Annapolis River 2005 Annual Water Quality Monitoring Report

including results from the

Annapolis River Guardians Volunteer Water Quality Monitoring Program

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This report is available electronically at *www.annapolisriver.ca*

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Executive Summary

In 2005, the Annapolis River Guardians completed their 14th year of continuous water quality monitoring on the Annapolis River. Eleven volunteers monitored eight sites over the course of the season, which ran from April to October. A number of parameters were measured, including dissolved oxygen, fecal coliform bacteria, E.coli bacteria, nitrate-nitrogen, phosphorus, chloride, sulphate, air and water temperature, pH and conductivity, as well as local weather conditions.

Fecal bacteria levels along the Annapolis River during 2005 were generally lower than those observed in 2004. Although bacteria levels continued to be highly variable, there was a uniform decrease in the proportion of samples which exceeded key water quality thresholds of 50, 100 and 200 colony forming units (cfu) per 100 ml. Of the 149 fecal bacteria samples collected and analyzed, 14% (21) exceeded the contact water recreation guideline of 200 cfu/100ml. This compared favourably with the 2004 results, where 37% of samples exceeded this threshold. During 2005, of the 21 samples with fecal bacteria greater than 200 cfu/100 ml, 8 (38%) were collected at the Aylesford sample station. In 2005, water samples were collected at an additional monitoring station in the Aylesford area at Victoria Road. The comparison of monitoring results from this and the nearby, existing Aylesford station, has provided a number of useful insights into the nature of fecal contamination in this area.

Dissolved oxygen levels during 2005 remained within their normal range for much of the Annapolis River. Over 14 years of monitoring, mean dissolved oxygen saturation (DOSAT) levels have remained in the range of 80-94%. In 2005, the mean DOSAT level was just under 87%. As a result of the regular monitoring provided by the Annapolis River Guardian program, unusually low DO values (3.8 mg/L) were detected at Bridgetown in September. DO levels were sufficiently low so as to cause stress to aquatic life, including fish. Subsequent investigation revealed an extensive oxygen-depleted zone in the lower Annapolis River.

The mean summer water temperature for the Annapolis River during 2005 was 20.0ºC or 1.4ºC warmer than for the same period in 2004. As in previous years, water temperatures during 2005 continued to reach levels stressful to aquatic life regularly during the summer months. The Aylesford, Middleton, Lawrencetown and Paradise stations recorded the warmest summer water temperatures.

A limited nutrient monitoring program was undertaken in 2005. Sample analyses for nitrate-N were found to be in the range of 0.22 to 0.64 mg/L These results are similar to those observed in 2004. Of the 15 phosphorus samples collected in 2005, 10 (67%) were at or above the 0.030 mg/L water quality guideline level.

The pH levels at each of the River Guardians sites were consistently within the recommended range for the protection of aquatic life (6.5-9.0). When the 2005 results were compared with those recorded in 2003 and 2004 though, a statistically significant downward shift was observed. While the cause of this downward shift of pH during 2005 is unknown, it was observed uniformly across the eight monitoring stations, throughout the 2005 season.

Split and blank water samples were analysed during 2005 as part of CARP's Quality Assurance Project Plan. The accuracy of River Guardian dissolved oxygen readings were estimated at +/- 0.32mg/L, compared with 0.85 mg/L recorded in 2004. Field and travel blank samples analysed for fecal coliforms consistently produced plates with 0 cfu/100ml.

Introduction

History

The Annapolis River Guardians volunteer monitoring program began collecting water quality data in the Annapolis River watershed in 1992. The Clean Annapolis River Project (CARP) initiated the program as a public awareness project, and has had numerous volunteer sample collectors over the years. It is one of the longest running and most extensive volunteer based water quality programs in Eastern Canada. It is also CARP's longest running and only on-going project. At least 90 volunteers from the Annapolis Valley community have participated in the program over the years, with over 3500 water samples being collected and analyzed.

The program was initiated in the early 1990's by Dr. Graham Daborn and Dr. Mike Brylinsky of the Acadia Centre for Estuarine Research. Many groups were involved in the planning process for the program, including staff with the Nova Scotia Department of Health, the Nova Scotia Department of Environment, Nova Scotia Community College, and CARP. Although the program has undergone slight changes over the last ten years, the core program has remained the same.

The initial program design called for 11 sites to be monitored by 17 volunteers. The initial response from the community was excellent and the project was significantly expanded between 1992 and 1994. In 1994, 38 sites were monitored by 43 River Guardians from 36 households (Pittman *et al*/2001). This intensity of monitoring placed considerable strain on the capacity of CARP. While some of the initial enthusiasm surrounding the program has diminished, a core group of 10 to 15 dedicated volunteers has been maintained over the past number of years.

Program Objectives

The Annapolis River Guardians program has four objectives:

- To establish and support a regular observation system that provides an early warning of environmental problems.
- To provide a long-term record of the river's health.
- To develop interest in the Annapolis River and community stewardship to ensure a viable resource for future generations.
- To provide a knowledgeable group of local individuals who can promote the preservation, rehabilitation, and use of these aquatic resources in the future.

Overview of 2005 Monitoring Season

The 2005 monitoring season commenced on April 17 and concluded on October 30. Samples were collected fortnightly, with a total of approximately 120 sampling events during the season. Samples were analysed for a variety of parameters, including fecal coliform bacteria, E.coli bacteria, dissolved oxygen, temperature, nitrate-N, chloride, sulphate, total phosphate, pH and conductivity. Further information on the testing procedures can be found in Appendix A.

Eight stations were sampled along the Annapolis River. Further information on these sampling locations is contained in Appendix B. Figure 1 shows the Annapolis Watershed and the 2005 monitoring sites. The data collected by the volunteers is stored in an in-house Microsoft Access database, as well as a publicly accessible web-based, searchable, database at www.fundybay.com

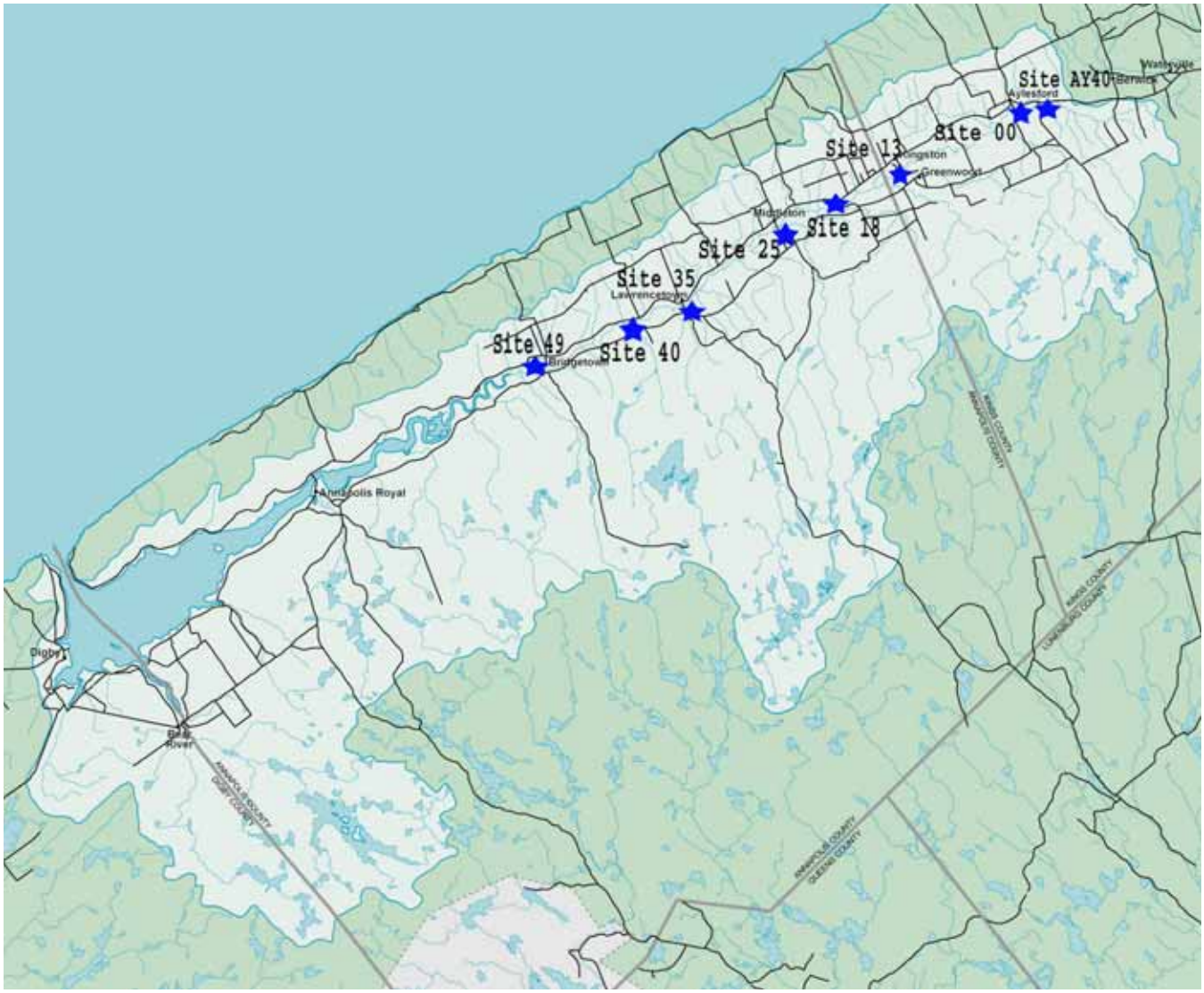

Figure 1. Annapolis Watershed with 2005 Monitoring Sites

The 2005 River Guardian sampling locations (with their identification numbers) were:

49 — Bridgetown	40 — Paradise	35 — Lawrencetown	25 — Middleton
18 — Wilmot	13 — Kingston	00 — Victoria Road, Aylesford	AY40 — Aylesford Road, Aylesford

2005 Monitoring Results

Fecal Coliform/E.coli Bacteria

Introduction

Fecal coliforms are rod-shaped, aerobic, lactose fermenting bacteria. They are gram-stain negative, thermotolerant and appear as dark blue colonies when cultured in the laboratory. Fecal matter of warm-blooded animals is the predominant source of fecal coliform bacteria. Because they occupy the same ecological niche as many human pathogens, fecal coliforms are used as indicators for the possible presence of other potentially dangerous pathogens. Fecal coliforms have been identified in the past as a major cause of concern in the Annapolis River watershed (Pittman *et al*/2001). The potential sources of fecal contamination in the watershed include central sewage treatment plants, malfunctioning on-site septic systems, aquatic wildlife (i.e. beavers, muskrats, waterfowl), domestic animals, and agricultural livestock.

Many factors in a particular ecosystem affect the abundance of fecal coliforms in rivers. These include the type of source, the transport mechanism with which the fecal coliform is deposited, and precipitation. The result is that fecal coliform densities in surface waters can be highly variable. Their survival in surface waters is not well understood, and is dependent on many factors. These include predation by other organisms, amount of sunlight, salinity of the water, temperature, as well as composition and abundance of sediment (Davies *et al*/1995). There is a range of estimates for the survival times of the commonly monitored fecal coliform, *Escherichia coli (E.coli)* in various media:

- Cow pats: 49 days at 37°C, 70 days at 5°C (also dependent on moisture content) (Chalmers *et al*/2000)
- Drinking water: Between 28 and 84 days (Edberg *et al*/2000)
- Soil Cores with grass roots: 130 days (Chalmers *et al*/2000)
- In situ Freshwater Sediment: 57 days (Davies *et al*/1995)

Spatial and temporal trends in fecal coliform data over the last fourteen years are analyzed below. Over the period of 1992 to 2005, numerous initiatives have been undertaken which have contributed to the improvement of water quality in the Annapolis River. For example, in the winter of 1994, 14 Wing Greenwood discontinued the discharge of untreated aircraft wash-water into a tributary of the Annapolis River. In August 1998, the base discontinued the operation of its own sewage treatment plant, redirecting its waste to the Greenwood municipal facility.

While the core River Guardian monitoring program has been maintained over the period of 1992 to 2005, a number of modifications have been made. For example, in 1996, the collection of fecal coliform samples was standardised to a fortnightly basis. During the period of 1997 to 2002, fecal coliform numbers were determined using the IDEXX Colilert procedure, which specifically identifies *E. coli*. With the change to a new laboratory, the 2003 and 2004 samples were analyzed using the Membrane Filtration procedure, which enumerates fecal coliforms (See Appendix A).

Prior to the start of the 2005 sampling season, the program's Science Advisory Committee advised that bacteria monitoring be switched from fecal coliforms to E.coli, to bring the program more in line with current guidance at a national level. To ensure the continuity of the historic dataset, it was decided to collect split samples for the first two months of the season, to allow parallel testing for fecal coliform and E.coli. This process confirmed that the two methods do not give statistically different results. Further information on the parallel testing and statistical analysis can be found in Appendix C. Samples were analyzed for E.coli for the remainder of the season, using the IDEXX Colilert

procedure. E.coli results are reported as Most Probable Number - colony forming units per 100 ml of sample (cfu/100 ml).

Canadian Water Quality Guidelines

Various governmental agencies have developed water quality guidelines to protect the safety of the general public. Health Canada is responsible for the guidelines for drinking and recreational waters. The Canadian Council of Ministers of the Environment (CCME) has incorporated these guidelines in the comprehensive Canadian Water Quality Guidelines (CCME 2002). CARP has summarized the guidelines for fecal coliform contamination into a concise table for public awareness purposes, shown in Table 1.

Table 1. Summary of Water Quality Guidelines for Fecal Coliforms

cfu/100ml	Water Use	Source
0	Acceptable for drinking	Health Canada, fecal coliforms/100ml.
< 50	Acceptable for livestock watering	Interpretation of CCME narrative "high-quality water given to livestock."
< 100	Acceptable for food crop irrigation	CCME Guidelines, cfu/100ml.
< 200	Acceptable for recreational use	Health Canada, Geometric Mean should not exceed 200 cfu/100 ml.

It should be noted that some guidelines are in maximum concentrations, while others are in geometric means over a period of time. Also, the numeric "50" in the table for acceptable livestock watering is based on total coliforms, rather than fecal coliforms.

