# TECHNICAL MEMORANDUM

**TO:** Ken Reimer, Chair of Independent Expert Advisory Committee (IEAC)

**FROM:** Iris Koch

**SUBJECT:** Measurement uncertainty associated with methylmercury concentrations in the Lower Churchill River and Lake Melville from October 2016 to November 2017

**DATE:** December 12, 2017

**CC:** Marina Biasutti-Brown, Research Director of IEAC

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The purpose of this technical memorandum is to summarize work carried out to support the monitoring of methylmercury concentrations in the Lower Churchill River and Lake Melville from October 2016 to November 2017.

***Summary***

Measurement uncertainty was estimated for water sampling results from the monitoring program being conducted in the Lower Churchill River and Lake Melville. The measurement uncertainty applies to results from October 2016 to November 2017 and was estimated from data obtained from a "Ten + Ten Study" reported in a memorandum from Azimuth (2017). The data were acquired for two different sites (a station upstream of the Muskrat Falls dam impoundment area, and one downstream near Goose Bay) and represented replicates associated with field sampling as well as laboratory subsampling/analysis. The measurement uncertainty was estimated on the basis of duplicate data only, obtained from the Ten + Ten Study data, following recommended procedures published by the Canadian Association for Laboratory Accreditation (CALA). The standard uncertainties (obtained from a calculated relative standard deviation, RSD, for duplicate data) for the measurement of dissolved methylmercury were 17.5% for field sampling and 19% for laboratory subsampling/analysis, and for total methylmercury they were 20.3% for field sampling and 16.7% for laboratory subsampling/analysis. Using the assumption that the largest of standard uncertainties between the two stages of the measurement contains the uncertainty from the other, as recommended by CALA, and using an expansion factor of two to obtain an expanded uncertainty, the measurement uncertainty was 38% for dissolved methylmercury and 41% for total methylmercury. The expanded uncertainty is the standard way of expressing measurement uncertainty and it provides a high confidence (95%) that the actual or true value is within the interval defined by it around the measured value. Consideration of these measurement uncertainties when examining time trends at the reference station (N1) showed that differences in dissolved methylmercury at station N4 (in the impoundment), N5 (just downstream of the impoundment), and N8 (near Goose Bay) were obscured by the measurement uncertainty, since most values at stations N4, N5 and N8 were within 40% of

values at N1. Values of total methylmercury differed by slightly higher amounts at N4, but most were still within 80% of the N1 values. General practice suggests that differences would be considered discernible when they are more than twice the expanded uncertainty (greater by more than approximately 80%). The size of the expanded uncertainty of around 40% is not surprising considering the proximity of most measured values to date to the detection limit. Lowering of the laboratory detection limit may help to lower the measurement uncertainty. However, if laboratory methods are altered to obtain lower detection limits, the project team should consider conducting another estimation of measurement uncertainty, ideally using a "Ten + Ten Study" again, or similar experimental design.

***Introduction, Procedure, and Results***

The objective of the work was to review water sampling results of methylmercury concentrations provided by the Independent Expert Advisory Committee (IEAC) and determine the analytical and field variability for the indicated analyses. The variability was determined by estimating a parameter known as the measurement uncertainty, which is the spread of values around a measured value that is attributed to the measurand (or the "true value" that is being sought through the measurement process). The measurement uncertainty is a parameter that is often overlooked when interpreting data produced by analytical laboratories, when users typically interpret a reported concentration as a single stand-alone value. However, the concept of measurement uncertainty is especially important when attempting to discern differences over time or spatially, as is the case in the present monitoring study.

The Canadian Association for Laboratory Accreditation (CALA) provides a Measurement Uncertainty Policy (CALA 2010) and in it CALA recommends using data from (among other sources) proficiency testing programs, accuracy checks (like fortified samples or reference materials), and inserted duplicates[1]. Only one of these components was available for the estimation procedure in the present work, and this was a proxy of inserted duplicate data.

The proxy was provided by a "Ten + Ten Study" (Azimuth 2017) in which ten samples were collected from each of two field sites – one at Lower Churchill River at station N1, and the other at the estuary near Goose Bay at station N8 – and analyzed separately for dissolved and total methylmercury. Additionally one 10 L sample was collected at each of these stations, and the analytical laboratory, Flett Research Ltd (referred to as Flett), split the sample into ten samples for separate analysis for dissolved and total methylmercury. The ten samples collected in the field represented field replicates, and the ten samples obtained from splitting the sample in the laboratory represented laboratory replicates. (Please see slides 11 and 12 for a schematic of the sampling design, and slide 26 for a map of the sampling stations).

The duplicate data were obtained by pairing independent results in all ways possible (please see slide 14 for a pictorial representation), and calculating a relative percent difference (RPD) for each pair, according to Equation 1.

