinity in % per sample site in the Waterford River.* 

Fresh water is generally characterised as having a very low level of salinity that is normally less than 1000ppm, or 0.1% salinity (UCAR, 2002). Above this concentration, water would begin to become brackish. The mean levels of salinity in the Waterford are well below this amount, with the highest level being less than 0.02% in site 2 (*Figure 40*). Site 2 had a higher level of salinity likely due to the birds using the site. The salinity was constant at 0.01% for all of the other locations, indicating that salt was not a significant input into the Waterford at the time of testing, and that it was naturally occurring for the most part.

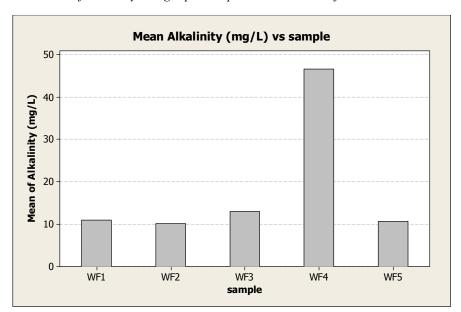
# 4.7 HACH Kit Analysis Results

The parameters alkalinity, ammonia, nitrite, and chloride were tested using a HACH field-testing kit. Descriptions of each parameter are listed in the following subsections along with the mean results obtained per sample site. Discussions of the results are also included in the subsections. The raw data obtained with the HACH kit are found in Appendix A.

## 4.7.1 Alkalinity

Depending on the presence of bicarbonate, carbonate or other anions, alkalinity is essentially a measure of the buffering ability of water with regards to changes in pH (Murphy, 2002). It is a very important parameter of water quality because a certain level of natural alkalinity would have the ability to stabilize the pH in a body of water, such as during acid rainfall, or in industrial runoff. The lower the alkalinity, however, the more susceptible water would be to pH fluctuations. Additionally, when more acid is added to the system, the buffering capacity will weaken and the alkalinity will be lowered (Murphy, 2002). A higher level of alkalinity will tend to be associated with harder water

and a higher concentration of sodium salts (Province of BC, 1998). However, because of the binding properties of carbonate and bicarbonate, water with a higher alkalinity may be able to cause metals to precipitate out of the water column, lowering the degree of metal toxicity in the water (Murphy, 2002).



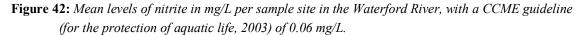
**Figure 41:** *Mean levels of alkalinity in mg/L per sample site in the Waterford River.* 

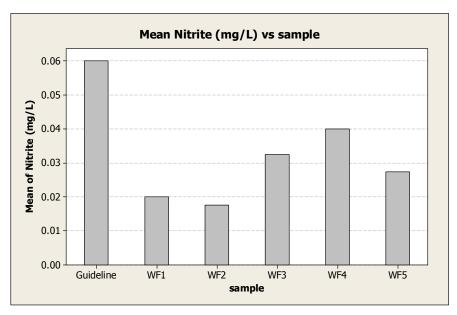
Alkalinity is measured as an equivalent amount of calcium carbonate (mg/L CaCO<sub>3 EQ.</sub>), whether CaCO<sub>3</sub> is present or not. Thus, since the bedrock in this region is mainly mud and sand derived, and not very carbonaceous, the Waterford should naturally have low values of alkalinity. However, natural fresh water generally has an alkalinity of between 20 and 200 mg/L, hence below this range the aquatic system would tend to be fairly sensitive to situations in which the pH would be likely to change (Murphy, 2002). With the exception of site 4, this means that although the river seems to be fairly buffered in some regards (*Sections 4.3 & 4.6.1*), a sudden input of a strongly acidic substance, for example, might have a drastic effect upon pH in the rest of the sites (*Figure 41*). Site 4, on the other hand, would not be as sensitive because at a mean value of 46.7 mg/L its alkalinity was within the normal buffering range for freshwater. A reason why site 4 had a higher alkalinity may have been due to an input of additional anions to the water from another source, such as the heavily trafficked bridge overhead, and it was noted from the raw data that site 4 had the highest mean concentration of Ca of all the sites at 10.5 ppm (*Appendix A*).

### 4.7.2 Ammonia & Nitrite

Ammonia (NH<sub>3</sub>) and nitrite (NO<sub>2</sub>), two nitrogenous compounds, can be particularly toxic to aquatic life (Province of BC, 1998), but their toxicity is dependant on many factors such as pH, temperature, DO, or the presence of other substances (CCME, 2003). Under normal conditions, these compounds are temporarily present as a function

of bacterial metabolism. They are usually present at very low levels and are used by plants and bacteria to their own benefit. Nitrite can be toxic at lower concentrations than ammonia, causing blood disorders in fish, but it tends to be short lived as it is quickly oxidized to nitrate (NO<sub>3</sub>) by bacteria. Ammonia is even less stable in water, especially with a lower pH, as it is easily converted to the relatively un-toxic ammonium ion (NH<sub>4</sub><sup>+</sup>) [Murphy, 2002]. However, certain forms of industrial discharge can add these compounds to the aquatic system in addition to residential discharge such as sewage, since human waste contains high amounts of nitrite and ammonia (Murphy, 2002). The mean results for nitrite per sample site are displayed in the following graph. Note that there will be no graph for ammonia because this parameter was not detected in the Waterford River at all.





A CCME guideline for the protection of aquatic life (2003) had been set for nitrite at 0.06 mg/L. Although none of the mean values at any of the sites exceeded this, site 4 was on average higher in nitrite than the other sites at 0.04 mg/L, which was somewhat close to the guideline (*Figure 42*). It should be noted as well that on the first sweep, site 3 had a value of 0.05 mg/L, which was even closer to the limit (*Appendix A*).

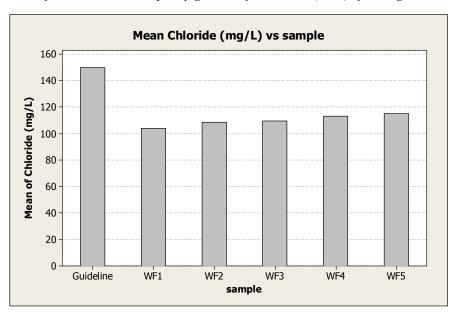
High amounts of ammonia and nitrite are found in raw sewage, but not water itself (Murphy, 2002). Thus, if there were sewage present it would probably have been quite diluted by the flowing water, and/or decomposed by bacteria within the river and the sewage, significantly lowering the ammonia and nitrite levels. There would probably have to be quite a high concentration of sewage in the water for the proper detection of these compounds. The  $E.\ coli$  testing would be a much better indication of sewage in this case, and the Kjeldahl test would also be a good indication. Testing for nitrate (NO<sub>3</sub>) rather than nitrite (NO<sub>2</sub>) would be a recommendation for future testing, since it is also

found in high concentrations in sewage and is quite stable in water (Province of BC, 1998).