Monitoring Results

The high variability of fecal bacteria measurements presents a number of challenges with respect to data analysis. Samples collected from a single site, on separate occasions, can vary by two and sometimes three orders of magnitude (e.g. 3 cfu per 100 ml to 3000 cfu per 100 ml). The use of standard data analysis methods, such as calculating and comparing mean values, inadequately describes the distribution of fecal bacteria results. The following analysis is therefore based on the proportion of samples analysed that exceed particular water quality thresholds. This approach was chosen as it best presents, to decision-makers and resource managers, whether the water at a site is unsuitable for particular uses.

While this approach eliminates the bias of calculating means with highly variable data, it presents another type of bias. If the majority of samples one year fall slightly below a guideline threshold (e.g. 200 cfu/100 ml), a small increase in fecal coliform concentration the next year may cause the proportion of samples above 200 cfu/100 ml to increase significantly. This would give the appearance that the water quality had worsened considerably, when in fact the mean coliform concentration may have only increased slightly. In order to ensure the differences observed in the following analysis are real, a box-whisker plot was prepared to compare the distribution of the 2004 and 2005 fecal bacteria results (See Figure 2). The box plot shows the 25th and 75th percentiles as well as the median for each site. The minimum and maximum results are also shown. The three water quality guidelines for fecal coliforms discussed in the report are shown as dotted lines at 50, 100, and 200 cfu/100ml. It is important to note that the y-axis of the graph is plotted using a logarithmic scale (Log Fecal Coliform).

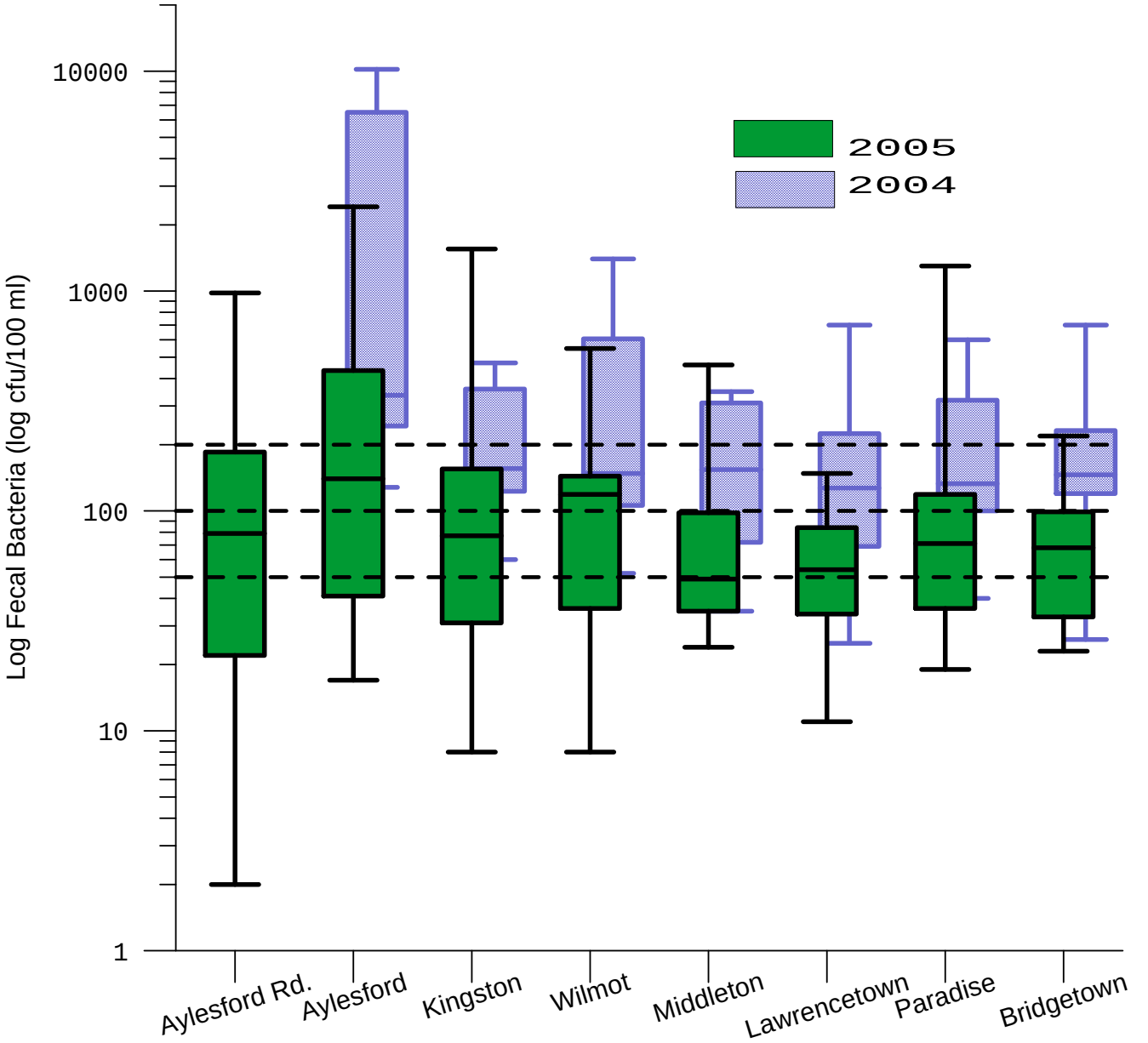

Figure 2. Box and Whisker Plot of Fecal Bacteria Results for 2004 and 2005

From Figure 2, it is evident that there has been a significant decrease in fecal bacteria counts between 2004 and 2005. Fecal bacteria levels are seen to be highly variable across most monitoring sites. The consistent trend in decreased fecal bacteria levels in 2005 is reflected in the median values. The Aylesford (Site 00) station had its median fecal bacteria value decrease from > 200 cfu/100 ml to the 100 to 200 cfu/100 ml range. The Kingston, Middleton, Lawrencetown, Paradise and Bridgetown monitoring sites had their median fecal bacteria values decrease from the 100 to 200 cfu/100 ml range, to the 50 to 100 cfu/100 ml range.

Table 2 presents the proportion of fecal bacteria samples exceeding 50 cfu/100 ml, the water quality guideline for livestock watering. For example, at Aylesford in 2005, 0.61 or 61% of water samples collected had fecal bacteria counts in excess of 50 cfu/100ml, as compared to 94% in 2004. From the data presented in Table 2, it is evident that all sites had a decrease in the number of samples that exceeded 50 cfu/100 ml.

Table 2. Proportion of Fecal Coliform Samples Exceeding 50 cfu/100 ml

	Aylesford Road	Aylesford	Kingston	Wilmot	Middleton	Lawrencetown	Paradise	Bridgetown
1992		1.00	0.33	1.00	1.00	1.00	1.00	
1993		0.91	0.79	0.81	0.86	0.93	0.86	
1994		0.83	0.73	0.88	0.91	0.81	0.86	0.92
1995		0.40	0.14			0.80	0.50	0.71
1996		0.50	0.80		0.75	0.93	0.75	0.80
1997		0.86	0.81	0.81	0.88	0.71	0.50	0.65
1998		0.92	0.75	0.40	0.50	0.55	0.60	0.75
1999		0.86	0.67	0.71	0.55	0.33	0.43	0.65
2000		0.60	0.53	0.45	0.46	0.50	0.57	0.36
2001		0.67	0.83	0.83	0.54	0.33	0.55	0.20
2002		1.00	0.53	0.64	0.38	0.38	0.20	0.60
2003		1.00	0.90	1.00	0.56	0.50	0.50	0.55
2004		0.94	0.93	1.00	0.85	0.79	0.86	0.86
2005	0.53	0.61	0.53	0.63	0.47	0.53	0.61	0.56

Table 3 presents the proportion of samples exceeding the water quality guideline for food crop irrigation (100 cfu/100 ml). Again in 2005, it is evident that there was a decrease in the number of fecal bacteria samples exceeding 100 cfu/100 ml for all monitoring sites, when compared with 2004. The 2004 and 2005 exceedences of this threshold are also compared in Figure 3.

Table 3. Proportion of Fecal Bacteria Samples Exceeding 100 cfu/100 ml

	Aylesford Road	Aylesford	Kingston	Wilmot	Middleton	Lawrencetown	Paradise	Bridgetown
1992		1.00	0.00	0.67	0.67	0.67	1.00	
1993		0.82	0.57	0.69	0.71	0.79	0.71	
1994		0.67	0.55	0.88	0.82	0.75	0.57	0.69
1995		0.40	0.14			0.80	0.50	0.57
1996		0.50	0.50		0.63	0.79	0.56	0.60
1997		0.71	0.44	0.69	0.63	0.36	0.14	0.53
1998		0.83	0.50	0.10	0.50	0.27	0.40	0.25
1999		0.71	0.53	0.43	0.45	0.00	0.29	0.41
2000		0.60	0.40	0.27	0.23	0.33	0.43	0.07
2001		0.56	0.42	0.50	0.31	0.08	0.45	0.13
2002		1.00	0.33	0.29	0.06	0.38	0.10	0.27
2003		0.70	0.80	0.45	0.33	0.29	0.25	0.36
2004		0.94	0.79	0.79	0.62	0.50	0.64	0.79
2005	0.42	0.50	0.47	0.58	0.21	0.21	0.28	0.11

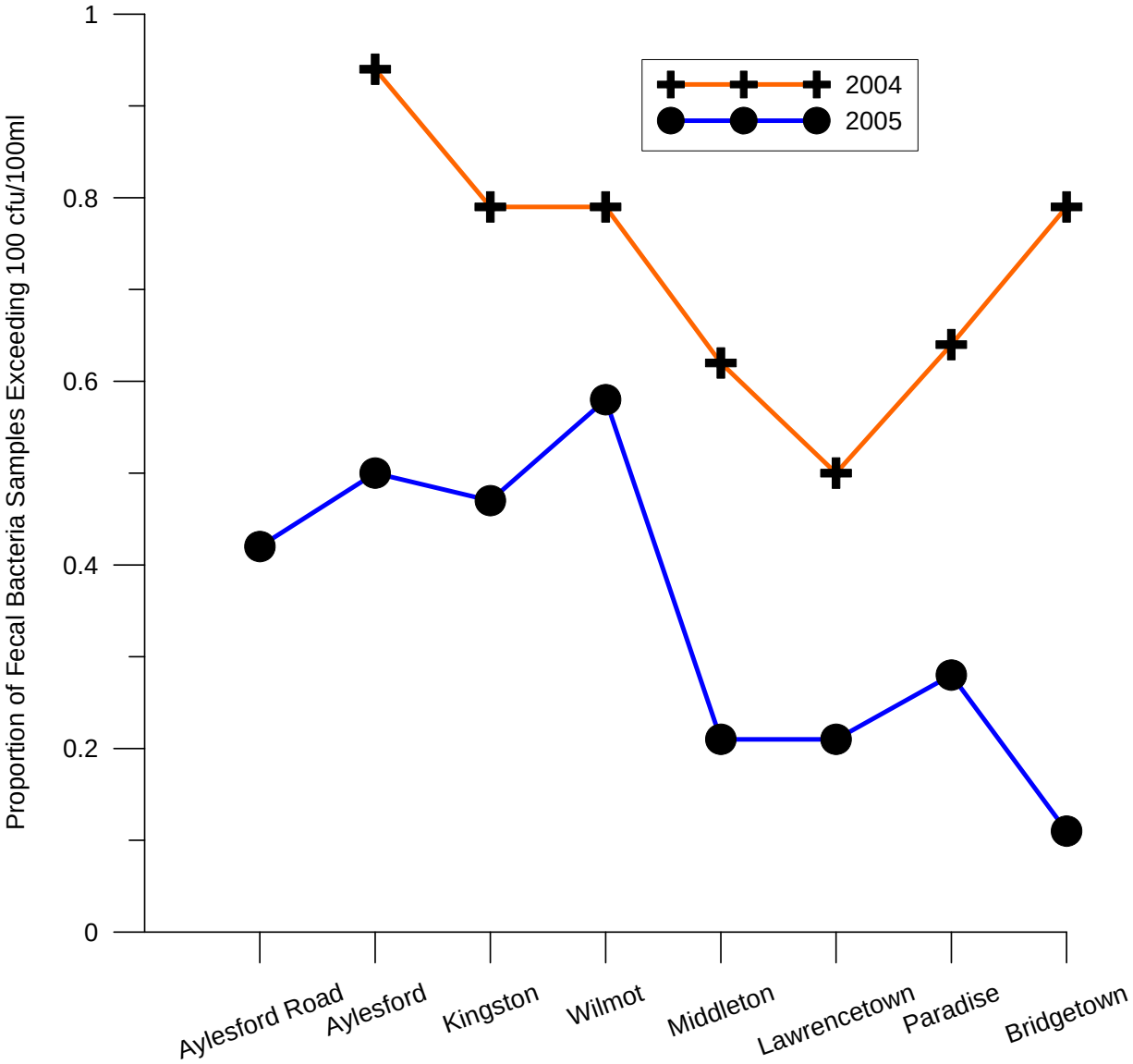

Figure 3. Proportion of Fecal Bacteria Samples Exceeding 100 cfu/100ml, 2004 and 2005.

As is evident is Figure 3, all monitoring sites exhibited a significant decrease in the number of samples exceeding 100 cfu/100ml in 2005 when compared to 2004. It should be noted that for most sites, fecal bacteria levels in 2004 were unusually high, with the 2005 results returning to more typical levels. The cause of the high fecal bacteria levels in 2004 is not fully understood.

Table 4 presents the proportion of fecal bacteria samples exceeding 200 cfu/100 ml, the water quality guideline for contact water recreation. The table shows a general decrease with respect to this threshold. Figure 4 presents the proportion of fecal bacteria samples collected at Aylesford that exceed 200 cfu/100 ml. Over 14 years of monitoring, the data from this site is observed to be highly variable, with the 2005 result returning to more typical values.

