2015 Brooks Rand Instruments Interlaboratory Comparison Study for Total Mercury and Methylmercury (Intercomp 2015)

Joel Creswell, Ph.D

Philip I. Kilner

Colin Davies

Brooks Rand Instruments
4415 6th Ave NW
Seattle, WA 98107 USA
bri@brooksrandinc.com
www.brooksrandinc.com

Original release date:

May 15, 2015

This corrected version released

June 3, 2015

Revision History

May 15, 2015 – Original report released

June 3, 2015 (this revision) – Corrected version released. Error bars on Figs. 4-5 were corrected to extend to ± 1 standard deviation of the mean from each date samples were analyzed. In the previous version (May 15, 2015), an average standard deviation across all analysis dates was used for each sample.

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Introduction

The Brooks Rand Instruments Interlaboratory Comparison Study (Intercomp) for Total Mercury (THg) and Methylmercury (MeHg), now in its fifth year, was initiated to take the place of the Mercury Round Robin, which was conducted by the Florida Department of Environmental Protection (DEP) on an annual basis between 2001 and 2009. This exercise provides a reliable means for laboratories to test their competency in the analysis of total mercury and methylmercury in natural waters, as well as a metric for assessing the intercomparability of data generated by different laboratories. Brooks Rand Instruments undertook the organization of the Intercomp in 2011, upon learning that the Florida DEP no longer planned to continue the exercise.

Intercomp 2011 [*Creswell et al.,* 2011] was organized to replicate, to the extent feasible, the methods followed in the Mercury Round Robins organized by the Florida DEP. The four week analysis and reporting period for methylmercury data, introduced and validated in Intercomp 2012 [*Creswell et al.*, 2012, 2015], was maintained in Intercomp 2015 (this study). The organization and methods of Intercomp 2015 were kept as similar to Intercomps 2011-2014 as possible, with the goal of producing a multiyear record of laboratory performance and data intercomparability [*Creswell et al.*, 2011, 2012, 2013, 2014].

Some of the key features of Intercomp 2015 were a broad invitation to participate; anonymous data submission, analysis, and reporting; and the inclusion of analytical method reporting. The initial invitation to participate was sent to Brooks Rand Instruments' email database of more than 3,000 unique addresses. 59 laboratories in nine countries signed up to participate and were sent samples. Participants submitted 55 sets of total mercury results and 39 sets of methylmercury results. Intercomp 2015 had seven fewer participants than Intercomp 2013, which was, to our knowledge, the largest interlaboratory comparison study for total mercury and methylmercury in un-spiked natural waters on record.

Methods

Sample Collection and Distribution

Samples were collected on January 31, 2015 from three sites in the western Washington State, USA. Site UJ (Uncle John Creek at Chapman Cove; Shelton, Washington) is an estuarine site where Uncle John Creek flows into Chapman Cove and Oakland Bay in southern Puget Sound (Figure 1). This site was sampled just below the Agate Loop Road bridge. Site CC (Cranberry Creek; Shelton, Washington) is a freshwater stream that was sampled upstream of the Highway 3 bridge, shortly before it empties into Oakland Bay (Figure 2). Site LS (Lake Sammamish State Park; Redmond, Washington) is a freshwater wetland hydrologically connected to Lake Sammamish (Figure 3). It was sampled from the hiking trail that connects the boat launch parking lot to the main parking lot, on the side of the trail closest to the lake (northwest).

Figure 1. Sampling site UJ

Figure 2. Sampling site CC

Figure 3. Sampling site LS

At all three sites, samples were collected with two peristaltic pumps, through 0.45 µm inline filter capsules (Voss Technologies, San Antonio, Texas), into acid-cleaned 20 L fluorinated polyethylene (FLPE) carboys. We used fluorinated ethylene propylene (FEP) sampling lines connected to silicone tubing through the pump head. Ten percent of the filters in each manufacturer's lot were checked for contamination by analyzing DI water passed through them. The average total mercury level was less than 10 pg per capsule. Filters were rinsed with sample prior to filling carboys. We followed strict trace metal clean techniques [*U.S. Environmental Protection Agency*, 1996] at the field sites to avoid sample inhomogeneity to the extent possible. Approximately 120 L of water was collected at each of the three sites.

