ENVIRONMENTAL CONSULTING Tri-Star

A Comparative Study of Site-specific Guideline Methods
Results from the 2008 Testing Program

Prepared for the Department of Environment and Labour for the

Government of

Newfoundland and Labrador

and for

Environment Canada

November 2008

Executive Summary

In 2007, the Newfoundland Department of Environment and Labour initiated a project to develop site-specific water quality guidelines (SSGs) in selected water bodies in the province. This initiative resulted from the fact that under national reporting on water quality through the Canadian Environmental Sustainability Initiative (CESI) of the federal government, site-specific guidelines are recommended to determine the status of water quality. A number of water bodies were considered for evaluation, and eventually Pound Cove Brook in north-eastern Newfoundland and Pinchgut Brook in western Newfoundland were selected for development of SSGs.

In developing SSGs, there are several possible methods that can be used. These include the Background Concentration Approach, typically used in most situations, and the Water Effects Ratio (WER) Approach that is used when the Background Concentration Approach is not practical and where more certainty is required in the SSGs that are developed. The WER Approach requires that toxicity testing be performed on actual site waters and also using laboratory test waters. A ratio of the toxicity in the site water to the laboratory water is developed and the generic guideline is multiplied by the ratio that has been determined in order to calculate a SSG.

In the case of Newfoundland and Labrador, it was decided that the WER Approach would be used for the two water bodies, and that aluminum would be the variable tested in each. Aluminum was determined to be a concern in both water bodies, as well as being considered a concern throughout Newfoundland and Labrador and the Maritime provinces in general. Aluminum has two separate CCME (Canadian Council of Ministers of the Environment) guidelines depending on the pH of the water body; 5 µg/L for water bodies with pH , 6.5 and 100 µg/L for water bodies with pH > 6.5. The pH of Pound Cove Brook is < 6.5 while that of Pinchgut Brook is > 6.5. Although a more recent draft aluminum guideline has been considered by CCME as recently as 2005, aluminum is

currently not on the work plan for updating by CCME. For this reason, the current CCME guideline was used in the development of the SSGs.

In order to develop SSGs for the two water bodies for aluminum, toxicity tests were conducted using the actual site waters and the laboratory waters (hardness adjusted to match site water). The fact that actual toxicity data were generated for the two water bodies means that actual SSGs can be developed for the water bodies with great confidence, since guidelines are not being developed using studies conducted by other researchers who may have been performing tests for totally different purposes and under restrictive conditions with potentially arbitrary safety factors applied.

Tests performed for both Pound Cove Brook and for Pinchgut Brook were acute toxicity tests using Rainbow trout (*Oncorhynchus mykiss*) with measurements after 24 hours and the standard 96 hours. In addition, reproduction and survival tests using the Cladoceran *Ceriodaphnia dubia* were measured with effects measured and reported for survival as LC_{50}, NOEC (No Observed Effects Concentration), LOEC (Lowest Observed Effects Concentration), and for reproduction as NOEC, LOEC, IC_{25} and IC_{50}. Results were reported both as total and dissolved concentrations.

WER values for the chronic and acute tests for Pound Cove Brook were similar, being up to a ratio of 1.41:1 for the IC_{25} total aluminum value and 4.9:1 for the IC_{25} dissolved aluminum value. Interestingly, the IC_{50} ratios were 1:1 for total aluminum and 5.14:1 for dissolved aluminum. These ratios are very close to what was determined using the acute toxicity tests for Rainbow trout.

Since the water quality guideline for aluminum is currently expressed as dissolved aluminum, the resulting SSG for Pound Cove Brook was calculated by applying the geometric mean of the IC_{25} and IC_{50} data (5:1). Thus, using the WER, the SSG for Pound Cove Brook was calculated to be 25 μg/L. This SSG value was confirmed based on the toxicity data from this work. The lowest value showing an impact is the IC_{25} value for reproduction at 202 µg/L, while all survival data exceed 400 µg/L. Thus the calculated SSG seems to be reasonable considering the concentrations where effects were noted..

For Pinchgut Brook, the resulting SSG was calculated by applying the ratio for the IC_{25} value of 1.21:1. The geometric mean for the IC_{25} and IC_{50} in this case could not be used since no WER for the IC_{50} data could be calculated. Thus, using the WER, the calculated SSG would be 120 µg/L based on the generic guideline of 100 µg/L at pH levels > 6.5. This SSG was confirmed based on the toxicity data from this work. The lowest value showing an impact was the IC_{25} value for reproduction at 176 µg/L and all survival data were above 400 µg/L. Thus based on the toxicity data from this test, no adverse implications on either *Ceriodaphnia dubia* or rainbow trout would be expected from applying the proposed SSG.

It should be noted that while the laboratory test water had hardness adjusted to match the harnesses in the water bodies, the pH in the laboratory waters was not adjusted. This could be an important factor in toxicities in laboratory waters, especially for Pound Cove Brook. It is suspected that if the pH had been adjusted downward in the laboratory water to more closely match Pound Cove Brook water, that the toxicity results would have been at lower concentrations and the resulting WER values may have been higher than reported. It is recommended that future testing programs where pH can be an important variable such as for aluminum ensure that the hardness (as was done for this testing) and the pH of the laboratory test waters be adjusted to match that of the water body.

Finally, it is recommended that development of the next SSGs using the WER should be in the Virginia River in eastern Newfoundland should an assessment of the data indicate the need. This assessment should also identify variables for testing and critical periods. In western Newfoundland, Wild Cove Brook should be tested to determine the influence of the refuse site located upstream on the SSG that will ultimately be developed.

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Acknowledgements

This project is the result of considerable collaboration among individuals from the beginning. Haseen Khan and Ali Khan from Newfoundland Department of Environment and Labour conceived of the project in collaboration with Joe Pomeroy from Environment Canada. Meetings were held, advice obtained and field visits conducted with Jennifer Bonnell of Newfoundland Department of Environment and Labour and Donald Bourgeois from Environment Canada. Ken Doe from Environment Canada provided crucial advice on toxicity testing. Keith Holtze and Martina Rendas of Aquatox Testing and Consulting Inc. coordinated the toxicity testing program and provided valuable insights into the testing results.

To these people our thanks are given. We alone are responsible for errors and omissions in this report.

1. Introduction:

Water quality guidelines have been used in Canada for many decades as a means of managing water quality. The guidelines apply to individual water uses and identify levels above which effects might be noted in that user group. For nearly as long as guidelines have been used in Canada, the need to modify these because of site-specific factors has been known.

There are numerous methods available to develop site-specific water quality guidelines (SSG) or objectives (SSO). These include:

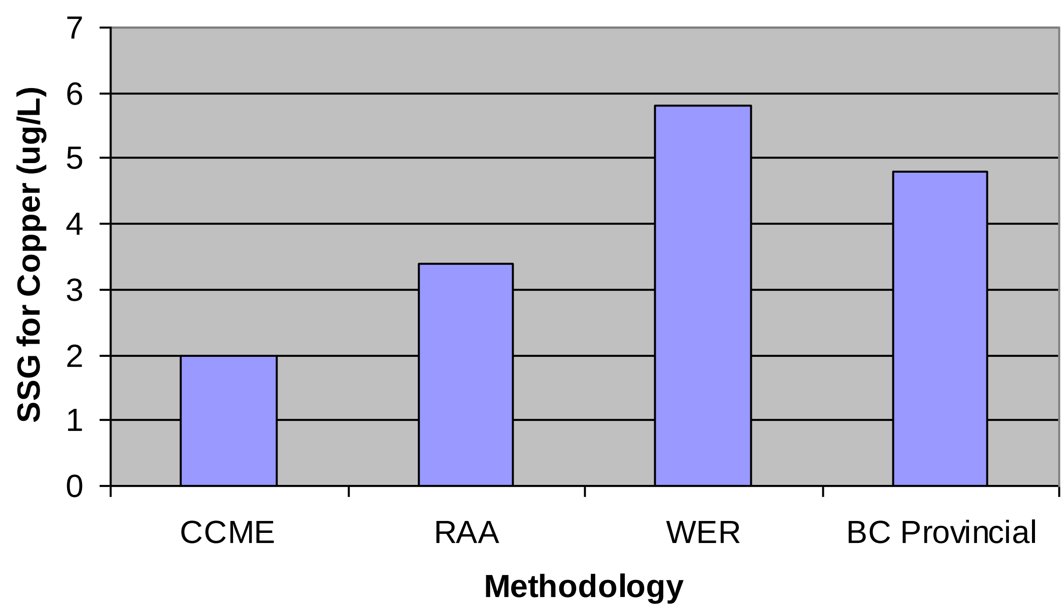
1. Making physio-chemical adjustments to the generic equation based on the site water characteristics (e.g., adjusting SSG value to reflect water hardness),
2. Using the Background Concentration Approach (taking a value to reflect "normal" values such as a 90th or 95th percentile and using that as the SSG),
3. Using an upstream value and allowing no increase at a downstream site (characterized by a maximum increase of 20% at the downstream site to allow for precision and accuracy),
4. Using the Rapid Assessment Approach (RAA) (to identify variables of concern and then using the background concentration approach, possibly in conjunction with a turbidity correction factor),
5. Using the Re-calculation procedure (if the most sensitive species used to derive the generic guideline is not present, re-calculating the SSG with data for that species removed),
6. Using a Water Effects Ratio (developed using the toxicity of site water relative to lab water), and
7. Using the Resident Species Approach (re-calculating the SSG by performing toxicity tests on species used to derive the generic guideline using site water).

In addition, the Biotic Ligand Model can be used for copper.

As is obvious from the process descriptions, the costs of developing SSGs increases as one proceeds down the list.

There has been a minimal amount of work performed in Canada to determine the relevance of guidelines developed using the methods above. The single case to date is from the Pacific and Yukon Region of Environment Canada for copper in the Sumas River (British Columbia). The Sumas River is a tributary of the Fraser River in the Fraser Valley, and drains predominantly agricultural land from the United States and Canada. Generally, agricultural type wastes and associated pesticides are of concern in this watershed. Environment Canada performed a series of toxicity tests on copper using 96-h Chinook salmon, 96-h rainbow trout and 48-h Daphnia magna tests[1].

Figure 1 - Guideline Comparison: Generic vs. RAA vs. WER for the Sumas River



[1] Source: Environment Canada. Poster Presentation to the CCME WQI Workshop, Victoria, B.C. January 2006.

Figure 1 illustrates the fact that the generic CCME guideline is quite overly protective, relative to a background concentration value determined using the Rapid Assessment Approach, and the generic guideline value for a maximum concentration derived from the B.C. Water Quality Guidelines, and that calculated using the Water Effects Ratio (WER). In fact, the WER allows as much as three times the amount of copper in the system with no obvious impact to either aquatic life or the safety factor used to derive the original generic guideline.

1.1 National Reporting on Water Quality

In 2005, annual reports began to be released by Statistics Canada and Environment Canada on the quality of ambient waters in Canada. The reports provide information on water quality as calculated using the Water Quality Index. The basis for the Index is that comparisons between ambient water quality measurements are made with either ambient guidelines or site-specific objectives (guidelines adjusted to reflect ambient ameliorating factors).

The province of Newfoundland and Labrador is interested in investigating the use of the WER because there have been no site-specific objectives developed in the province and a number of water bodies with no human influence do not receive the WQI score in line with what is expected from the experts. CCME advice on use of the WQI is that site-specific objectives should be used and not national guideline values.

1.2 Principle Behind the Water Effects Ratio

The guiding principles behind the use of the WER are that during the testing of aquatic organisms in the laboratory (to generate the data from which guidelines are eventually derived), very pure water is used which does not have any of the inherent attributes that may be present in a water body to ameliorate the toxicity of particular contaminants. To adjust for this shortfall, the WER procedure calls for the use of water body-specific water for testing in side-by-side toxicity tests with the traditional laboratory water used for toxicity testing. Since an ambient guideline developed using toxicity data has an inherent safety factor incorporated into it that is to compensate for effects or un-tested organisms and additive or synergistic effects of multiple contaminants, the logic employed in the WER is that the guideline value for a specific water body tested in side-by-side tests can be multiplied by a ratio of the toxicity test value determined using site water to that determined using laboratory water.

1.3 Contaminants Considered for use of the WER

Six metals lend themselves for adjustment using the seven methods listed because the generic guidelines are based on hardness concentrations and/or other actors such as total organic carbon concentrations. These metals are aluminum, lead, nickel, copper, cadmium, and zinc. In addition, guidelines for metals such as iron are quite dated and it is not known whether a hardness relationship exists. It is known that when B.C. Ministry of Environment attempted to have some traditional toxicity testing performed on iron in the late 1990's, that iron precipitation became a problem at higher iron concentrations, making testing quite difficult. This is unlikely to be a problem in many of the Newfoundland water bodies where pH is normally near or less than 7.0.

Although there are many water bodies in Newfoundland and Labrador with naturally elevated aluminum concentrations, performing work related to aluminum is possibly premature because there is no revised CCME guideline even though it has been drafted for several years. Some jurisdictions such as Ontario and British Columbia use aluminum guidelines based on dissolved concentrations. However, the draft CCME guideline suggests monomeric aluminum as the critical aluminum form[2]. The availability of performing these tests for monomeric aluminum is limited. However, it would still be possible to do work on aluminum using the information in the draft CCME guideline, if a laboratory were available to measure both dissolved and monomeric aluminum concentrations during the test periods. At worst, testing on aluminum might involve

[2] CCME. Draft 2005. Water Quality Guidelines for the Protection of Aquatic Life – Aluminum.

testing for dissolved and total concentrations and developing an appropriate ratio for use in the short-term.

The guidelines for the other metals, other than cadmium, relative to pending CCME guidelines also do not have up-to-date guideline values. It is our suspicion that cadmium may be difficult to test because of the extremely low concentrations involved at the guideline level. The national Canadian Environmental Sustainability indicator (CESI) reporting project has used the B.C. guideline for zinc; however, it suggests one value at hardness less than 90 mg/L and values based on hardness for hardness values greater than 90 mg/L. Developing a SSG for zinc should be considered carefully since there is no CCME guideline that is appropriate.

This leaves four other potential metals that could be tested: copper, iron, lead, and nickel. For these metals, CESI has used EPA guidelines – the most up-to-date EPA guideline is for copper.

In order to initiate this work and the project, a one-day meeting was held in St. John's on June 26, 2007 followed by a one-day field reconnaissance visit to potential sites that might be useful in the second phase of this project. These results are discussed in later sections of this report. However, the results of that meeting in general were that two candidate water bodies (using a draft report on a number of Newfoundland water bodies) were identified (Pound Cove Brook and Wild Cove Brook) and three metals based on that analysis were chosen for consideration: copper, iron and aluminum.

2. Discussion:

2.1 General Principles of the Water Effects Ratio

The general principle behind the use of the WER is that the natural attribute of many systems will ameliorate toxic effects seen in testing in a laboratory, and that if side-by-side tests are performed using laboratory water and water from source water, that the amount of a contaminant (say a metal) can be increased in the natural source water. This was illustrated in Figure 1 for the Sumas River in British Columbia.

To generate these ratios, generally a vertebrate and an invertebrate are tested, with preference given to chronic tests and tests carried out during different seasons. Generally, only one test is needed for the vertebrate species (usually a fish). When all of this testing occurs, the results are then "averaged" using a geometric mean of the values to derive one WER. This then leads to one new guideline value, derived by multiplying the generic guideline by the WER. This can be an expensive method given that five toxicity tests are performed on two different water sources (laboratory and natural) and the associated chemistry needs to be performed at a minimum of seven points for each test. As well, the chemistry has to be measured at these seven points at the beginning, middle and ends of the tests. If each toxicity test nominally cost $1000, and each chemistry sample nominally was only $100, testing for the WER would cost $10,000 for the actual toxicity tests and $21,000 for the associated chemistry.

The geometric mean value generally reduces the impact of high values on the resulting "average". From a management perspective, this can be both a plus and minus. The negative of this is that a larger ratio than the minimum obtained is used, thereby potentially reducing the available safety factor. On the positive side, the impact of high extreme ratios on the "average" is reduced.

To address all these concerns, it might be possible for some water bodies with adequate database to generate a ratio at a "worst-case" time of year, producing the lowest possible ratio. Tests to generate WER should be performed for both vertebrate and invertebrate species in these situations and should be performed when the lowest hardness and dissolved organic carbon are expected in a water body. To define the "worst-case", the agency responsible for establishing the guideline could use one of three possible ratios: the lowest ratio derived (maximum safety factor), the ratio derived from the geometric mean of the two ratios, or finally the arithmetic average of the ratios. The latter two potentially reduce the available safety factor; however, it must be remembered that this might be compensated for at other times of year when higher concentrations of hardness or dissolved organic carbon might be present.

2.2 Water Bodies Under Consideration and Potential Metals of Concern

As noted in the Introduction, two water bodies for testing in Newfoundland and Labrador were identified at the kick-off meeting for the project. These water bodies were Wild Cove Brook in western Newfoundland and Pound Cove Brook in north-eastern Newfoundland. These sites are shown in Figure 2. These were selected because both were relatively pristine sites, there was the potential ability to collect samples using existing Department staff, and because a good historical data set existed for each water body. The latter fact is critical if a truly meaningful testing program is to be developed. After due consideration by Department staff, it was decided that Wild Cove Brook might not be suitable because it was not as pristine as anticipated and was replaced by Pinchgut Brook (Figure 3).

Other sites near St. John's were also the subject of a field investigation following the meeting and recommendations for further testing of water bodies near St. John's are included in a later section of the report.

Sites were not considered in Labrador because of the lack of good long-term data sets and the difficulties in collecting samples. The former problem will be addressed through a concerted sampling program in future years.