Table 4. Proportion of Fecal Bacteria Samples Exceeding 200 cfu/100 ml

	Aylesford Road	Aylesford	Kingston	Wilmot	Middleton	Lawrencetown	Paradise	Bridgetown
1992		0.50	0.00	0.67	0.67	0.33	0.33	
1993		0.55	0.21	0.50	0.29	0.57	0.36	
1994		0.50	0.55	0.56	0.55	0.31	0.57	0.46
1995		0.20	0.14			0.40	0.33	0.29
1996		0.50	0.40		0.38	0.43	0.44	0.40
1997		0.43	0.13	0.19	0.13	0.07	0.07	0.06
1998		0.58	0.13	0.00	0.25	0.09	0.20	0.08
1999		0.43	0.33	0.29	0.18	0.00	0.14	0.18
2000		0.40	0.07	0.18	0.15	0.25	0.43	0.00
2001		0.22	0.25	0.33	0.15	0.08	0.09	0.13
2002		0.50	0.13	0.14	0.00	0.00	0.00	0.13
2003		0.10	0.40	0.27	0.22	0.21	0.08	0.27
2004		0.71	0.36	0.21	0.23	0.29	0.43	0.29
2005	0.21	0.44	0.21	0.05	0.11	0.00	0.06	0.06

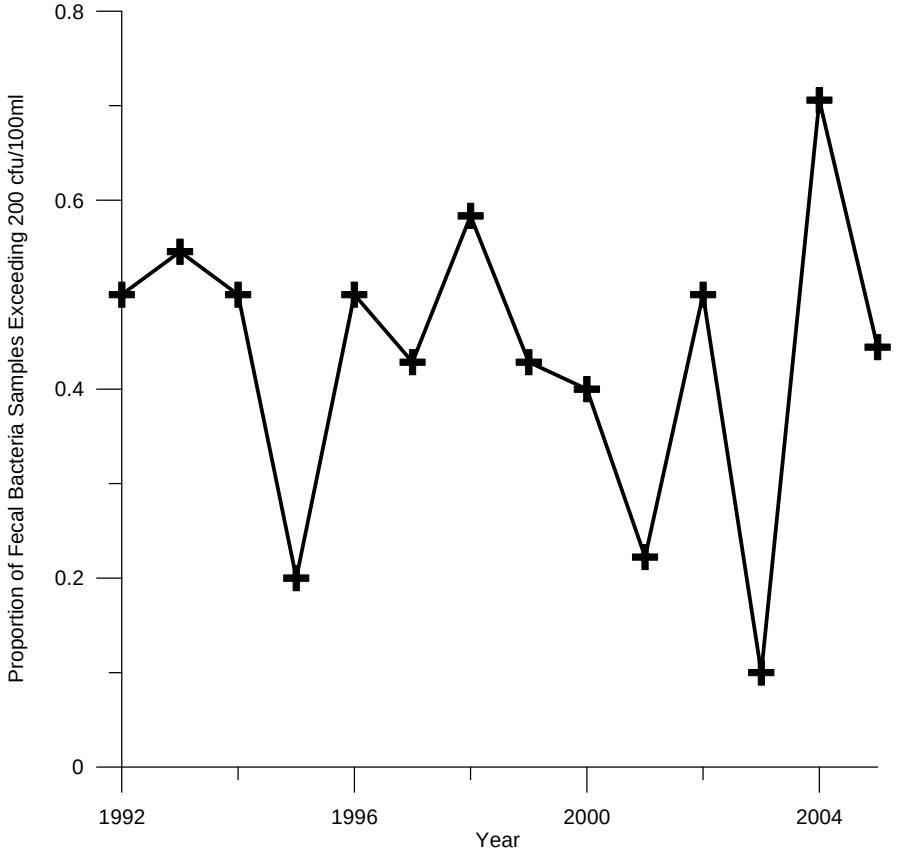

Figure 4. Proportion of Fecal Bacteria Samples Collected at Aylesford Exceeding 200 cfu/100 ml.

During the summer of 2003, CARP staff undertook a survey of tributaries to the Annapolis River in the Aylesford area, as part of the larger Aylesford East Project, to identify watercourses with impaired water quality (Sharpe & Sullivan 2004). A number of tributaries were identified as having elevated fecal coliform and nutrient levels, including Patterson, Parker

and Skinner Brooks. These tributaries originate on the North Mountain and enter the Annapolis River approximately 2km above the Aylesford River Guardian sample site (Site 00 – Aylesford).

During the 2005 monitoring season, an additional monitoring site was added (Site AY40) at Aylesford Road, approximately 2.5 km upstream of the Site 00 Aylesford location. The purpose of this was to collect regular samples above and below the mouth of the above brooks, to assess if there was a significant difference in fecal bacteria results. Figure 5 presents the monitoring results for the AY40 (Aylesford Road) and 00 (Aylesford) locations.

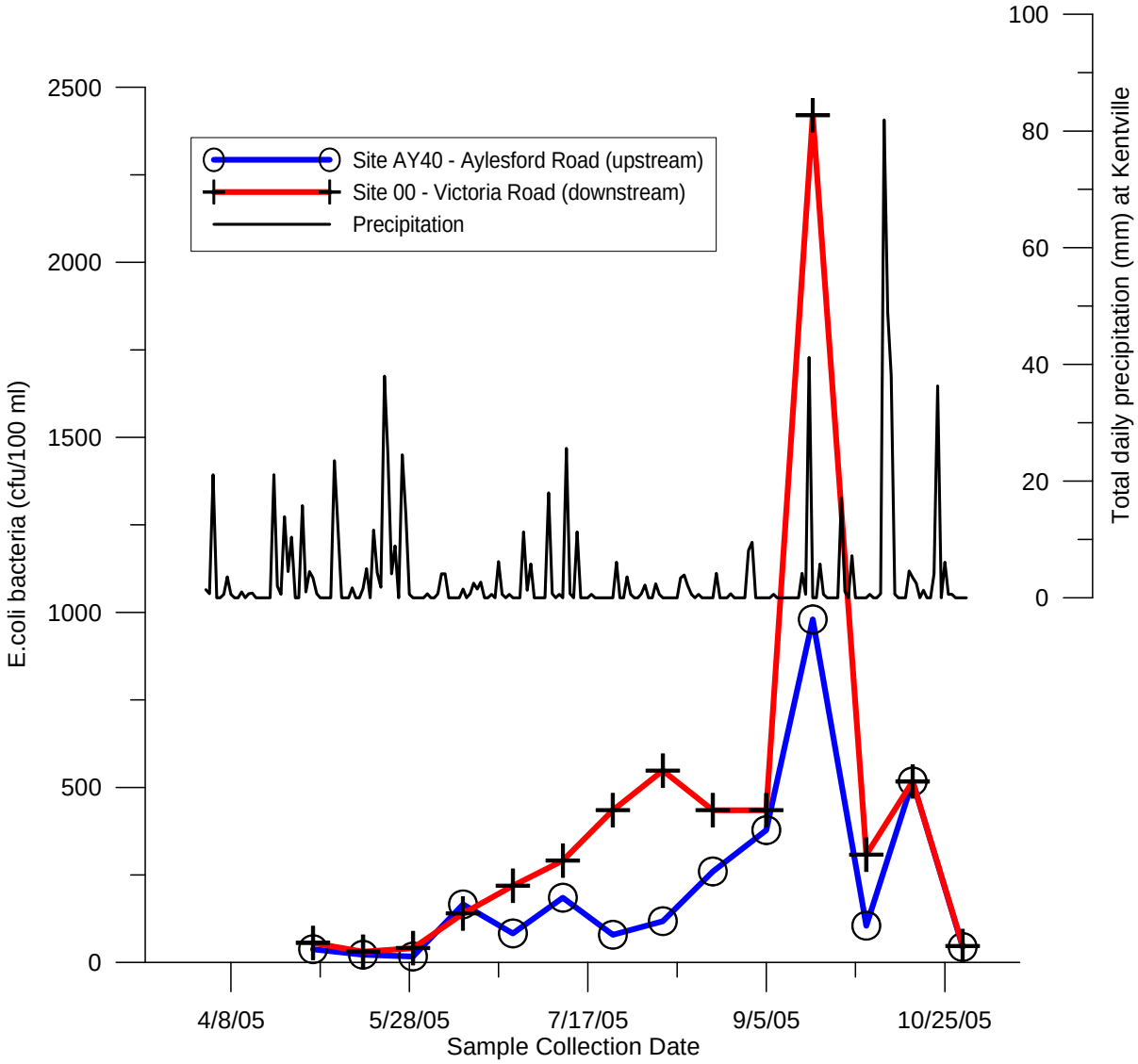

Figure 5. E.coli monitoring results for Aylesford (Site 00) and Aylesford Road (Site AY40) locations

The fecal bacteria levels for the two monitoring sites are very similar from April to mid June, after which the downstream Aylesford site (00) consistently exhibits significantly higher bacteria levels until mid October. The 2005 geometric mean for the Aylesford Road (Site AY40) was 88 cfu/100 ml, and 183 cfu/100 ml for Aylesford (Site 00). The 2005 results are consistent with those observed in the 2003 survey, noted above, where the downstream site (Site 00) had consistently higher fecal coliform counts. From this data, a number of tentative conclusions can be drawn:

- a source of fecal bacteria appears to be entering the Annapolis River between these two sample locations.
- the fecal coliform source is time based, occurring between June and late September.
- fecal inputs occur during the summer months when there is limited rainfall.
- the heavy autumn rains resulted in a spike in fecal coliform inputs. Two possible explanations of this include (1) the progressive accumulation of fecal material on land over the summer months, rapidly being flushed into watercourses with the heavy rain, and (2) the over topping and/or release of fecal material from a holding facility as a result of the heavy rain.

From the daily precipitation plot, it can be seen that after a relatively dry summer, the first heavy rainfall event of the season occurs in early October. This rain event coincides with a peak in E.coli results for both the Aylesford and Aylesford Road stations.

Patterson Brook was identified by MacMillon *et al* (2003) as one of the few streams in the Annapolis watershed with consistently cool water temperatures throughout the summer months. The stream was also found to contain high populations of brook trout (MacMillon and Crandlemere, 2003). Patterson Brook may therefore have the appropriate combination of cool water and necessary habitat to serve as nursery and/or summer refuge for brook trout. For these reasons, any contamination presents should be investigated and remediated where possible.

It is recommended that in 2006, monitoring be continued at both the Aylesford and Aylesford Road locations, as well as on the tributaries entering the Annapolis River between these two sites. As well, it is suggested that the length of the river between these two sites, and the tributaries, be surveyed on foot to identify possible contamination sources.

For the past several years, CARP has collaborated with Acadia University (Dr. Greg Bezanson) and Environment Canada in the testing of Microbial Source Tracking (MST) technologies (Sullivan, 2004). During 2005, CARP participated in an Atlantic-wide trial of the *Bacteroides-Prevotella* MST genomic method. The *Bacteroides* method has the ability to discriminate fecal contamination between human, ruminant animal (e.g. cattle) and other sources. Samples were collected on October 18, 2005 from Patterson Brook, Parker/Skinner Brook and the Annapolis River at Aylesford Road (Site AY40). Of the three samples collected, only Patterson Brook yielded a positive result for the human specific *Bacteroides* primer. Due to the preliminary nature of this trial, this result should not be used to conclude that ruminant fecal material was absent from the three sample locations. Should the opportunity become available, additional *Bacteroides* analysis will be conducted in 2006. A limiting factor with this is financial, as each sample costs approximately $140.

Recommendations

- Continue regular River Guardian E.coli monitoring at the eight main river sample locations.
- Conduct simultaneous monitoring at Sites 00 and AY40, together with intervening tributary streams.
- Conduct a foot survey of the Annapolis River between these two sites, and the intervening tributary streams, to identify possible contamination sources.
- Review current and historic air photos of this area to identify land use changes and possible sources of contamination.
- Collect samples for MST analysis in Aylesford and other areas, to determine the sources of fecal bacteria contamination.

Dissolved Oxygen

Introduction

Dissolved oxygen (DO) is a widely used and important general indicator of the health of a river system (Addy *et al* 1997). Aquatic organisms require oxygen in solution, just as terrestrial organisms need oxygen for internal respiration. Oxygen in the atmosphere, which is readily available to terrestrial organisms, must be dissolved into the water and is present at much lower concentrations. Wind, wave action, rainfall, and photosynthesis help aerate waterways and increase dissolved oxygen levels. Sewage, other highly organic inputs, lower rates of photosynthesis and diffusion from the atmosphere due to ice cover can lead to decreased oxygen levels.

As the temperature of water decreases, a greater concentration of oxygen is able to dissolve in the water. The amount of oxygen in water can be reported in two ways, either as a concentration measurement (mg/L) or as percent saturation. Water reaches its saturation point when it can no longer dissolve any additional oxygen for a given temperature. As water temperature decreases, more oxygen can be dissolved. High levels of photosynthesis or turbulent conditions can "supersaturate" the water, resulting in saturation levels greater than 100%. Dissolved oxygen levels below 60% saturation are known to cause stress to aquatic life, including fish.

Monitoring Results

a) How have dissolved oxygen levels changed over 14 years of monitoring on the main Annapolis River?

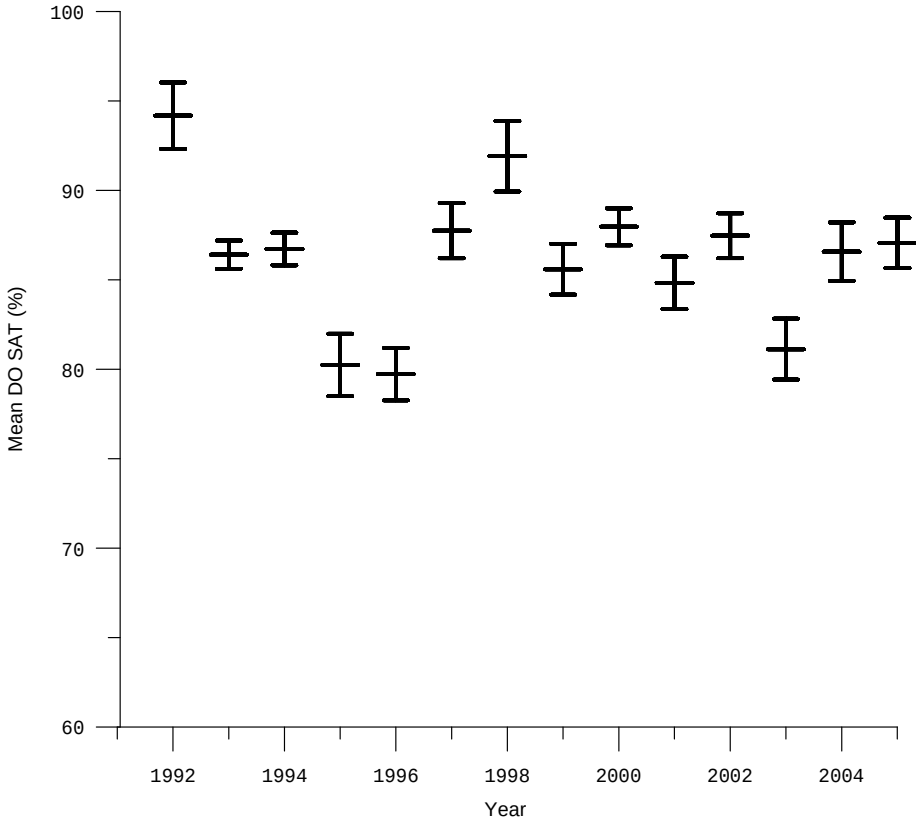

Figure 6. Mean Dissolved Oxygen Saturation (DO SAT) by year 1992 to 2005 (showing standard error of the mean)

Figure 6 shows that during the period of 1992 to 2005, annual mean dissolved oxygen (percent saturation) levels have varied from a high of 94.2% in 1992, to a low of 79.7% in 1996. For the values recorded during 2005, the mean dissolved oxygen saturation was 87.1%, which is within the normal range. The standard error of the mean is shown with error bars.