[1] An inserted duplicate is a quality control sample that commercial laboratories include with every batch of samples (batches are groups of 10–20 samples), consisting of a sample that has been subsampled twice, and each subsample is taken through the entire analytical testing procedure. Its purpose is to monitor and ensure precision (the nearness of two measurements) during the analysis of the batch.

$$RPD = \frac{|(value\ 1 - value\ 2|}{[(value\ 1 + value\ 2)/2]} \times 100\% = \frac{|difference\ between\ value\ 1\ and\ value\ 2|}{mean\ of\ value\ 1\ and\ value\ 2} \times 100\%$$

Equation 1

All possible pairings of independent data values gave 45 RPDs for each of the four groups: N1 field replicates, N8 field replicates, N1 laboratory replicates, and N8 laboratory replicates for each of dissolved and methylmercury (eight groups altogether). The RPDs are provided in Appendix A of this memorandum.

To obtain a value representing a parameter referred to as a "relative standard deviation", or RSD (CALA 2010), for duplicate data, Equation 2 was used (adapted from CALA 2010).

$$RSD = \sqrt{\frac{[\sum_{n=1}^{45}(RPD_n)^2]}{2N}}$$

Equation 2

The results for the eight groups of data are presented in slides 16 and 17 and in Appendix A, and indicate that RSD values range from 14 to 20% for dissolved methylmercury measurements, and from 12 to 23% for total methylmercury measurements. There was no discernible systematic pattern indicating lower RSDs for different sites, different concentrations, or field vs laboratory replicates.

Measurement results for field replicates inherently contain the variability associated with analytical laboratory replicates, and in these circumstances, when the uncertainty of one component is nested within another, CALA recommends using the highest value (CALA 2010). Additionally, because there was no systematic association of RSD values with sampling station, and to allow for the estimation of a generalized measurement uncertainty for all sampling stations, data for both sites were combined. This resulted in Equation 2 being used for 90 values instead of 45 (for each type of analysis), and the calculation of new RSDs (Appendix A).

As the RSDs represented the only component used for the uncertainty estimate, they were equivalent to the standard uncertainty. International standard practice for reporting measurement uncertainty includes the calculation of a parameter known as expanded uncertainty, and this is obtained by multiplying the standard uncertainty by an expansion factor, k, of two (CALA 2010). Using this factor of two means that the unknown true value of what is being measured is believed to lie in the interval defined by the expanded uncertainty with a level of confidence of approximately 95 %. If the standard uncertainty is used (no expansion factor), the level of confidence is approximately 68%. The CALA policy states that uncertainty should be reported to a confidence of 95% (CALA 2010) and this is consistent with the uncertainty statement provided by Flett (see Appendix B for an example of a Flett laboratory report).

When data for both sites were combined and the highest value between the field and laboratory replicate groups was used, the expanded uncertainty was 38% for dissolved methylmercury measurements and 41% for total methylmercury measurements.

These values are not unexpected given the proximity of measurements near the detection limit of 0.01 ng/L. The average concentrations of total and dissolved methylmercury in the Ten + Ten Study were 0.024 (range 0.017–0.036 ng/L) and 0.013 (range <0.01–0.019 ng/L), respectively. Flett reported an expanded uncertainty estimate of 13% at 0.1 ng/L (ten times higher than the detection limit) and provided an estimate of the uncertainty at the detection limit of 46% (taking into account primarily standard deviation of the blank, but not including duplicate data or reference sample data near the detection limit). High uncertainties, up to 100%, at or near the detection limit are known to be typical in analytical testing, and typical uncertainty at three times the detection limit is around 30% (CALA 2010).

***Implications for Monitoring Data (October 2016–November 2017)***

The concept of measurement uncertainty was considered in an examination of time trend data for stations N1, N4, N5, and N8. These stations were selected as examples that were judged to be of interest to committee members, since N1 is used as the reference station, N4 is in the impoundment and is predicted to be likeliest to show changes in water methylmercury concentrations, N5 is just downstream of the impoundment, and N8 is near Goose Bay and considered to be the first indicator station of changes in Lake Melville. (Please see map in slide 26 for the location of these stations.)

A simplified way of looking at the data was to compare the time trends of monthly means[2] at the different stations on the same set of x (time) and y (methylmercury concentrations) axes. An interval was also shown for N1, the reference site, representing the measurement uncertainty of approximately 40%[3]. The monthly means for the other stations were found inside this interval and the conventional way of interpreting this is that differences were therefore not discernible. (Please see slide 27 for the graphic described). The interval defined for the monthly means at N1 was likely underestimated since the variability resulting from different sampling times over the month was not taken into account.

When the same time trends were examined for individual sampling points a similar picture was seen, except for some individual points from N4 that were higher than the N1 upper measurement uncertainty interval value (please see slide 28).

Monthly time trends for total methylmercury were also examined and some of the N4 values were above the N1 interval but the data for all other stations were not discernible from the N4 data in the June to November time period (slide 29). Higher values were seen in March at N5, which has been attributed to a high total suspended solids event (Azimuth 2017). The examination of time trends did not exhibit intervals for N4, N5 and N8 stations, which would also be subject to 40% measurement uncertainty estimates.