Figure 2

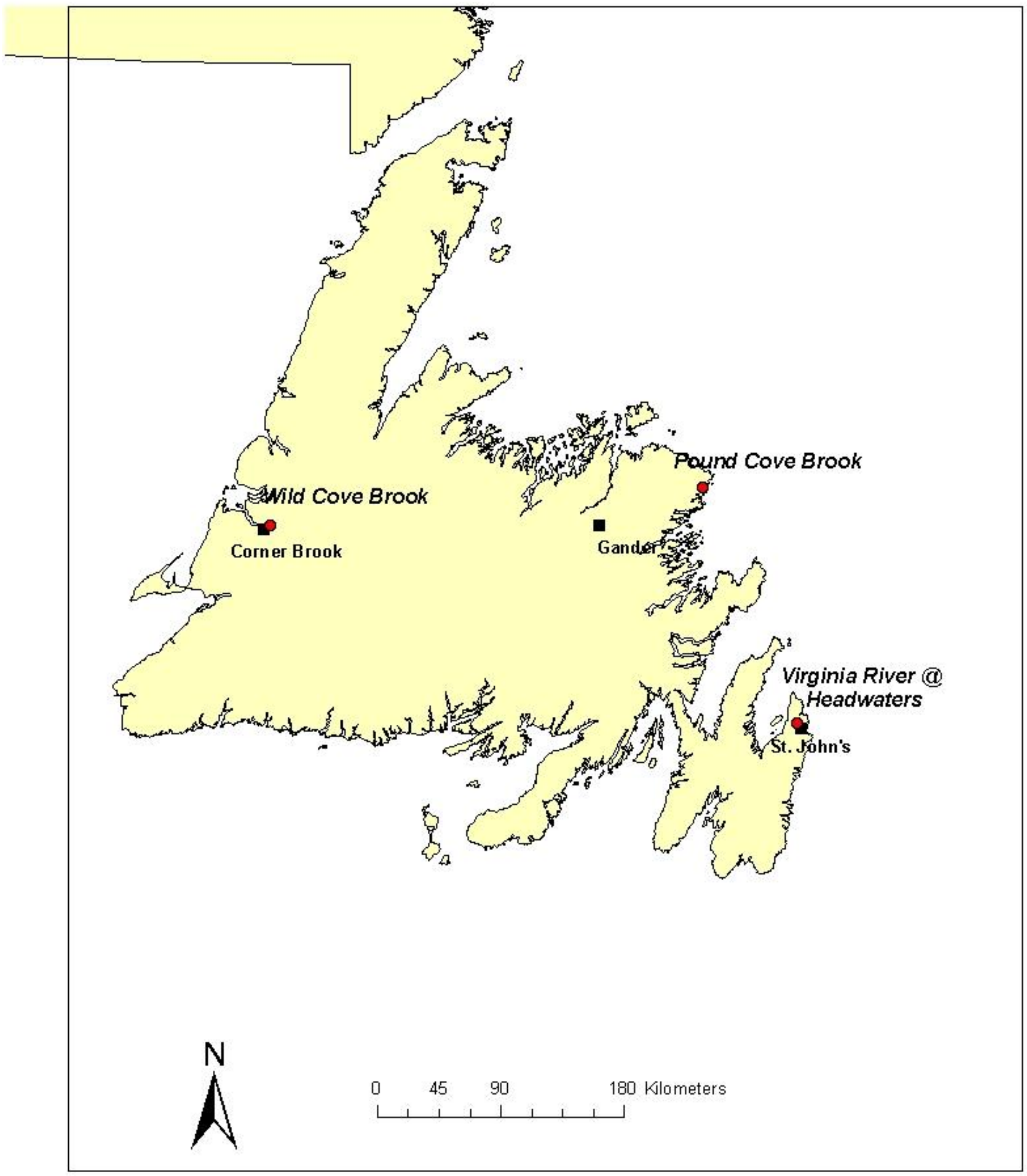


Figure 2 – Locations of Pound Cove Brook and Wild Cove Brook

Figure 3 – Locations of Pound Cove Brook and Pinchgut Brook

2.3 Evaluation of the Water Bodies

2.3.1 Pound Cove Brook

Pound Cove Brook (at Route 330) has been sampled since August 1986 at site NF02YR0001 (latitude 49 10 41.40; longitude 53 33 32.70) which is only 4.0 metres above sea level. Pound Cove Brook is located about 75 m north-east from the navigation light at Pound Cove.

The headwaters of Pound Cove Brook are at Rocky Ridge Pond, located about 23 km west from the sampling site. Before reaching Pound Cove, the brook also passes through Powder Hill Pond. Numerous tributaries connect to the brook along its 23 km path.

Table 1 – Watershed Statistics for Pound Cove Brook

Drainage Area	120.4 km^2
Forested Area	85.6 km^2
Lakes	23.6 km^2
Organic Terrain	11.2 km^2
Mean channel length	27.5 km
Mean channel gradient	0.22%
Elevation drop	60 m

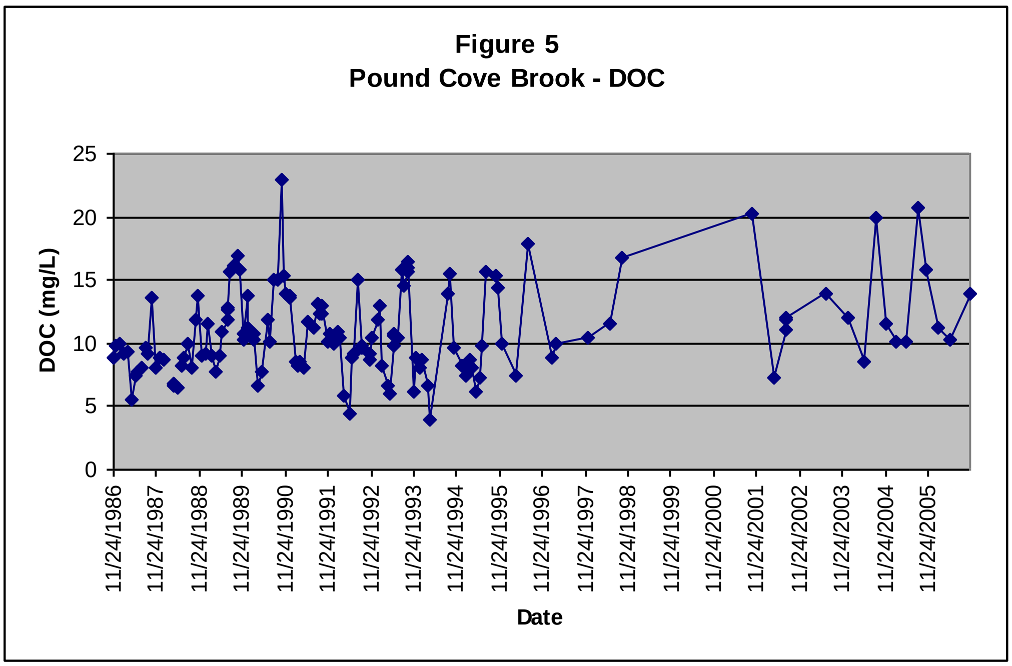
The Pound Cove Brook watershed receives a mean annual precipitation volume of 1030 mm that provides a mean annual runoff volume equivalent of 750 mm. This means that there is minimal storage of water in the soil, which would result in a low pH reflective of precipitation chemistry and minimal buffering. Open water is present on a mean annual basis about 250 days per year.

The basin is dominated by poorly developed soil originating from glacial till that rarely exceeds 1.5 m in depth. There are no active or past mines in the watershed. Development pressure in the water basin is considered to be low.

Figure 4 – Pound Cove Brook

2.3.1.1 Dissolved Organic Carbon and Hardness

There is a good long-term data set for Pound Cove Brook that has been analyzed by Water Resources Division (draft 2007). In the period between 1987 and 1996, 126 measurements were made of dissolved organic carbon while only an additional 22 measurements were made to the end of 2006. The fluctuation of the DOC values through that period is shown in Figure 5. Hardness values for Pound Cove Brook are plotted in Figure 6.



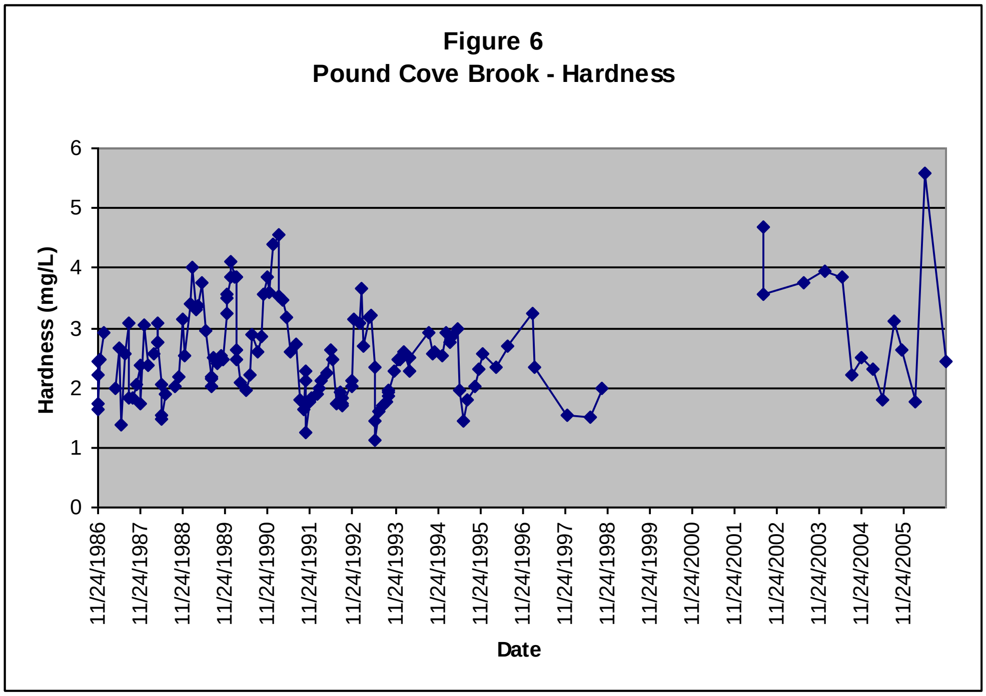
As can be seen from Figure 5, the lowest DOC values were generally recorded in either April or May in the 1987 to 1996 period of time. These low values ranged from 4 mg/L in April 1994 to a high of 8.1 mg/L in May 1991. **This indicates that the April – May period will be a key sampling period when we could expect the lowest DOC values**.

It is interesting to compare this to hardness concentrations plotted in Figure 6. The lowest hardness values coincided with the low DOC period, indicating again that the April – May period will be a key window for testing Water Effects Ratio in Pound Cove Brook. Total organic carbon would have the largest ameliorating potential impact on reducing toxicity of metals such as copper; however, its influence on other metals such as aluminum or iron is currently not known. It might therefore be important that some sampling be carried out when TOC values might be expected to be at their highest concentrations.

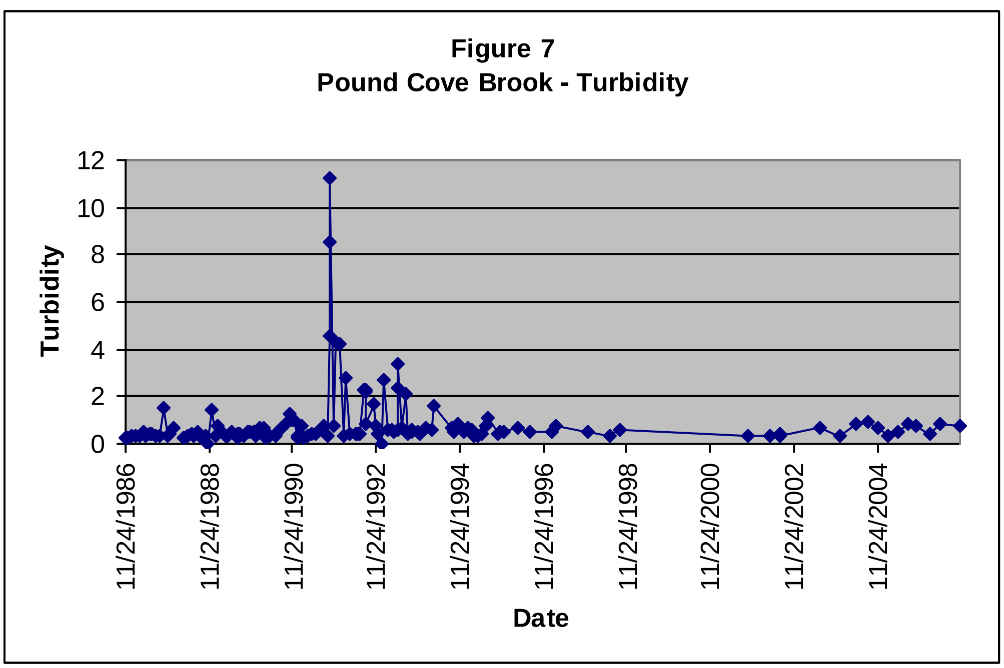
Since increased TOC values likely would originate from runoff that carries organic matter, one might expect that these higher concentrations would occur during periods of high water flow (and low hardness concentrations due to dilution effects). In general, high TOC values seem to correspond (Figure 5) to the period from late June to the end of the summer on a yearly basis, with July being one of the most frequent months with lowest values. It must be noted that the low hardness concentrations (Figure 6) are generally 2 mg/L or slightly less, but that peak concentrations are only in the 4 to 5 mg/L range. **This suggests that we are unlikely to see great differences among any of the sampling periods because of the small range of hardness values**.

Table 2 – Summary of DOC and Hardness Concentrations (mg/L) in Pound Cove Brook

	DOC	Hardness
Number of Values	148	145
Maximum	22.9	5.6
Minimum	4.0	1.1
Mean	10.9	2.6
Standard Deviation	3.4	0.79
90th %ile	15.6	3.71
95th %ile	16.4	3.94
Mean + 2 SD	17.6	4.2



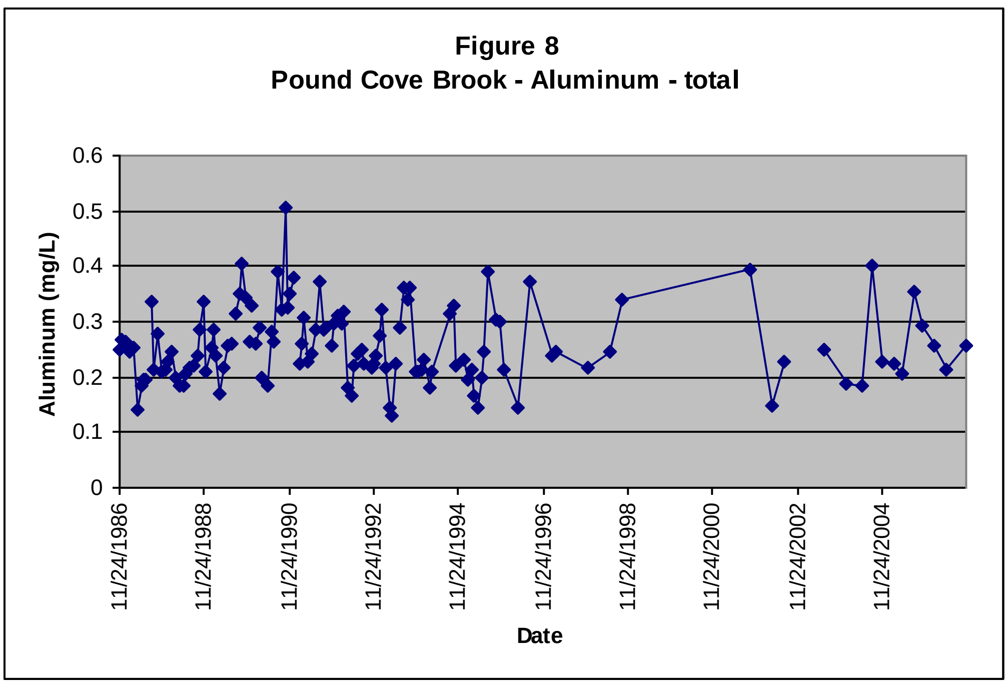
In an attempt to see whether another variable might help to predict higher TOC values, we plotted turbidity values through time on the assumption that higher turbidity would reflect periods of higher runoff and higher TOC concentrations. The data are plotted in Figure 7 below.



It is apparent from the graph that turbidity is generally low, likely meaning that runoff is not a large component of the flow. Peak values, if they are to occur, seem to take place in the autumn of many years (October through December).

2.3.1.2 Aluminum

As noted earlier, the CCME guideline for aluminum is being revised; however, there has not been a draft document produced since about 2005. The present CCME guideline value for waters with pH less than 6.5 is 5 µg/L as dissolved aluminum. This guideline is a value that is well below all total aluminum measurements in Pound Cove Brook. Aluminum concentrations in Pound Cove Brook do not appear to be increasing (Figure 8) and have no relationship to turbidity levels (Figure 9).



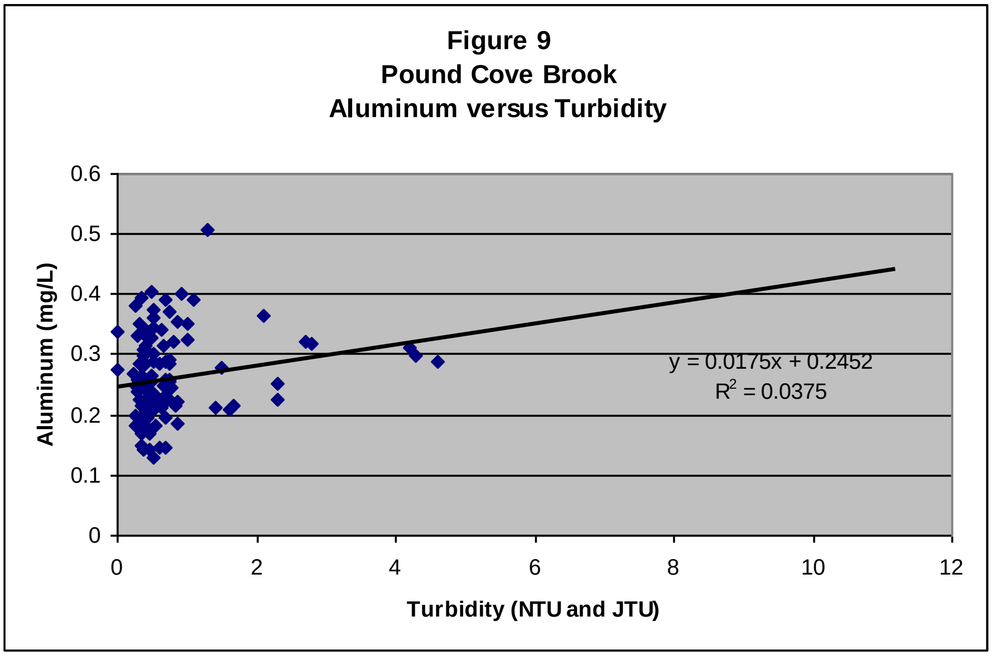
One technique used in most cases to develop a site-specific guideline is the background concentration approach. Inherent in this approach is to develop a site-specific guideline value that reflects background yet still provides an adequate degree of safety to aquatic life.