### 4.7.3 Chloride

The chloride ion occurs naturally in freshwater systems, however its occurrence is in much lower concentrations than in saline water. It is sometimes associated with industrial discharge, but in fact higher levels of chloride can react with nitrite and make it less toxic (CCME, 2003).

**Figure 43:** Mean concentrations of chloride in mg/L per sample site in the Waterford River, with a Province of BC ambient water quality guideline for chloride (2003) of 150mg/L.



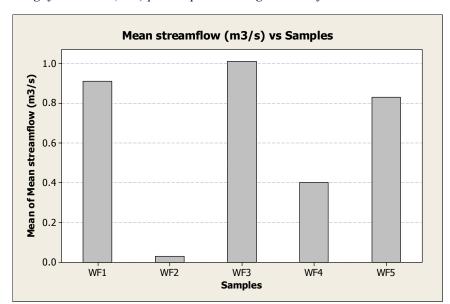
There is no specific guideline set by the CCME in relation to chloride and it can exist in high concentrations without being harmful. However, the Province of BC (1998), recognised that chloride levels in excess of 600 mg/L at any given time could be quite toxic to aquatic life. They also mentioned that mean chloride values in freshwater should not exceed 150 mg/L on a continuous basis. This is the guideline referred to in Figure 43. Mean chloride levels in the Waterford did not exceed this guideline, but they were approaching it, suggesting that there may have been a slight additional input of chloride to the system. Since there were moderate levels of chloride in the river, it may have been enough to moderate the toxicity of the nitrite present as well.

#### 4.8 Flow

Any river with sufficient depth and width will naturally have a higher volume of water flowing through it per unit of time at a given point (streamflow). It is possible for rivers having a smaller width and shallower depth to have a strong current with respect to a larger river, however their channel capacity would be significantly less, resulting in a lower streamflow than in a larger river. Likewise, a river of a certain width but also

having a deeper channel may have a larger area but a slower current, resulting in a reduction of overall streamflow. Flow is important to the health of the river ecosystem, but it would be expected to change naturally on a yearly, to monthly, to daily basis. Constant unnatural interruptions to flow could thus disrupt this natural balance.

The mean values of streamflow for each sample site along the Waterford River are displayed in the following graph. The raw data associated with these values are located in Appendix A, and the depth profiles from which these data are derived are located in Appendix C.



**Figure 44:** Average flow values  $(m^3/s)$  per sample site along the Waterford River.

It can be noted that all of the sites showed a visually healthy flow along the Waterford, however sites 2 and 4 showed a much lower flow at 0.03 and 0.4 m<sup>3</sup>/s respectively (*Figure 44*). This was due in part to the fact that site 2 had a very small channel relative to the other sites, and that site 4 was a relatively shallow section. Although site 5 had larger flow than sites 2 and 4, it may have been impeded slightly due to the amount of debris observed in that part of the river, which ranged from gravel to shopping carts and bicycles. Otherwise, the streamflows at each site appeared healthy when taking into consideration their individual morphologies and the drier summer conditions.

There was no observable correlation between the streamflows and the rain event that occurred on sweep three, however it should be noted that site one was quite inflated on the first sweep with an instantaneous flow of  $1.72 \,\mathrm{m}^3/\mathrm{s}$ , and was most likely due to the minor rain event that occurred during the morning of that day (*Appendix A*).

# 5.0 Conclusions

The results show that the main stretch of the Waterford River was somewhat affected by urban activities, however they also showed that the river was not in a critical state of poor health. Of note, many parameters such as pH, DO, temperature, hardness, conductivity, and flow exhibited values that would be considered normal for an urban river during summer conditions, although the unique conditions at site 2, which was not along the main stretch, did pose for a few minor abnormalities in this regard.

Of constituents entering the system, some metals were in elevated concentrations; and was especially so in site 1, which was to be expected since it was located on the downstream end of the industrial park in Mount Pearl. These raised mean concentrations in site 1 were also probably related to the short but heavy rainfall that occurred just before the first sample was taken. Site 2 also tended to show higher concentrations of certain metals at times. This was so in the other sites, however usually in lower concentrations than the first two. There were also some situations where CCME guidelines related to aluminum, iron, copper, zinc, and lead were exceeded in many of the water samples in many of the sites. The sediment also showed some potentially harmful metals, such as chromium, copper, zinc, arsenic, cadmium, and lead in excess of CCME guidelines in most circumstances, indicating a possible input of these traces to the system.

Sewage was another component suspected to be present and degrading the water quality in the river. This was correlated with the fact that there were high counts of E. coli and occasionally high levels of TKN present in the river. Occasional discharges of sewage from nearby storm sewers or direct outfalls in the river were believed to be the cause. Overflow of these storm passages during a rain event could also contribute extra amounts of sewage to the river.

The fact that there were moderate to occasionally high amounts of solids present in the water provided more evidence of constituents entering the Waterford, and was most likely directly related to the river's passage through the urban region and, thus, to the type of runoff it was receiving. Elevated chloride levels and moderate conductivity values reflected this as well.

The low alkalinity values in most of the sites also indicated the river's possible susceptibility to potential environmental degradation. Although the pH and hardness of the river seemed fairly stable, the buffering ability of the water within the river, with exception to site 4, was considered to be fairly low. Since the awareness of various chemical constituents, such as pesticides or petroleum type components were unknown within the boundaries of this report, it could not be determined how much pressure was being put on the Waterford from these types of environmental degraders.

Essentially, the Waterford River does not appear to be exceedingly stressed as a result of the various constituents shown to be present in it. It does, however, experience the impact and pressures placed upon it from the urban developments along most of its length.

## 6.0 Recommendations

The continued monitoring of the Waterford River would be essential to ensure that any future changes to the system would be accurately observed and recorded. A more thorough analysis on the water and sediment in the river would also be recommended; there was not much information available on certain substances such as pesticides or PAHs in the Waterford River, and these types of contaminants were not possible to test for beyond the scope of this report.