N4 station data were also compared as ratios (of monthly means) to N1 station data. All of the monthly means at N4 were within 40% of the N1 data for dissolved methylmercury, and for total methylmercury, three monthly means were more than 40% higher than N1 monthly

[2] Means were calculated as arithmetic means: mean = $(a_1 + a_2 + \ldots a_n)/n$.
[3] Intervals were calculated as: lower line = mean N1 – 0.4*mean N1; upper line = mean N1 + 0.4*mean N1

means (two within 60%, and the third was attributed to a large total suspended solids event (Azimuth 2017)).

The Eurachem/CITAC Guide to Setting and Using Target Uncertainty in Chemical Measurement recommends that when measurements are performed to measure a trend (such as the depletion or increase of a chemical in a river), two measurement results should differ by four times the standard uncertainty (Bettencourt da Silva and Williams 2015), or two times the expanded uncertainty when the expansion factor is two. Following this guidance suggests that two values would be considered different if they differ by approximately 80%. In the case of increases in the Lower Churchill River or Melville Lake, a result would have to be 1.76 times higher than the reference result for dissolved methylmercury, and 1.82 times higher for total methylmercury.

***Comments on Azimuth 2017***

This work does not include a review of Azimuth technical memorandum (2017) but there are a few points of comparison that may be instructive in the context of measurement uncertainty.

Azimuth's interpretation of the Ten + Ten Study results was limited to ascertaining the validity of the laboratory analysis, with respect to field and analytical precision. Similar to the methods used in the present work, Azimuth generated RPD[4] values from the pairing of results from the Ten + Ten Study in eight groups. However, Azimuth conducted random pairings, which presumably included samples paired with themselves, and calculated RPDs for 10,000 pairings. Azimuth then calculated a (presumed arithmetic) mean of the 10,000 RPD values. The Azimuth values were very similar to the RSD values obtained in the present work (slides 16 and 17).

Azimuth compared the mean RPDs obtained with their stated acceptance limits of 20% for laboratory duplicates and 30% for field duplicates, and considered the data valid and sufficiently precise for the purposes of the statistical analysis undertaken because the mean of RPDs were close to or below these acceptance limits. A minor point is that generally RPDs are intended to be assessed individually and when this is done with the RPD results in the present work, a failure rate of 11–58% was observed.

Azimuth carried out comparisons of monthly means taking into account the variability in the data from different time points in the months, and for N4, also different depths, using Bayesian statistics to generate the posterior (modeled) means and 95% credibility intervals (similar to confidence intervals). (Comparisons did not include measurement uncertainty). Azimuth also calculated ratios of stations to N1 monthly concentrations on the basis of the Bayesian modeled means. Thus although the comparisons carried out in Azimuth 2017 and the present work were similar, the means are likely to be different because of the way in which they were estimated.

[4] The RPD formula reported in Azimuth 2017 (page 10) erroneously did not include the absolute value function; this was likely a typo, since it is probable that the mean RPD value would be closer to zero if both positive and negative values had been used.

Azimuth did not carry out statistical comparisons of total methylmercury data, only dissolved methylmercury data. They rationalized this by observing that the dissolved methylmercury was usually 75% of the total methylmercury concentrations with exceptions when high total suspended solids events occurred. On the basis of this constant, they concluded that "comparisons of spatial and temporal patterns using dissolved MeHg is reasonable" (Azimuth 2017). The committee will likely wish to ascertain if examination of total methylmercury is required.

Azimuth used mixed-effects models to test for differences in dissolved methylmercury trends between the sites, and found that the increase in slope for N4 relative to N1 was marginally statistically significantly higher, with no differences for the remaining sites. Consideration of measurement uncertainty suggests a similar conclusion.

***Recommendations***

As discussed during the question period following the webinar presentation of this material, the way in which uncertainty can be improved is possibly through the lowering of detection limits. However, the Ten + Ten Study was not able to distinguish differences in uncertainty from field sampling compared with uncertainty from laboratory subsampling/analysis, and the latter is nested within field sampling uncertainty. Therefore, it is possible that while a lower detection limit may be achieved by the analytical laboratory, there could be field sampling or inherent sample conditions that may override an improved laboratory measurement uncertainty and still cause the overall measurement uncertainty to remain at its current level.

Therefore it would be prudent to consider conducting a study to assess measurement uncertainty in the eventuality of changed analysis conditions at the laboratory (i.e., a lowered detection limit). Another Ten + Ten Study would be useful, although a study design that allows for the sampling and analytical variances to be distinguished could also be considered (e.g., five splits of a five field replicates) (Miller and Miller 2000).

Please do not hesitate to contact me with any questions.