Samples were preserved upon returning from the field, by adding either concentrated (12 M) Trace Metal Grade hydrochloric acid (freshwater samples: sites CC and LS) or concentrated (18M) Trace Metal Grade sulfuric acid (saline samples: site UJ) to each carboy. The final acid concentration in the freshwater samples was 0.4% (v/v) or approximately 50 mM and in the saline samples was 0.2% (v/v) or approximately 36 mM. We distributed the samples into 500 mL FLPE bottles for shipment to laboratories the following day, February 1, 2015. In an effort to maximize sample uniformity, we shook and transferred samples from the field carboys into acid-cleaned, fluorinated HDPE 30 gallon (113.6 L) drums. We filled the 500 mL FLPE bottles through a fluoropolymer spigot installed in the bottom of each drum. These bottles were all from the same manufacturer's lot, and prior to use we tested a random selection of ten percent of the cases received. Ten percent of the bottles from each case selected were filled with a 1% (v/v) bromine monochloride (BrCl) solution, stored at room temperature overnight, and analyzed the following day. The mean total mercury concentration in these bottle blanks was 0.148 ± 0.173 ng/L, less than the 0.4 ng/L limit established for this study.

The 500 mL FLPE sample bottles were placed in single plastic zip-top bags and stored overnight. Prior to shipping, the samples from each site were separated into three groups and randomly assigned ID numbers (Table 1). They were then grouped into sets, each set containing nine samples, three from each site, but numbered such that it was not possible for participants to identify which samples were from which site. Each bottle was labeled as to whether it contained fresh or saline water. Sample sets were sent to 59 laboratories on Monday, February 2, 2015, by express courier. Most deliveries were completed within three days, but in a few cases, international customs delays prevented timely delivery and samples were not delivered for several days. Participating laboratories were asked to analyze samples for total mercury and/or methylmercury following their standard operating procedures, and were given no further guidance on analytical methodology. All results were requested to be reported by March 2, 2015, four weeks after the samples were shipped; however, results were generally accepted for samples analyzed by the March 2 deadline. This deadline is based on the results of the 2012 bottle storage study, which demonstrated that analyte concentrations did not change substantially over a four week holding time [*Creswell et al.*, 2012, 2015].

Table 1. Sample identification table.

Site	**Sample Numbers**
UJ (Uncle John Creek)	1, 7, 9
CC (Cranberry Creek)	2, 3, 8
LS (Lake Sammamish State Park)	4, 5, 6

Three laboratories participated in a holding time study as part of Intercomp 2015. Brooks Rand Labs, the Jožef Stefan Institute Department of Environmental Sciences, and the U.S. Geological Survey Wisconsin Mercury Research Lab each received two replicate sets of samples to analyze at the beginning and end of the reporting period. The results of these analyses were used to determine whether the analyte concentrations changed over the course of the study.

All results were reported to an independent third party, EcoChem, Inc. (Seattle, Washington, USA), a data validation company who had no role in the study other than data management. At EcoChem, the dataset was compiled, and a unique identifier was assigned to each laboratory, before it was transmitted to Brooks Rand Instruments. Following delivery of this report, each participating laboratory received an e-mail containing their own unique identifier, but identifiers were not disclosed to any other parties, including Brooks Rand Instruments. This research design ensured that there would be no bias by the preparers of this report against any participating laboratory and that participants could submit data without fear their scores would be publicly identifiable.

Data Analysis and Calculations

Each laboratory was asked to report an analytical result, detection limit, and date analyzed for each sample and analyte. These data are the basis of the scores in this report. In addition, each laboratory reported information on sample preparation and analytical methodology and equipment. These data were used to compile assessments of the performance of various analytical methods, but were not used in laboratory scoring.

Statistical data analysis was carried out largely following the recommendations of Lin & Niu [1998]. Samples were pooled by site (Table 1) for the calculation of consensus statistics and outliers. The consensus mean, median, standard deviation, and inter-quartile range for each site were calculated using the Kaplan-Meier method, which is an unbiased estimator of these statistics for datasets with undetected values [*Helsel*, 2010, 2012]. The median and inter-quartile range, which are unbiased in the presence of extreme values, were computed prior to the removal of outliers (described below). The mean and standard deviation, which are biased by extreme values, were computed after the removal of outliers.