In terms of the preservation of the Waterford, keeping an urban river healthy is a difficult task, however it is by no means impossible. Thus, in this regard it would be recommended that steps be taken to ensure city runoff to the river would be minimalised, if possible. Parking lots could be upgraded, or new lots could be properly engineered to reduce direct runoff and to encourage rainwater infiltration instead; industry and business could be educated and convinced to use less contaminating techniques in their operations, and to dispose of waste and wastewater properly if they are already not doing so; and new building developments could utilize procedures to minimalise erosion and better contain any sedimentation caused by loose earth particles transported during runoff.

With respect to sewage, essentially no sewage should ever enter the Waterford River untreated. Thus, any outfalls to the river should be properly redirected, and the storm sewers should be inspected and upgraded where cross connections and overflows are known to occur in order to prevent any sewage from entering the system.

Continued public outreach is also recommended, since the public can help keep the Waterford clean as well. In particular, education about the proper disposal of garbage in order to prevent litter from polluting the river is important. The more aware a person is about what is occurring in their community in and around the river, then the more likely that person would be to adopt a watchdog or river guardian role and report an environmental spill or other such adverse occurrence upon the river.

## 7.0 References

- CCME Canadian Council of Ministers of the Environment (2001). Canadian sediment quality guidelines for the protection of aquatic life: Introduction. Updated. In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.
- CCME Canadian Council of Ministers of the Environment (2003). Canadian water quality guidelines for the protection of aquatic life: Guidance on the Site-Specific Application of Water Quality Guidelines in Canada: Procedures for Deriving Numerical Water Quality Objectives. In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.
- CCME Canadian Council of Ministers of the Environment (2003). Summary Table In: Canadian environmental quality guidelines, 1999. Canadian Council of Ministers of the Environment, Winnipeg.
- Green Lane, the. (2003). Canada and Newfoundland/Labrador Aqua Link (CANAL).
  Prepared for Environment Canada, Ottawa. Retrieved 09/09/05 from <a href="http://map.ns.ec.gc.ca/canal/root/main/main.asp">http://map.ns.ec.gc.ca/canal/root/main/main.asp</a>.
- Murphy, S. (2002). *BASIN: Information on Water Quality Standards*. Retrieved 09/09/05 from http://bcn.boulder.co.us/basin/data/FECAL/info/.
- Patel, J. (2004). *Microbiology Laboratory Manual*. St. John's: Fisheries and Marine Institute.
- Powell, S. (1999). Surface Run-Off Contributions to St. John's Harbour from the Waterford River Drainage Basin. Prepared for St. John's Harbour ACAP, Inc., St. John's.
- Province of British Columbia (1998). *Guidelines for Interpreting Water Quality Data*. Retrieved 09/09/05 from <a href="http://srmwww.gov.bc.ca/risc/pubs/aquatic/interp/index.htm">http://srmwww.gov.bc.ca/risc/pubs/aquatic/interp/index.htm</a>.
- Ullah W., et al (1992). Urban Hydrology of the Waterford River Basin, Main Report. Prepared for the Department of Environment, Water Resources Division, St. John's; Environment Canada, Inland Waters Directorate, Dartmouth; and Environment Canada, National Water Research Institute, Burlington.
- United States Environmental Protection Agency (1986). Ambient Water Quality Criteria for Bacteria. Office of Water Regulations and Standards, Criteria and Standards Division. Washington, DC: EPA.
- University Corporation for Atmospheric Research, UCAR (2002). Salinity, Dissolved Salts, Measuring Salinity. Retrieved 09/09/05 from <a href="http://www.windows.ucar.edu/tour/link=/earth/Water/dissolved\_salts.html&edu=high">http://www.windows.ucar.edu/tour/link=/earth/Water/dissolved\_salts.html&edu=high</a>
- Whiteway, G. (2004). *Chemistry 4100 Lab Procedures*. St. John's: Fisheries and Marine Institute.

# 8.0 Appendix A

The raw results and their associated means derived from all water quality and characteristic tests performed on the Waterford River samples for each sweep are listed in the following tables. Bolded values indicate exceedances to CCME guidelines (for the protection of aquatic life, 2003).

sample	Date	TSS (mg/L)	TDS (mg/L)	TS (mg/L)	VOC (mg/L)	Total Kjeldahl N (%) Water
WF1	20-Jul-05	28	682	710	278	0.01
	3-Aug-05	10	852	862	686	0.95
	18-Aug-05	54	548	602	284	N/A
	Mean	30.7	694	724.7	416	0.48
WF2	20-Jul-05	4	716	720	256	0.13
	3-Aug-05	50	612	662	416	0
	18-Aug-05	58	750	808	364	0
	Mean	37.3	692.7	730	345.3	0.04
WF3	20-Jul-05	10	718	728	320	0.45
	3-Aug-05	16	950	966	726	0
	18-Aug-05	34	584	618	314	0
	Mean	20	750.7	770.7	453.3	0.15
WF4	20-Jul-05	4	748	752	378	0.96
	3-Aug-05	68	642	710	596	0
	18-Aug-05	44	546	590	286	0
	Mean	38.7	645.3	684	420	0.32
WF5	20-Jul-05	18	772	790	468	0.09
	3-Aug-05	56	1150	1206	698	0
	18-Aug-05	54	628	682	334	N/A
	Mean	42.7	850	892.7	500	0.05

sample	Date	Hardness (mg/L)	Non-Fecal Coliforms (# of Colonies/100ml)	E. coli (# of Colonies/100ml)	рН	Conductivity (uS/cm)
WF1	20-Jul-05	32.7	TNTC	TNTC	6.54	329
	3-Aug-05	36.8	550	23.5	6.45	428
	18-Aug-05	37.2	1886.5	137.5	6.86	386
	Mean	35.6			6.62	381
WF2	20-Jul-05	28.4	TNTC	TNTC	6.97	930
	3-Aug-05	25.2	1840	2690	6.74	475
	18-Aug-05	29.3	2350	1030	7.12	545
	Mean	27.6			6.94	650
WF3	20-Jul-05	30.6	TNTC	TNTC	7.21	350
	3-Aug-05	36.6	4215	1730	7.06	415
	18-Aug-05	34.9	TNTC	1665	7.39	378
	Mean	34			7.22	381
WF4	20-Jul-05	37.5	TNTC	55.3	7.42	294
	3-Aug-05	35	649	367	6.79	265
	18-Aug-05	33.3	732.5	6600	7.22	282
	Mean	35.3		2340.8	7.14	280.3