Respectfully,

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***References***

Azimuth 2017. Technical Memorandum RE: Relationship Between Muskrat Falls Reservoir Elevation and Mercury Concentrations, Lower Churchill River October 2016 – September 2017. Prepared for Peter Madden, Nalcor Energy. Azimuth Consulting Group Partnership, Vancouver, BC. 50 pages (including appendices).

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Miller JN and Miller JC 2000. Statistics and Chemometrics for Analytical Chemistry. Fourth Edition. Pearson Prentice Hall, U.K. pp 77–78

## APPENDIX A: TABLES OF DATA FROM TEN + TEN STUDY

Abbreviations for tables

CALA RSD = relative standard deviation from Canadian Association for Laboratory Accreditation (see memo text for equation)

DMeHg = dissolved methylmercury

DOC = dissolved organic carbon

dups = duplicates

MU = measurement uncertainty

N1 = Station N1

N8 = Station N8

not calc = not calculated

RPD = relative percent difference (see memo text for equation)

TMeHg = total methylmercury

TOC = total organic carbon

TSS = total suspended solids

**Table A1: Ten+Ten Study data. All values <RDL have been included as RDL for analysis, indicated in RED.**

| Replicate Type | Sample ID | Sample Location | DOC (mg/L) | TSS (mg/L) | TOC (mg/L) | TMeHg (ng/L) | DMeHg (ng/L) |
|---|---|---|---|---|---|---|---|
| Lab | MS1 | N1 | 5.8 | 5 | 7.4 | 0.029 | 0.018 |
| Lab | MS2 | N1 | 5.6 | 5 | 5.8 | 0.028 | 0.018 |
| Lab | MS3 | N1 | 5.4 | 5 | 5.8 | 0.027 | 0.019 |
| Lab | MS4 | N1 | 6.1 | 5 | 6 | 0.032 | 0.010 |
| Lab | MS5 | N1 | 5.9 | 5 | 6.4 | 0.027 | 0.017 |
| Lab | MS6 | N1 | 6.3 | 5 | 6.1 | 0.023 | 0.014 |
| Lab | MS7 | N1 | 6 | 5 | 5.9 | 0.023 | 0.016 |
| Lab | MS8 | N1 | 5.4 | 5 | 6.3 | 0.028 | 0.012 |
| Lab | MS9 | N1 | 5.8 | 6 | 6 | 0.028 | 0.015 |
| Lab | MS10 | N1 | 6.2 | 5 | 6.3 | 0.022 | 0.017 |
| Lab | ES1 | N8 | 6.6 | 5 | 6.9 | 0.033 | 0.015 |
| Lab | ES2 | N8 | 6.8 | 5 | 6.4 | 0.024 | 0.013 |
| Lab | ES3 | N8 | 6.2 | 5 | 6.7 | 0.029 | 0.016 |
| Lab | ES4 | N8 | 6.4 | 5 | 7.3 | 0.021 | 0.014 |
| Lab | ES5 | N8 | 6.5 | 5 | 7.5 | 0.019 | 0.012 |
| Lab | ES6 | N8 | 7.2 | 5 | 8.3 | 0.017 | 0.010 |
| Lab | ES7 | N8 | 6.4 | 5 | 7.4 | 0.028 | 0.010 |
| Lab | ES8 | N8 | 7.2 | 5 | 7.6 | 0.024 | 0.010 |
| Lab | ES9 | N8 | 7.7 | 6 | 7.5 | 0.027 | 0.010 |
| Lab | ES10 | N8 | 6.5 | 5 | 7.4 | 0.024 | 0.011 |
| Field | MS1 | N1 | 6.6 | 5 | 6.7 | 0.019 | 0.013 |
| Field | MS2 | N1 | 7.3 | 5 | 7.5 | 0.022 | 0.015 |
| Field | MS3 | N1 | 7.1 | 5 | 7.5 | 0.022 | 0.014 |
| Field | MS4 | N1 | 6.8 | 5 | 7.3 | 0.031 | 0.019 |
| Field | MS5 | N1 | 6.3 | 5 | 6.9 | 0.018 | 0.017 |
| Field | MS6 | N1 | 6.2 | 5 | 6.5 | 0.022 | 0.018 |
| Field | MS7 | N1 | 5.2 | 9 | 6.1 | 0.027 | 0.011 |
| Field | MS8 | N1 | 5.1 | 5 | 5.4 | 0.036 | 0.011 |
| Field | MS9 | N1 | 4.9 | 5 | 5.2 | 0.019 | 0.011 |
| Field | MS10 | N1 | 4.7 | 5 | 5 | 0.025 | 0.016 |
| Field | ES1 | N8 | 4.4 | 7 | 4.7 | 0.021 | 0.014 |
| Field | ES2 | N8 | 4.3 | 8 | 4.4 | 0.024 | 0.010 |
| Field | ES3 | N8 | 3.9 | 6 | 4.2 | 0.020 | 0.010 |
| Field | ES4 | N8 | 3.8 | 10 | 4.2 | 0.024 | 0.012 |
| Field | ES5 | N8 | 3.8 | 7 | 4.2 | 0.026 | 0.013 |
| Field | ES6 | N8 | 2.9 | 6 | 3.9 | 0.018 | 0.010 |
| Field | ES7 | N8 | 4.1 | 8 | 4 | 0.027 | 0.013 |
| Field | ES8 | N8 | 5.1 | 9 | 5.3 | 0.017 | 0.010 |
| Field | ES9 | N8 | 5.7 | 12 | 5.8 | 0.018 | 0.010 |
| Field | ES10 | N8 | 6.5 | 8 | 6 | 0.017 | 0.012 |