The Canadian Water Quality Guideline for the Protection of Freshwater Aquatic Life for Dissolved Oxygen is 5.5 mg/L (CCME, 2002). Only two of the ninety-five water samples analyzed by the Annapolis River Guardians in 2005 had a dissolved oxygen level below this guideline level (Bridgetown, September 5, 2005 3.8 mg/L; September 18, 2.6 mg/L).

b) How do Dissolved Oxygen levels differ between each of the main river sampling sites?

Figure 7 presents the 14-year mean dissolved oxygen (percent saturation) values for each of the main river monitoring sites. The standard error of this mean is shown with error bars. This is overlaid with the mean values for the 2005 monitoring season. From these data, there does not appear to be a significant increasing or decreasing trend for any of the sites. A 14-year mean for Middleton is not available, as dissolved oxygen monitoring was not conducted at this site during 1995, 1996, and 1997.

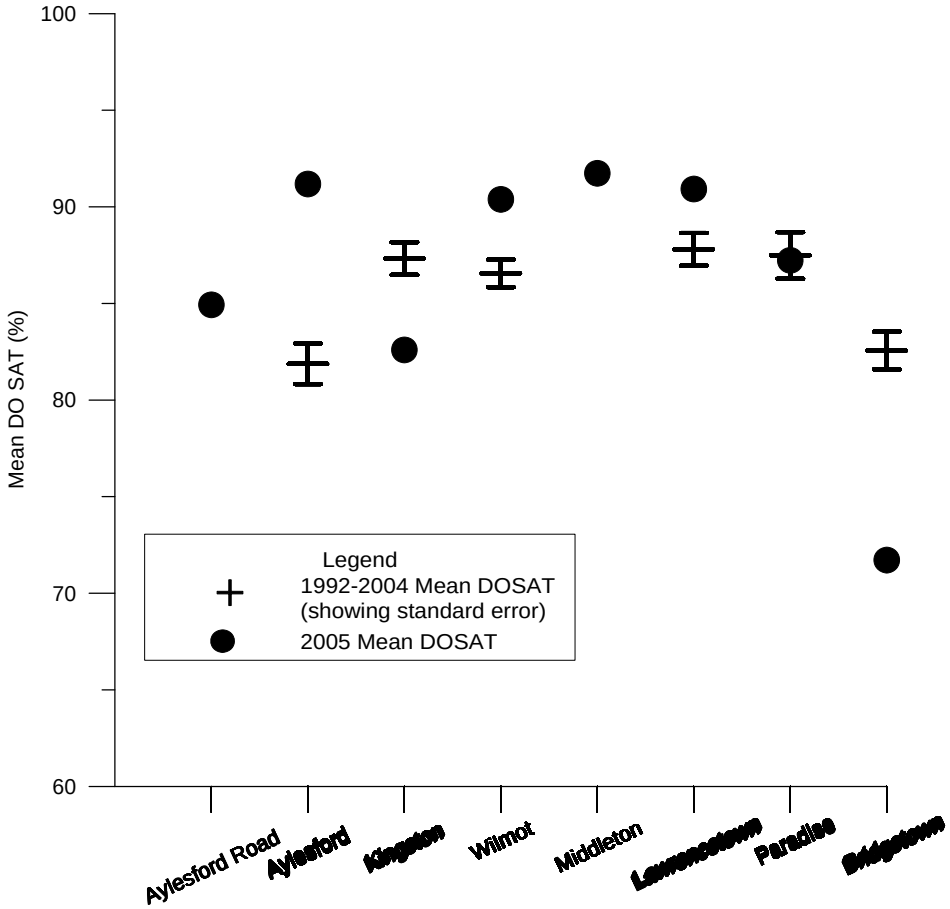

Figure 7. Mean Dissolved Oxygen Saturation (DO SAT) by sampling site, 1992 to 2005 (showing standard error of the mean)

c) Which River Guardian monitoring sites experienced low dissolved oxygen levels in 2005?

Table 5. Dissolved Oxygen Percent Saturation (DOSAT) Thresholds for Annapolis River.

Site	Number of Samples Collected in 2005	Number of Samples with DOSAT below 60%	Number of Samples with DOSAT below 75%	Number of Samples with DOSAT above 75%
Aylesford Road	14	0	3	11
Aylesford	14	0	2	12
Kingston	15	0	2	13
Wilmot	14	0	1	13
Middleton	15	0	1	14
Lawrencetown	12	0	2	10
Paradise	11	0	3	8
Bridgetown	14	2	6	8

As is indicated in Figure 7 and Table 5 above, Bridgetown had the greatest number of low dissolved oxygen (DO) results of the eight main river sample locations. In both 2004 and 2005, observed DO levels at Bridgetown were sufficiently low so as to cause stress to aquatic life, including fish (September 6, 4.80 mg/L; September 5, 2005 3.8 mg/L). The proximity of date and location of these low DO results prompted a more in-depth investigation of oxygen levels on the lower Annapolis River during the autumn of 2005. This investigation revealed that it was the underlying salt water in this tidal section of the river that was oxygen depleted. Further information on this investigation can be found in Appendix D.

Recommendations

- Continue regular River Guardian DO monitoring program at eight main river sample locations.
- Conduct investigation into low DO levels in the tidal section of the Annapolis River during 2006.
- For samples at Bridgetown (the only station to be tidally influenced), monitor conductivity/salinity with DO.

Temperature

Introduction

Water temperature, like dissolved oxygen, serves as a broad indicator of water quality. The temperature of water has a direct bearing on the aquatic species present and their abundance. For example, trout and salmon species experience stress at water temperatures in excess of 20ºC, with lethality occurring with prolonged exposures to temperatures over 24ºC (MacMillan *et al*, 2003).

Annapolis River Guardian Monitoring Results

The mean summer water temperature for the Annapolis River in 2005 was 20.0ºC or 1.4ºC warmer than for the same period in 2004. As in previous years, water temperatures during 2005 continued to reach levels stressful to aquatic life regularly during the summer months. Figure 8 presents the mean summer water temperature (July, August, September) by year for all the mainstem monitoring sites. Figure 8 also includes the 1992 to 2005 mean summer water temperature (18.7 *ºC*). Five of the past six summers had summer water temperatures well above this mean.

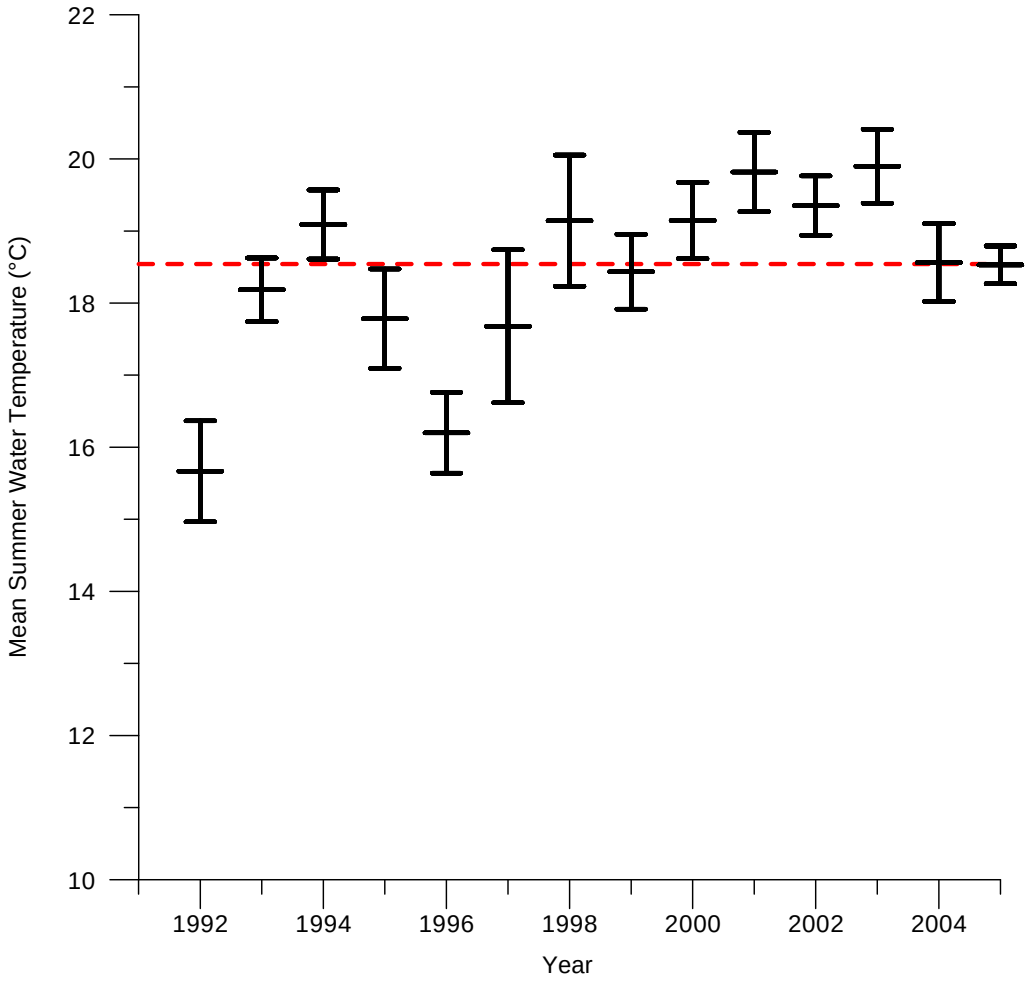

Figure 8. Mean Summer Water Temperature by Year (showing standard error of the mean) with 1992-2005 mean shown as dashed line.

The data from the 2003 & 2004 River Guardians annual reports suggested a gradual increase in temperature in the lower river sites, particularly in the summer data. Figure 9 presents the mean summer water temperature along the main Annapolis River in 2005, and shows that this spatial trend was not evident during 2005. Of the 41 temperature measurements recorded during the months of July, August and September in 2005, approximately half (49%) exceeded 20ºC. This compared with one-third of measurements exceeding 20ºC in 2004. The maximum temperature observed was 25.7ºC, recorded at Middleton on August 7, 2005.

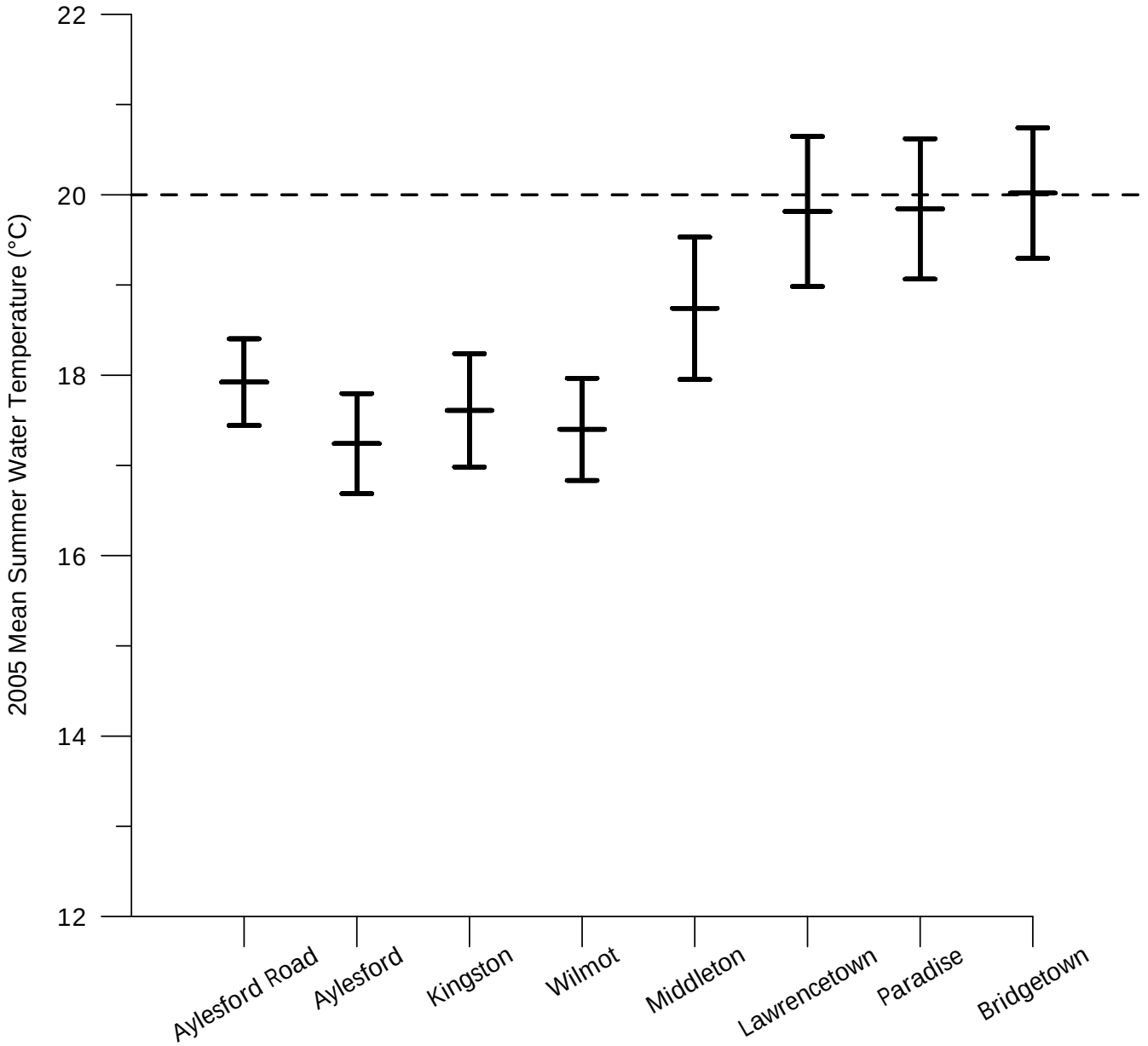

Figure 9. Mean 2005 Summer Water Temperatures by Site, with standard error of the mean and 20 ℃ threshold

Diurnal Temperature Monitoring

It is known that surface waters undergo a daily cycle of warming and cooling. To date, the magnitude of this cycle for the Annapolis River was not well understood. This, coupled with fact that River Guardian volunteers do not all collect their water samples at the same time, introduced an unknown level of variability into the River Guardian temperature results. During 2005, a small study was undertaken to better understand the nature of this cycle for the Annapolis River and its impact on the temperature readings collected by the Annapolis River Guardians. The results for this study are reported in Appendix E, (Quality Assurance/Quality Control Data).