The scoring method used for the Intercomp requires the flagging of outlier measurements, which we identified using the modified Z score method [*Filliben*, 2012] because it is robust for both small and large sample sizes, and is not affected by the magnitude of extreme outliers. The modified Z score is calculated as follows:

$$Z_i = \frac{0.6745(x_i - \tilde{x})}{MAD}$$

Z_i	Modified Z score for laboratory i
x_i	an individual measurement of a sample by laboratory i
$\tilde{x}$	the median measurement of sample x across all laboratories and replicates
MAD	median absolute deviation = $median(\lvert x_i - \tilde{x}\rvert)$ across all measurements of a given sample

Any measurement with a modified Z score greater than 3.5 was labeled as an outlier [*Filliben*, 2012] and excluded from the calculation of laboratory performance scores, described below. If any of a lab's results for a given site were flagged as outliers, that lab received a score of 0 for that site.

Undetected values present a challenge for the calculation of outliers and performance scores. An undetected value is effectively a censored data point, the actual value of which falls between zero and the detection limit. In some cases, such as when the true concentration of a sample is below a laboratory's detection limit, reporting an undetected value is "correct," however in other cases, a lab may report an undetected value as a result of incorrectly measuring the concentration as being too low. Because the true concentration of the Intercomp samples is unknown, it is difficult to distinguish between undetected values for the purposes of identifying outliers and calculating performance scores. In Intercomp 2015, for the first time, we treated undetected values differently than in previous Intercomps. We substituted a laboratory's detection limit for any undetected values. These substituted detection limits were treated as reported measurements for the purpose of identifying outliers and calculating scores. If a substituted detection limit was identified as an outlier by the modified Z score method and was less than the site median, we labeled it an outlier and assigned a score of 0 to that lab for that site. This is because the detection limit represents the highest possible value of the undetected result, and if that highest value was low enough to be an outlier, any lower value would also be an outlier. If a substituted detection limit was identified as an outlier and was greater than the site median, it was flagged as a possible outlier and was not assigned a score. The actual value of the undetected result may not be an outlier, because its range of possible values from zero to the detection limit includes the median, however, it is impossible to be certain. If a substituted detection limit was not identified as an outlier, that lab was assigned a score for that site, but the score is marked with an asterisk (*) on the tables in this report to identify it as speculative because the true value of the measurement is not known and could be an outlier.

Following outlier removal, a series of exploratory statistical plots was generated to verify that the removal of outliers resulted in a dataset with improved normality (a more Gaussian distribution). Although the method of outlier removal used did not always result in a normal distribution of data (e.g., Figure 17a), outlier removal improved normality for every site.

In order to assign a score to each laboratory's performance, we calculated a t-statistic and Cook-Weisberg distance [*Cook and Weisberg*, 1980; *Lin and Niu*, 1998; *Niu and Tintle*, 2008; *Niu and Miller*, 2009] for the measurement of each analyte at each site by each participating laboratory. For example, if a lab analyzed total mercury and methylmercury in all nine samples, with no outliers, that lab would receive six scores: one for each analyte for each of the three sites.

If a lab measured two samples from a site, that lab received a score for that site, but the score is marked with a dagger (†) in the tables in this report to identify is as being derived from only two measurements. If a lab analyzed one or no samples from a site, that lab did not receive a score for that site. The t-statistic was calculated as follows:

$$t_i = \frac{\bar{Y}_i - \tilde{\mu}}{\tilde{\sigma}\sqrt{1/r - 1/n_0}}$$

t_i	t statistic for lab i
$\bar{Y}_i$	the mean measurement for site Y by lab i
$\tilde{\mu}$	mean of all measurements by labs with no flagged outliers
$\tilde{\sigma}$	standard deviation of the residuals of all measured values for site Y
r	number of replicates from site Y analyzed by lab i
n_0	total number of measurements taken by laboratories with no flagged outliers

The t-statistic reflects the distance of an individual laboratory's mean value from the consensus mean for the site.

The Cook-Weisberg distance (C-W distance) was calculated as follows:

$$D_i = \frac{r(\bar{Y}_i - \bar{Y}_{..})^2}{p \cdot s^2}$$

D_i	C-W distance for lab i
r	number of replicates of site Y analyzed by lab i
$\bar{Y}_i$	mean of all measurements of site Y by lab i
$\bar{Y}_{..}$	the consensus mean of site Y
p	number of labs with no flagged outliers
s^2	variance of the residuals of all measured values for site Y

The C-W distance reflects the influence that each laboratory's average value has on the consensus mean.