**Table A2: Summary statistics of Ten+Ten Study data for TMeHg.**

| Replicate Type | Sample Location | Minimum (ng/L) | Maximum (ng/L) | Mean (ng/L) | Standard deviation (ng/L | %RSD |
|---|---|---|---|---|---|---|
| Lab | N1 | 0.022 | 0.032 | 0.027 | 0.003 | 12 |
| Lab | N8 | 0.017 | 0.033 | 0.025 | 0.005 | 20 |
| Lab | All | 0.017 | 0.033 | 0.026 | 0.004 | 16 |
| Field | N1 | 0.018 | 0.036 | 0.024 | 0.006 | 24 |
| Field | N8 | 0.017 | 0.027 | 0.021 | 0.004 | 18 |
| Field | All | 0.017 | 0.036 | 0.023 | 0.005 | 22 |

**Table A3: Summary statistics of Ten+Ten Study data for DMeHg.**

| Replicate Type | Sample Location | Minimum (ng/L) | Maximum (ng/L) | Mean (ng/L) | Standard deviation (ng/L | %RSD |
|---|---|---|---|---|---|---|
| Lab | N1 | 0.010 | 0.019 | 0.016 | 0.003 | 18 |
| Lab | N8 | 0.010 | 0.016 | 0.012 | 0.002 | 19 |
| Lab | All | 0.010 | 0.019 | 0.014 | 0.003 | 22 |
| Field | N1 | 0.011 | 0.019 | 0.015 | 0.003 | 21 |
| Field | N8 | 0.010 | 0.014 | 0.011 | 0.002 | 14 |
| Field | All | 0.010 | 0.019 | 0.013 | 0.003 | 22 |

**Table A4: RPD values (%), lab duplicates**

| Sample Location | TMeHg | DMeHg |
|---|---|---|
| N1 | 3.5 | 0.0 |
| N1 | 7.1 | 5.5 |
| N1 | 10.3 | 49.2 |
| N1 | 7.0 | 6.1 |
| N1 | 21.7 | 25.0 |
| N1 | 22.2 | 12.5 |
| N1 | 3.7 | 38.7 |
| N1 | 3.7 | 19.4 |
| N1 | 26.2 | 6.4 |
| N1 | 3.6 | 5.4 |
| N1 | 13.8 | 51.1 |
| N1 | 3.5 | 6.2 |
| N1 | 18.2 | 25.6 |
| N1 | 18.8 | 12.8 |
| N1 | 0.0 | 39.6 |
| N1 | 0.0 | 19.8 |
| N1 | 22.7 | 6.5 |
| N1 | 16.9 | 62.1 |
| N1 | 0.0 | 13.0 |
| N1 | 14.7 | 33.3 |
| N1 | 15.2 | 19.7 |
| N1 | 3.8 | 47.7 |
| N1 | 3.7 | 27.2 |
| N1 | 19.0 | 13.3 |
| N1 | 16.9 | 51.9 |
| N1 | 32.9 | 29.3 |
| N1 | 34.3 | 42.1 |
| N1 | 15.0 | 14.5 |
| N1 | 14.9 | 35.7 |
| N1 | 38.3 | 48.5 |
| N1 | 16.0 | 19.4 |
| N1 | 16.4 | 6.4 |
| N1 | 4.0 | 33.9 |
| N1 | 3.9 | 13.5 |
| N1 | 19.9 | 0.0 |
| N1 | 0.0 | 13.3 |
| N1 | 20.3 | 14.3 |
| N1 | 19.6 | 7.0 |
| N1 | 4.0 | 20.3 |
| N1 | 19.6 | 28.6 |
| N1 | 19.0 | 7.0 |
| N1 | 4.0 | 6.7 |
| N1 | 0.0 | 22.2 |
| N1 | 23.1 | 34.1 |
| N1 | 24.0 | 12.5 |
| minimum | 0.0 | 0.0 |
| maximum | 38.3 | 62.1 |
| mean | 13.5 | 22.4 |
| CALA RSD | 11.8 | 19.4 |
| % > 20% | 22 | 44 |