The investigation indicated that the time of temperature measurement represents a moderate source of variability within the River Guardians program, comparable to that introduced through the use of glass thermometers. The current recommended time of temperature measurement of 12:00 pm occurs at a period of rapid water temperature change. If different volunteers were to collect water samples either slightly before or after this time, this has the potential to introduce variability into the temperature dataset. There are two periods of the day where water temperatures exhibited limited change: mornings (e.g. 7.00 to 10.00 am) and evenings (5.00 to 8.00 pm). CARP's principal concern with respect to surface water temperature is the impact of increased temperatures on cold water fish such as trout and salmon. In order to reduce the potential for variability being introduced into the dataset and ensure the entire dataset remains usable, it is recommended that: (1) River Guardian volunteers be encouraged to collect water samples at a consistent time (12:00 noon) and (2) a temperature data logger be deployed at a single sample location for the full season, to allow the determination of a correction factor to be applied against field temperature observations.

Thermal Status Monitoring

During 2005, the thermal status of two tributaries in the Annapolis watershed were examined to assess their suitability for fish habitat improvements. Temperature measurements were made by placing pre-programmed temperature data loggers within the watercourses during spring, summer and autumn. Table 6 describes the location information for these placements.

Table 6. Placement Information for Temperature Data Loggers

Tributary	Location of Data Logger Placement	UTM Easting	UTM Northing	Instrument Used	Sampling Interval
Leonard Brook	100 m upstream of Hwy 1 Bridge	326200 (Zone 20)	4970986	Onset Instruments, Stowaway	1 hr 36 min
Moose River	40 m upstream of Clementsport Community Swimming Park	294660 (Zone 20)	4947804	MiniLog-T; Model 4903A	1 hr 00 min

The framework for assessing water temperature data developed by MacMillan *et al*, (2005) was used to assess the temperature monitoring results. MacMillan *et al.* found that the number of trout in a system was directly related to the amount of cool water habitat available in the summer. Summer average water temperatures were used to rank sites into three categories: cool, intermediate and warm. Cool water sites had a summer average temperature of less than 16.5ºC. Intermediate sites had a summer average water temperature between 16.5 and 19.0 ºC. Warm sites had a summer average temperature greater than 19.0ºC. As part of a province wide temperature study, Leonard Brook was

classified as intermediate in 2000 by MacMillon, with a summer average temperature of 16.7ºC, and a daily maximum of 22.2ºC. Table 7 summarizes the 2005 results for Leonard Brook and Moose River. The 2005 summer average for Leonard Brook is found to be 1ºC higher than that reported in 2000. This is felt to be within expected year-to-year climatic variability (J. MacMillan, pers. com).

Table 7. Thermal Status Monitoring Results

Tributary	Number of Days Cool (< 16.5ºC)	Number of Days Intermediate (16.5 to 19ºC)	Number of Days Warm (> 19ºC)	15 June to 5 Sept. Daily Average (ºC)	Warmest Daily Average (ºC)	Number of Days > 20ºC *(daily average)*	Rank (Cool, Intermediate or Warm)
Leonard Brook	22	39	22	17.73	21.64 (July 20)	11	Intermediate
Moose River	9	28	46	19.09	23.50 (July 20)	30	Warm

The use of automated temperature data loggers in 2005 was found to be an inexpensive and relatively easy method to assess the thermal status of watercourses. From this analysis, it can be concluded that lower main stem of the Moose River may not be suitable for trout and salmon habitat improvements, given its limited cold water habitat. Additional monitoring is recommended for the two main branches of the Moose River to assess if cold water habitat exists in the headwaters.

Recommendations

- Continue regular River Guardian temperature monitoring program at eight main river locations.
- Install temperature loggers in candidate streams to assess for fish habitat improvements.
- Install temperature loggers on the two main branches of the Moose River during 2006 assess the thermal status of headwaters.
- Temperature data loggers be calibrated immediately prior to deployment and at least once *in situ*. These procedures be added to the QA/QC Project Plan.
- River Guardian volunteers be encouraged to collect water samples at a consistent time (12:00 noon).
- A temperature data logger be deployed at a single sample location for the full season, to allow the determination of a correction factor to be applied against field temperature observations.

Nutrients (Nitrogen and Phosphorus)

Introduction

Elevated levels of nitrate in aquatic systems can originate from a variety of sources, including domestic on-site and municipal wastewater discharges, the use of chemical fertilizers and manure on urban and agricultural land, industrial discharges, and atmospheric deposition. Nitrogen concentrations in water can be reported in a number of forms, including: nitrate, nitrate + nitrite, ammonia and total dissolved nitrate. The following guidelines as well as the data collected by River Guardians are expressed as nitrate-nitrogen (NO_3-N), and represent the amount of nitrogen in the nitrate form. The Canadian Water Quality Guideline for the Protection of Freshwater Aquatic Life for nitrate is 13 mg/L (CCME, 2002). It should be noted that this level is for protection from direct toxic effects, and does not consider indirect effects due to eutrophication. Table 8 shows nitrate guidelines for various freshwater uses, as either maximum or 30-day average concentrations.

Table 8. Water Quality Guidelines for Nitrate-N (mg/L)

NO_3-N (mg/L)	Water Use
< 10 (maximum)	Acceptable for recreational use
< 40 (average)	Protection of freshwater aquatic life
< 100 (maximum)	Acceptable for livestock watering

Source: Province of British Columbia (Website: http://www.env.gov.bc.ca/wat/wq/BCguidelines/nitrogen/nitrogen.html)

Elevated nitrate-N levels, as low as 2.5 mg/L, have been shown to cause chronic effects in a number of amphibian species (Chambers *et al*, 2001). Generally, nitrate-N levels above 1-2 mg/L indicate that the water body may be affected by anthropogenic sources. Historic nitrogen monitoring results for the Annapolis River are shown in Table 9.

Table 9. Historic Nitrogen Levels in the Annapolis River

Period	Number of Samples		Nitrate-N	Total Nitrogen	Nitrate + Nitrite-N	Ammonia	Source
			(mg/L)	(mg/L)	(mg/L)	(mg/L)	
1992 to 1996	14	Mean			0.519	0.030	Dalziel et al, 1998[1]
		Max			1.466	0.060	
		Min			0.151	0.012	
2004	2	Mean	0.40	0.74			CABIN, 2004[2]
2004	96	Mean	0.48				Sullivan & Sharpe, 2005[3]
		Max	1.52				
		Min	0.11				
2005	6	Mean	0.54	0.60			CABIN, 2005[4]

[1] Dalziel, J.A., P.A. Yeats and B.P. Amirault. 1998. Inorganic Chemical Analysis of Major Rivers Flowing Into The Bay Of Fundy, Scotian Shelf and Bras D'Or Lakes, Canadian Technical Report of Fisheries and Aquatic Sciences 2226. Science Branch, Department of Fisheries and Oceans, Dartmouth. Samples collected at Paradise.

[2] CABIN, 2004 — Canadian Aquatic Biomonitoring Network protocol. Samples collected by CARP staff at Aylesford and Kingston on Annapolis River (18/10/04 and 20/10/04, respectively).

[3] Sullivan D. & A. Sharpe, CARP 2004 Annual Water Quality Monitoring Report

Phosphorus is an essential nutrient required by plants and animals, with phosphorus-containing organic compounds found in all living matter. Orthophosphate (PO_4^{3-}) is the only form readily used as a nutrient by plants and organisms. Because of its low dissolved concentrations, phosphorus can be the limiting nutrient in fresh waters. Elevated phosphorus levels in surface waters can lead to algal blooms (Ironside, 2001).

While phosphorus is a naturally occurring element in rocks and soils, anthropogenic sources are the predominant cause of elevated concentrations leading to impaired water quality. Anthropogenic sources include human and animal waste, atmospheric inputs, industrial waste and artificial fertilizers. A total phosphorus concentration of 0.030 mg/L is a recommended water quality guideline to avoid excessive plant growth in rivers and streams (OMEE, 1994). Total phosphorus levels in excess of 0.030 mg/L are an indicator of eutrophic surface waters (Mackie, 2001). Historic phosphorus monitoring results for the Annapolis River are shown in Table 10.

Table 10. Historic Phosphorus Levels in the Annapolis River

Period	Number of Samples		Phosphate-P	Total Phosphorus	Source
			(mg/L)	(mg/L)	
1992 to 1996	14	Mean	0.017		Dalziel et al, 1998[1]
		Max	0.032		
		Min	0.007		
2004	2	Mean		0.055	CABIN, 2004[2]
2005	6	Mean		0.087	CABIN, 2005[4]
		Max		0.142	
		Min		0.043	

2005 Monitoring Results

Table 11 shows the chloride, sulphate, nitrate-N and total phosphorus monitoring results for 2005. Analytical methods and procedures are shown in Appendix A. For each location, samples were collected on June 13, July 25 and August 22. The frequency and number of stations sampled in 2005 was scaled back from that undertaken in 2004, due to financial limitations and relatively low nitrate levels found in 2004. Chloride, sulphate and nitrate-N concentrations were similar to those observed in 2004 and well below guideline levels.

Of the 15 phosphorus samples collected in 2005, 10 (67%) were at or above the 0.030 mg/L guideline level. Given the relatively lower values observed in the 1992 to 1996 period, this gives some cause for concern. The sample having the highest observed phosphorus concentration (0.28 mg/L) was collected on July 25 at Kingston. No algal blooms were observed. The cause of this unusually high result is not known. As this single result is significantly higher than all other samples from 2005, the possibility of sample contamination or laboratory error must be considered as one possible explanation. This is unlikely though, as two of the water samples collected as part of the CABIN program also had total phosphorus levels in excess of 0.100 mg/L (Aylesford-0.117 mg/L, Kingston-0.142 mg/L, September 13, 2005).

[4] CABIN, 2005 — Canadian Aquatic Biomonitoring Network protocol. Samples collected by CARP staff at Aylesford, Kingston and Paradise on Annapolis River (Samples collected 13/9/05 and 14/9/05).

Table 11. River Guardian Data for Chloride, Sulphate, Nitrate-N and Total Phosphorus

Site #	Site Name		Mean Chloride (mg/L)	Mean Sulphates (mg/L)	Mean Nitrate-N (mg/L)	Mean Total Phosphorus (mg/L)
AY40	Aylesford at Aylesford Road	Mean	12.51	5.05	0.46	0.037
		Max	15.12	5.43	0.59	0.040
		Min	9.00	4.41	0.22	0.030
00	Aylesford at Victoria Road	Mean	20.33	9.47	0.64	0.050
		Max	25.40	10.62	0.75	0.069
		Min	14.80	8.40	0.51	0.035
13	Kingston	Mean	12.69	6.34	0.38	0.118
		Max	18.48	9.27	0.46	0.28
		Min	9.30	4.84	0.28	0.021
25	Middleton	Mean	13.85	11.07	0.22	0.034
		Max	22.95	20.70	0.32	0.054
		Min	8.99	6.10	0.06	0.024
40	Paradise	Mean	10.78	6.35	0.24	0.036
		Max	11.24	8.22	0.62	0.058
		Min	10.20	3.80	0.04	0.020

As was noted earlier in the fecal bacteria section, an additional sample location was added in Aylesford during 2005, where Aylesford Road crosses the Annapolis River. This sample location (AY40) is located approximately 2.5 km upstream of the long-standing Aylesford sample location (OO). Several brooks entering the Annapolis River between these two locations have for some time been suspected as a source of fecal bacteria and nutrient contamination. The addition of the Aylesford Road (AY40) sample station has allowed for simultaneous samples to be taken above and below these potential contamination sources.

A comparison of nutrient results for this pair of upstream (AY40) and downstream (00) stations is shown in Table 12. Of the three sample pairs, the June 13, 2005 results showed the most significant change for both nitrate and phosphate. This temporal pattern differed from that observed for E.coli bacteria, which exhibited the greatest change between the two sample stations over the period of June 26 to October 3. In the past, it has been assumed that fecal bacteria (e.g. E.coli) and nutrients, arising from a common source, would result in concentrations increasing in close correlation with each other. The above results may suggest that two mechanisms may be at work in the Aylesford area, resulting in fecal bacteria and nutrient enrichment occurring separately.

Table 12. Comparison of Nutrient Results for Site AY 40 (Aylesford at Aylesford Road) (Upstream Station) and Site OO (Aylesford at Victoria Road) (Downstream Station)

Date	Sample Location	Nitrate-N	Total Phosphorus
June 13, 2005	AY 40 (Aylesford Road)	0.22	0.040
	OO (Aylesford)	0.75	0.069
July 25, 2005	AY 40 (Aylesford Road)	0.56	0.040
	OO (Aylesford)	0.66	0.047
August 22, 2005	AY 40 (Aylesford Road)	0.59	0.030
	OO (Aylesford)	0.51	0.035

Recommendations

- Given the significant number of total phosphorus results in 2005 that exceeded the 0.030 mg/L water quality guideline, it is recommended that additional monitoring of this parameter be conducted in 2006 to provide confirmation of these results. This should include main stem locations which have had elevated phosphorus concentrations, and pristine tributary streams.
- Nutrient monitoring (nitrate and total phosphorus) should continue at the two Aylesford sample stations, in combination with E.coli monitoring, to better understand the temporal pattern of contamination sources in this area.

pH and Conductivity

Introduction

pH is a measure of the acidic/basic nature of water and is determined by measuring the concentration of the hydrogen ion (H^+). It is expressed on a logarithmic scale from 0 to 14, zero being the most acidic. Because the scale is logarithmic, every unit decrease in the pH scale represents a tenfold increase in acidity. To ensure the health of freshwater aquatic life, pH levels should not vary beyond the range of 6.5-9.0 (CCME, 2002). Levels below 5.0 are known to negatively affect many species of fish, including salmon and trout. pH varies naturally depending on the underlying soil type and its buffering capacity; however it can also be influenced by anthropogenic means, such as acid precipitation.