We assigned scores following the rating system of Niu and Tintle [2003; Table 2].

Table 2. Rating system for laboratory performance [*Niu and Tintle*, 2003].

Rating	*t*-value	C-W distance
5 (Very good)	$0.00 \leq t$-value ≤ 2.00	C-W distance < 3.00
4 (Good)	$2.01 \leq t$-value ≤ 4.00	C-W distance < 3.00
3 (Satisfactory)	t-value > 4.00	C-W distance < 3.00
2 (Questionable)	t-value > 4.00	$3.00 \leq$ C-W distance ≤ 10.00
1 (Poor)	t-value > 4.00	$10.01 \leq$ C-W distance
0 (Unacceptable)	With one or more outliers	With one or more outliers

Results

We received 58 unique sets of results. 55 of these contained total mercury data and 39 contained methylmercury data. We accepted results with analysis dates up to the reporting deadline of March 2, 2015.

Holding time data

Due to differences in sample receipt and preparation times, holding time samples were not analyzed on the same dates by all three laboratories participating in the holding time study. However, the dates of analysis shown in Figures 4 and 5 below span the majority of the reporting period for both analytes. There are several instances in which one or more labs observed a change in analyte concentration in a sample greater than ± 1 standard deviation of three replicate measurements (indicated by error bars). In the THg data, this is true for the USGS results from site UJ. In the MeHg data, this is true for the USGS results from site CC and the IJS results from sites CC and LS. However, due to some instrument downtime, the later IJS samples were analyzed well after the end of the reporting period, which likely contributed to the variability in the results [*Creswell et al.*, 2012, 2015]. Additionally, the IJS samples were analyzed by three different methods, which may have contributed variability to the results. However there is no trend of a consistent, directional (up or down) concentration change over time in all results from any one lab. If a lab exhibited increasing concentrations over time in all samples, this might indicate a contamination problem, while the reverse might indicate poor sample storage conditions. The lack of any such trend indicates that the changes over time in these holding time samples exemplify the variability that can be expected in all samples over the course of the reporting period.

Laboratory results

There were four instances in which a participant did not receive a score because they reported undetected results with a detection limit that was higher than the site median and which, when substituted for a result, was flagged as an outlier. Because a detection limit represents the maximum point of the range in which the actual measured concentration lies, these results were not treated as outliers, given the possibility that the unknown actual results from these labs ($0 \leq$ actual result $\leq$ detection limit) might not be outliers. There were seven instances in which a lab's detection limit was substituted for a reported value which was not flagged as an outlier. These labs received nonzero scores for those sites. There were two instances in which a detection limit was lower than the site median and, when substituted for a result, was flagged as an outlier. These were treated as outliers and assigned scores of zero because every possibility for the actual result would be less than the detection limit and therefore also an outlier. The remainder of the scores are based on measured concentrations as reported.