**Table A5: RPD values (%), lab duplicates**

| Sample Location | TMeHg | DMeHg |
|---|---|---|
| N8 | 31.6 | 14.3 |
| N8 | 14.0 | 6.8 |
| N8 | 44.9 | 6.9 |
| N8 | 55.6 | 21.4 |
| N8 | 67.1 | 37.5 |
| N8 | 20.5 | 38.9 |
| N8 | 36.9 | 40.0 |
| N8 | 24.3 | 40.9 |
| N8 | 36.6 | 33.1 |
| N8 | 18.9 | 20.7 |
| N8 | 12.2 | 7.0 |
| N8 | 21.5 | 7.3 |
| N8 | 31.8 | 23.1 |
| N8 | 17.4 | 24.0 |
| N8 | 0.0 | 24.7 |
| N8 | 12.7 | 25.3 |
| N8 | 0.0 | 17.0 |
| N8 | 32.0 | 13.3 |
| N8 | 43.5 | 28.6 |
| N8 | 55.8 | 46.2 |
| N8 | 4.4 | 48.4 |
| N8 | 21.7 | 50.0 |
| N8 | 8.5 | 51.2 |
| N8 | 21.2 | 43.0 |
| N8 | 10.0 | 15.4 |
| N8 | 21.1 | 33.3 |
| N8 | 32.9 | 34.8 |
| N8 | 13.8 | 35.7 |
| N8 | 26.5 | 36.4 |
| N8 | 13.1 | 27.3 |
| N8 | 11.1 | 18.2 |
| N8 | 42.2 | 18.8 |
| N8 | 22.7 | 19.0 |
| N8 | 34.8 | 19.2 |
| N8 | 21.6 | 9.5 |
| N8 | 48.9 | 0.0 |
| N8 | 30.4 | 0.0 |
| N8 | 41.7 | 0.0 |
| N8 | 29.2 | 9.8 |
| N8 | 15.4 | 0.0 |
| N8 | 3.8 | 0.0 |
| N8 | 15.5 | 9.8 |
| N8 | 11.8 | 0.0 |
| N8 | 0.0 | 9.7 |
| N8 | 11.8 | 9.5 |
| minimum | 0.0 | 0.0 |
| maximum | 67.1 | 51.2 |
| mean | 24.2 | 21.7 |
| CALA RSD | 20.4 | 18.7 |
| % > 20% | 58 | 49 |

**Table A6: RPD values (%), field duplicates**

| Sample Location | TMeHg | DMeHg |
|---|---|---|
| N1 | 14.6 | 14.3 |
| N1 | 14.3 | 7.1 |
| N1 | 51.1 | 39.3 |
| N1 | 4.5 | 25.6 |
| N1 | 13.4 | 31.3 |
| N1 | 34.8 | 13.1 |
| N1 | 69.0 | 13.6 |
| N1 | 0.0 | 14.0 |
| N1 | 24.9 | 20.7 |
| N1 | 0.0 | 6.9 |
| N1 | 36.0 | 25.0 |
| N1 | 17.2 | 12.3 |
| N1 | 0.0 | 18.1 |
| N1 | 21.1 | 25.5 |
| N1 | 55.1 | 26.7 |
| N1 | 12.2 | 27.6 |
| N1 | 12.2 | 6.8 |
| N1 | 34.0 | 30.3 |
| N1 | 16.9 | 18.0 |
| N1 | 0.0 | 23.5 |
| N1 | 20.8 | 19.0 |
| N1 | 53.8 | 20.0 |
| N1 | 12.0 | 20.8 |
| N1 | 12.0 | 13.7 |
| N1 | 53.1 | 11.1 |
| N1 | 38.0 | 5.6 |
| N1 | 16.3 | 49.2 |
| N1 | 18.7 | 52.6 |
| N1 | 47.1 | 55.2 |
| N1 | 23.6 | 20.4 |
| N1 | 20.0 | 5.7 |
| N1 | 40.3 | 39.1 |
| N1 | 69.9 | 42.1 |
| N1 | 4.1 | 44.1 |
| N1 | 28.6 | 7.1 |
| N1 | 20.4 | 48.3 |
| N1 | 49.4 | 52.5 |
| N1 | 11.5 | 54.9 |
| N1 | 11.6 | 14.9 |
| N1 | 28.6 | 0.0 |
| N1 | 29.3 | 0.0 |
| N1 | 7.5 | 40.8 |
| N1 | 61.8 | 0.0 |
| N1 | 41.3 | 39.5 |
| N1 | 27.3 | 37.0 |
| minimum | 0.0 | 0.0 |
| maximum | 69.9 | 55.2 |
| mean | 26.2 | 24.3 |
| CALA RSD | 22.8 | 20.5 |
| % > 30% | 33 | 33 |