WF5	20-Jul-05	31	TNTC	42.3	7.53	377
	3-Aug-05	34	654.5	235	6.91	424
	18-Aug-05	31.2	1550	440	7.43	405
	Mean	32.1		239.1	7.29	402

sample	Date	DO (mg/L)	Turbidity (NTU)	Temperature ('C)	Salinity (%)	Alkalinity (mg/L)	Ammonia (ppm)	Nitrite (mg/L)
WF1	20-Jul-05	7.76	65	17.5	0.01	5	0	0.02
	3-Aug-05	8.13	2	14.3	0.01	14	0	0.02
	18-Aug-05	6.81	7	15.6	0.01	14	0	0.02
	Mean	7.57	24.7	15.8	0.01	11	0	0.02
WF2	20-Jul-05	7.04	6	22.8	0.02	9	0	0.02
	3-Aug-05	6.91	0	18.1	0.01	13	0	0.03
	18-Aug-05	6.96	6	19.2	0.02	8	0	0
	Mean	6.97	4	20	0.02	10	0	0.02
WF3	20-Jul-05	8.5	6	20.5	0.01	5	0	0.05
	3-Aug-05	8.7	0	16	0.01	11	0	0.02
	18-Aug-05	7.72	3	18.1	0.01	23	0	0.03
	Mean	8.31	3	18.2	0.01	13	0	0.03
WF4	20-Jul-05	9.2	50	17.1	0.01	6	0	0.04
	3-Aug-05	7.62	0	16	0.01	39	0	0.04
	18-Aug-05	8.48	1	17.5	0.01	95	0	0.04
	Mean	8.43	17	16.9	0.01	46.7	0	0.04
WF5	20-Jul-05	8.83	13	19	0.01	9	0	0.04
	3-Aug-05	8.56	0	15.7	0.01	18	0	0.04
	18-Aug-05	8.46	0	17.5	0.01	5	0	0
	Mean	8.62	4.3	17.4	0.01	10.7	0	0.03

		Chloride	Flow					
sample	Date	(mg/L)	(m <sup>3</sup> /s)	Li (ppb)	Be (ppb)	B (ppb)	Mg (ppb)	Al (ppb)
WF1	20-Jul-05	93.7	1.72	1.7	<0.15	<101.8	1455.5	278
	3-Aug-05	107.5	0.54	1.15	<0.15	<97.67	1868.8	60.9
	18-Aug-05	110.5	0.48	1.25	<0.14	12.39	1712.5	99.7
	Mean	103.9	0.91	1.37	0.07	37.38	1678.94	146.19
WF2	20-Jul-05	15.5	0.01	1.82	<0.14	<96.49	1473.8	55.9
	3-Aug-05	137.2	0.05	1.72	<0.14	<97.17	1286.4	85.2
	18-Aug-05	172.7	N/A	<1.02	< 0.17	7.46	1541.8	69.6
	Mean	108.5	0.03	1.35	0.08	34.76	1434.0	70.2
WF3	20-Jul-05	95.3	1.5	0.99	<0.15	<98.47	1670.4	66.2
	3-Aug-05	118.1	0.88	13.31	0.15	<96.66	2034.5	36.4
	18-Aug-05	115.4	0.66	< 0.84	<0.14	10.66	1870.9	42.0
	Mean	109.6	1.01	4.91	0.1	36.08	1858.6	48.2
WF4	20-Jul-05	110.7	0.37	1.54	0.32	<100.08	2015.4	61.5
	3-Aug-05	117.9	0.34	1.24	<0.15	<99.35	1754.7	47.0
	18-Aug-05	111.8	0.49	1.25	<0.15	10.38	1643.9	60.1
	Mean	113.5	0.4	1.34	0.16	36.7	1804.7	56.2
WF5	20-Jul-05	108.5	0.84	1.06	<0.15	<98.71	1592.6	68.0
	3-Aug-05	122.3	0.78	1.00	<0.14	<95.56	1776.2	37.0

18-Aug-05	114.7	0.86	<1.04	<0.18	14.27	1565.1	84.5	
Mean	115.2	0.83	0.86	0.08	37.14	1644.7	63.2	

sample	Date	Si (ppb)	P (ppb)	S (ppb)	CI (ppb)	Ca (ppb)	Ti (ppb)	V (ppb)
WF1	20-Jul-05	1375	<1308	<15764	93025.5	8435	6.34	<1.51
	3-Aug-05	1855	<1264	<15232	114685	10938	2.25	<1.46
	18-Aug-05	1865	<2239	<5328	95759.5	11245.5	5.62	1.13
	Mean	1698.45	801.8	6054	101156.5	10206.1	4.74	0.87
WF2	20-Jul-05	675	<1248	<15047	155328	7682	1.73	<1.44
	3-Aug-05	665	<1257	<15154	132940	6752	1.76	<1.45
	18-Aug-05	603	<2718	<6537	151517	7821	1.67	1.55
	Mean	648	870.5	6123	146595	7418	1.72	1
WF3	20-Jul-05	1608	<1274	<15357	98631	9050	2.17	<1.47
	3-Aug-05	1999	<1251	16378	119785	10918	1.86	<1.45
	18-Aug-05	1844	<2243	<5395	101130	10628	1.55	1.30
	Mean	1817	794.7	8918	106515	10199	1.86	0.92
WF4	20-Jul-05	2026	<1295	24483	134345	11191	2.55	<1.50
	3-Aug-05	1885	<1285	<15494	118427	10118	1.93	<1.49
	18-Aug-05	2363	<2315	6728	95972	10279	2.69	1.30
	Mean	2091	815.8	12986	116248	10529	2.39	2.8
WF5	20-Jul-05	1527	<1277	<15395	101900	9277	2.56	<1.48
	3-Aug-05	1801	<1236	<14902	119681	10279	1.80	<1.43
	18-Aug-05	1634	<2777	<6678	120524	9467	3.06	0.66
	Mean	1654	881.7	6162.5	114035	9675	2.47	0.71