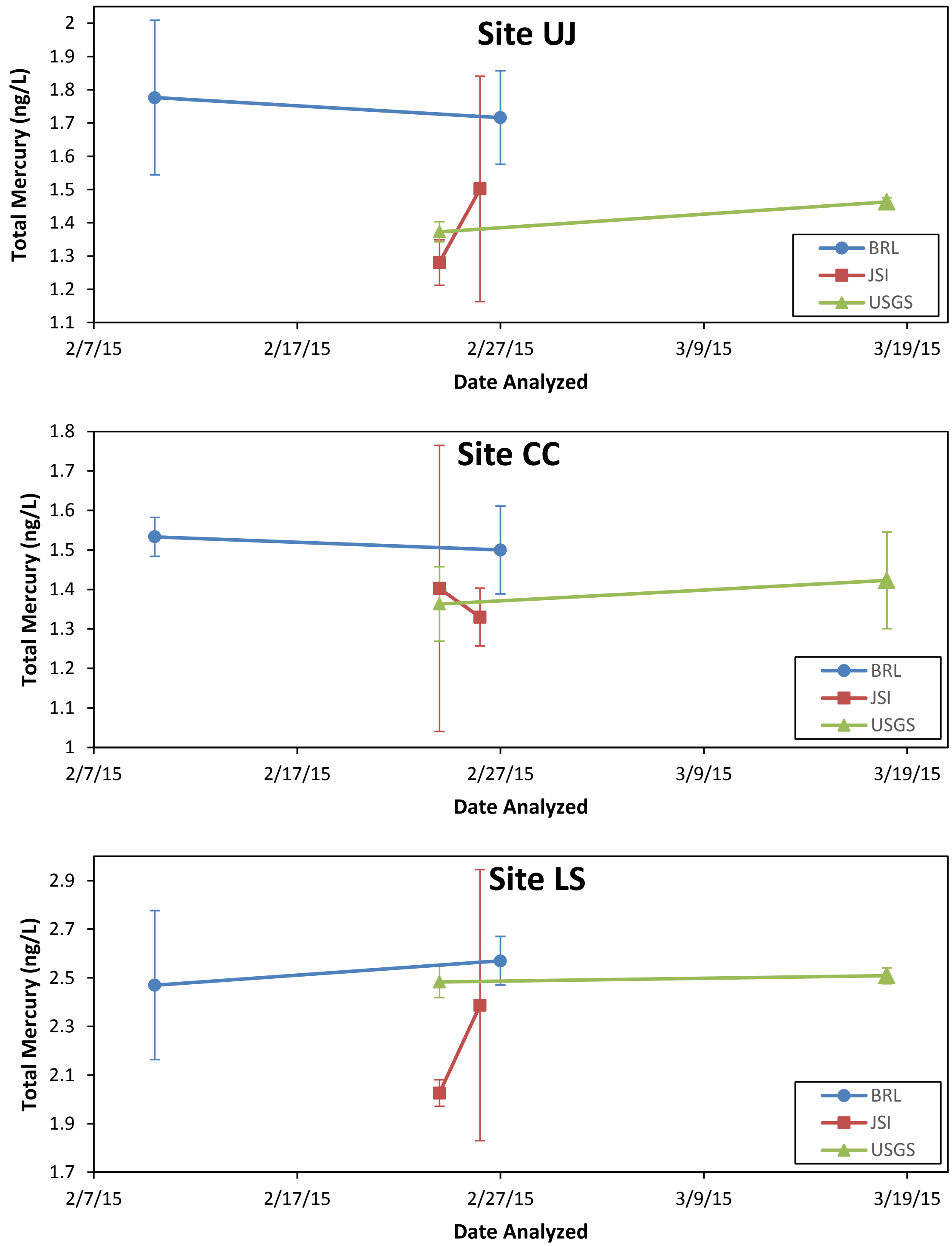

Figure 4. Holding time data for total mercury. Error bars are ± 1 standard deviation of replicate measurements. Where error bars are not visible, they are smaller than the chart symbol to which they pertain. Note that the vertical scales are not identical. BRL = Brooks Rand Labs; JSI = Jožef Stefan Institute; USGS = U.S. Geological Survey.