Table 3 – Summary of Aluminum Concentrations (mg/L) in Pound Cove Brook

Number of Values	128
Maximum	0.506
Minimum	0.130
Mean	0.257
Standard Deviation	0.066
90th %ile	0.351
95th %ile	0.378
Mean + 2 SD	0.390

From Table 3, it is apparent that a site-specific guideline using the existing data would lead to a value in the order of 0.35 to 0.40 mg/L total aluminum. Such a value, although justifiable using this approach eliminates any safety factor used to derive the original guideline, and reinforces the need to use other techniques to develop a site-specific guideline.

The Rapid Assessment Approach is a technique to identify, for long-term data sets, variables that may be a concern due to values approaching or exceeding guidelines, or showing a deteriorating trend. Aluminum, using this technique, becomes a candidate variable. Using the second method associated with the RAA, where a relationship is developed with turbidity to eliminate high values associated with turbidity that are not likely a problem for aquatic life, this technique also fails since there is no turbidity-aluminum relationship present (Figure 9).



2.3.1.3 Copper

The current CCME guideline for total copper is a maximum of 2 µg/L for hardness values from 0 to 120 mg/L. This is the range of hardness concentrations applicable to Pound Cove Brook.

Total copper concentrations for the period of record have been plotted in Figure 10 and are summarized in Table 4. Although the guideline value has been exceeded on occasion, the maximum value of 0.0087 mg/L is only about four times higher than the guideline, and certainly within the range of safety factors. Most importantly, the guideline has not been exceeded since 1994.

If the background concentration approach were used to develop a site-specific copper guideline, the site-specific guideline would only exceed the guideline if the 95th percentile (0.0020 mg/L) or the mean plus two standard deviations were used (0.0036 mg/L) as the SSG value. Using the background concentration technique, we would likely select a value of about 2 µg/L as the site-specific guideline, or the same as the generic guideline value.

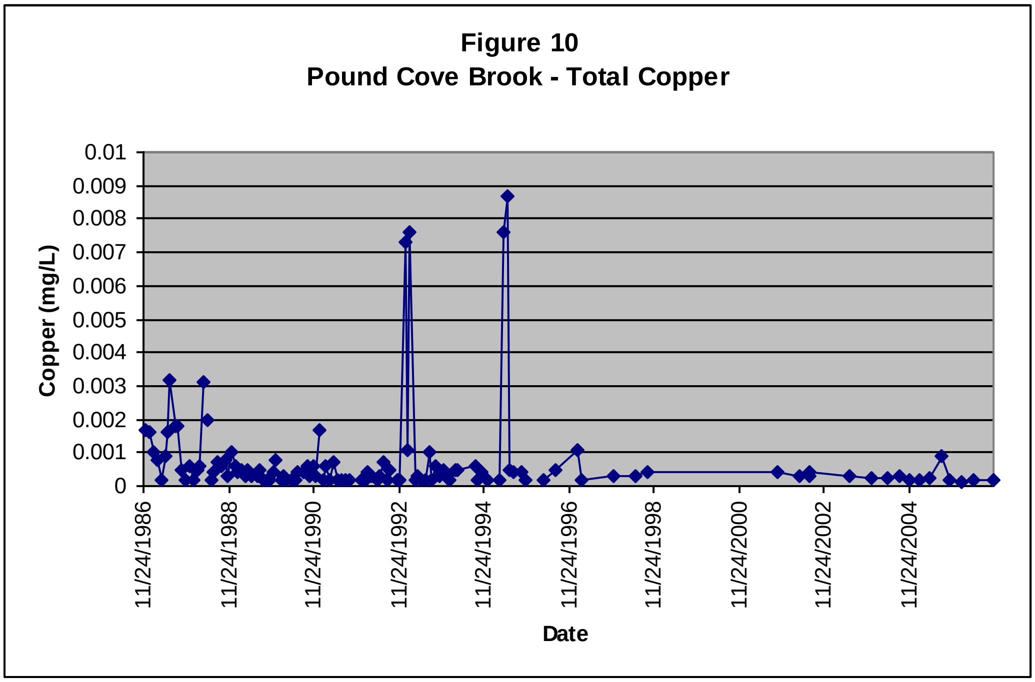
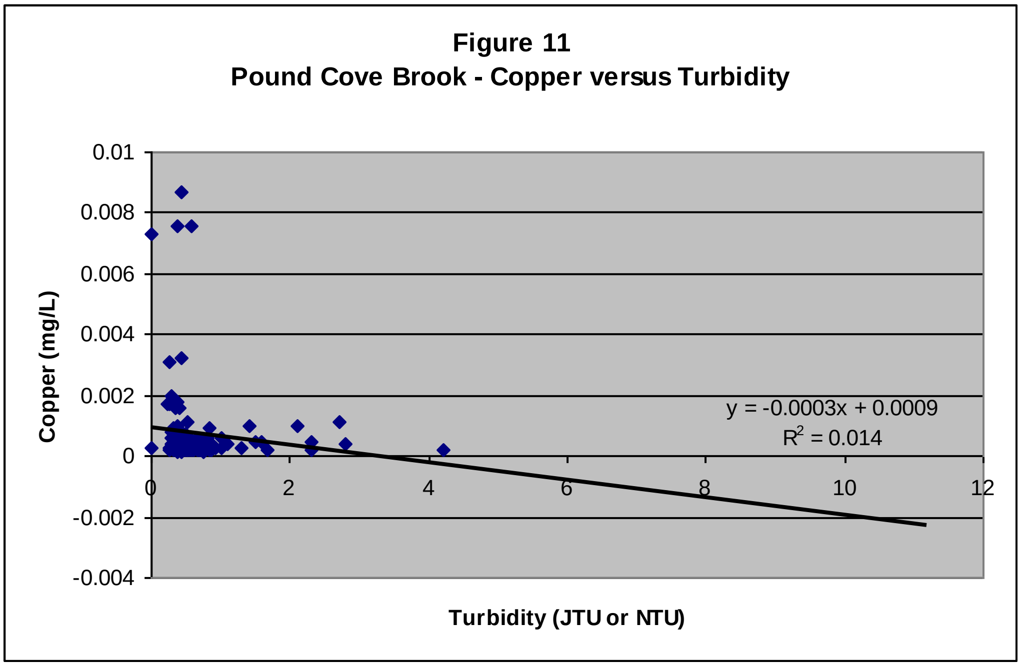


Table 4 – Summary of Copper Concentrations (mg/L) in Pound Cove Brook

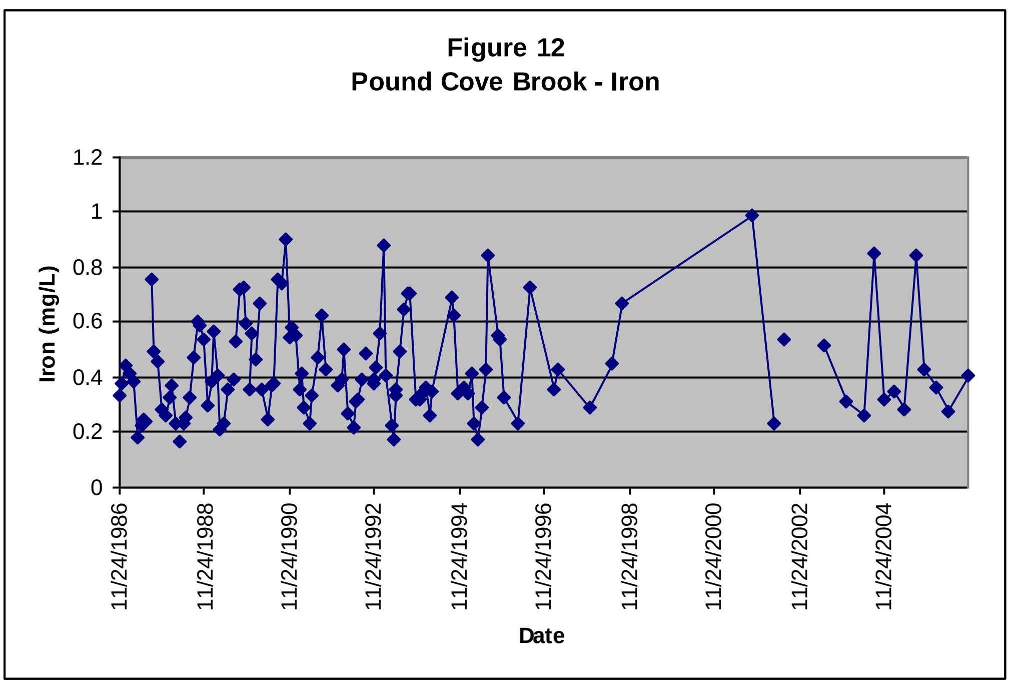
Number of Values	123
Maximum	0.0087
Minimum	0.0001
Mean	0.0008
Standard Deviation	0.0014
90th %ile	0.0015
95th %ile	0.0020
Mean + 2 SD	0.0036

If the RAA approach is used, copper which has exceeded the guideline would certainly be a candidate variable; however, there is no correlation between copper and turbidity concentrations (Figure 11), so the background concentration approach would be used to develop a site-specific guideline. The fact that the potential site-specific guideline does not eliminate a large proportion of the safety factor, and copper values have met the generic guidelines during the last ten years, it is difficult to recommend strongly the need to develop a WER for copper in this water body.



2.3.1.4 Iron

The CCME water quality guideline to protect aquatic life from iron is a maximum concentration of 0.3 mg/L. This guideline is regularly exceeded in Pound Cove Brook.



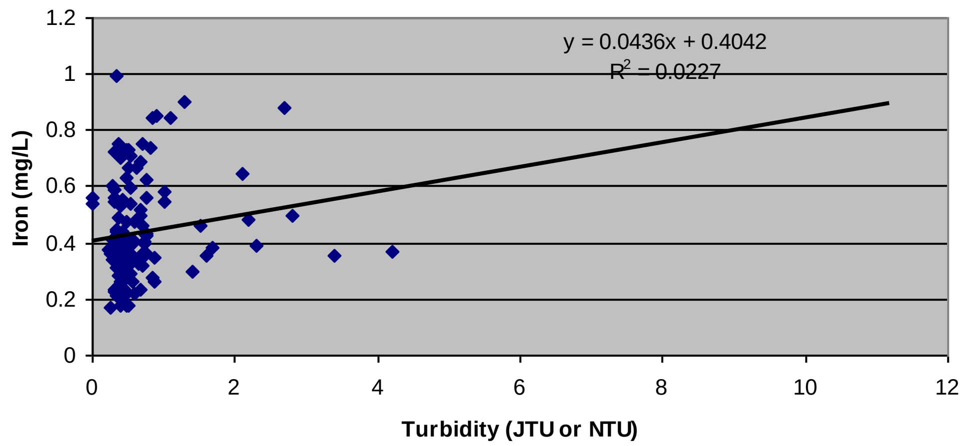
The data in Table 5 confirm that the guideline is regularly exceeded. If the background concentration approach were used to develop a site-specific iron guideline, the site-specific guideline would likely be the 95th percentile (0.756 mg/L) or the mean plus two standard deviations (0.79 mg/L). Using the background concentration technique, we would likely select a value of about 0.75 mg/L as the site-specific guideline. This reduces the safety factor only minimally.

Table 5 – Summary of Iron Concentrations (mg/L) in Pound Cove Brook

Number of Values	126
Maximum	0.992
Minimum	0.167
Mean	0.433
Standard Deviation	0.179
90th %ile	0.705
95th %ile	0.756
Mean + 2 SD	0.790

If the RAA approach is used, iron which has exceeded the guideline would certainly be a candidate variable; however, there is no correlation between iron and turbidity concentrations (Figure 13), so the background concentration approach would be used to develop a site-specific guideline. **The potential site-specific guideline would eliminate a proportion of the safety factor, so we would recommend developing a WER for iron in this water body.** However, as pointed out in earlier sections of this report, iron can be a difficult variable to test because it can precipitate out. For this reason, iron would be a less desirable candidate for testing than aluminum.

Figure 13
Pound Cove Brook - Iron versus Turbidiity



2.3.2 Pinchgut Brook

Pinchgut Brook (at TCH bridge) has been sampled since August 1986 at site NF02YJ0004 (latitude 48 47 51.00; longitude 58 03 43.00) which is three kilometres upstream from its confluence with George's Lake (which is drained by Harry's Creek into the Gulf of St. Lawrence).

The headwaters of Pinchgut Brook consist of heavily forested hilly and mountainous slopes draining into Pinchgut Lake. Watershed characteristics are summarized in Table 6 and the watershed is depicted in Figure 14.

Table 6 – Watershed Statistics for Pinchgut Brook

Drainage Area	119 km^2
Forested Area	102.3 km^2
Barren	4.8 km^2
Lakes	6 km^2
Organic Terrain	6 km^2
Mean channel length	16.6 km
Mean channel gradient	2.8 %
Elevation drop	464 m

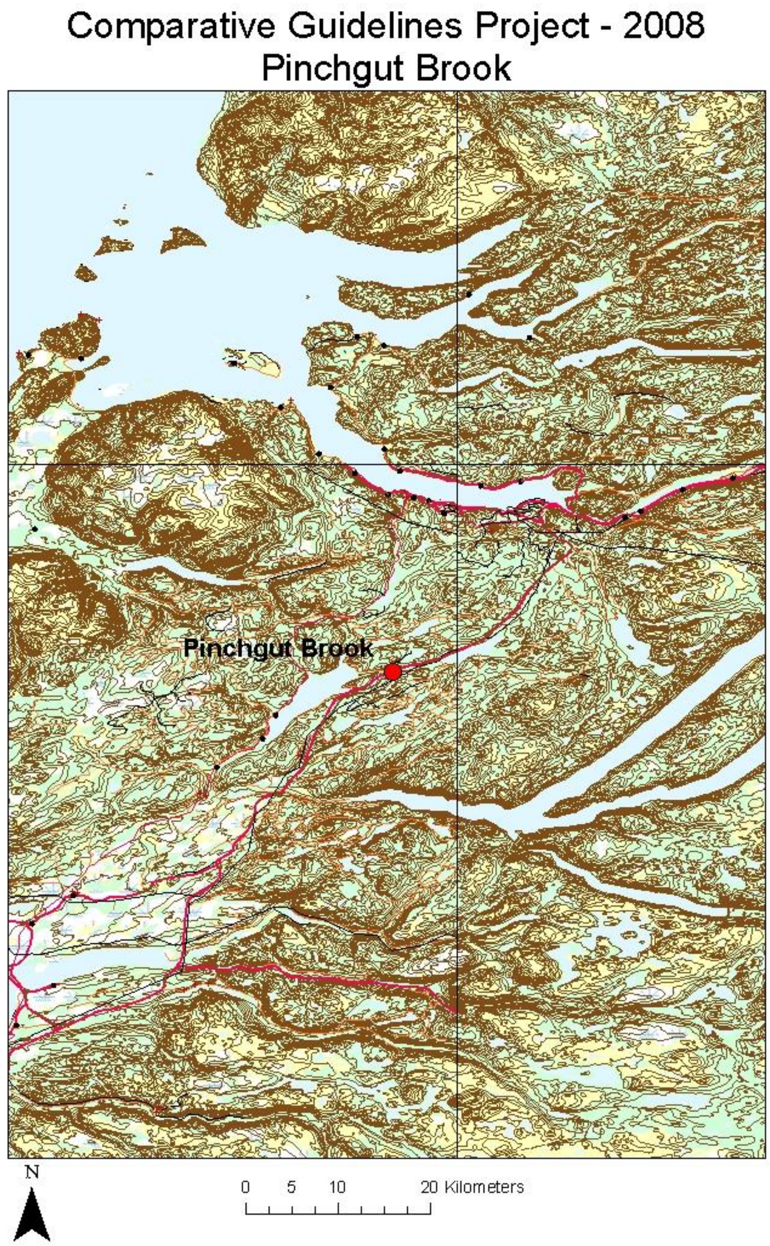


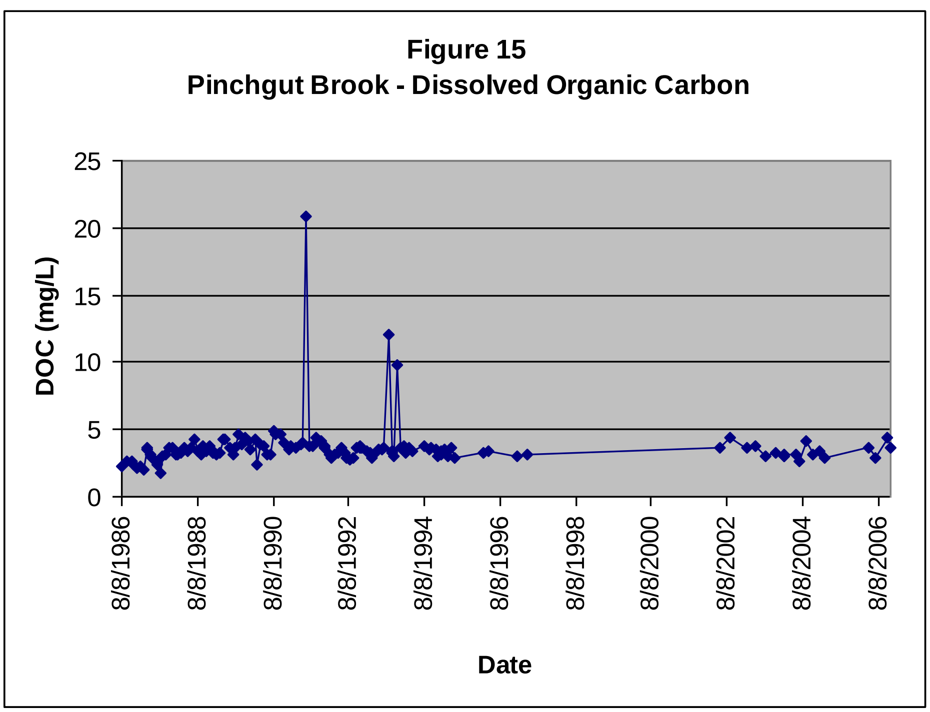
Figure 14 – Pinchgut Brook

The Pinchgut Brook watershed receives a mean annual precipitation volume of 1175 mm that provides a mean annual runoff volume equivalent of 1200 mm. This means that there is no storage of water in the soil, which would result in a low pH reflective of precipitation chemistry and minimal buffering. Open water is present on a mean annual basis about 108 days per year.