Conductivity is a measure of water's ability to conduct an electrical current, measured in milliSiemens per centimeter (mS/cm). The greater the conductivity, the greater the amount of ions in the water. Some sources of pollution, including industrial and municipal effluent as well as road salt, increase the number of ions contained in the water. Sharp increases (or decreases) in conductivity can therefore signal anthropogenic inputs in a river system. There is currently no national guideline for conductivity in freshwater. Rivers and streams that are not influenced by anthropogenic sources typically have conductivity in the range of 0.05-1.5 mS/cm. Seawater has much higher conductivity due to the dissolved salts, and can reach values as high as 50 mS/cm.

pH and conductivity were measured on the Monday following River Guardian collection by CARP staff using the portable HydroLab Quanta water meter (See Appendix A for more details on sampling procedure and meter calibration).

Monitoring Results

Table 13 shows that pH values all along the Annapolis River are generally good, being only very slightly acidic. In total, 106 individual pH measurements were made during 2005. The pH values are consistently well within the range recommended by the CCME for the protection of freshwater aquatic life. A number of the principal tributaries of the Annapolis River pass through the Torbrook formation that buffers rivers and streams in the watershed from acidification.

Table 13. Mean pH and Conductivity Values at Each River Guardian Monitoring Site, 2005

Site	Mean pH	Standard Deviation	Mean Conductivity (mS/cm)	Standard Deviation
AY40-Aylesford Road	6.54	0.40	0.10	0.03
00-Aylesford	6.60	0.22	0.15	0.04
13-Kingston	6.50	0.20	0.11	0.04
18-Wilmot	6.60	0.28	0.15	0.07
25-Middleton	6.30	0.32	0.11	0.07
35-Lawrencetown	6.34	0.35	0.11	0.11
40-Paradise	6.49	0.59	0.11	0.07
49-Bridgetown	6.62	0.59	5.33	11.73

Conductivity values for all the River Guardian sites were also well within the natural variability of fresh/brackish water. The range of conductivity for all sites (expect Bridgetown) was 0.10-0.15 mS/cm. No sharp increase or decrease in conductivity was observed at either of the River Guardian sites throughout the sampling season. In Bridgetown, the high conductivity values are due to the brackish water in that part of the estuary.

pH data collected from all seven main river sites for 2003, 2004 and 2005, using the Quanta Hydrolab meter, are presented below as a Box and Whisker plot (Figure 10). From the plot, it is apparent that a downward shift in pH occurred between 2004 and 2005. The downward pH shift is observed, upon closer examination of the data, across all seven of the monitoring sites (Aylesford to Bridgetown). This would appear to indicate that that the factors causing this shift were present at a watershed or larger scale. The 2005 pH values were relatively consistent throughout the entire sample season, with the lowest observation of 5.69 being recorded on October 31. The 2004 and 2005 data was compared using a two-sample t-test, and were found to be significantly different[5]. To ensure that the normality of the data was not impairing the result, the t-test was re-run after a natural log (ln) transformation of the data, with similar conclusions observed.

During the early years of the Annapolis River Guardians program, pH was regularly measured at many of the main river sample locations. During this period, the mean pH was 6.95, based on 620 individual measurements. This historic pH is similar to that observed in 2003 & 2004, but appears to differ significantly from that in 2005.

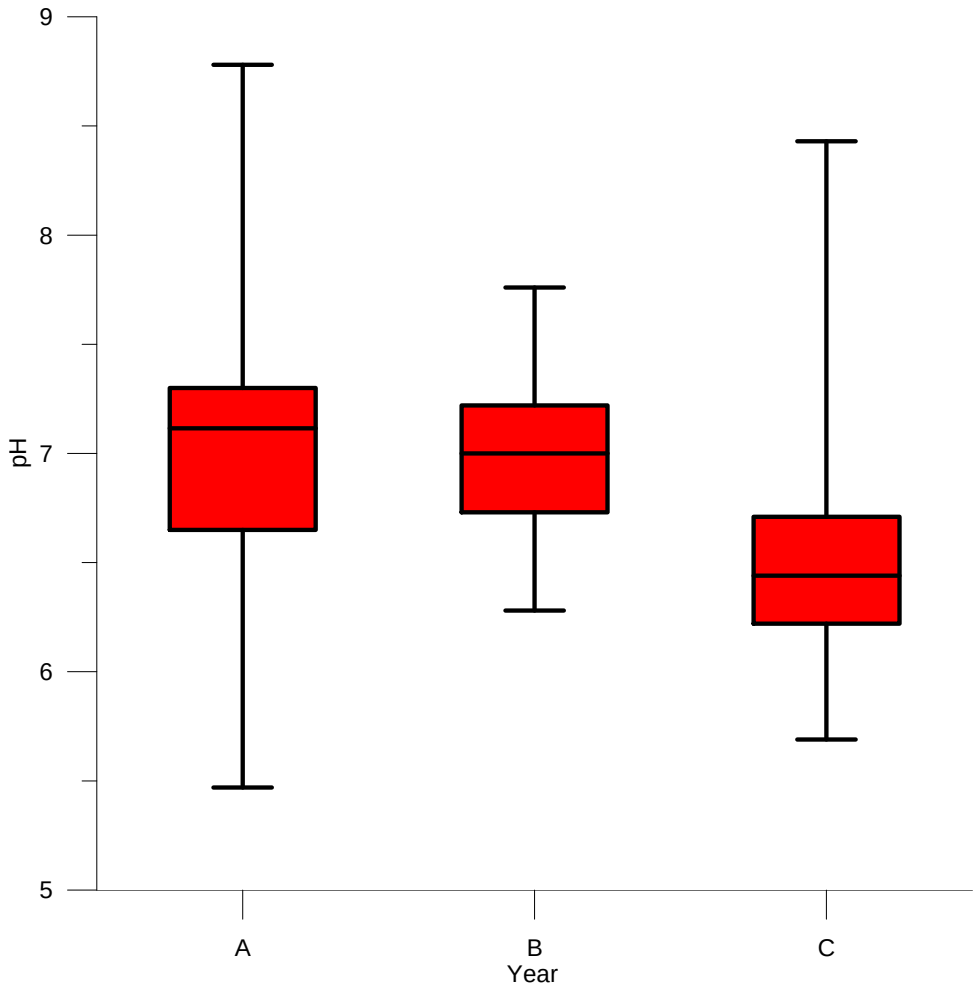

Figure 10. Box & Whisker Plot of pH measurements from Annapolis River, A = 2003, B = 2004, C = 2005

[5] T-test Results: n_{2004} = 77 samples; n_{2005} = 106 samples; alpha 0.05; df = 177; t Stat = 8.51, t Critical = 1.97; P(T<=t) (two tailed) = 7.3×10^{-5}

During 2005, Kejimikujik National Park and Historic Site conducted a trout movement study, which included observations of pH levels in the Mersey River system. This study recorded lower than expected pH levels at a number of locations during September and October 2005 (Gary Corbett, pers. com.), which were particularly associated with storm systems giving heavy rainfall. Given the pH observations on both the Annapolis and Mersey Rivers, it is possible to conclude that large scale atmospheric inputs (acid rain?) may have played a contributing factor in the reduction of pH in surface waters in south western Nova Scotia.

Recommendations

- Regular pH monitoring should be continued at the eight Annapolis River Guardian monitoring locations.

Conclusions

In 2005, the Annapolis River Guardians completed their 14th year of continuous water quality monitoring on the Annapolis River. Eleven volunteers monitored eight sites over the course of the season, which ran from April to October. A number of parameters were measured, including dissolved oxygen, fecal coliform bacteria, E.coli bacteria, nitrate-Nitrogen, chloride, sulphate, air and water temperature, pH and conductivity, as well as local weather conditions.

Fecal bacteria levels along the Annapolis River during 2005 were generally lower than those observed in 2004. Although bacteria levels continued to be highly variable, there was a uniform decrease in the proportion of samples which exceeded key water quality thresholds of 50, 100 and 200 colony forming units (cfu) per 100 ml. Of the 149 fecal bacteria samples collected and analyzed, 14% (21) exceeded the contact water recreation guideline of 200 cfu/100ml. This compared favourably with 2004 were 37 samples exceeded this threshold. During 2005, of the 21 samples with fecal bacteria greater than 200 cfu/100 ml, 8 (38%) were collected at the Aylesford sample station. In 2005, water samples were collected at an additional monitoring station in the Aylesford area at Victoria Road. The comparison of monitoring results from this and the nearby, pre-existing, Aylesford station have provided a number of useful insights into the nature of fecal contamination in this area.

Dissolved oxygen levels during 2005 remained within their normal range for much of the Annapolis River. Over 14 years of monitoring, mean dissolved oxygen saturation (DOSAT) levels have remained in the range of 80-94%. In 2005, the mean DOSAT level was just under 87%. As a result of the regular monitoring provided by the Annapolis River Guardian program, unusually low DO values (3.8 mg/L) were detected at Bridgetown in September. DO levels were sufficiently low so as to cause stress to aquatic life, including fish. Subsequent investigation revealed an extensive oxygen-depleted zone in the lower Annapolis River.

The mean summer water temperature for the Annapolis River during 2005 was 20.0ºC or 1.4ºC warmer than for the same period in 2004. As in previous years, water temperatures during 2005 continued to reach levels stressful to aquatic life regularly during the summer months. The Aylesford, Middleton, Lawrencetown and Paradise stations recorded the warmest summer water temperatures.

A limited nutrient monitoring program was undertaken in 2005. Samples analysed for nitrate-N were found to be in the range of 0.22 to 0.64 mg/L. These results are similar to those observed in 2004. Of the 15 phosphorus samples collected in 2005, 10 (67%) were at or above the 0.030 mg/L water quality guideline for the protection of freshwater aquatic life.

pH levels at each of the River Guardians sites were consistently within the recommended range for the protection of aquatic life (6.5-9.0). When the 2005 results were compared with those recorded in 2003 and 2004 though, a statistically significant downward shift was observed. While the cause of this downward shift of pH during 2005 is unknown, it was observed uniformly across the eight monitoring stations, throughout the 2005 season.

Split and blank water samples were analysed during 2005 as part of CARP's Quality Assurance Project Plan. The accuracy of River Guardian dissolved oxygen readings were estimated at +/- 0.32mg/L, compared with 0.85 mg/L recorded in 2004. Field and travel blank samples analysed for fecal coliforms consistently produced plates with 0 cfu/100ml.

Recommendations

Recommendations for the River Guardians Program

- Continue regular River Guardian E.coli monitoring at the eight main river sample locations.
- Conduct simultaneous monitoring at Sites 00 and AY40, together with intervening tributary streams.
- Conduct a foot survey of the Annapolis River between these two sites, and the intervening tributary streams, to identify possible contamination sources.
- Review current and historic air photos of this area to identify land use changes and possible sources of contamination.
- Collect samples for MST analysis in Aylesford and other areas, to determine the sources of fecal bacteria contamination.
- Continue regular River Guardian DO monitoring program at eight main river sample locations.
- During 2006, conduct investigation into low DO levels in the tidal section of the Annapolis River, which were observed in 2005.
- For samples at Bridgetown (the only station to be tidally influenced), monitor conductivity/salinity with DO.
- Continue regular River Guardian temperature monitoring program at eight main river locations.
- Install temperature loggers in candidate streams to assess for fish habitat improvements.
- Install temperature loggers on the two main branches of the Moose River during 2006 to assess the thermal status of headwaters.
- Temperature data loggers be calibrated immediately prior to deployment and at least once *in situ*. These procedures be added to the QA/QC Project Plan.
- River Guardian volunteers be encouraged to collect water samples at a consistent time (12:00 noon).
- A temperature data logger be deployed at a single sample location for the full season, to allow the determination of a correction factor to be applied against field temperature observations.
- Given the significant number of phosphate results in 2005 that exceeded the 0.030 mg/L water quality guideline, it is recommended that additional monitoring of this parameter be conducted in 2006 to provide confirmation of these results. This should include main stem locations which have had elevated phosphorus concentrations, and pristine tributary streams.
- Nutrient monitoring (nitrate and phosphate) should continue at the two Aylesford sample stations, in combination with E.coli monitoring, to better understand the temporal pattern of contamination sources in this area.
- Regular pH monitoring should be continued at the eight Annapolis River Guardian monitoring locations.

Recommendations for CARP

- Continue supporting Microbial Source Tracking (MST) methods in order to more effectively identify and remediate the sources of fecal contamination in the Annapolis River.
- Complete the Quality Assurance Project Plan for all of CARP's Water Quality monitoring programs.
- Complete the benthic invertebrate survey of the mainstem Annapolis River to help identify some of the major sources of contamination.

Additional Recommendations (carried forward from previous years)

- Examine the relation between observed increases in water temperature to air temperature data to determine if increases are due to climate trends, riparian changes, or other factors that may be influencing flow patterns.

- Examine in further detail the water temperature data to determine whether any statistically significant trends are occurring.
- Given the high contributions of fecal coliforms observed in 2004 from the Fales River, conduct further investigations on this tributary (i.e.: monitoring upstream/downstream of suspected point sources) to gain a better understanding of the sources of fecal coliforms.
- Examine the relationship between fecal coliform levels at each site over 5-10 years and the monthly precipitation data in order to better understand the influence from different sources (i.e.: surface vs. on-site sources).

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Appendices

Appendix A — Parameters Tested and Methodologies

Parameters Analyzed in 2005	Additional Parameters Analyzed in Previous Years of the Program
Fecal coliform and E.coli densities	Salinity
Dissolved Oxygen	Chlorophyll a
Temperature (Water and Air)	Total Suspended Solids (TSS)
Weather conditions	Colour
Nitrate-N, Chloride, Sulphate, Total Phosphate	Transparency
pH, Conductivity, Total Dissolved Solids	

Water Collection for Fecal Bacteria Analysis

Following the contamination of some sampling equipment in 2003, a new collection procedure for fecal coliform samples was developed and used during the 2004 and 2005 seasons. The sample collection unit is shown in Figure A1.

Figure A1 — Collection Unit Used for Fecal Coliform Samples in 2005.

The open sample bottle is secured in the clamp, and lowered from the mid-span of the bridge into the river, to a depth of 1 meter. Samples are collected on the upstream side of bridges, where a safe pedestrian walkway exists. After collection, water samples are refrigerated until delivery to the lab, typically within 24 hours of collection.