**Table A7: RPD values (%), field duplicates**

| Sample Location | TMeHg | DMeHg |
|---|---|---|
| N8 | 13.3 | 33.3 |
| N8 | 4.6 | 35.3 |
| N8 | 13.5 | 17.4 |
| N8 | 21.7 | 8.5 |
| N8 | 13.5 | 34.8 |
| N8 | 26.3 | 8.5 |
| N8 | 18.1 | 34.8 |
| N8 | 13.8 | 35.3 |
| N8 | 18.9 | 17.5 |
| N8 | 18.2 | 0.0 |
| N8 | 0.0 | 18.8 |
| N8 | 8.5 | 26.7 |
| N8 | 26.8 | 0.0 |
| N8 | 12.9 | 26.5 |
| N8 | 31.4 | 0.0 |
| N8 | 27.6 | 0.0 |
| N8 | 33.0 | 18.0 |
| N8 | 18.2 | 18.2 |
| N8 | 25.7 | 25.7 |
| N8 | 9.1 | 0.0 |
| N8 | 30.4 | 25.9 |
| N8 | 13.6 | 0.0 |
| N8 | 9.3 | 0.0 |
| N8 | 14.4 | 17.8 |
| N8 | 8.0 | 8.0 |
| N8 | 26.5 | 17.1 |
| N8 | 12.6 | 8.3 |
| N8 | 31.3 | 17.2 |
| N8 | 27.7 | 17.6 |
| N8 | 33.3 | 0.0 |
| N8 | 36.4 | 26.1 |
| N8 | 4.2 | 0.0 |
| N8 | 40.9 | 26.1 |
| N8 | 37.7 | 26.8 |
| N8 | 43.9 | 8.8 |
| N8 | 40.0 | 26.1 |
| N8 | 4.8 | 0.0 |
| N8 | 0.0 | 0.0 |
| N8 | 5.2 | 18.2 |
| N8 | 45.5 | 26.1 |
| N8 | 43.5 | 27.3 |
| N8 | 50.6 | 8.9 |
| N8 | 5.7 | 0.0 |
| N8 | 0.0 | 18.8 |
| N8 | 5.7 | 18.2 |
| minimum | 0.0 | 0.0 |
| maximum | 50.6 | 35.3 |
| mean | 20.6 | 15.6 |
| CALA RSD | 17.5 | 13.8 |
| % > 30% | 29 | 11 |

**Table A8: Summary statistics of % RPD values for TMeHg**

| Statistic | N1 | N8 | N1 | N8 | All | All |
|---|---|---|---|---|---|---|
| | Lab dups | Lab dups | Field dups | Field dups | Lab dups | Field dups |
| minimum | 0 | 0 | 0 | 0 | 0 | 0 |
| maximum | 38 | 67 | 70 | 51 | 67 | 70 |
| mean | 13 | 24 | 26 | 21 | 19 | 23 |
| CALA RSD | 11.8 | 20.4 | 22.8 | 17.5 | 16.7 | 20.3 |
| Azimuth mean | 12 | 21 | 23 | 19 | not calc | not calc |
| Expanded MU | 24 | 41 | 46 | 35 | 33 | 41 |

MU = measurement uncertainty

x Value selected for TMeHg MU

**Table A9: Summary statistics of % RPD values for DMeHg**

| Statistic | N1 | N8 | N1 | N8 | All | All |
|---|---|---|---|---|---|---|
| | Lab dups | Lab dups | Field dups | Field dups | Lab dups | Field dups |
| minimum | 0 | 0 | 0 | 0 | 0 | 0 |
| maximum | 62 | 51 | 55 | 35 | 62 | 55 |
| mean | 22 | 22 | 24 | 16 | 22.0 | 20.0 |
| CALA RSD | 19 | 19 | 21 | 14 | 19.0 | 17.5 |
| Azimuth mean | 20 | 19 | 22 | 14 | not calc | not calc |
| Expanded MU | 39 | 37 | 41 | 28 | 38 | 35 |

MU = measurement uncertainty

x Value selected for DMeHg MU

## APPENDIX B: EXAMPLE LABORATORY REPORT FROM FLETT RESEARCH LTD

# Dissolved Methyl Mercury Results



**Flett Research Ltd.**
440 DeSalaberry Ave. Winnipeg, MB R2L 0Y7
Fax/Phone (204) 667-2505
E-mail: flett@flettresearch.ca Webpage: http://www.flettresearch.ca

**CLIENT:** AGAT Labs - Dartmouth: 17x219002
Unit 122-11 Morris Drive
Dartmouth, NS B3B 1M2

**Date Received:** June 1, 2017
**Sampling Date:** May 25, 2017

**Matrix:** Water
**Transaction ID:** 718
**PO/Contract No.:**
**Date Analysed:** July 29, 2017
**Analyst(s):** Jason S.

**Analytical Method:** M10210: Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap, and CVAFS with Automated Instruments (Version 3)

**Comments:** Samples filtered at AGAT. No Filter Blank included with this set.

**Detection Limit:** 0.010 ng/L. The MDL is based on replicates of method blanks and is expressed with a 98% confidence level.