The basin is mostly till veneer and moraine deposits of variable thickness overlaying bedrock. Tills vary from silt-sand to clay-silt and locally include ice contact sand and gravel.

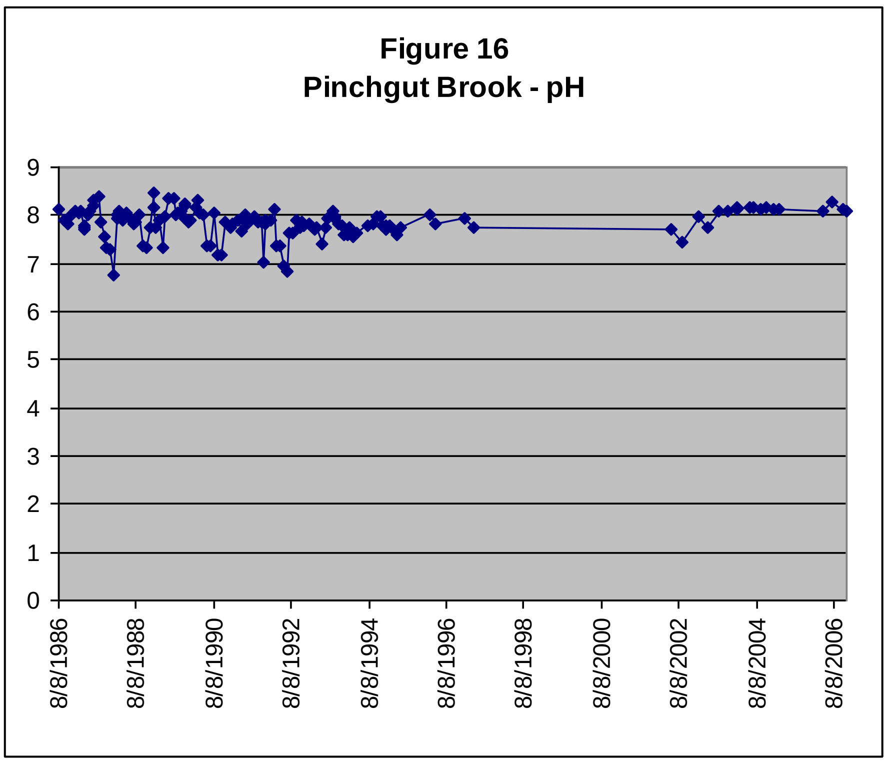
2.3.2.1 DOC, pH and Hardness

There is a good long-term data set for Pinchgut Brook that began in 1986 but that was terminated for about five years between 1997 and 2002. The fluctuation of the DOC values through that period is shown in Figure 15, while ph values are plotted in Figure 16 and hardness values in Figure 17.



As can be seen from Figure 15, the lowest DOC values were generally recorded in the summer months with values as low as1.7 mg/L but usually no higher than 5 mg/L. Exceptions to this have been as high as about 21 m/L in June 1991. There is usually only a small variation in DOC levels however with the 5th percentile value of 2.5 mg/L and the 95th percentile of 4.4 mg/L **This indicates that the summer period will be a preferred sampling period when we could expect the lowest DOC values; however, it is likely that any time would be acceptable.**.

The pH in Pinchgut Brook is higher than expected based on the runoff and rainfall values. The pH is generally higher than 7.0 and as high as about 8.5.



It is interesting to compare this to hardness concentrations plotted in Figure 17 to the DOC. The lowest hardness values coincided with the low DOC period, indicating again that the summer period will be a key window for testing Water Effects Ratio in Pinchgut Brook; however, the 5th percentile was 58 mg/L and the 95th percentile was 76 mg/L, indicating that hardness is in a relatively narrow band. This means that timing of sampling with respect to hardness is not crucial. As well, we suspect that the minimum hardness value recorded was an outlier, which if removed form the data set, would result in a smaller range between the 5th and 95th percentile values.

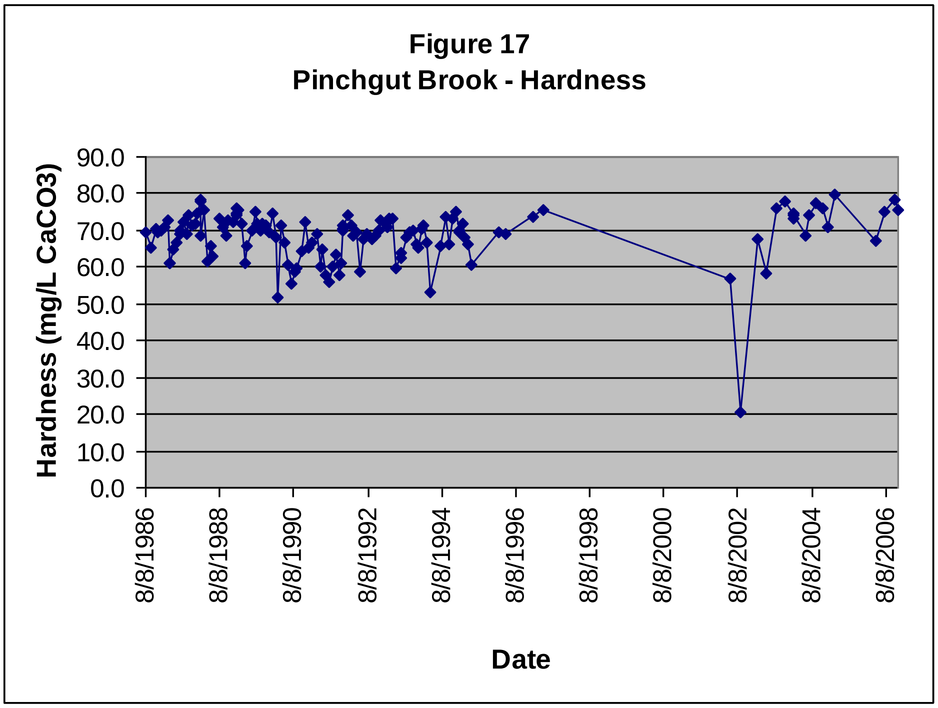
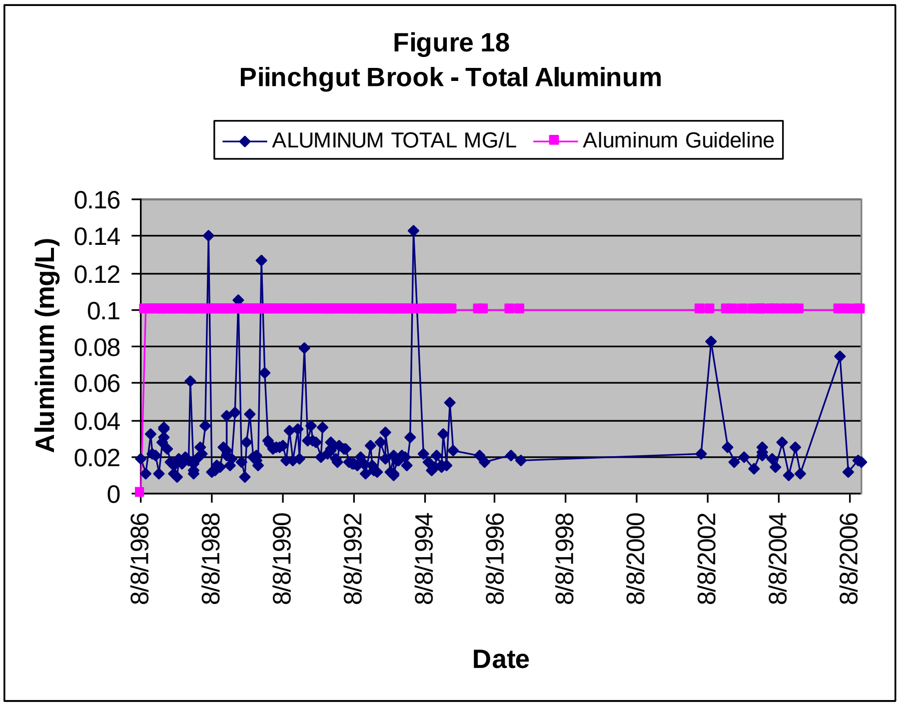


Table 7 – Summary of DOC and Hardness Concentrations (mg/L) in Pinchgut Brook

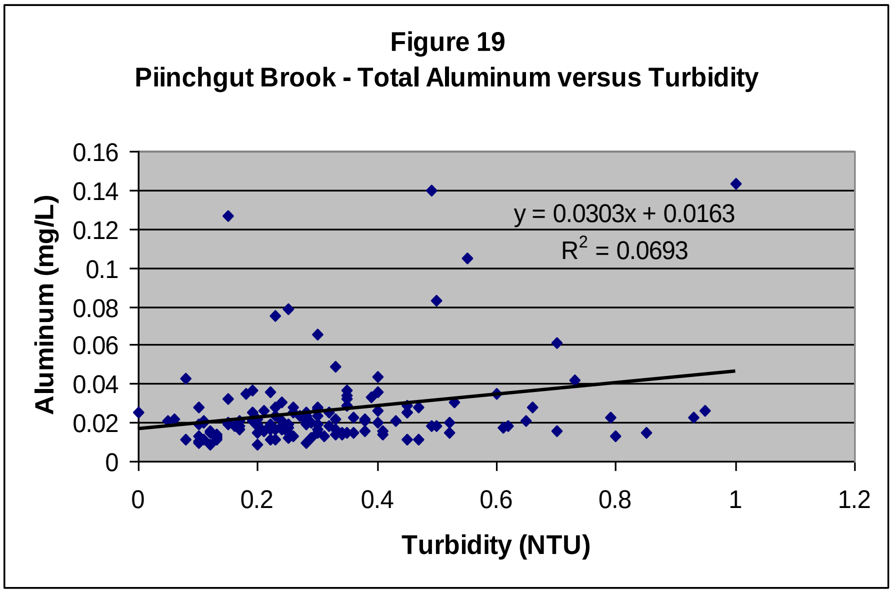
	DOC	Hardness
Number of Values	140	139
Maximum	20.8	79. 6
Minimum	1.7	20. 7
Mean	3.7	68.4
Median	3 5	69. 8
95th %ile	4.4	76.1
5th %ile	2. 5	58.0

2.3.2.2 Aluminum

As noted earlier, the CCME guideline for aluminum is being revised; however, there has not been a draft document produced since about 2005 and it is not on the CCME work plan[3]. The present CCME guideline value for waters with pH greater than 6.5 is 100 µg/L as dissolved aluminum. This guideline is a value that is well above many aluminum measurements in Pinchgut Brook. Aluminum concentrations in Pinchgut Brook do not appear to be increasing (Figure 18) and have no relationship to turbidity levels (Figure 19).



[3] Personal Communication. Susan Roe, National Guidelines and Standards Office, to L. Swain. August 28, 2008



2.3.2.3 Copper

The current CCME guideline for total copper is a maximum of 2 µg/L for hardness values from 0 to 120 mg/L. This is the range of hardness concentrations applicable to Pinchgut Brook.

Total copper concentrations for the period of record have been plotted in Figure 20 and are summarized in Table 8. Although the guideline value has been exceeded on occasion, the maximum value of 0.014 mg/L is about seven times higher than the guideline, and within the range of safety factors. Most importantly, the guideline has not been exceeded since 1994.

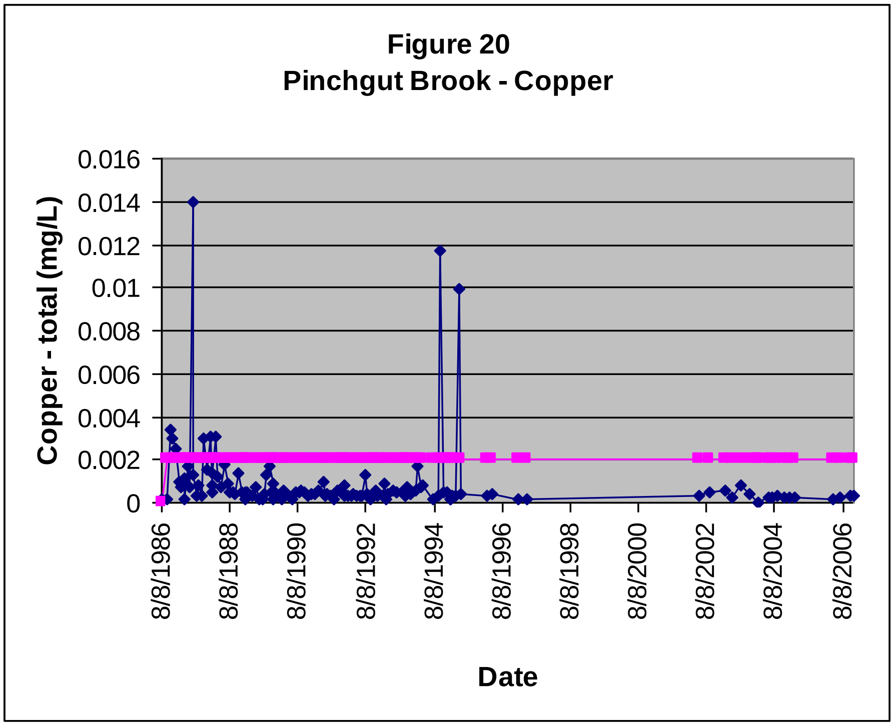
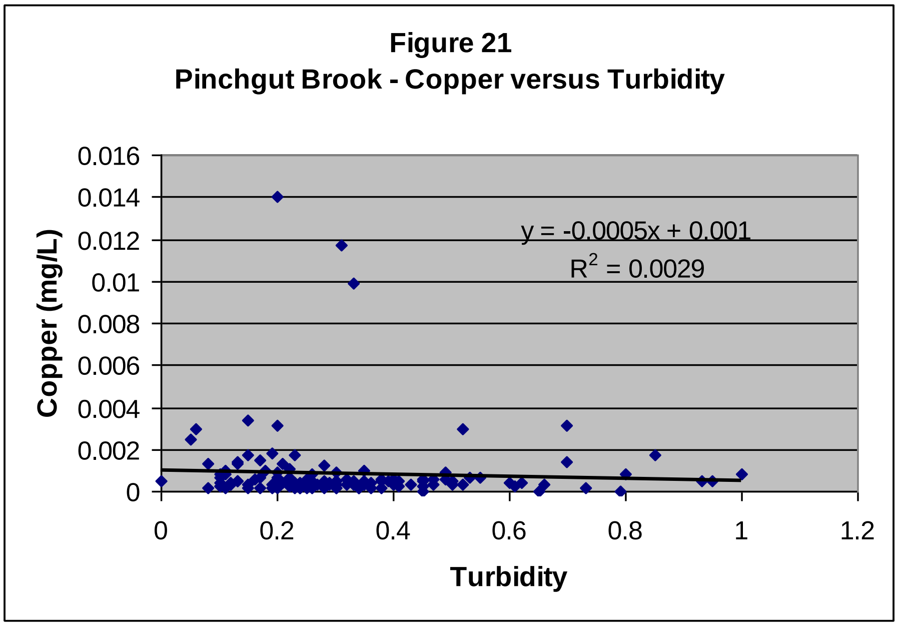


Table 8 – Summary of Copper Concentrations (mg/L) in Pinchgut Brook

Number of Values	137
Maximum	0.014
Minimum	0.00002
Mean	0.0009
Median	0.0004
95th %ile	0.003
5th %ile	0.0002

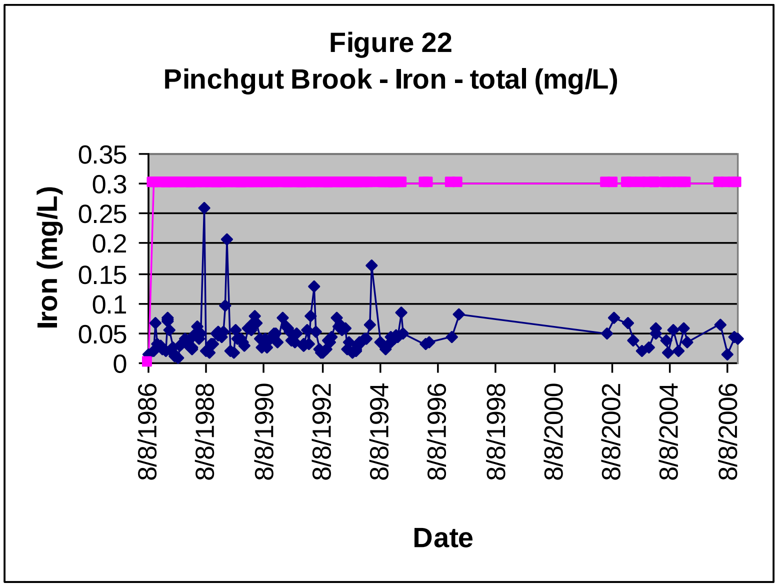
Most values have been low, with the 95th percentile value of 0.003 mg/L. As with other variables, there is no relationship between total copper concentrations and turbidity (Figure 21).



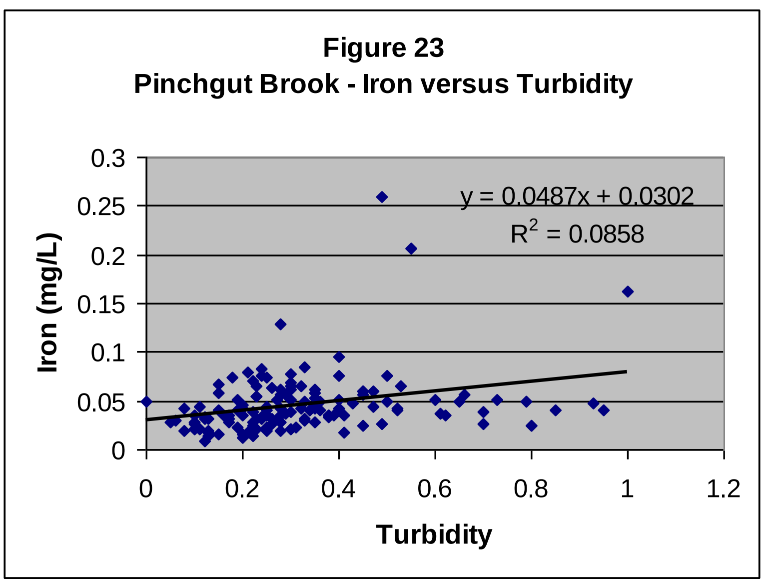
If the RAA approach is used, copper which has exceeded the guideline would certainly be a candidate variable; however, there is no correlation between copper and turbidity concentrations (Figure 21), so the background concentration approach would be used to develop a site-specific guideline. The fact that the potential site-specific guideline does not eliminate a large proportion of the safety factor, and copper values have met the generic guidelines during the last ten years, it is difficult to recommend strongly the need to develop a WER for copper in this water body.