sample	Date	Cr (ppb)	Mn (ppb)	Fe (ppb)	Co (ppb)	Ni (ppb)	Cu (ppb)	Zn (ppb)
WF1	20-Jul-05	4.39	588.32	1941	2.01	<16.54	9.64	111.22
	3-Aug-05	0.87	256.07	598	0.45	<15.98	2.35	22.18
	18-Aug-05	1.59	194.1	680.5	0.36	<3.76	5.42	<37.65
	Mean	2.28	346.16	1073.23	0.94	6.05	5.8	50.74
WF2	20-Jul-05	1.36	459.40	1148	0.36	<15.79	11.22	153.48
	3-Aug-05	1.42	439.46	1047	0.67	<15.90	10.15	156.06
	18-Aug-05	2.84	318.58	1400	0.47	<4.11	32.94	<45.70
	Mean	1.87	405.81	1198	0.50	5.97	18.10	110.8
WF3	20-Jul-05	1.22	125.00	340	0.29	<16.11	6.20	33.71
	3-Aug-05	0.65	74.04	274	0.20	<15.82	4.49	50.64
	18-Aug-05	0.97	55.33	208	0.15	<3.28	3.67	<37.72
	Mean	0.95	84.79	274	0.21	5.87	4.79	34.4
WF4	20-Jul-05	0.81	66.74	474	0.25	<16.38	5.17	32.71
	3-Aug-05	0.59	69.93	297	0.21	<16.26	5.71	57.71
	18-Aug-05	0.86	29.52	293	<0.13	<3.76	3.35	<38.92
	Mean	0.76	55.40	355	0.18	6.07	4.74	36.63
WF5	20-Jul-05	0.73	94.58	440	0.27	<16.15	5.48	24.76
	3-Aug-05	0.52	110.52	334	0.19	<15.64	2.56	23.12
	18-Aug-05	0.86	59.98	329	0.16	<4.31	3.06	<46.68
	Mean	0.71	88.36	368	0.21	6.02	3.70	23.74

sample	Date	As (ppb)	Br (ppb)	Se (ppb)	Rb (ppb)	Sr (ppb)	Mo (ppb)	Ag (ppb)
WF1	20-Jul-05	0.63	181.53	<0.74	1.35	36	0.26	<0.02
	3-Aug-05	0.36	294.31	< 0.73	0.98	45	0.18	0.03
	18-Aug-05	<0.54	2666.66	<2.7	1.25	51	0.36	< 0.05
	Mean	0.42	1047.5	0.7	1.19	44	0.26525	0.02
WF2	20-Jul-05	0.66	66.07	<0.69	1.75	47	0.16	0.03
	3-Aug-05	0.72	98.68	<0.70	2.06	40	0.13	<0.02
	18-Aug-05	< 0.69	<382.41	< 0.90	1.87	47	0.34	< 0.07
	Mean	0.58	118.65	0.38	1.89	45	0.21	0.03
WF3	20-Jul-05	0.34	94.67	<0.70	1.21	44	<0.11	<0.02
	3-Aug-05	0.37	163.94	<0.70	1.13	55	0.15	< 0.02
	18-Aug-05	<0.55	<315.61	<0.80	1.12	50	0.31	<0.06
	Mean	0.33	138.81	0.37	1.16	50	0.17	0.02
WF4	20-Jul-05	0.41	398.06	<0.77	1.15	44	0.15	0.03
	3-Aug-05	0.27	203.75	<0.73	1.11	43	<0.12	<0.02
	18-Aug-05	<0.56	1673.05	<1.94	1.23	45	0.30	<0.06
	Mean	0.32	758.29	0.57	1.16	44	0.17	0.02
WF5	20-Jul-05	0.33	481.67	<0.77	1.09	41	0.19	<0.02
	3-Aug-05	0.26	187.47	<0.70	0.97	44	<0.11	<0.02
	18-Aug-05	<0.67	<390.66	<1.07	1.16	40	0.29	<0.07
	Mean	0.31	288.16	0.42	1.07	41	0.18	0.02

sample	Date	Cd (ppb)	Sn (ppb)	Sb (ppb)	I (ppb)	Cs (ppb)	Ba (ppb)	La (ppb)
WF1	20-Jul-05	<0.11	0.23	0.21	9.6	0.06	33.54	0.91
	3-Aug-05	<0.11	0.28	0.11	10.75	0.04	24.96	0.26
	18-Aug-05	<0.07	0.52	0.14	13.67	0.06	28.64	0.33
	Mean	0.05	0.34	0.15	11.34	0.05	29.05	0.5
WF2	20-Jul-05	<0.11	0.17	0.06	7.15	0.05	53.87	0.40
	3-Aug-05	<0.11	0.21	0.10	9.30	0.05	45.67	0.43
	18-Aug-05	<0.09	0.66	0.08	11.34	0.06	44.46	0.42
	Mean	0.05	0.35	0.08	9.26	0.05	48.00	0.42
WF3	20-Jul-05	<0.11	0.15	0.14	7.69	0.05	14.57	0.30
	3-Aug-05	<0.11	0.17	0.13	9.25	0.05	124.71	0.18
	18-Aug-05	<0.07	0.44	0.14	10.84	0.05	11.92	0.15
	Mean	0.05	0.25	0.13	9.26	0.05	50.40	0.21
WF4	20-Jul-05	<0.11	0.23	0.12	10.24	0.05	24.86	0.29
	3-Aug-05	<0.11	0.25	0.11	9.94	0.04	29.15	0.23
	18-Aug-05		0.42	0.16	13.95	0.05	20.20	0.20
	Mean	0.05	0.30	0.13	11.38	0.05	24.74	0.24
WF5	20-Jul-05	<0.11	0.23	0.11	9.95	0.06	20.32	0.29
	3-Aug-05	<0.11	0.17	0.08	9.61	0.04	18.20	0.19
	18-Aug-05	<0.09	0.74	0.15	11.52	0.05	13.21	0.25
	Mean	0.05	0.38	0.11	10.36	0.05	17.25	0.24

sample	Date	Ce (ppb)	Hg (ppb)	TI (ppb)	Pb (ppb)	Bi (ppb)	U (ppb)
WF1	20-Jul-05	1.83	<0.07	0.02	4.05	0.04	0.03