**Estimated Uncertainty:** The estimated uncertainty of this method has preliminarily been determined to be ± 10 % at methyl mercury concentrations of 0.5 and 2.5 ng/L (95 % confidence). Uncertainty at 0.1 ng/L is 13% (95% confidence).

**Results authorized by Dr. Robert J. Flett, Chief Scientist**

## QUALITY DATA

| Blanks | | Pg of CH3Hg in the Ethylation Blank | Gross Peak Area | CH3Hg in the Ethylation Blank (ng/L) |
|---|---|---|---|---|
| | Ethylation blank ($H_2O$+Reagents) | 0.24 | 1156 | 0.01 |
| | Mean Eth. Blank (last 30 runs) | 0.49 | | |
| | | Net Pg CH3Hg in the Method Blank (Eth. Blank subtracted) | Gross Peak Area | Net CH3Hg in the Method Blank (ng/L) [Eth. Blank subtracted] |
| | Method Blank 1 | 0.47 | 3366 | 0.010 |
| **Mean Calibration Factor** (area untis / pg) | 8054 ± 4.2 %RSD | | | |

| Spike Recovery Matrix Spike (MS) and Matrix Spike Duplicate (MSD) | Sample ID (Details) | Sample Type | Gross Peak Area | Volume of Water Sample Distilled (mL) | % $CH_3Hg$ Recovery Used for Calculations | Net $CH_3Hg$ as Hg (ng/L) | **$CH_3Hg$ Recovery (%)** | |
|---|---|---|---|---|---|---|---|---|
| | 8417563F (MS8 (filtered)) | MS1 | 211947 | 47.64 | 100% | 0.95 | 90.0 | |
| | 8417563F (MS8 (filtered)) | MS1D | 209738 | 47.64 | 100% | 0.95 | 89.3 | %RPD=0.7 |
| | **Mean of Spike Recoveries** | | | | | | **89.7** | |
| **QC Samples** Ongoing Precision & Recovery (OPR) | MeOPR ID1502 (1000ng/L) | (beginning of run) | 122804 | 0.050 | 100% | 955 | 95.5 | |
| | MeOPR ID1502 (1000ng/L) | (end of run) | 100315 | 0.050 | 100% | 889 | 88.9 | |
| | MeOPR ID1502 (1000ng/L) | (beginning of run) | 128244 | 0.050 | 100% | 929 | 92.9 | |
| | MeOPR ID1502 (1000ng/L) | (end of run) | 89326 | 0.050 | 100% | 867 | 86.7 | |
| | **Mean of MeOPR** | | | | | 910 | 91.0 | |
| Alternate Source Standard (A.S.S) | A.S.S.-Alfa ID1302 (1000 ng/L) | | 243851 | | 100% | 1025 | **102.5** | |

| LAB ID | Sampling Details | Sample ID | Date Sampled | Time Sampled | Sample Type | Gross Peak Area | Volume of Water Sample Distilled (mL) | % $CH_3Hg$ Recovery Used for Calculations | Net $CH_3Hg$ in the Sample as Hg (ng/L) [Ethylation & Method Blank subtracted] [recovery corrected] |
|---|---|---|---|---|---|---|---|---|---|
| 81591 | 8417545F | MS6 (filtered) | May 25, 2017 | | | 6822 | 48.83 | 89.7% | **0.018** |
| 81592 | 8417554F | MS7 (filtered) | May 25, 2017 | | | 5664 | 47.64 | 89.7% | **0.011** |
| 81593 | 8417563F | MS8 (filtered) | May 25, 2017 | | | 5511 | 48.37 | 89.7% | **0.011** |
| 81594 | 8417572F | MS9 (filtered) | May 25, 2017 | | | 5681 | 48.55 | 89.7% | **0.011** |
| 81595 | 8417581F | MS10 (filtered) | May 25, 2017 | | **DupA1** | 6433 | 48.59 | 89.7% | **0.016** |
| 81595 | 8417581F | MS10 (filtered) | May 25, 2017 | | **DupA2** | 5660 | 47.22 | 89.7% | **0.012** |
| 81596 | 8417590F | ES1 (filtered) | May 25, 2017 | | | 6051 | 48.13 | 89.7% | **0.014** |
| 81597 | 8417599F | ES2 (filtered) | May 25, 2017 | | | 4893 | 48.18 | 89.7% | **0.010** |
| 81598 | 8417608F | ES3 (filtered) | May 25, 2017 | | **DupB1** | 5139 | 49.17 | 89.7% | **0.010** |
| 81598 | 8417608F | ES3 (filtered) | May 25, 2017 | | **DupB2** | 5595 | 47.06 | 89.7% | **0.012** |

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* : See 'Comments' section above for discussion.

*This test report shall not be reproduced, except in full, without written approval of the laboratory.*

*Note: Results relate only to the items tested.*

Dup : Duplicate - two subsamples of the same sample carried through the analytical procedure in an identical manner.

ISO/IEC/17025:2005 Accredited with the Canadian Association for Laboratory Accreditation

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