2.3.2.4 Iron

The CCME water quality guideline to protect aquatic life from iron is a maximum concentration of 0.3 mg/L. This guideline has not been exceeded in Pinchgut Brook (Figure 22).



If the RAA approach is used, iron which has been within 80% of the guideline would certainly be a candidate variable; however, there is no correlation between iron and turbidity concentrations (Figure 23), so the background concentration approach would be used to develop a site-specific guideline. **The SSG based on this approach would be 0.3 mg/L**.



2.4 Timing of Monitoring and Variables for the Water Bodies

2.4.1 Critical Monitoring Periods

Two variables are considered potentially important for testing metals: hardness and organic carbon. For the water bodies under consideration, the critical lowest periods of time when DOC should be measured is between April and May for Pound Cove Brook, and during the summer time for Pinchgut Brook.

For hardness, the lowest concentrations are usually seen in April to May in Pound Cove Brook and summer in Pinchgut Brook. The critical periods of time are summarized in Table 9.

Table 9 Critical Sampling Periods and Expected Concentrations

Water Body	DOC	Hardness
Pound Cove Brook	April – May (5 – 7 mg/L)	April – May (1 -2 mg/L)
Pinchgut Brook	Summer (2.5 – 4.4 mg/L)	Summer (58 – 76 mg/L)

2.4.2 Metals That Should Be Tested for WER

We have considered three metals in our analysis: aluminum, copper, and iron. Aluminum is certainly a variable in the Atlantic provinces and Newfoundland that frequently exceeds the generic guidelines, be it for water bodies with pH less than 6.5 or for those where pH is greater than 6.5. Based on using the background concentration approach, we speculate that site-specific guidelines for aluminum might be in the order of 350 µg/L in Pound Cove Brook, and 100 µg/L in Pinchgut Brook.

The pH and therefore the generic guidelines of the water bodies is different, meaning that the "intrusion" into the safety factor for the SSG for each water body is significantly different. This could be quite an interesting aspect if part of the goal of the project is to compare the impact on the two different levels. We do have concerns and speculate that the high natural levels of aluminum might somehow make developing a WER of any significance possible. What we mean is that the WER developed may be so low as to be of virtually no use in setting a SSG. However, until testing is tried, there is no information to confirm or refute this argument.

There is also the concern that when testing for aluminum, one might not be able to measure the monomeric form of aluminum as well as say dissolved or total concentrations. However, there are no recent indications that the CCME plan to continue developing the aluminum guideline based on monomeric aluminum in the near future (not on the CCME plans).

The potential SSGs put forth in earlier sections for copper are summarized in Table 10. As can be seen, it is suggested that the generic guidelines for copper may be suitable for use in the Pound Cove Brook and Pinchgut Brook.

Table 10 Possible SSGs for the Water Bodies

Water Body	**Aluminum (Total)**	**Copper (Total)**	**Iron (Total)**
Pound Cove Brook	350 – 400 μg/L	2 μg/L	0.75 mg/L
Pinchgut Brook	100 μg/L	2 μg/L	0.3 mg/L

Iron is a variable that appears to be a bit more consistent between the two water bodies, at least where development of the SSG is concerned. The maximum suggested SSG is only two and one-half times the generic guideline.

2.4.3 Conclusions

Critical monitoring periods appear to be during the early months of the year for both DOC and hardness. The actual program design will depend on the ability to collect samples and on the ability of the laboratory to analyze those samples. Laboratory considerations are looked at in Chapter 3.

Table 11 Suggested Months for Sampling the Water Bodies

Water Body	**DOC**	**Hardness**
Pound Cove Brook	April	May
Pinchgut Brook	Summer	Summer

As for the metal to test, we feel that aluminum offers the most potential. This is based on:

- Possible SSGs based on other techniques for aluminum in one of the water bodies (Pound cove Brook) far exceed the available safety factor.
- A new guideline for aluminum based on monomeric aluminum is unlikely to be available for many years.
- There is little benefit to testing for copper because the suggested SSGs are at the generic guideline values for the water bodies.
- There is no known relationship for iron with DOC or hardness. In that case, the use of the WER could be a means to develop a meaningful SSG while contributing to the scientific literature on whether these variables influence iron toxicity. However, the proposed SSGs may be sufficient for reporting purposes.

3.0Testing Protocol – A Practical Guide for the Project

It is imperative that testing be performed uniformly and according to Protocols established by the US EPA or CCME. MacDonald (1997) has simplified these for Canada and specifically for British Columbia and these are repeated here in context of the Newfoundland situation. MacDonald (1997) noted the following:
"The procedures recommended in this document for calculating the final WER are less complicated than those that have been applied in the United States (see USEPA 1994). The recommended simplification of the procedures is intended to make the procedure more accessible and understandable to potential practitioners. In addition, the modifications reflect the mechanics of the WQG derivation process in Canada, in which a safety factor is applied to the lowest observed effect level. This conservative approach provides room for flexibility in the derivation of the site-specific WQOs, while still providing a margin of safety for protecting designated water uses."

The following information should be collected during WER studies:

- **We need to characterize both the site water and laboratory water used in the study**, including conventional variables (*e.g*., hardness, pH, D.O., water temperature, alkalinity, conductivity, suspended solids, and total organic carbon during collection and at start of test), and total and dissolved metals;
- **At the same schedule, temperature, pH, and dissolved oxygen must be measured in the chemistry controls of each treatment group for both site water and laboratory water**;
- **Nominal concentrations can be used in the range-finding test**;
- **As a minimum, the concentrations of the toxicant must be measured in all treatments in which some of the test organisms were adversely affected**, the highest treatment that did not adversely affect any test organism, and the lowest treatment that adversely affected all of the test organisms.
- **The concentrations of the toxicant should be measured in all test solutions at the midpoint of the test** (for static tests) or the midpoint of each renewal period

(for static renewal tests). Alternatively, toxicant concentrations may be measured at the beginning and end of the test or each renewal period;

- **For metals, both total and dissolved concentrations must be measured in all test solutions**.
- The response data for all of the concentrations in the dilution series should be reported to facilitate more detailed evaluation of the toxicity data; and,
- Appropriate quality assurance/quality control measures (e.g., replicates, sample splits, matrix spikes, etc.) must be performed to support all analytical results.

3.1 Selection of Toxicity Tests

The following selection criteria that were developed by MacDonald (1997) for cost-effective application in British Columbia and Yukon:

- A minimum of two distinct toxicity tests should be conducted, including **one acute bioassay and one short-term chronic** bioassay. (**Acute toxicity tests are conducted over a short period of time in relation to the organism's life span**, generally lasting minutes, hours, or a few days. By comparison, **chronic bioassays span a significant portion of the organism's life span (often more than 10%)** and are particularly appropriate for evaluating substances that are persistent in the aquatic environment). A third toxicity test (preferably a short-term chronic test) should be conducted if the results of the range-finding tests suggest that the two primary tests are likely to produce substantially different WERs (*i.e*., more than a factor of 3);
- The test species used to determine WERs should be in different orders and should **include at least one vertebrate and one invertebrate**;
- The toxicity tests should be conducted on sensitive life stages of sensitive species of aquatic organisms and measure sensitive endpoints for that life stage;
- The **test organism should be sensitive to the substance** or substances that are being tested;

- The duration of the toxicity test should be appropriate for the species and life stage that is tested and for the endpoint that is being measured; and,
- **Static renewal or flow-through tests must be used when exposure durations exceed 48 hours**.

Based on the review of the available literature, the following tests are likely to be the most appropriate for determining WERs using the WER procedure:

- 48-hour acute toxicity test using water fleas, including *Daphnia magna, Daphnia pulex*, or *Ceriodaphnia dubia* (static test; EC_{50} or LC_{50} as preferred endpoints);
- 7-day short-term chronic toxicity test using the water fleas, *Ceriodaphnia dubia* (static renewal test; IC_{50} for survival and reproduction as preferred endpoints);
- 96-hour acute toxicity test using the amphipod, *Gammarus* sp. (static renewal test; EC_{50} or LC_{50} as preferred endpoints);
- 48-hour acute toxicity test using fathead minnows (*Pimephales promelas*; static test; LC_{50} as preferred endpoint);
- 96-hour acute toxicity test using fathead minnows (*Pimephales promelas*; static renewal test; LC_{50} as preferred endpoint);
- 7-day short-term chronic toxicity test using larval fathead minnows (*Pimephales promelas*; static renewal test; IC_{50} for survival and growth as preferred endpoints); and,
- 96-hour acute toxicity test using a salmonid within the genus *Oncorhynchus* or *Salmo* (static renewal test; EC_{50} or LC_{50} as preferred endpoints).

A listing of the preferred toxicity tests for determining WERs for various metals in freshwater systems is presented in the following Table. **Among the species commonly tested, rainbow trout and C. dubia generally provide the lowest WERs; therefore, at least one of these species should be tested whenever possible**.

Table 12. Preferred toxicity tests for determining water effect ratios (WERs) for metals and metalloids in freshwater systems

Metal	**Primary Tests**	**Secondary Tests**
Aluminum	7-d IC_{25} on survival and/or reproduction for *Ceriodaphnia* sp.	48-hr EC_{50} for Daphnid (Ce, Da or Si)
Copper	48-hr EC_{50} for Daphnid (Ce, Da or Si) 48-hr LC_{50} for minnow (PP) larvae 96-hr EC_{50} for *Gammarus* sp.	7-d IC_{25} on survival and/or reproduction for *Ceriodaphnia* sp. 48-hr LC_{50} for minnow (PP) larvae
Iron	Hyalella? TBD	TBD

Ce: *Ceriodaphnia* species; **Da**: *Daphnia* species; **Si**: *Simocephalus* species;
On: *Oncorhynchus* species; **Sa**: *Salmo* species; **PP**: *Pimephales promelas*.

3.2 Range-finding Tests

A range-finding test should be conducted for all of the toxicity tests that will be used to determine WERs. The purpose of the range-finding test is to determine the range of chemical concentrations that are likely to cause a response in the test organism in order to design definitive toxicity tests. Considerations for conducting range-finding tests include:

- For each species, life stage, and endpoint, the information in the toxicological data set should be used to estimate the effective concentration of the toxicant;

- Range-finding tests should be conducted using the type of site water that will be used in the definitive toxicity test (*i.e*., upstream water, actual downstream water, or simulated downstream water);
- Range-finding tests should include appropriate negative control treatments (solvent only) to assure the validity of each test;
- Range-finding tests must be initiated within 36 hours of collecting the site water;
- Range-finding tests should be conducted for 8 to 96 hours using the same life stages of the same species that will be used in the definitive toxicity tests;
- The concentrations tested in the range-finding tests should increase from roughly a factor of 10 below the value indicated in the toxicological data set for the appropriate endpoint, life stage, and species. The concentrations in the dilution series should increase by a factor of 3.2 to 10 from the lowest concentration tested. Generally, six to eight concentrations should be tested to span the possible range of effective concentrations of the toxicant. For example, if the lowest 96-hr LC_{50} of copper to Daphnia magna in the toxicological data set was reported to be 6.5 mg/L, then the dilution series for the range-finding test might include concentrations ranging from 0.6 to 201 mg/L (*e.g.*, 0.0, 0.6, 1.9, 6.1, 19.7, 62.9, and 201 mg/L);
- All of the dose-response data generated during the toxicity test should be reported; and,
- Appropriate statistical procedures (*e.g*., Probit analysis) should be applied to the results of the range-finding test to determine median effective concentrations of the toxicant in site water (based on nominal toxicant concentrations).

3.3 Definitive Toxicity Tests

Definitive toxicity tests must:

- be conducted using site water and appropriate laboratory dilution water;

- be conducted using the same type of site water that was used in the range-finding test;
- include appropriate positive (reference toxicant) and negative (solvent only) control treatments to assure the validity of each test;
- be initiated within 36 hours of collecting the site water;
- use the results of the range-finding test and toxicological database to identify an appropriate dilution series for the toxicity tests that are conducted using site water. The concentrations in the dilution series should increase by a factor of 1.1 to 1.5 from the lowest concentration tested (a factor of 1.4 is recommended). Generally, six to nine concentrations should be tested to span the possible range of effective concentrations of the toxicant; and,
- use appropriate statistical procedures (e.g., Probit analysis) should be applied to the results of the definitive toxicity tests to determine median effective concentrations of the toxicant in site water and in laboratory water (based on measured concentrations of the toxicant).

3.4 Laboratory Dilution Water

Some considerations for selecting and preparing laboratory dilution water for conducting toxicity tests include:

- should be available in adequate supply, acceptable to the test organisms, be of uniform quality, and not unnecessarily affect the results of the test;
  The laboratory dilution water must be a ground water, surface water, de-chlorinated tap water, diluted mineral water, or reconstituted water that has been demonstrated to be acceptable to aquatic organisms;
- must satisfy the requirements identified in the protocol for the toxicity tests that will be used in the study. At minimum, test organisms should survive through acclimation and testing without showing signs of stress, such as discolouration, unusual behaviour, or death;

- should be similar to those of the site water in terms of water hardness, alkalinity, and pH;
- should have concentrations of total organic carbon and total suspended solids less than 5 mg/L; and
- the results of the toxicity tests conducted in laboratory dilution water should be comparable to those conducted at other laboratories (*i.e*., similar to the data represented in the toxicological database).

3.5 Site Dilution Water

Dilution water for the toxicity tests conducted using site water should be obtained at times when the WERs are likely to be the lowest (*i.e*., when the factors that are likely to mitigate toxicity are at the lowest levels).

3.6 Test Organisms

Test organisms should:

- be obtained, cultured, held, acclimated, fed, and handled in accordance with the guidance provided in the protocol for the specific toxicity test;
- be acclimated to the laboratory dilution water for at least 48 hours prior to the initiation of toxicity tests;
- must be drawn from the same population and tested under identical conditions for a pair of side-by-side tests;
- must be assigned to treatment groups in a random or impartial basis;
- must be added to the test chambers for the side-by-side tests at the same time; and,
- must be observed at the intervals specified in the toxicity test protocol and relevant observations must be appropriately recorded.

3.7 Spiking Procedures

Considerations for spiking laboratory and site water include:

- A stock solution should be prepared using a highly soluble form of the toxicant. For metals, it is generally acceptable to use nitrate, chloride, and sulphate salts;
- Reagent or better grade chemicals must be used to prepare stock solutions for spiking water samples;
- The same stock solution must be used to add the toxicant to all of the tests that are conducted at the same time;
- For the toxicity tests conducted using site dilution water, the test solutions should be prepared using one of the four spiking procedures involving the following steps:
    - divide the mixture into two portions;
    - prepare a large volume of the highest test concentration of the toxicant using one portion of the water;
    - perform serial dilutions using the well-mixed spiked and unspiked samples of the water (*i.e.*, using a graduated cylinder); and,
    - allow the samples to equilibrate for a period of 1 to 3 hours.
- For the toxicity tests conducted using laboratory dilution water, the test solutions should be prepared using one of the two spiking procedures involving the following steps:
    - prepare a large volume of the highest test concentration of the toxicant in the laboratory dilution water;
    - perform serial dilutions using the well-mixed spiked and un-spiked samples of the laboratory dilution water (*i.e.*, using a graduated cylinder); and,
    - allow the samples to equilibrate for a period of 1 to 3 hours.
- For each treatment group, sufficient identical replicates must be prepared to support both biological testing and chemical analyses (i.e., chemistry only controls).

4.0 Results from the Water Effects Ratio Testing Program

It was decided by Departmental staff following the initial analyses performed for Pound Cove Brook and Wild Cove Brook that the latter water body may not be suitable for testing at this time. Staff recommended tat Pinchgut Brook should be the water body substituted for the testing program. In addition, it was decided that aluminum toxicity would be tested in both water bodies, since this metal was a concern throughout Newfoundland and Labrador and the Maritime provinces in general.

The CCME (Canadian Council of Ministers of the Environment) guidelines for aluminum are expressed as dissolved aluminum and are based on the 1987 CCREM (Canadian Council of Resource and Environment Ministers) document. These guidelines are that dissolved aluminum concentrations should not exceed 5 μg/L at pH < 6.5 nor 100 μg/L at pH $\geq$6.5. The latter document cites higher toxicity at lower pH values although the "toxicity of aluminum is greatly reduced at circumneutral pH levels." More recently, CCME (2005 draft) have proposed new guidelines for aluminum for pH <6.7, in terms preferably of monomeric aluminum (Table 13) although interim total aluminum guidelines (Table 14) are also cited. Aluminum is currently not on the work plan for updating by CCME[4].

Table 13: Draft CCME Water Quality Guidelines for Inorganic Monomeric Aluminum for the Protection of Aquatic Life

	pH Range		
	<5.7	**5.7 – 6.7**	**>6.7**
Al_{im} (μg/L)	2.8	0.18	N/A

N/A = not applicable

Since the existing guidelines are expressed as dissolved aluminum, toxicity tests that were conducted measured both dissolved and total aluminum concentrations. We were

[4] Personal Communication. Susan Roe, National Guidelines and Standards Office, to L. Swain. August 28, 2008.

not aware of any laboratories with the analytical capability to measure inorganic monomeric aluminum at the time of the testing. The important fact to remember is that the purpose of the testing was to establish site-specific guidelines (SSGs) for aluminum, likely using a water effects ratio (WER) procedure. The fact that actual toxicity data were generated for the two water bodies means that actual SSGs can be developed for the water bodies with great confidence, since we are not using studies conducted by chance by other researchers who may have been performing tests for other purposes and under restrictive conditions with potentially arbitrary safety factors applied.

Table 14: Draft CCME Water Quality Guidelines for Total Aluminum (µg/L) for the Protection of Aquatic Life

	DOC (mg/L)				
pH	**0.5**	**2.5**	**5.0**	**7.5**	**10.0**
4.4	6.1	6.1	6.3	6.5	6.7
4.8	6.7	7.2	8.1	9.6	11.9
5.2	8.4	8.7	12	15.4	20.3
5.6	9.8	11.6	14.9	19.3	25.2
6.0	9.2	10.8	13.7	17.8	23.2
6.4	7.4	8.2	9.7	12.1	15.6

Tests performed for both Pound Cove Brook and for Pinchgut Brook were acute toxicity tests using Rainbow trout (*Oncorhynchus mykiss*) with measurements after 24 hours and the standard 96 hours. In addition, reproduction and survival tests using the Cladoceran *Ceriodaphnia dubia* were measured with effects measured and reported for survival as LC50, NOEC, LOEC, and for reproduction as NOEC, LOEC, IC_{25} and IC_{50}. Tests were performed using laboratory water (hardness adjusted to match site water) as well as site waters. Results were reported both as total and dissolved concentrations. It should be noted that LOEC and NOEC values are actual values that will depend on the dilutions selected, whereas IC_{25} and IC_{50} values are determined statistically from the actual testing. Thus there can be situations where an IC_{25} might be higher than a LOEC.