	3-Aug-05 18-Aug-05	0.48 0.65	<0.07 <0.04	0.01 0.26	0.47 0.88	<0.01 0.03	0.01 0.01
	Mean	0.99	0.03	0.1	1.8	0.03	0.02
WF2	20-Jul-05	0.56	<0.07	0.01	1.95	<0.01	<0.01
	3-Aug-05	0.89	<0.07	<0.01	2.06	<0.01	0.01
	18-Aug-05	0.84	<0.04	0.33	1.86	<0.01	0.06
	Mean	0.76	0.03	0.12	1.96	0.01	0.03
WF3	20-Jul-05	0.38	<0.07	0.01	0.94	0.01	0.01
	3-Aug-05	0.21	<0.07	0.02	0.79	<0.01	0.01
	18-Aug-05	0.21	<0.04	0.27	0.64	<0.01	0.01
	Mean	0.27	0.03	0.10	0.79	0.01	0.01
WF4	20-Jul-05	0.34	<0.07	0.02	0.49	0.02	<0.01
	3-Aug-05	0.37	<0.07	<0.01	0.61	<0.01	<0.01
	18-Aug-05	0.37	<0.04	0.26	0.78	<0.01	0.01
	Mean	0.36	0.03	0.1	0.63	0.01	0.01
WF5	20-Jul-05	0.47	<0.07	0.01	0.99	0.01	0.01
	3-Aug-05	0.30	<0.07	0.02	0.36	<0.01	<0.01
	18-Aug-05	0.46	<0.05	0.29	0.87	<0.01	0.01
	Mean	0.41	0.03	0.11	0.74	0.01	0.01

# 8.1 Appendix B

The results obtained from the ICP-MS tests performed on the Waterford River sediment samples are listed in the following tables. Duplicate sample tests are indicated in the first column of each table with a star (\*). All values are in ppm.

Name	Ca	Ti	٧	Cr 52 (+)	Cr 53 (-)	Fe 54	Mn
Limit of Detection	71	0.926	0.164	0.324	0.329	99	3.404
WATERFORD SED 1	5703	3208.904	66.219	37.181	98.973	45407	5725.937
WATERFORD SED 2	2088	3636.458	70.960	32.628	107.137	52355	4514.601
WATERFORD SED 2*	2667	3525.127	69.451	31.806	103.562	52532	4499.660
WATERFORD SED 3	10632	3080.730	70.383	72.312	125.024	37958	5001.402
WATERFORD SED 4	19119	2797.593	66.462	242.712	293.927	40494	10288.482
WATERFORD SED 5	7481	2624.029	59.831	82.069	140.426	44297	12560.375
WATERFORD SED 5*	7538	2682.756	61.433	84.444	125.738	45710	12911.775
BK	32	0.616	0.118	5.409	5.345	440	-0.360

	Ī						
Name	Fe 57	Co	Ni	Cu	Zn	As	Se 77
Limit of Detection	29	0.047	0.184	0.120	2.329	0.227	0.828
WATERFORD SED 1	44725	30.523	26.884	40.305	287.927	9.163	2.300
WATERFORD SED 2	53034	20.352	20.638	33.687	180.307	11.048	6.147
WATERFORD SED 2*	51025	19.671	19.881	32.971	174.718	10.488	4.069
WATERFORD SED 3	38378	18.082	65.081	50.070	429.511	5.632	3.751
WATERFORD SED 4	40222	38.534	129.531	53.603	411.229	11.724	5.733
WATERFORD SED 5	41983	36.586	28.632	91.767	696.454	11.393	5.008
WATERFORD SED 5*	42840	37.006	28.678	91.947	713.208	11.782	3.045
BK	19	0.184	3.349	20.868	5.500	-0.098	0.197

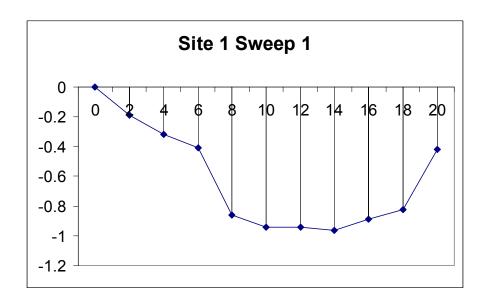
Name	Se 82	Br 79	Мо	Ag 107	Ag 109	Cd	Sn
Limit of Detection	2.319	233.527	0.311	0.020	0.010	0.160	0.023
WATERFORD SED 1	966.950	231.553	3.634	0.305	0.183	0.639	24.966
WATERFORD SED 2	823.800	218.741	2.584	0.332	0.161	0.400	9.898
WATERFORD SED 2*	793.857	222.282	2.917	0.337	0.158	0.478	9.528
WATERFORD SED 3	1639.158	597.439	3.339	0.915	0.795	0.671	122.123
WATERFORD SED 4	3340.785	1223.573	6.764	0.304	0.208	0.789	370.844
WATERFORD SED 5	791.918	236.131	4.347	0.262	0.168	0.991	13.673
WATERFORD SED 5*	573.823	173.915	4.540	0.253	0.144	1.222	13.379
BK	1900.945	219.929	-0.121	0.021	0.022	-0.062	2.468

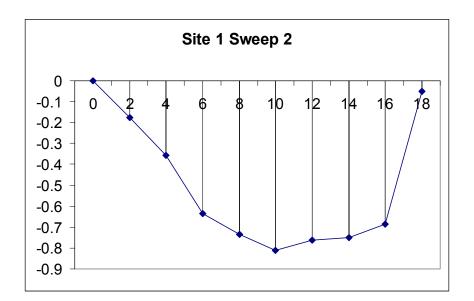
Name	Sb	Te	I	La	Ce	Pr	Nd
Limit of Detection	0.037	0.243	1.530	0.013	0.006	0.009	0.065
WATERFORD SED 1	0.998	-0.419	7.552	34.118	74.878	8.704	34.508
WATERFORD SED 2	0.659	-0.055	7.936	32.226	72.199	8.243	31.824
WATERFORD SED 2*	0.680	0.089	9.547	32.764	70.629	8.104	30.668
WATERFORD SED 3	1.177	0.468	12.166	25.816	51.583	6.505	25.661
WATERFORD SED 4	1.128	-0.379	26.712	25.925	62.473	6.456	25.964
WATERFORD SED 5	1.559	-0.150	7.307	32.285	66.693	7.982	31.982
WATERFORD SED 5*	1.595	0.406	8.808	33.192	68.603	8.110	32.317
BK	0.019	0.174	-0.920	0.038	0.031	0.030	-0.016