Enumeration of Fecal Bacteria

Prior to the 2005 season, bacterial samples collected by Clean Annapolis River Project's Annapolis River Guardians program were tested for Fecal Coliforms (FC), using the Membrane Filtration method. During the winter of 2005, the program's Science Advisory Committee suggested that the program switch to testing for E.coli (EC) using the Most

Probable Number method, to bring testing more in line with National Guidelines. In order to ensure the continuity of the dataset, a period of duplicate analysis with the two methods was conducted. Duplicate samples were analysed using the two methods over a two-month period (four biweekly sample events at eight locations along the river). Further information on this period of parallel testing is contained in Appendix C.

All fecal bacteria samples were submitted to the Synova Diagnostics laboratory in Lawrencetown, Nova Scotia. The Synova lab is accredited by the Canadian Association for Environmental Analytical Laboratories (CAEAL) to perform the membrane filtration (Fecal Coliform) and most probable number (MPN) (E.coli) procedures. For Fecal coliform determination, a measured volume of the sample is filtered through a filter pad, which is in turn transferred onto an absorbent pad containing fecal coliform selective growth media. Samples are incubated for 24 hours (+/- 2 hrs) at 44.5 ºC. Visible colonies of navy blue colour are counted and expressed as the number of colony forming units (cfu) per 100 ml of sample.

As part of its internal quality control procedures, the Synova laboratory regularly assesses the precision of their procedures. The laboratory reports precision levels for fecal coliform (mFC) samples in the range of 0 to 50 cfu/100 ml of 11% and 10.4% for E.coli (MPN). See Appendix D for further information on the precision testing procedures.

From 1997 to 2003 and again in 2005, fecal bacteria densities were determined using the IDEXX Colilert procedure, to give a Most Probable Number of *E. coli* bacteria present.

Dissolved Oxygen Content

Dissolved Oxygen samples are collected from the mid-span of bridges using a horizontal Van Dorn sampler, at a depth of 1 meter. Dissolved Oxygen in mg/L is determined using the modified Winkler Titration using pre-packaged Hach reagents. The Winkler titration procedure is a widely recognized standard for determining dissolved oxygen. The procedure is reported to have an accuracy of at least +/- 1 mg/L. Dissolved oxygen as percent saturation is determined using Rawson's nomogram. Further information on the collection and analysis procedure for dissolved oxygen can be found in the Annapolis River Guardians Procedure Manual.

Temperature

The Annapolis River Guardians used a combination of glass / alcohol and digital thermometers during 2005. Prior to the start of the season, all thermometers were compared with the temperature reading from CARP's HydroLab Quanta water meter. This unit had recently been serviced and calibrated, with a reported accuracy of +/- 0.10 ºC. From this comparison, a correction factor was determined for each River Guardian thermometer. These correction factors were applied to all River Guardian temperature measurements.

Nitrate-N, Chloride, Sulphate, Total Phosphorus

Water samples for nitrate-N, chloride, sulphate and total phosphorus analysis were collected using the sampling equipment described above for fecal coliforms and shown in Figure A1. Water samples were refrigerated following collection and transported to Environment Canada's Moncton laboratory within one to two days. The analysis of nitrate-N, chloride and sulphate was conducted using a Dionex Ion Chromatograph, which allows for the measurement of several parameters simultaneously. The average recovery for each parameter is reported to be 100%, 101% and 101% for nitrate-N, chloride and sulphate, respectively. Total phosphorus was determined using the AAII system. The Environment Canada lab is accredited by the Canadian Association for Environmental Analytical Laboratories (CAEAL) to perform these procedures.

pH, Conductivity

Water chemistry data including pH and conductivity was collected using CARP's portable HydroLab Quanta Water Quality Monitoring System. Data was collected on a fortnightly basis by CARP staff, typically the Monday following the volunteers' sampling day, at a set location on the riverbank at each River Guardian site. The meter was placed in the river approximately 1 to 2 meters away from the bank, and allowed to stabilize, usually two to three minutes. Once stabilized, the values were stored in the meter's memory and recorded on the data sheets upon return at the CARP office. The data was also stored in an in-house Microsoft Access database. Approximately every two to three weeks, the multi-sensor water meter was calibrated for pH, conductivity and dissolved oxygen according to the directions in the Operating Manual (Hydrolab Corporation, 2002).

Appendix B — Sites Monitored

Water samples were collected during 2005 by the Annapolis River Guardians program at the following sites. Coordinates are reported in Universe Transverse Mercator (Zone 20) and Latitude/Longitude, as recorded on a hand-held GPS unit.

SITE	LOCATION	Easting	Northing
AY40	Aylesford, Aylesford Road, bridge	357328.48	4987755.13
00	Aylesford, Victoria Road, bridge at the Post Office	353313.34	4985418.70
13	Kingston, Bridge Street, bridge	346748.46	4982480.39
18	Wilmot, Old Mill Road, bridge	342100*	4979500*
25	Middleton, Highway 10, bridge	336981.58	4978044.59
35	Lawrencetown, Lawrencetown Lane, bridge	329581.15	4971984.70
40	Paradise, Paradise Lane, bridge	325738.51	4970620.51
49	Bridgetown, Queen Street, bridge	318900.00	4967621.30

** coordinates determined from 1:50,000 map sheet*

Appendix C — Comparison of Fecal Coliform and E.coli Bacterial Results for the Annapolis River Guardian Program

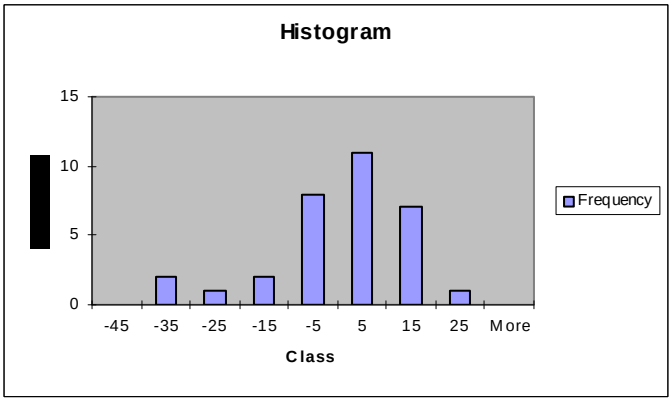
Background

Prior to the 2005 season, bacterial samples collected by Clean Annapolis River Project's Annapolis River Guardians program were tested for Fecal Coliforms (FC), using the Membrane Filtration method. At the last meeting of the program's Science Advisory Committee, it was suggested that the program switch to testing for E.coli (EC) using the Most Probable Number method, to bring testing more in line with National Guidelines. In order to ensure the continuity of the dataset, a period of duplicate analysis with the two methods was conducted. Two months (four biweekly sample events at eight locations along the river) was agreed to be appropriate for this.

A total of 32 water samples were collected during April and May 2005, split at the Synova Laboratory, and tested for the two methods. The results obtained from these two tests, therefore, are not independent of one another, but are linked or "paired". There is evidence to suggest that the two methods of testing are interchangeable, and so it is hypothesized that the difference between the results obtained from each method will be zero, or at least reasonably small. Therefore, regardless of the test that is performed, the null hypothesis (H_0) will be that the difference between sample X (FC) and sample Y (EC) is equal to zero.

Distribution of Paired Results

When the difference between the paired results was calculated, a new sample made up of the values X- Y for all of the values of n (x_i-y_i, i = 1,2…..n) was created. The sample distribution was examined in order to determine which statistical test may be performed on the data. The following histogram is inconclusive, showing some skew, but not indicating how much.



The mean, median and mode of the sample are also indicative of skew, with the median lying slightly to the left of the mode, and the mean lying farther to the left of both. When the kurtosis and skewness are divided by the standard error, they are both found to lie between –2 and + 2, indicating that the skew is not severe. As the sample size is also relatively large (n > 25), it is acceptable to perform a Paired T-test on the sample mean.

Mean	-4.28125
Standard Error	2.500094504
Median	-0.5
Mode	2
Kurtosis	1.619004812
Skewness	-1.223963607

Paired T-Test

The null hypothesis for the test, H_0, will be that the mean difference is equal to zero, with the alternative hypothesis, H_a, stating that the mean difference is not equal to zero.

$$H_0: \mu_d = D_0$$
$$H_a: \mu_d \neq D_0$$

The value of alpha (α) is set at 0.05, as this gives a higher chance of not rejecting H_0 in the case that H_0 is true.

t-Test: Paired Two Sample for Means

	Variable 1	*Variable 2*
Mean	45.78125	50.0625
Variance	869.9829	1447.22177
Observations	32	32
Pearson Correlation	0.943424	
Hypothesized Mean Difference	0	
df	31	
t Stat	-1.71244	
P(T<=t) one-tail	0.048402	
t Critical one-tail	1.695519	
P(T<=t) two-tail	0.096804	
t Critical two-tail	2.039515	

Using the t values, H_0 is rejected if the absolute value of the test statistic is greater than or equal to the critical value of t.

$$\text{Reject } H_0 \text{ if } |t_0| \geq t_{\alpha/2}$$

In this case we find that

$$|-1.71244| < 2.039515$$

and so H_0 is not rejected.

According to the Paired T-test, the mean of the sample does not differ significantly from zero, but this test is only valid if the sample comes from a normal distribution.

Transformation of Data Follow By Paired T-Test

If the data do indeed come from a non-normal distribution, then the previous t-test is not valid. The data can be transformed by taking the square root of all data points, a process which reduces the effects of outliers, helping to counteract skew and making the data closer to normal. Another Paired T-test was performed on the population mean, μ_d, using the set of "normalized" data. The null hypothesis, H_o will again be that the mean difference is equal to zero, with the alternative hypothesis, H_a, that the mean difference is not equal to zero.

$$H_o: \mu_d = D_0$$
$$H_a: \mu_d \neq D_0$$

The test statistic was calculated for the new set of data, and the test conducted as before, with alpha set at 0.05, and H_o being rejected for values of the test statistic that are greater than t-values from the T-distribution.

Mean	-0.70892
Standard deviation	3.125946
Standard error	0.552594
Test statistic	-1.2829

It was shown that H_o is rejected when

$$| t_o | \geq t_{\alpha/2}$$

but when the t-value from the table is compared to the test statistic it is found that

$$| -1.2829 | < 2.0395$$

and so H_o is not rejected.

Paired Sign Test

A Paired Sign Test for the median difference does not require the sample to follow any distribution at all (it is non-parametric), and only stipulates that the variables in question be continuous. This description fits the population, and it would not violate any assumptions if it were used. The Paired Sign Test examines the signs (positive or negative) associated with each of the differences x_i-y_i in the sample. For this test it is hypothesized that the median difference (M_d) in the population is equal to zero (D_0). In other words

$$H_o: M_d = D_0$$
$$H_a: M_d \neq D_0$$

where H_o is the null hypothesis, and H_a is the test hypothesis. To find the probability that H_o is true, the following equation is used

$$\text{P-value} = 2P(X \leq a)$$

where $a = \min(x_+, x_-)$. The notation x_+ represents the number of positive differences in the sample (x_i-$y_i > 0$), and x_- represents the number of negative differences in the sample (x_i-$y_i < 0$). The size of the test sample is defined as n', where n' is the sum of x_+ and x_-. For a two-tailed test the P-value is obtained by finding the appropriate value in the table ($n' = 29$, $x = 13$) and doubling it. The P-value is 0.711, indicating very strong evidence supporting H_o. The Paired Sign Test clearly indicates that the median difference between the samples is approximately equal to zero.

Conclusions

The above tests all indicate that there is not sufficient evidence to assume that the difference between the two samples is significantly different from zero. Thus it can be assumed that the use of the E.coli method for measuring bacteria levels (MPN/100ml) does not produce significantly different results from the Fecal Coliform method of measuring bacteria levels (cfu/100ml). CARP can switch its method for measuring bacteria in the Annapolis River without compromising the comparability between previous and future data.

Appendix D – Preliminary Observations of Low Dissolved Oxygen Levels in the Annapolis River Estuary — Autumn 2005

During September 2005, the salt wedge of the Annapolis River estuary was found to have reduced levels of dissolved oxygen (DO). Using a variety of sampling and analysis methods, dissolved oxygen in the underlying saltwater was found to be in the range of 3 to 5 mg/L, with the lowest value being 1.69 mg/L. The zone of oxygen depleted saltwater was found to extend from at least 1 km above the Town of Bridgetown to at least 8 km downstream, the farthest extent of the survey. The DO levels observed are well below those recommended by the Canadian Water Quality guidelines for the protection of freshwater and marine aquatic life. At this time, the causal mechanism for the reduced oxygen levels is not known. Given the potential impacts of reduced oxygen levels on aquatic life, a DO surveillance-monitoring program for 2006 is recommended.

Introduction

Over the past 15 years, Clean Annapolis River Project (CARP) has undertaken a number of water quality monitoring programs on the Annapolis River and its tributaries. The Annapolis River Guardians is a volunteer based program that collects water samples spring through autumn along the river's length.

The Annapolis River above Annapolis Royal is tidally influenced, with the effects of the tides reaching as far as Paradise, a distance of approximately 42 km. The region of the river immediately above the causeway and tidal generating station at Annapolis Royal is well mixed and vertically homogeneous, due to the turbulent flow through the sluice gates twice daily. Above this region, the river becomes a two-layered salt-wedge type estuary, with fresh to brackish water overlying salt water. The stability of this stratification has been found to be highly variable, being influenced by river discharge, tidal flow, and the occurrence of storm and high wind events. (Daborn, et al, 1982)

Monitoring Results

Clean Annapolis River Project (CARP) undertakes a number of monitoring programs on the fresh and tidal sections of the Annapolis River. Samples collected by boat at Bridgetown on July 4, 2005 had a mean DO of 5.22 mg/L in the underlying saltwater, and 6.88 mg/L in the overlying freshwater.

As part of its regular Annapolis River Guardians water quality monitoring program, volunteer Ronald Jones recorded a DO level of 3.80 mg/L at Bridgetown on September 5, 2005. This low result triggered a period of additional monitoring on the Annapolis River. Over the next three weeks, approximately 36 measurements were made of DO in the tidal section of the Annapolis River at various depths. An area of the river ranging from near the Britex plant at Centrelea to above the Town of Bridgetown was surveyed by boat, a distance of approximately 8 km. At sample locations from Bridgetown to Centrelea, a sharp stratification was observed between the overlying freshwater and the underlying saltwater. This thermo/haline stratification occurred at a depth of between 1.3 and 1.7m. For these locations, the mean DO from 17 salt water samples was 3.52 mg/L (Minimum 1.69 mg/L, Maximum 4.90 mg/L). The overlying fresh water at these locations had a mean DO of 8.15 mg/L.