It must be remembered that in reviewing these results that we provide in the Tables in the following sections that there are confidence limits associated with each of these reported endpoints. For this reason, when WER values have a ratio calculated as <1:1, we have reported it as 1:1 since confidence limits in such cases usually overlap. We have not done the same should ratios be greater than 1:1.

In addition, it should be noted that where values for an endpoint have been reported as greater than a concentration, that a WER has not been calculated. Similarly, we have done the same for the reported NOEC concentrations since these could occur at any number of points in the continuum. .

4.1 Pound Cove Brook

Pound Cove Brook water was sampled April 28, 2008 and arrived in the testing facility May 1, 2008. Testing began May 2, 2008. Results are reported for the test endpoints in Tables 15 and 16 and water effects ratios are also calculated. Hardness in the laboratory water was about 90 mg/L to match that in Pound Cove Brook at the time of sampling.

Water Effects ratios for the chronic and acute tests are similar, being up to a ratio of 1.41:1 for the IC_{25} total value and 4.90:1 for the dissolved value. Interestingly, the IC_{50} values were 1:1 for total and 5.14:1 for dissolved aluminum. These ratios are very close to what was determined using the acute toxicity tests for Rainbow trout.

Table 15. Toxicity Testing Results for Pound Cove Brook – Total Aluminum (µg/L)

Test	Pound Cove Brook	Laboratory Water	Water Effects Ratio (WER)
Rainbow Trout			
24-hour (survival)	671	525	1.28:1
96-hour (survival)	671	490	1.37:1
Ceriodaphnia dubia			
LC_{50} (survival)	632	900	1:1
NOEC (survival)	525	635	-
LOEC (survival)	850	1300	1:1
NOEC (reproduction)	365	315	-
LOEC (reproduction)	525	635	1:1
IC_{25} (reproduction)	240	170	1.41:1
IC_{50} (reproduction)	430	523	1:1

Table 16. Toxicity Testing Results for Pound Cove Brook – Dissolved Aluminum (µg/L)

Test	Pound Cove Brook	Laboratory Water	Water Effects Ratio (WER)
Rainbow Trout			
24-hour (survival)	539	110	4.9:1
96-hour (survival)	539	98	5.5:1
Ceriodaphnia dubia			
LC_{50} (survival)	474	110	4.31:1
NOEC (survival)	410	55	-
LOEC (survival)	595	375	1.59:1
NOEC (reproduction)	315	47.75	-
LOEC (reproduction)	410	55	7.45:1
IC_{25} (reproduction)	202	41.2	4.90:1
IC_{50} (reproduction)	355	69	5.14:1

Since the water quality guideline for aluminum is currently expressed as dissolved aluminum, the resulting SSG from this work would be calculated by applying the geometric mean of the IC_{25} and IC_{50} data (5:1). The guideline for dissolved is 5 µg/L at pH <6.5 and 100 µg/L at pH $\geq$6.5. The Pound Cove Brook water that was tested was at about the pH 6.5 level which makes application of the WER difficult. However, the historic data for Pound Cove Brook indicate that the pH is always <6.5. Thus, using the WER, the calculated SSG would be 25 µg/L.

Before this is accepted, we need to confirm that such a concentration is reasonable based on the toxicity data from this work. Looking at the data in Table 16, the lowest value showing an impact is the IC_{25} value for reproduction at 202 µg/L. This is about eight times higher than the SSG suggested from our analysis, and is in the same order as the safety factors often applied (10:1). As well, all survival data exceed 400 µg/L. Thus it seems like a reasonable SSG. The other option for the Department would be to apply a safety factor of 10:1 to the IC25 value and apply a SSG of 20 µg/L; however, that safety factor is arbitrary and we would recommend that the SSG based on the WER is better.

4.2 Pinchgut Brook

Pinchgut Brook water was sampled April 7, 2008 and arrived in the testing facility April 9, 2008. Testing began April 15, 2008. Results are reported for the test endpoints in Tables 17 and 18 and water effects ratios are also calculated. Hardness was about 10mg/L in the laboratory water to match the hardness in Pinchgut Brook at the time of sampling.

Table 17. Toxicity Testing Results for Pinchgut Brook – Total Aluminum (µg/L)

Test	Pinchgut Brook	Laboratory Water	Water Effects Ratio (WER)
Rainbow Trout			
24-hour (survival)	10539	10577	1:1
96-hour (survival)	10539	10577	1:1
Ceriodaphnia dubia			
LC_{50} (survival)	>2100	>2100	-
NOEC (survival)	>2100	>2100	-
LOEC (survival)	>2100	>2100	-
NOEC (reproduction)	170	600	-
LOEC (reproduction)	320	1150	1:1
IC_{25} (reproduction)	282	496	1:1
IC_{50} (reproduction)	478	655	1:1

Table 18. Toxicity Testing Results for Pinchgut Brook – Dissolved Aluminum (µg/L)

Test	Pinchgut Brook	Laboratory Water	Water Effects Ratio (WER)
Rainbow Trout			
24-hour (survival)	772	800	1:1
96-hour (survival)	772	800	1:1
Ceriodaphnia dubia			
LC_{50} (survival)	>407	>218.8	-
NOEC (survival)	>407	>218.8	-
LOEC (survival)	>407	>218.8	-
NOEC (reproduction)	143.8	218.8	-
LOEC (reproduction)	268.8	186.3	1.44:1
IC_{25} (reproduction)	176	146	1.21:1
IC_{50} (reproduction)	293	>218.8	-

As noted earlier, the water quality guideline for aluminum is currently expressed as dissolved aluminum; the resulting SSG from this work would be calculated by applying the ratio for the IC_{25} value of 1.21:1. We could not apply the geometric mean for the IC_{25} and IC_{50} in this case as we did for Pound Cove Brook since no WER for the IC_{50} data could be calculated. The guideline for dissolved is 5 μg/L at pH <6.5 and 100 μg/L at pH $\geq$6.5. The Pinchgut Brook water that was tested was at about the pH 8.0 level while the historic data for Pinchgut Brook indicate that the pH generally is always >6.5. Thus, using the WER, the calculated SSG would be 120 μg/L based on the generic guideline of 100 μg/L.

Before this SSG is accepted, we need to confirm that such a concentration is reasonable based on the toxicity data from this work. Looking at the data in Table 18, the lowest value showing an impact is the IC_{25} value for reproduction at 176 μg/L although the NOEC for reproduction was about 144 μg/L and all survival data were above 400 μg/L. Thus based on the toxicity data from this test, we would not expect any adverse implications on either Daphnia or rainbow trout using the proposed SSG, which therefore seems to be a reasonable SSG. The other option for the Department would be to apply a safety factor of 10:1 to the IC_{25} value and apply a SSG of 17.5 μg/L; however, that safety factor is arbitrary and we would recommend that the SSG based on the WER is a better choice.

4.3 Discussion and Conclusions

The two water bodies used for this testing program in 2008, Pound Cove Brook and Pinchgut Brook had distinctly different pH values which generally coincided with being below the pH of 6.5 or above that pH, respectively. When the laboratory test water had hardness adjusted to match the harnesses in the water bodies, the pH in the laboratory waters was not adjusted. This could be an important factor in toxicities in laboratory waters, especially for Pound Cove Brook. It is suspected that if the pH had been adjusted downward in the laboratory water to more closely match Pound Cove Brook water, that the toxicity results would have been lower and the resulting WER values higher than reported. We recommend that future testing program where pH can be an important variable such as for aluminum ensure that the hardness (as was done for this testing) and the pH of the laboratory test waters be adjusted to match that of the water body.

The existing aluminum guidelines, expressed as dissolved aluminum, are quite different at pH levels below or above 6.5. As such, the testing provides important information for water bodies in Newfoundland and Labrador, as well as in the Maritime Provinces.

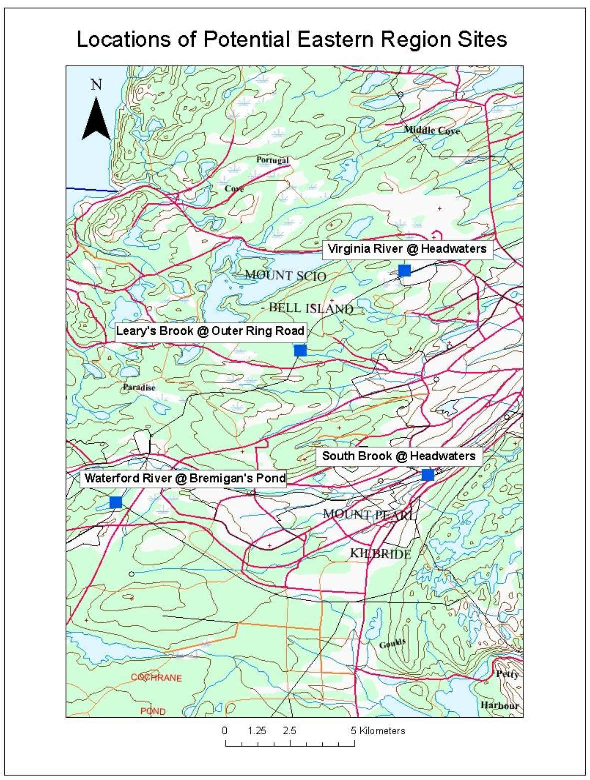
The WER procedure for Pound Cove Brook lead to a SSG of 25 μg/L compared to a generic guideline of 5 μg/L. This SSG is about eight times lower than the lowest values where chronically toxic effects were noted. For Pinchgut Brook, the SSG was only 120 μg/L compared to the generic guideline of 100 μg/L. The lowest measured effects level is less than twice this concentration.

5.0Future Testing Programs

In June 2007, four water bodies near St. John's were ground-truth to determine whether these might be suitable for future testing. The four water bodies (proceeding from north to south on Figure 21) were:

- Virginia R at headwaters Envirodat site number NF02ZM0098,
- Leary's Brook at Outer Ring Road Envirodat site number NF02ZM0184,
- South Brook at Headwaters Envirodat site number NF02ZM0185, and
- Waterford River Envirodat site number NF02ZM0182.

Figure 24



The four water bodies are discussed according to the priority for sampling each. A description of the watershed characteristics is also included. Prior to testing, data for the water bodies needs to be reviewed to identify the variables of concern and the critical sampling periods.

5.1 **Virginia R at Headwaters**

The Virginia River at Headwaters site (NF02ZM0098) has been operational since August 17, 1998 (Figure 21). It is located in St. John’s downstream from the Pippy Park Golf Course at an elevation of 170 m and at Latitude: 47 35 56.00 and Longitude: 52 45 17.00. Development Pressure at the site is considered to be low. The site is at the end of Firdale Place; approximately 50 m further alongside the fence toward the stream; and down a slight embankment; with sampling site located in center of stream.

The headwaters to Virginia River are marshes located near Penetanguishene in Airport Heights. The river runs southeast through some urban areas before draining into Virginia Lake. Virginia River continues from Virginia Lake and eventually drains into Quidi Vidi Lake and then into Quidi Vidi Harbour. The main channel length from the headwaters to the sampling site is 0.5 km and the length from the sampling site to the mouth of the river is 8.51 km.

The drainage area is only 1.00 km^2 with a mean channel length of 0.50 km. The mean stream gradient: 2.00 %. The basin consists mostly of bedrock with little or no surficial sediment and a blanket of till (greater than 1.5 m). There is a small portion at the north of the basin where a veneer of till (less than 1.5 m) over the bedrock. Till consists of a mixture of grain sizes from clay to boulders, and was deposited by glacial action.

The mean annual precipitation: 1400 mm with a mean annual runoff of 1200mm. The river has ice for less than 55 days on average. Fish species present include Atlantic salmon, Brown Trout, Brook Trout, Rainbow Smelt and Stickleback. A 1981 study by fisheries biologists found a trout biomass of up to 50 g per square metre in Virginia River.

Water Survey of Canada operated a hydrometric station (02ZM019) from 1985-1998 on the Virginia River at Cartwright Place, 4.3 km further downstream. At that site (drainage area of 5.55km^2), the mean daily discharge was 0.24 m^3/s, with a maximum daily discharge of 3.56 m^3/s in May 1985 and a minimum of 0.010 m^3/s in September 1988.

The Virginia River near its headwaters is easily reached by road and although relatively near to residential construction, appears to be a suitable site (Plate 1). Other sites just upstream from the existing site are easily reached by foot and showed good flows. The only possible concern with the existing site is that it is immediately adjacent to a residential development.

Plate 1 – Virginia River at Headwaters (Site NF02ZM0098)

For this reason we looked at possible locations upstream from the existing site. The best possible site is shown in Plates 2-4, at the entrance to the site, looking upstream from the site, and looking downstream from the site.

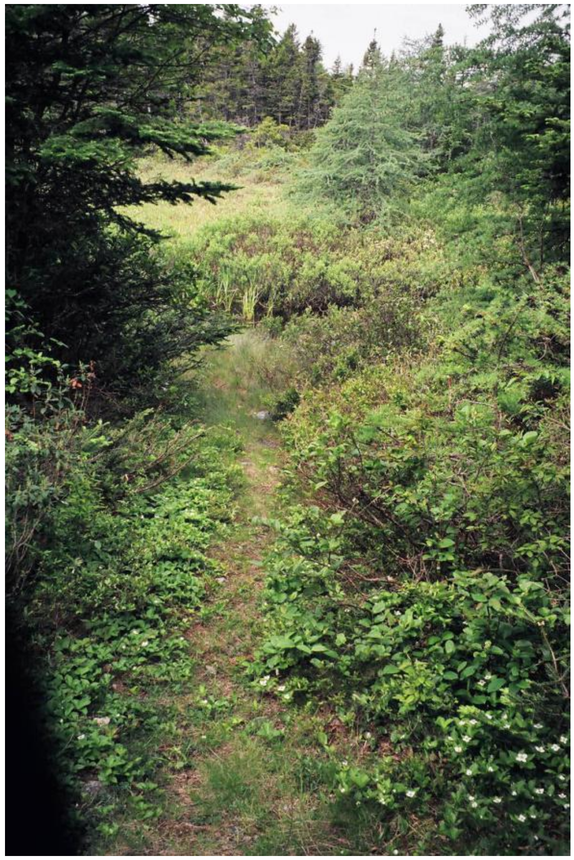


Plate 2 – Entrance to Best Possible Site – Virginia River

Plate 3 – Looking Upstream at Best Possible Site – Virginia River

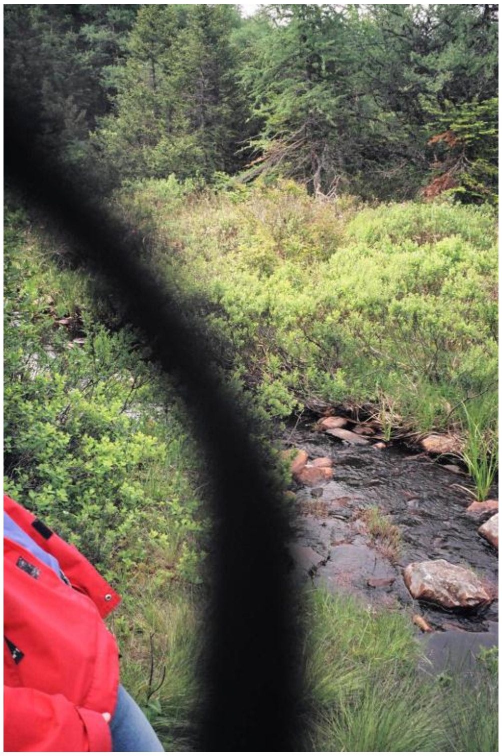


Plate 4 – Looking Downstream at Best Possible Site – Virginia River

5.2 **South Brook at Headwaters**

South Brook at Headwaters (NF02ZM0185) has been operational since August1998. It is located at latitude: 47 29 37.00 and longitude: 52 51 2.00 at an elevation of 160.00m. Development pressure near the site is considered to be low. It is located just outside of Mount Pearl in St. John’s.

The site is accessed from the Trans Canada Highway (left onto Ruby Line and then right onto Great Southern Drive and park vehicle on corner of this road and Treetop Drive (near bridge). Sampling is from the centre of the stream; approximately 5 m upstream from the bridge.

South Brook starts in a marshy area south from Mount Pearl. This marshy area is within the Southlands subdivision although very is contributed to this sampling site. The main channel length from the headwaters to the sampling site is 3 km and the length from the sampling site to the mouth of the river at St. John's Harbour is 11.5 km. After the sampling site at the headwaters, South Brook joins Waterford River in Bowring Park as a major tributary to this system.

The drainage area:6.20 km^2 with a perimeter length: of 6.80km. The mean channel length is 3.00 km at a gradient of 0.70 %. The mean annual precipitation is1400 mm with a mean annual runoff of 1200mm. There is usually less than 55 days of ice cover.

Water Survey of Canada operated a hydrometric station (02ZM021) on the brook at Pearl Town Road from 1986 until 1998. The drainage area at that station is 9.21km^2. It had a mean daily discharge: 0.41 m^3/s, with a maximum daily discharge of 10.7 m^3/s in February 1991 and a minimum daily discharge of 0.015 m^3/s in September 1987.

The basin is mostly covered by a veneer (less than 1.5m) of till over bedrock. Till consists of a mixture of grain sizes from clay to boulders, and was deposited by glacial action. In the eastern and western regions of the basin there may be a blanket (greater than 1.5m) of till over the bedrock, however the majority is veneer covered.

Fish species present include Atlantic Salmon, Brown Trout, Brook Trout, Rainbow Smelt and Stickleback.

The headwaters are near the Trans Canada Highway (Route 1). The sampling site is located alongside secondary roads in Southlands subdivision. "The Woods" golf course is located within the basin near Southlands subdivision.

South Brook near its headwaters (Plate 5) is easily reached by road but seems to be an area where residential development is occurring (Plate 6). Other sites just upstream from the existing site can be reached by foot and showed some flow.