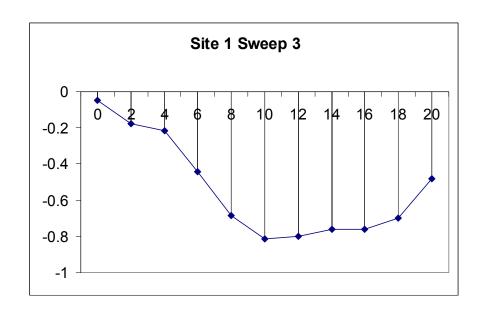
Name	Er	Tm	Lu	W	Hg	Pb	Bi	Th
Limit of Detection	0.026	0.003	0.015	0.000	0.008	0.543	0.004	0.061
WATERFORD SED 1	3.197	0.464	0.420	9.938	-0.022	47.673	0.248	7.231
WATERFORD SED 2	2.942	0.453	0.447	3.693	-0.010	31.087	0.373	9.085
WATERFORD SED 2*	2.980	0.449	0.439	3.809	-0.030	30.972	0.378	8.983
WATERFORD SED 3	2.614	0.379	0.352	9.342	-0.029	61.880	0.323	6.375
WATERFORD SED 4	3.041	0.409	0.393	6.251	-0.139	41.933	0.148	6.327
WATERFORD SED 5	2.983	0.429	0.388	7.889	-0.018	97.906	0.202	5.629
WATERFORD SED 5*	3.012	0.427	0.398	7.968	-0.035	98.608	0.213	5.793
BK	0.031	0.023	0.030	0.165	0.003	-0.580	0.032	0.048

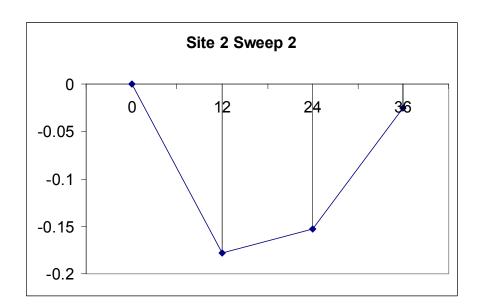
# 8.2 Appendix C

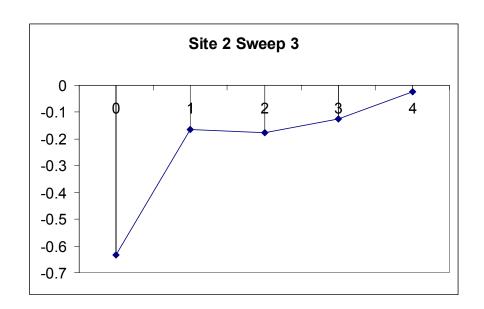
Depth profiles for each site along the Waterford with respect to each sweep are displayed in the following diagrams. The "x" regions show the widths of the river (in feet), and the "y" regions show the depths of the river (in metres). Although both are listed in different units, due to the nature of the diagram, the depths and widths are still proportional to each other. Some minor distortions resulting from the resizing of graphs during the input from one program to another may have occurred. Each profile represents the area of each specific section of stream measured along its width at a given point.