A YSI data logger was used to record continuous DO levels at Bridgetown from October 2 to 11. Within the salt wedge, the mean DO over this period was 4.71 mg/L (Minimum 3.27 mg/L, Maximum 5.98 mg/L). On the evening of October 9, the data logger abruptly shifted from salt water to fresh water, with a mean DO of 10.55 mg/L. While the reason for this sudden shift cannot be confirmed, it does coincide with three days of very heavy rainfall and the rapid rise in river water levels throughout south western Nova Scotia. It is thought that either debris may have become ensnarled on the

buoy rope resulting in the data logger being displaced, or the large pulse of fresh water pushed the salt wedge down the estuary.

It is interesting to note that on September 6, 2004, a single low DO value of 4.80 mg/L was reported at Bridgetown. This report was followed up by additional DO measurements being taken from shore using a portable water meter. All subsequent DO readings were found to be acceptable. It is possible that a similar low-DO event was occurring in the Annapolis River in the late summer of 2004, but because additional sampling was only conducted from shore, the event was not identified.

The Canadian Water Quality Guidelines recommend dissolved oxygen levels in the range of 5.5 to 9.5 mg/L for the protection of freshwater aquatic life, and greater than 8.0 mg/L for the protection of marine aquatic life. Acute mortality has been observed when dissolved oxygen levels fall below 6 mg/L and 4 mg/L for salmonid and non-salmonid fish embryo larva, respectively. For other fish life stages, acute mortality is observed at dissolved oxygen levels below 3 mg/L (CCME, 2002). The DO levels observed in September and October 2005 in the Annapolis River estuary have thus a significant potential to cause impairment on aquatic life.

Tidal Station Activity

During the first two weeks of September 2005, the Nova Scotia Power Tidal Generating Station at Annapolis Royal experienced unforeseen mechanical problems, resulting in the turbine being offline for a number of days. At the same time, the north sluice gate was not in operation, due to routine repairs. As a result of these circumstances, the normal, twice daily, tidal flooding of the lower Annapolis River was disrupted. The relationship between these factors, and the low DO values observed in the Bridgetown area, is not known at present. The activities of the Tidal Generating Station are noted here only in an attempt to document all possible factors that may have an effect on the river's DO levels.

Literature Review

Jessop (1976) conducted a physical survey of the Annapolis River following the construction of the causeway at Annapolis Royal, but prior to the installation of the tidal generating station. The river between the causeway and Bridgetown was observed to be a highly stratified estuary, with a wedge of saline water lying below the outflowing lower salinity water. Beyond the 10 km mark upriver of the causeway, the thermocline and halocline were found to be closely associated, lying at a depth of 1.5 to 2.0 m. The thermocline and salinity gradients were found to disappear at about 32 km above the causeway (between Bridgetown and Paradise).

Daborn et al (1982) conducted an ecological study of the lower Annapolis River and Basin, immediately prior to the installation of the tidal generating station. The lower river was found to be highly stratified, with thermocline and haloclines occurring at a depth of 2 to 4 m. Dissolved oxygen levels in the Annapolis River immediately above the causeway were found in the range of 75 to 100% saturation, over the period of May to November. Dissolved oxygen monitoring was not conducted further upstream.

Materials and Methods

DO samples by River Guardian Ronald Jones were collected using a horizontal Van Dorn sampler, from the mid-span of the bridge at Bridgetown and analysed using the modified Winkler titration method (Brylinsky, 2000). All other DO measurements were made using a Hydrolab Quanta multi-probe water meter. Most samples were collected by boat at mid-stream by lowering the probe to the appropriate depth. A small number of samples were also collected by wading into the river from shore.

A YSI Model 6920 Data Logger was placed in the river from October 2 to 11, 2005, at an approximate depth of 3 m. The data logger collected DO, temperature and conductivity readings every 15 minutes during this period.

Conclusions and Monitoring Plans for 2006

Based on available information, it is known that between early July and early September 2005, DO levels in the salt wedge of the Annapolis River decreased significantly. The zone of DO depleted saltwater extend over at least 9 km of the upper Annapolis River estuary. It is possible that a similar low DO event occurred in the late summer of 2004, but was not fully evaluated.

At present, it is not possible to identify the causal factors that resulted in depressed DO levels in the Annapolis River estuary. There are a number of possibilities though, including: strong thermal and haline stratification, low freshwater discharge from the Annapolis River during summer months, elevated nutrients levels and alteration of the tidal flushing within the estuary.

The following monitoring plan is proposed for the lower Annapolis River in 2006, to allow low DO levels to be more quickly identified, and the causal factors to be more fully understood.

1. Weekly samples be collected from the centre bridge span at Bridgetown over the period of May to October. Samples to be collected at two depths (0.5 m & 3.0 m), and analysed for DO, conductivity and temperature. Samples will be collected at high tide where possible.
2. A monthly survey of the Annapolis River from the Annapolis Royal causeway to the head of the tide be conducted by boat. DO, salinity, and temperature profiles to be compiled for a number of locations along the river.
3. In the event that low DO levels be observed, additional DO, salinity and temperature profiles to be completed at a finer spatial and temporal scale.
4. Collection of water samples for analysis of nitrates, phosphates and chlorophyll a from both the freshwater and saltwater zones, on a monthly basis a selected location.

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Appendix E — Quality Assurance / Quality Control Data

Introduction

Following a contamination event in 2003, Clean Annapolis River Project initiated a number of procedures to ensure the quality of data collected. In addition to instituting a new collection procedure for fecal bacteria, CARP has put in place a program of regular quality control checks on sampling equipment and methods. Further information on the quality assurance/quality control (QA/QC) program can be found in CARP's draft QA/QC Project Plan (Sharpe & Sullivan, 2006). An important initial step in the QA/QC program is the training of volunteers. A refresher session was held for all volunteers on April 12, 2005 at Middleton High School. Dr. Mike Brylinsky, Acadia University, and CARP staff conducted the session. During the 2005 season, CARP staff conducted visits with all eight volunteers on collection days in order to both collect a series of blank and split samples, as well as to ensure the consistency in collection procedures.

Background

For the purposes of CARP's Water Quality monitoring programs, a blank sample is one filled with water that is known not to contain any of the substance in question. For CARP's monitoring of fecal bacteria, either distilled or un-chlorinated tap water is added to the sample bottle. Over the 2005 season, two different types of blanks were collected: travel blanks and field blanks.

- Travel blanks are obtained by filling the sample bottle with distilled/tap water before the start of a sampling day, and placing them in the same cooler among other surface water samples. Travel blanks are used to ensure there is no cross contamination between samples while they are being transported in the same cooler and should always produce plates with no fecal bacteria growth.
- Field blanks are obtained by performing the entire sampling protocol (i.e.: attaching the bottle to the clamp, and lowering the apparatus to the water surface) but NOT submerging the bottle. The bottle is instead lifted up empty and filled with distilled/tap water on the bridge. This type of blank sample is used to test the sampling procedure and should also always produce plates with no fecal bacteria growth. A positive result on a field blank would lead to further investigations to determine the source of contamination (ie: operator, equipment, distilled water, etc).

Split samples are used to measure both precision and accuracy. Precision is expressed as the degree of agreement among repeated measurement of the same parameter and provides information on the reproducibility and consistency of the methods used. Accuracy, on the other hand, consists of how close a measurement is to the "true" value.

A split sample is single sample volume that is divided in two samples that are analysed separately. Split samples can provide information on the precision of the lab method (i.e.: the precision of Synova's Membrane Filtration Technique (MFT) and/or the precision of Environment Canada's Dionex Ion Chromatograph method, as well as CARP's own precision at the MFT). Split samples can also provide information on the accuracy of the method used (i.e.: the accuracy of volunteers at the Winkler titration).

The degree of variability between two split samples can be evaluated by calculating their relative percent difference (RPD). The RPD is expressed as the absolute difference of the two measurements multiplied by 100 and divided by the average of the two values:

$$RPD = \frac{|X_1 - X_2| \times 100}{(X_1 + X_2) / 2}$$

When more than two samples are to be compared, the degree of variability is estimated by calculating their Relative Standard Deviation (RSD). Both the RPD and the RSD are expressions of precision. The smaller the value, the greater the precision.

$$RSD = \frac{s}{X_m} X\ 100$$

s = standard deviation
X_m = mean of duplicate samples

Accuracy is estimated by taking the absolute difference between the "true" value and the "test" value. When there are multiple measurements, the true value is subtracted from the average of the test measurements. The result is compared to acceptable accuracy standards for each individual method.

Accuracy = Test/Average value — True Value

Dissolved Oxygen

Dissolved oxygen split samples were taken in 2005 using a single volume of water from a Van Dorn sampler. The accuracy of volunteer DO measurements was assessed through the collection of eight split samples, one from each of the volunteers. The Winkler Titration is widely recognized has a standard for determining dissolved oxygen and is reported to have an accuracy of at least +/- 1 mg/L. Results from the split samples shown below in Table C1, show that the volunteers attain an average accuracy of +/- 0.32 mg/L. For comparison purposes, the average DO accuracy during 2004 was +/- 0.85 mg/L. Such a high degree of accuracy gives greater confidence in the validity of the dissolved oxygen data.

Table E1. Volunteers' level of accuracy at Measuring Dissolved Oxygen Using the Winkler Titration

Site	Date	Volunteer Result mg/L	True Result* (mg/L)	Accuracy +/- (mg/L)
18	10-Jul-05	8.7	8.47	0.23
13	26-Jun-05	7.2	7.76	0.56
AY40	30-Oct-05	8.85	8.92	0.07
35	10-Jul-05	8.7	8	0.7
25	26-Jun-05	7.9	8.37	0.47
49	10-Jul-05	7.85	8.2	0.35
40	26-Jun-05	7.75	7.67	0.08
00	30-Oct-05	8.76	8.89	0.13
			Mean Accuracy	**0.32**

* The 'True' DO value was determined by calculating an average of three Winkler titrations, performed by CARP staff.

Fecal Bacteria

Throughout the sampling season, a series of blank samples were submitted blind for analysis at the Synova laboratory. The three travel blanks analysed had coliform counts of 0 cfu/100ml, indicating that there is no cross contamination between samples while they are being transported. Two field blanks collected also showed no fecal coliform growth, indicating that the fecal bacteria sample collection procedure is not contaminating the samples.

Throughout the 2005 sampling season, a total of nine split samples were collected during the sampling visits with the volunteers. These samples were submitted to the Synova laboratory under a fictitious sample identification number. The purpose of this was to assess the reproducibility of the E.coli MPN analysis method used at Synova. The results of this are presented in Table C2. The mean RPD for these split samples was found to be 14.2%.

As part of its internal quality assurance procedure, Synova conducted a replicate study to estimate the reproducibility of fecal coliform results in 2004. This was estimated by calculating the Relative Standard Deviation (RSD) of ten replicate samples collected and analysed using the Membrane Filtration Technique. The reported RSD for the ten samples was 11.1%. Given the similarity in the two RPD values, it is assumed that this represents the typical range of precision associated with fecal bacteria determinations.

Table E2. Relative Percent Difference in Duplicate Samples Analysed for Fecal Coliforms

Volunteer Result E.coli MPN (cfu/100ml)	QA/QC Result E.coli MPN (cfu/100ml)	Relative Percent Difference (RPD)
144	148	2.74
77	91	16.67
82	86	4.76
192	167	13.93
68	58	15.87
34	32	6.06
150	101	39.04
77	69	10.96
47	56	17.48
	Mean	**14.2**

Nitrate-Nitrogen

No nitrate or phosphate quality control samples were collected in 2005.

Temperature

It is known that surface waters undergo a daily cycle of warming and cooling. To date, the magnitude of this cycle for the Annapolis River was not well understood. This, coupled with fact that River Guardian volunteers do not all collect their water samples at the same time, introduces an unknown level of variability into the River Guardian temperature results.

On three occasions during the 2005 season, a StowAway Temperature Logger, (Number 002 - Onset Instruments) was deployed at Annapolis River Guardian site 40 — Paradise. During each deployment, the logger was anchored to the river bed and placed approximately 1 meter below the river's surface. The unit was deployed in late May, mid July and

mid September in an attempt capture the typical temperature profiles during the River Guardian season (April to October).

For the three deployments, a total of 25 days of monitoring data was recorded. For each calendar day, the minimum and maximum temperatures were extracted from the data sets, as well as the water temperature at noon (currently recommended time for River Guardians to collect temperature measurements).

The difference between daily minimum and maximum temperatures ranged from 0.3ºC to 3.5ºC, with the average being 1.75ºC. The sample periods in May, July and September all experienced one or more days having a daily min to max difference of at least 2.5ºC. Most of the daily minimum temperatures occurred during the period of midnight to 9.00 am. Most of the daily maximum temperatures occurred during the period of noon to 6.00 pm. Water temperatures were observed to increase rapidly during the period of 10 am to 5 pm and then decrease gradually through the night.

When the daily minimum and maximum temperatures were compared against the noon water temperature, they were found to differ on average by 0.62ºC and 1.1ºC. This result is not surprising, as noon tends to be midway through the daily warming cycle.

While the time of temperature measurement has been shown to be a source of variability, another source would be the particular thermometers used. The Annapolis River Guardians program uses combination of glass alcohol and digital thermometers. The glass thermometers have an accuracy of +/- 1ºC and precision of +/-10%. Glass thermometers are calibrated at the beginning of each sample season against a known standard. The digital thermometers have an accuracy of +/- 0.3ºC. The variability introduced to the data through the use of the glass thermometers is comparable to that arising from time of temperature measurement. The glass thermometers are gradually being phased out of active use.

Conclusions

This investigation has indicated that the time of temperature measurement represents a moderate source of variability within the River Guardians program, comparable to that introduced through the use of glass thermometers. The current recommended time of temperature measurement of 12:00 am occurs at a period of rapid water temperature change. If different volunteers were to collect water samples either slightly before or after this time, this could introduce significant variability into the temperature dataset. There are two periods of the day where water temperatures exhibited limited change: mornings (e.g. 7.00 to 10.00 am) and evenings (5.00 to 8.00 pm). CARP's principal concern with respect to surface water temperature is the impact of increase temperatures of cold water fish such as trout and salmon. In order to reduce the variability introduced from time of temperature measurement and track peak water temperatures, it is recommended that:

In order to reduce the potential for variability being introduced into the dataset and ensure the entire dataset remains usable, it is recommended that:

- River Guardian volunteers be encouraged to collect water samples at a consistent time (12:00 noon)
- A temperature data logger be deployed at a single sample location for the full season, to allow the determination of a correction factor to be applied against field temperature observations.