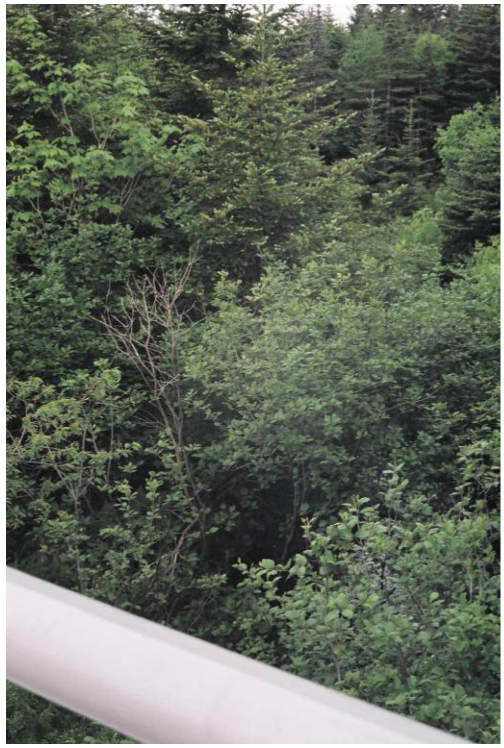


Plate 5 – South Brook at Headwaters (from bridge looking upstream)

Plate 6 – South Brook at Headwaters (Construction signs)

South Brook also looks like there may be some other human activities above the sampling site (Plate 7).

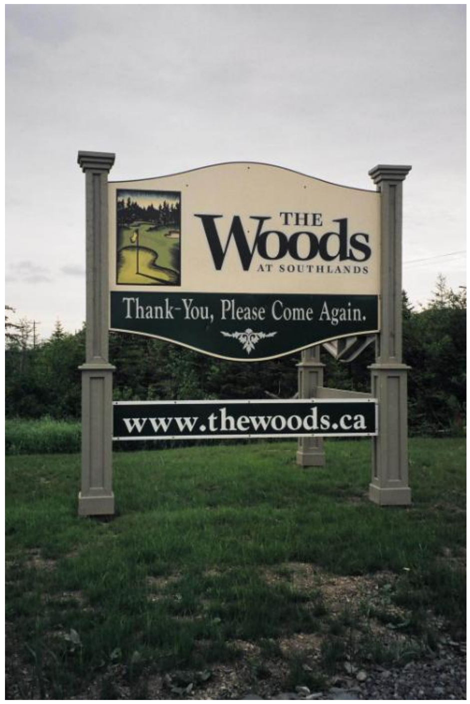


Plate 7 – Upstream from South Brook at Headwaters

5.3 **Leary's Brook at Outer Ring Road**

Leary's Brook at Outer Ring Road (NF02ZM0184) in St. John's was initiated in August 1998. It is located at latitude 47 34 16.00 and longitude 52 47 29.00 at an elevation of 144.00m. Development pressure at the site is considered to be low.

The site is located on the Outer Ring Road about 1 km before the Thorburn Road Exit (heading West on Outer Ring Road). The site is in the middle of the brook. The headwaters for Leary's Brook are Hummocky Marsh and Yellow Marsh. This sampling site (NF02ZM0184) is located very near the headwaters and only Hummocky Marsh has contributed to the river up to the sampling site.

The main channel length from the headwaters to the sampling site is 1.2 km. The length from the sampling site to the mouth of the river is 12.1 km. The drainage area is only 1.60 km^2. The perimeter length is 5.20km with a mean channel length of 1.20 km and a mean stream gradient of 1.70 %.

The basin consists mostly of a veneer of till (less than 1.5m) over the bedrock. There is a small portions at the east and west of the basin where there is bedrock with little or no surficial sediment and a blanket of till (greater than 1.5m). Till consists of a mixture of grain sizes from clay to boulders, and was deposited by glacial action.

The mean annual precipitation is1400 mm with a mean annual runoff of 1200mm. There are usually less than 55 days of ice cover. The Water Survey of Canada operated a hydrometric station (02ZM017) from 1983-1998 (drainage area of 15.3 km^2 . The mean daily discharge was 0.61 m^3/s with a maximum daily discharge of 18.5 m^3/s in May 1983 and a minimum daily discharge of 0.021 m^3/s in December 1996.

Fish species present include Atlantic Salmon, Brown Trout, Brook Trout, Rainbow Smelt and Stickleback.

A major concern about Leary's Brook at Outer Ring Road is the proximity of the sampling site to the Trans Canada Highway. In fact, the brook runs parallel to the highway ditch and would likely be subject to salt problems.

Plate 8 – Leary's Brook at Outer Ring Road

5.4 **Waterford River**

Waterford River at Bremigans Pond (NF02ZM0182) is located at latitude 47 31 7.00 and longitude 52 51 21.00 at an elevation of 166.00m. Development pressure is considered to be low although parts of the basin are in St. John's.

To access the site when heading west, turn off Outer Ring Road (approximately 500 m before the exit to CBS) onto a dirt road; drive approximately 1 km (over a hill) to the edge of the pond. The sampling site is located at dam on east end of pond. The sampling site is almost directly at the headwaters so the distance from the headwaters to sampling site is only about 1 km.

Very little human activity affects this sampling site (NF02ZM0182) because the headwaters are in a remote area. The distance from the sampling site to the mouth of the river is 14.33 km. The mouth of the river drains into St. John's Harbour. Downstream from Bremigan's Pond, the river flows through Mount Pearl and St. John's. The drainage area is only1.80 km^2 with the pond being 0.15 km^2. There is 0.30km^2 of forested area and a perimeter length of 5.90km. The man channel length is 1.50 km with a mean Stream Gradient of 0.66 %.

The surficial geology consists of a generally thin (0-5 m) overburden, composed of a very compact, poorly sorted lodgment till overlain by a till deposit which is looser and more permeable.

The mean annual precipitation:1400 mm results in a mean annual runoff of 1200mm. There is usually less than 55 days of ice cover.

The Water Survey of Canada operated a hydrometric station (02ZM011) from 1981-1984 near Donovan's Industrial Park. It had a drainage area of 11.40km^2, a mean daily discharge of 0.52 m^3/s, a maximum daily discharge of 4.56 m^3/s in October 1983 and a minimum daily discharge of 0.068 m^3/s in August 1984.

Fish species present include Brook Trout, Brown Trout, Stickleback and Eel. Brown trout are the dominant species in most parts of the river. Brook trout are most abundant in the upper portion of the South Brook tributary. Though the system has potential for recreational fishery, it is seldom fished due to concerns with pollution and fish quality.

When the Waterford River was examined at the outlet from Bremigan’s Pond, it was noted that there was no flow from the outlet structure (Plate 9). The weather in the previous week had been relatively wet, suggesting that because of the non-existent flows, that this would be a poor choice for future work.

Plate 9 – Waterford River at Bremigan's Pond – Outlet Structure

References Cited

CCME 1999. Canadian Environmental Quality Guidelines. Water Quality Guidelines for the Protection of Aquatic Life. Aluminum.

CCME 2005 Draft. Water Quality Guidelines for the Protection of Aquatic Life. Aluminum.

Environment Canada. Poster Presentation to the CCME WQI Workshop, Victoria, B.C. January 2006.

MacDonald, D. 1997. Methods for Deriving Site-Specific Water Quality Objectives in British Columbia and Yukon**.** Report prepared by MacDonald Environmental Sciences Ltd. November 1997

Personal Communication. Susan Roe, National Guidelines and Standards Office, to L. Swain. August 28, 2008

Appendix 1

Assessment of Wild Cove Brook

Wild Cove Brook drains a steeply hilled but small area into a deep valley. The brook is heavily forested, and drains Fox Bow Lake and Wild Cove Lake. The lowlands of the basin are dominated by an extensive marsh cover. The headwaters of Wild Cove Brook are only about 5 km upstream from the sampling site.

Wild Cove Brook (at Route 440) has been sampled since January1989 at site NF02YL0029 (latitude 48 58 28.00; longitude 57 53 2.00) which is only 7.0 metres above sea level. Wild Cove Brook drains into Humber Arm.

Watershed Statistics for Wild Cove Brook

Drainage Area	10.2 km^2
Forested Area	9.00 km^2
Lakes	0.6 km^2
Organic Terrain	0.6 km^2
Mean channel length	5.3 km
Mean channel gradient	6.1 %
Elevation drop	323 m

The watershed characteristics show that relative to Pound Cove Brook, Wild Cove Brook drains a much smaller area but is much steeper terrain than found at Pound Cove Brook. The Wild Cove Brook watershed receives a mean annual precipitation volume of 1150 mm that provides a mean annual runoff volume equivalent of 1050 mm, or virtually no retention in soil present. Although precipitation is about the same as for Pound Cove

Brook, the steep gradient of Wild Cove Brook area means that most of the precipitation ends up as runoff. Open water is present on a mean annual basis about 250 days per year.

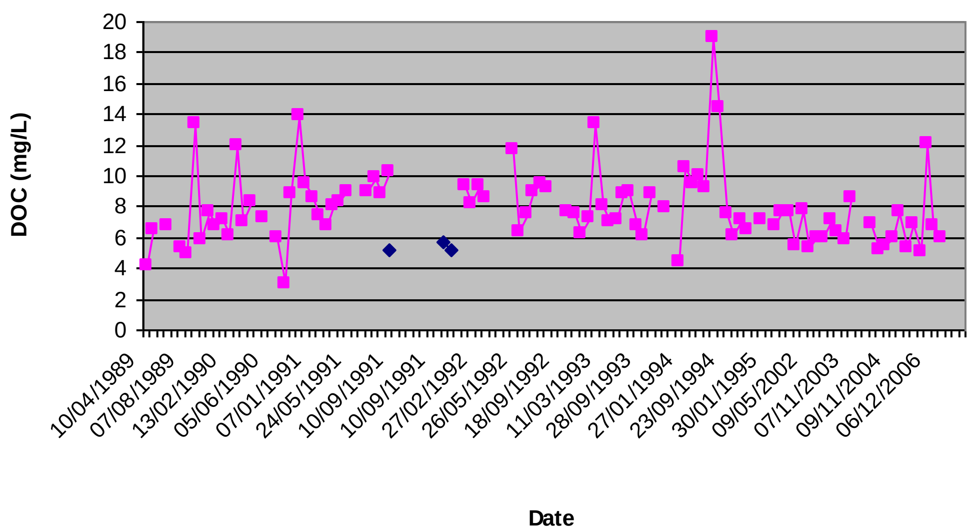
The basin is dominated by mostly sands, gravels, and silts. There are no active or past mines in the watershed. Development pressure in the water basin is considered to be low with no residents living in the basin perimeter.

1-1 Dissolved Organic Carbon and Hardness

In the period from 1989 to 1994, there were 86 DOC values while in the intervening period from 1995 to 2006, there were only 25 values in West Pound Cove Brook. DOC values for Wild Cove Brook are plotted in Figure 1-1 while hardness values are plotted as Figure 1-2.

DOC values for Wild Cove Brook are in the same ranges as found for Pound Cove Brook, with low values of about 6 mg/L and high values of about 15 mg/L.

Figure 1-1
Wild Cove Brook - DOC



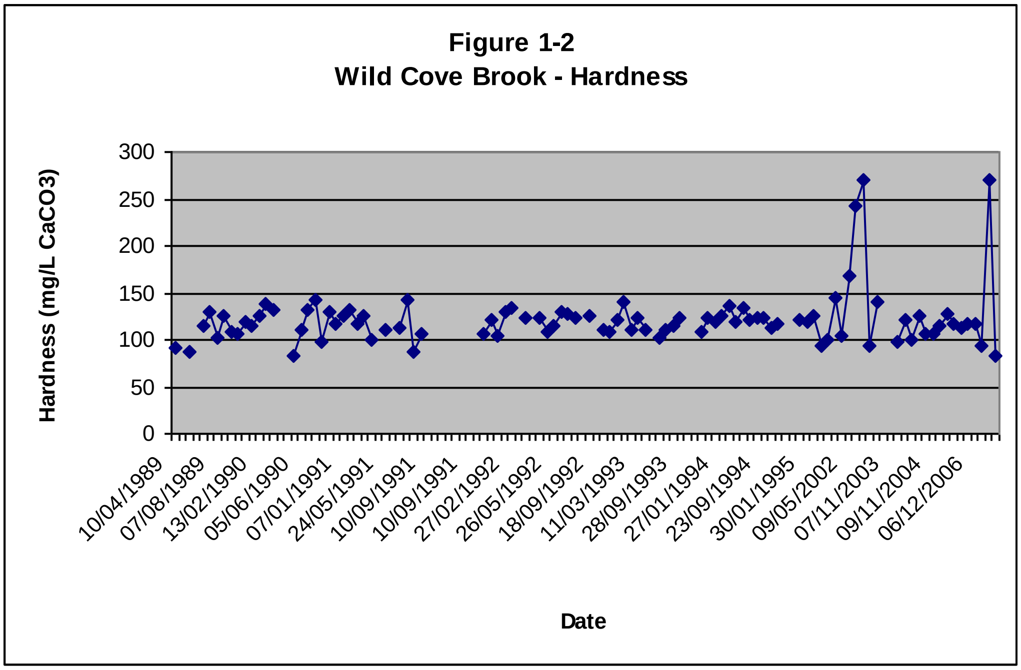
DOC values in Wild Cove Brook appear to be more stable than in Pound Cove Brook and are generally in the 6 to 15 mg/L range. Low DOC values generally occur in the spring period from February through April but have actually on an annual basis occurred in the autumn as well. **We are most likely to have success capturing low DOC events during the spring period.**

If, as stated earlier, increased TOC values likely originate from runoff that carries organic matter, one might expect that these higher concentrations would occur during periods of high water flow (and low hardness concentrations due to dilution effects). Thus, the period of lowest hardness may correspond to the period of highest TOC.

The hardness of Wild Cove Brook (Figure 1-2) is significantly higher than for Pound Cove Brook, generally being in the 100 to 150 mg/L range (Table 1-1). **Low values on an annual basis generally occur during the March through May period, so this will be a crucial period for testing for WER.**

Table 1-1 – Summary of Hardness (mg/L) in Wild Cove Brook

Number of Values	93
Maximum	269.9
Minimum	83.4
Mean	120.4
Standard Deviation	24.7
90th %ile	135.1
95th %ile	142.4
Mean + 2 SD	169.8



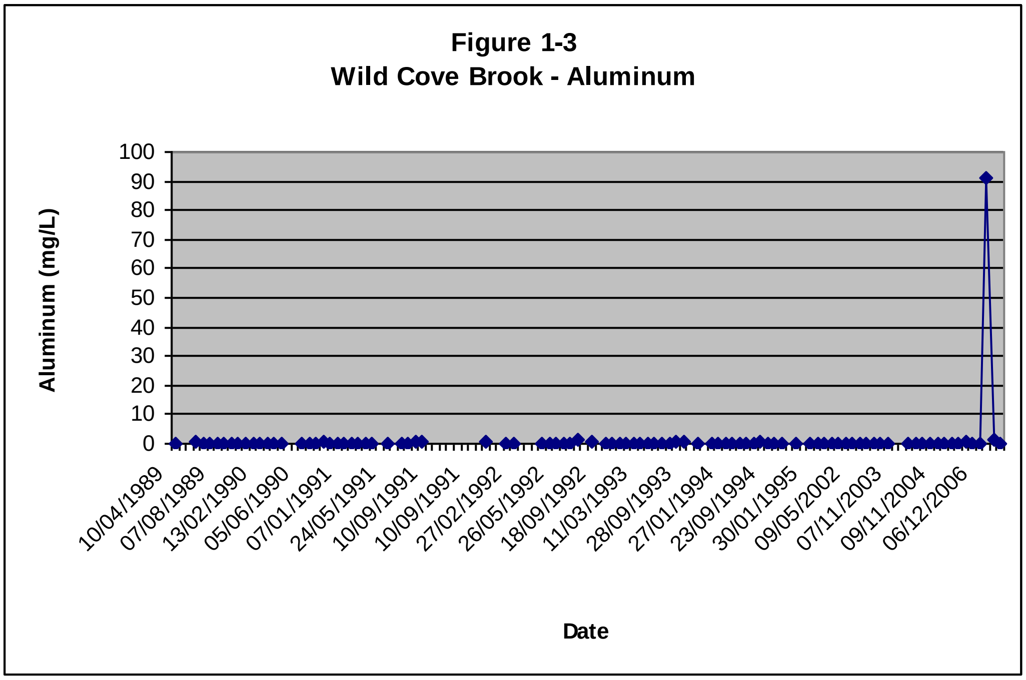
1-2 Aluminum

As noted earlier, the CCME guideline for aluminum is being revised. The current guideline is pH dependent and in Wild Cove Brook, pH is more basic than in Pound Cove Brook. A summary of pH is in Table 1-2.

Table 1-2 – Summary of pH in Wild Cove Brook

Number of Values	92
Maximum	8.33
Minimum	6.32
Mean	7.51
Standard Deviation	0.50
90th %ile	8.18
95th %ile	8.20
Mean + 2 SD	8.52

The present CCME guideline value for waters with pH greater than 6.5 is 100 µg/L. This guideline is a value that is well below many total aluminum measurements in Wild Cove Brook.



Aluminum concentrations in Wild Cove Brook exhibit no relationship to pH (Figure 1-4). A summary of aluminum values in Wild Cove Brook is shown in Table 1-3.