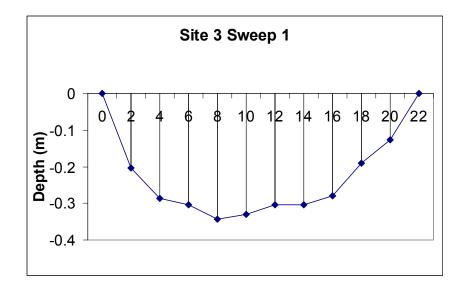


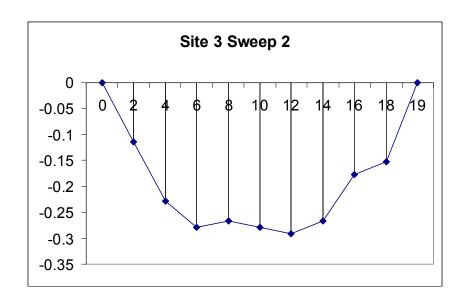


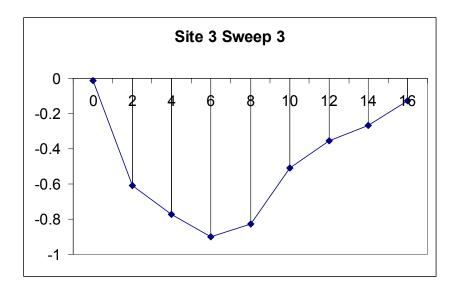


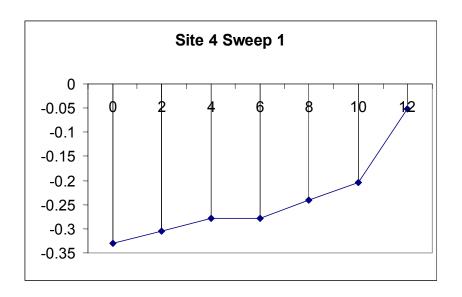


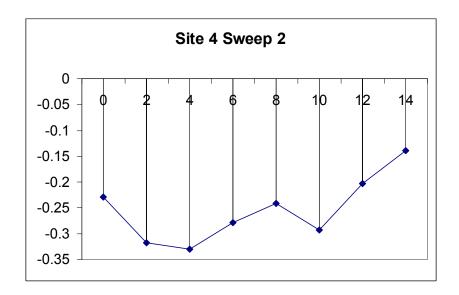


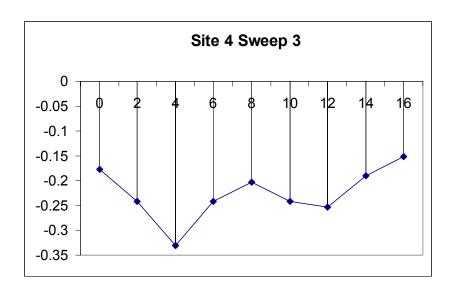


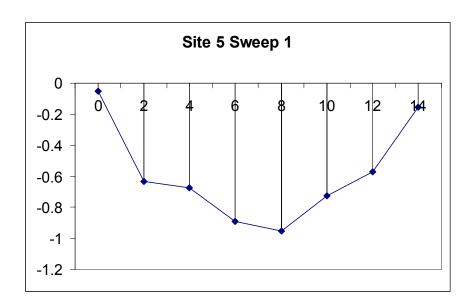


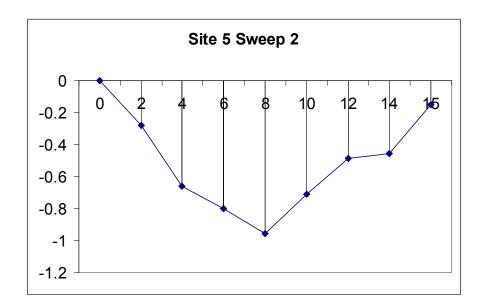


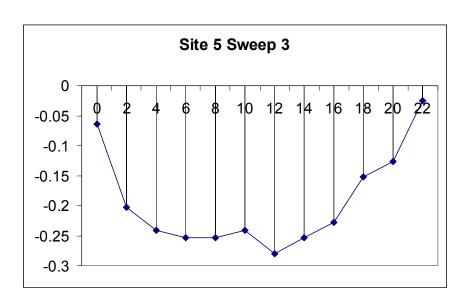












# 8.3 Appendix D

# **Procedure for Solids Analysis**

## Part I: Preparation

- 1. Pre-dry the crucible dishes, filters (Whatman #1) and filter dishes in an oven at  $\sim$ 40 50°C for about 30 minutes.
- 2. Cool dishes and filters for a few minutes and gravimetrically weigh them.
- 3. Assign a sample number to each crucible and filter.
- 4. Filter 50ml amounts of the samples using a suction hose apparatus and rinse everything down with deionised water. Let the samples filter for a few minutes.
- 5. Put the filter back on the silver filter dish and transfer the filtrate to the crucible.
- 6. Place filters in oven at 70 90°C to dry, note their location in the oven so they are not mixed up later.
- 7. Place crucibles in muffle furnace at low heat ( $\sim 100 110$ °C) to evaporate all of the water in them. Note their location so they will not be mixed up later.

### Part II: TSS

- 1. When filters have dried fully, let them cool and then gravimetrically weigh them. The increase in mass, calculated as the difference between the initial and final weight, is the concentration of total suspended solids (TSS) per 50ml.
- 2. Record this weight.

### Part III: TDS

- 1. When all water in the crucibles have evaporated, let them cool and then gravimetrically weigh them. The increase in mass, calculated as the difference between the initial and final weight, is the concentration of total dissolved solids (TDS) per 50ml.
- 2. Record this weight.

### Part III: VOC

1. Place the weighed crucibles back in the muffle furnace and set the temperature to about 550°C. Keep them in for a minimum of one hour (maybe two hours) or until all of the organic content has volatilized off the sample.

- 2. Remove the crucibles carefully (very hot), and let them cool for 30-35 minutes.
- 3. Re-weigh the crucibles and record the new weight. The decrease in mass, calculated as the difference in the weight of the crucible with the TDS and the final weight of the crucible, is the concentration of the volatile organic content (VOC) per 50ml.
- 4. Record this weight.

To get concentrations in mg/L just multiply result ( $\chi$ ) by 20,000

$$\chi [g/50ml] \rightarrow (20 ml/L * [50ml] * 1000mg/g)$$

# 8.4 Appendix E

# **Procedure for Kjeldahl Analysis**

Do each sample in duplicate.

Remember, meticulous cleaning of all glassware is essential.

# Part I: Preparation/Digestion

- 1. Weigh between 0.2 and 0.3 grams of sample (usually 6 to 7 drops) on a tared weigh boat.
- 2. Do the same with nanopure water for a blank.
- 3. Put the weighed sample or blank in a labeled Kjeldahl tube and re-weigh the boat. Subtract the difference and that is the weight of the sample used.
- 4. Record this value.
- 5. To each tube with sample, add one Kjeltab catalyst tablet.
- 6. To each tube with catalyst and sample or blank, add 20ml of concentrated sulphuric acid via Brinkman dispenser.
- 7. Digest the samples and blank in the digestion unit for about 30 minutes, or until the liquid becomes a pale yellowish colour (maybe 45 minutes).
- 8. Let the digested samples and blank cool for at least 15 minutes (probably a little more).
- 9. Prepare 250ml Erlenmeyer flasks for samples and blank by adding 25ml of 4% (w/v) boric acid solution + methyl red/methylene blue indicator to each.

### Part II: Distillation

- 1. When the samples and blank have cooled, add about 75ml of nano or deionised water to each tube.
- 2. Turn on distillation unit as per instructions on machine.
- 3. Properly insert tube with digested sample or blank in the left socket, and place the associated flask with boric acid and indicator on the right platform.
- 4. Make sure the plastic distillation tubes are in the digestion tube and flask below the surface of the solutions.
- 5. With the steam off, add two pumps of alkali (NaOH) solution to the tube and turn the steam back on.

Careful: make sure the platform is in the "up" position on the left side (best to hold it up) while pumping in the NaOH; otherwise it may spray out of the tube.

6. Distil the sample or blank until 150ml of condensate is collected in the flask. Remove the flask while simultaneously rinsing the exterior of the plastic tube into the flask with deionised water.

# Part III: Titration

- 1. Titrate the condensate in the flask with 0.1N HCl to a purple/red endpoint *(careful, it may not take much)*. It might go from light green to brown to red.
- 2. Record the final volume of titrant used.

# 8.5 Appendix F

# **Procedure for M-coli Blue Test**

### Do in triplicate

- 1. Sterilise the work area, filtration units, and glass tubes.
- 2. Place a sterile membrane filter on the filtration apparatus and securely attach the glass tubes with the clamps.
- 3. Turn on water for suction into the filtration unit.
- 4. Pour 100 ml of sample into each tube and open suction valves.
- 5. Rinse the sample bottles with clean water and add the rinse to the tubes. Wash the sides of the tubes with clean water from a squirt bottle.
- 6. When all water has been filtered, remove the tube, place the filter on a pad in an incubation dish with sterilized tongs, and add the M-coli blue solution.
- 7. Make sure the dishes have been labeled properly, and place them in an incubator at 37.5°C for 20 30 hours.
- 8. Properly clean and sterilise equipment and workspace.
- 9. Remove the dishes from the incubator when it is time, and count the colonies under a magnifying light plate. The red colonies are non-fecal coliforms, and the blue colonies are *E. coli*.

### To make a 1:10 dilution:

- 1. Remove 10 ml of sample with a sterile pipette and add it to 90 ml of clean water.
- 2. Add this dilution to the tube and filter.