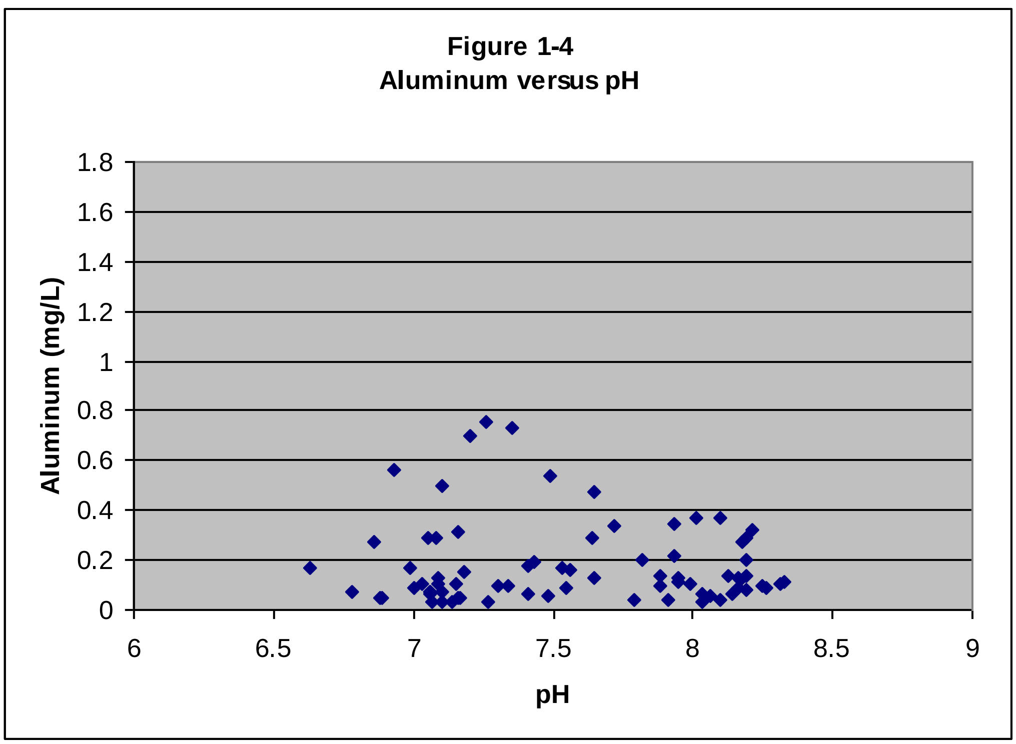
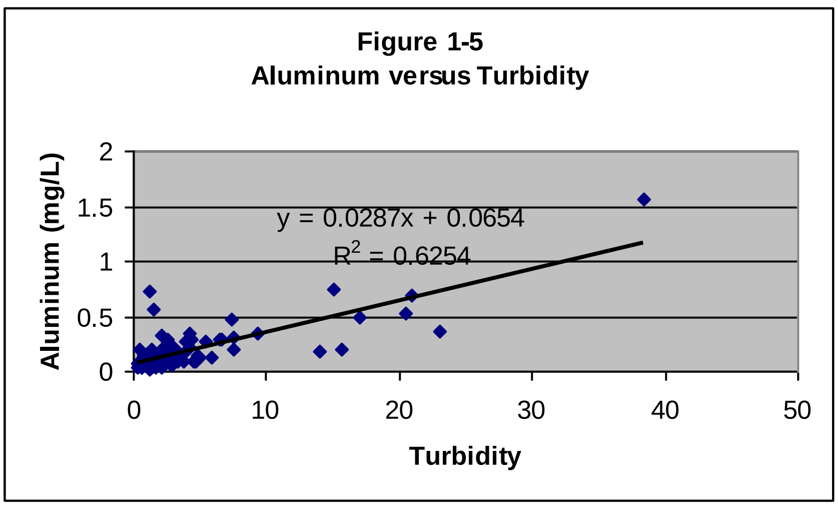


Table 1-3 – Summary of Aluminum Concentrations (mg/L) in Wild Cove Brook

Number of Values	91
Maximum	1.570
Minimum	0.023
Mean	0.186
Standard Deviation	0.215
90th %ile	0.370
95th %ile	0.547
Mean + 2 SD	0.615

If we were to establish a site-specific guideline for aluminum using the background concentration approach, the maximum aluminum would be 0.55 mg/L (95th percentile) or 0.62 mg/L (mean plus two standard deviations). These possible site-specific guidelines are about six times the generic guideline and extensively erode any safety factor associated with the guideline.

Aluminum concentrations in Wild Cove Brook do not appear to be increasing (Figure 1-3) but do seem to be related to turbidity levels (Figure 1-5).



If we were to use the RAA to establish a site-specific guideline, aluminum would be identified as a variable of concern. As well, we would be comfortable that a relationship appears to exist with turbidity (R^2 = 0.62). Based on this regression and the associated equation, we would indicate that the 100 µg/L guideline would apply at this site for concentrations of turbidity below about 1.2 NTU. Unfortunately, if the goal of the project is to have site-specific guidelines that then allows for calculation of a water quality index (WQI) score for national reporting, only one value collected in the last ten years could be used for this purpose. **Therefore, we would recommend that more work needs to be undertaken in the form of WER or other means to develop a meaningful site-specific guideline value for aluminum in Wild Cove Brook**.

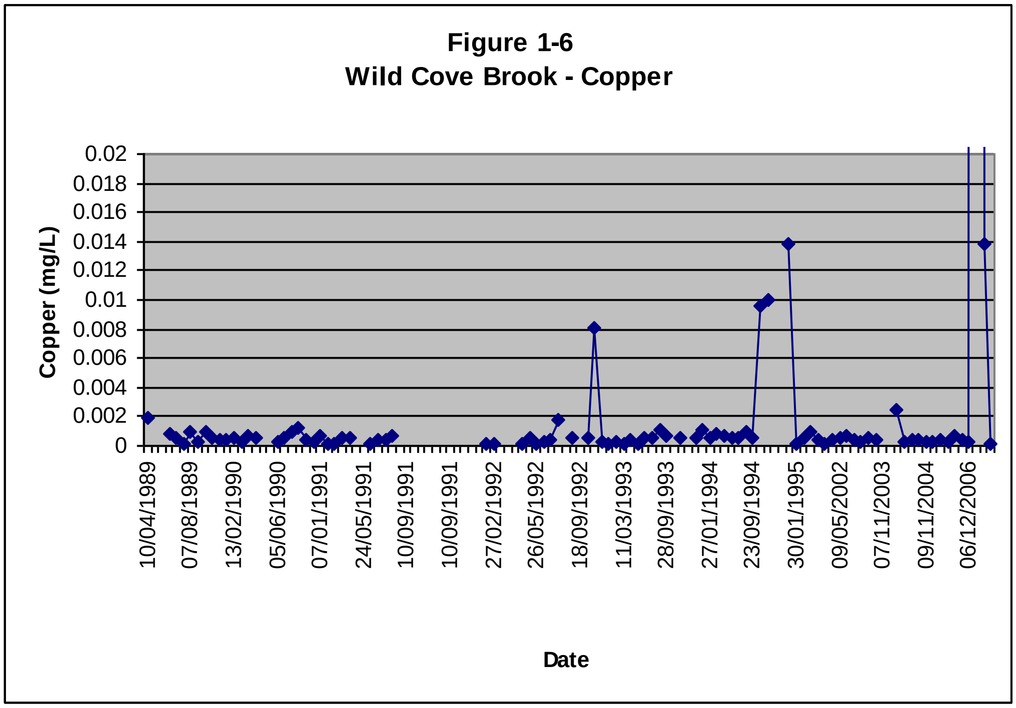
1-3 Copper

The CCME guideline for copper is that at hardness values up to 120 mg/L, the guideline is 2 µg/L and this increases to 3 µg/L for hardness concentrations between 120 and 180 mg/L. From Table 1-4, the mean hardness concentration is 120 mg/L, so that the 2 µg/L guideline would apply in many cases.

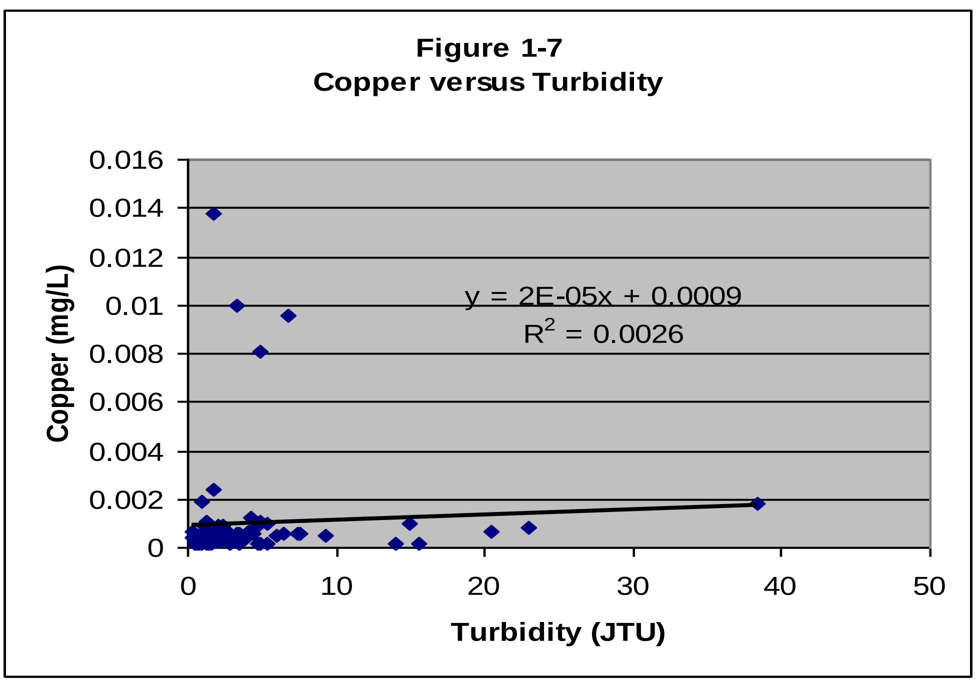
The 95th percentile is about 2 µg/L (Table 1-4). If we were to use the background concentration approach to establishing a site-specific guideline, we would likely adopt the generic guidelines using the hardness dependent relationship.

Table 1-4 – Summary of Copper Concentrations (mg/L) in Wild Cove Brook

Number of Values	89
Maximum	0.0138
Minimum	0.0002
Mean	0.0010
Standard Deviation	0.0021
90th %ile	0.0011
95th %ile	0.0022
Mean + 2 SD	0.0052



It is apparent from Figure 1-6 that most recent copper concentrations have met the national guideline. **It is therefore difficult to recommend performing additional guideline development work using the WER based on copper.**



Additionally, there is no evidence that the RAA could provide any benefit in terms of refining a site-specific guideline for copper in Wild Cove Brook because of the lack of a relationship between copper concentrations and turbidity levels (Figure 1-7).

1-4 Iron

The CCME guideline to protect aquatic life from iron concentrations is a maximum of 0.3 mg/L. The data in Table 1-5 indicate that this value is frequently exceeded in Wild Cove Brook.

Table 1-5 – Summary of Iron Concentrations (mg/L) in Wild Cove Brook

Number of Values	91
Maximum	2.480
Minimum	0.065
Mean	0.437
Standard Deviation	0.361
90th %ile	0.765
95th %ile	0.923
Mean + 2 SD	1.160

If one were to develop a site-specific guideline for iron using the background concentration approach, it would be in the order of 0.9 mg/L (95th percentile) to 1.2 mg/L (mean plus two standard deviations). These levels are three to four times the generic guideline and would erode any safety factor associated with the guideline.

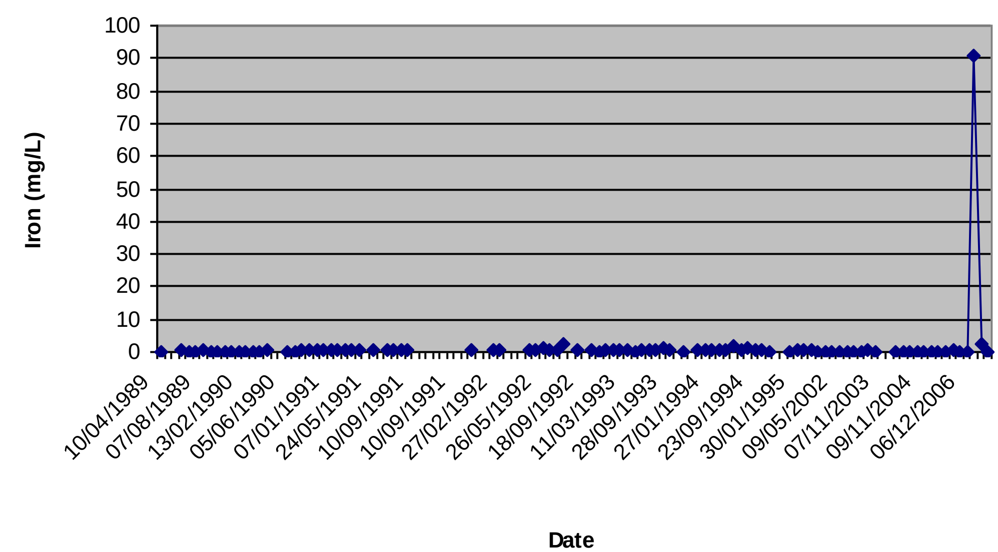
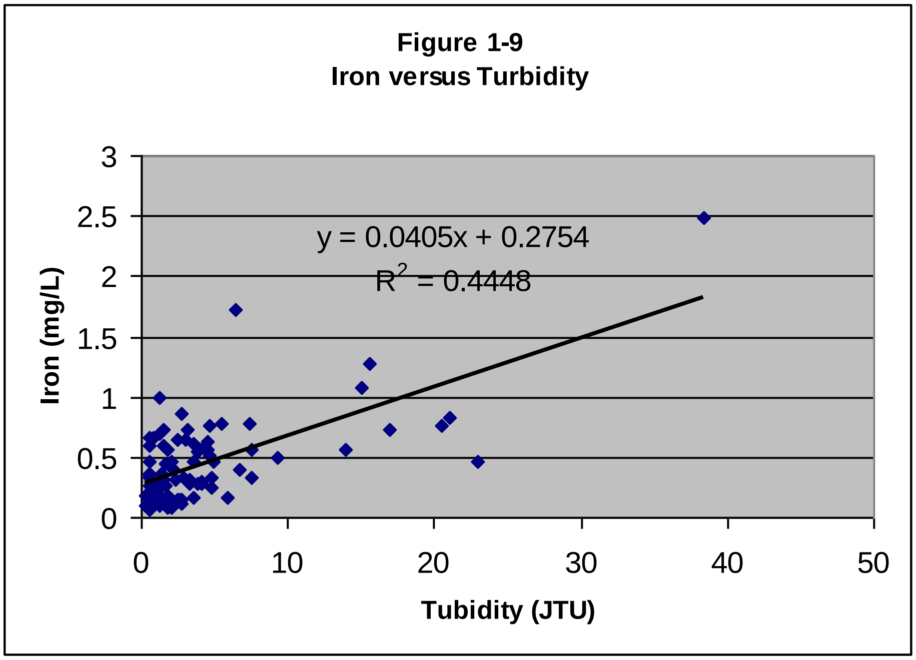


Figure 1-8
Wild Cove Brook - Iron

Although the generic guideline does not appear in Figure 1-8 to be being exceeded as frequently in recent years, this is likely a reflection of sampling frequency rather than real concentrations.

A second means to develop a site-specific guideline for iron would be to use the RAA. Using the RAA, iron would certainly be identified as a candidate variable for site-specific guideline development. In Figure 1-9, an apparent relationship also is apparent for iron concentrations in relation to turbidity levels present (R^2 = 0.45). Unfortunately, this technique would suggest that the generic iron guideline would apply only at turbidity levels less than 0.34 JTU. This level is very close to the minimum turbidity level in the Wild Cove Brook so that this is an unrealistic level if the purpose is for national reporting. **Iron would therefore be a good candidate for doing WER testing in Wild Cove Brook**, however, as noted in earlier sections of this report, iron can be difficult to test**.**



1-5 Critical Monitoring Periods

Two variables are considered potentially important for testing metals: hardness and organic carbon. For the water bodies under consideration, the critical lowest periods of time when DOC should be measured is between February to April for Wild Cove Brook.

For hardness, the lowest concentrations are usually seen in March to May in Wild Cove Brook. The critical periods of time are summarized below.

Table 1-6 Critical Sampling Periods and Expected Concentrations

Water Body	DOC	Hardness
Wild Cove Brook	February – April (6 mg/L)	March – May (100 mg/L)

1-6 Metals That Should Be Tested for WER

We have considered three metals in our analysis: aluminum, copper, and iron. Aluminum is certainly a variable in the Atlantic provinces and Newfoundland that frequently exceeds the generic guidelines, be it for water bodies with pH less than 6.5 or for those where pH is greater than 6.5. Based on using the background concentration approach, we speculate that site-specific guidelines for aluminum might be in the order of 350 µg/L in Pound Cove Brook, and 550 µg/L in Wild Cove Brook.

The pH and therefore the generic guidelines of the water bodies is different, meaning that the "intrusion" into the safety factor for the SSG for each water body is significantly different. This could be quite an interesting aspect if part of the goal of the project is to compare the impact on the two different levels. We do have concerns and speculate that the high natural levels of aluminum might somehow make developing a WER of any significance possible. What we mean is that the WER developed may be so low as to be of virtually no use in setting a SSG. However, until testing is tried, there is no information to confirm or refute this argument.

There is also the concern that when testing for aluminum, one might not be able to measure the monomeric form of aluminum as well as say dissolved or total concentrations. However, there are no recent indications that the CCME plan to continue developing the aluminum guideline based on monomeric aluminum.

The potential SSGs put forth in earlier sections for copper are summarized in Table 1-7. As can be seen, it is suggested that the generic guidelines may be suitable for use in Wild Cove Brook.

Table 1-7 Possible SSGs for the Water Bodies

Water Body	**Aluminum**	**Copper**	**Iron**
Wild Cove Brook	550 – 600 µg/L	2 µg/L	0.9 – 1.2 mg/L

Iron is a variable that appears to be a bit more consistent between the two water bodies, at least where development of the SSG is concerned. The maximum suggested SSG is only four times the generic guideline. If part of the goal of the project is to make comparisons among water bodies, especially when those selected to date have different hardness values (we are not certain whether hardness influences iron toxicity), but more consistent DOC concentrations, then iron might be the best candidate metal of the three examined.

1-7 Conclusions

Critical monitoring periods appear to be during the early months of the year for both DOC and hardness. The actual program design will depend on the ability to collect samples and on the ability of the laboratory to analyze those samples. Laboratory considerations are looked at in Chapter 3.

Table 1-8 Suggested Months for Sampling the Water Bodies

Water Body	**DOC**	**Hardness**
Wild Cove Brook	February	March

As for the metal to test, we feel that aluminum offers the most potential. This is based on:

- Possible SSGs based on other techniques for aluminum in one of the water bodies far exceed the available safety factor.
- A new guideline for aluminum based on monomeric aluminum is unlikely to be available for many years.
- There is little benefit to testing for copper because the suggested SSGs are at the generic guideline values for the water bodies.
- There is no known relationship for iron with DOC or hardness. In that case, the use of the WER could be a means to develop a meaningful SSG while

contributing to the scientific literature on whether these variables influence iron toxicity. However, the proposed SSGs may be sufficient for reporting purposes.