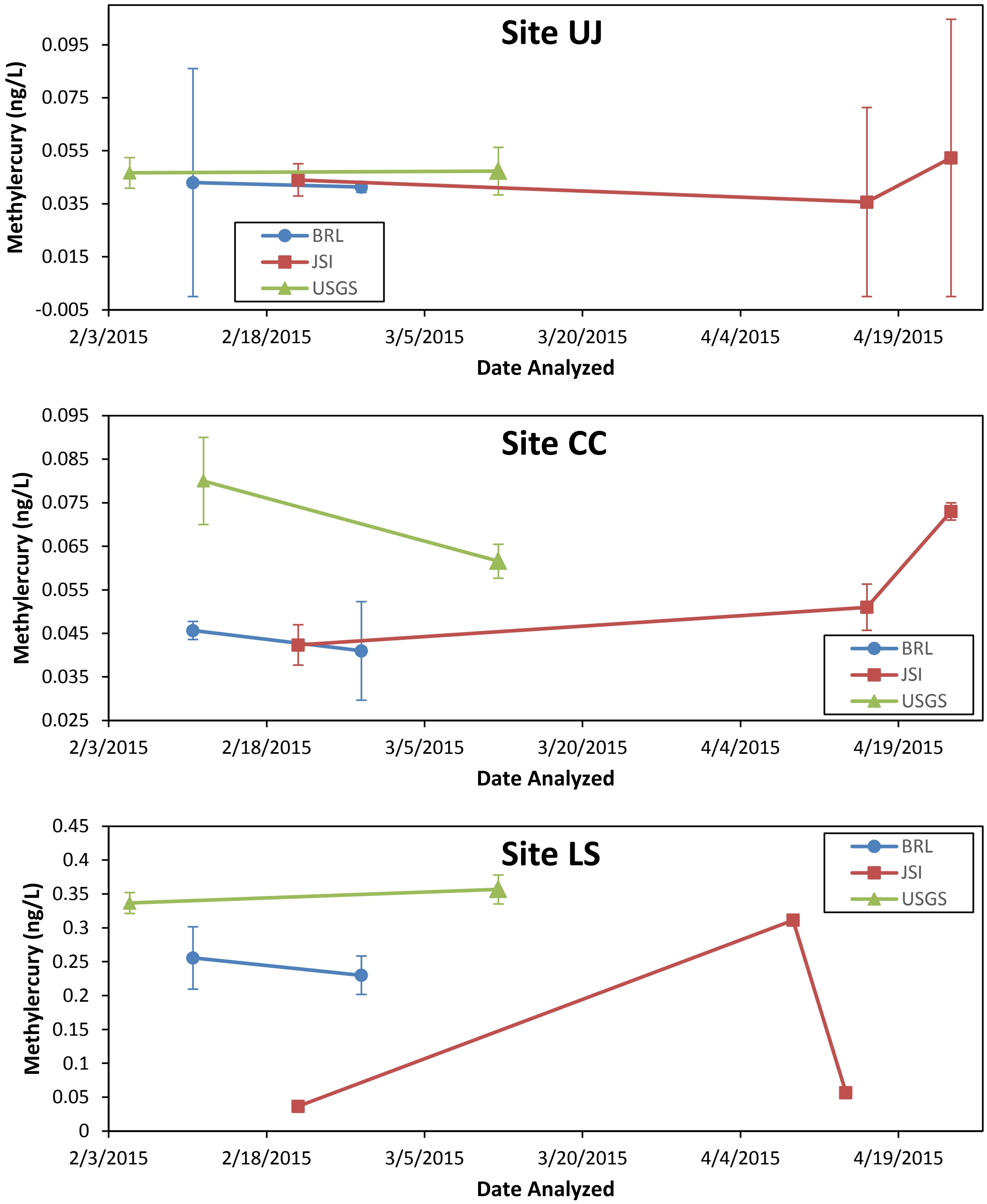

Figure 5. Holding time data for methylmercury. Error bars are ± 1 standard deviation of replicate measurements. Where error bars are not visible, they are smaller than the chart symbol to which they pertain. Note that the vertical scales are not identical. BRL = Brooks Rand Labs; JSI = "Jožef Stefan" Institute; USGS = U.S. Geological Survey. JSI samples were analyzed by three different methods. 2/21: direct hydride generation-GC-AFS; 4/16: distillation, ethylation, GC-AFS (Method 1630); 4/24: CH_2Cl_2 extraction, ethylation, GC-AFS.

Total mercury data, Site UJ

Table 3. Laboratory performance for total mercury, site UJ (samples 1, 7, 9). An asterisk (*) indicates that the lab mean includes at least one undetected value that was substituted with that lab's detection limit.

Consensus statistics:
Mean = 1.26 ng/L, Standard deviation = 0.30,
Median = 1.28 ng/L, Inter-quartile range = 0.33

Lab	Mean	t value	C-W Distance	Score
1	1.49	1.85	0.07	5
2	1.50	1.96	0.08	5
3	1.27	0.03	0.00	5
4	1.43	1.39	0.04	5
5	1.50*	1.96	0.08	5
6	1.65	With	outliers	0
7	1.24	0.24	0.00	5
8	1.04	1.98	0.08	5
9	1.39	1.02	0.02	5
10	1.10	1.47	0.04	5
11	1.33	0.50	0.00	5
12	1.29	0.16	0.00	5
13	1.31	0.36	0.00	5
14	1.35	0.65	0.01	5
15	1.48	1.76	0.06	5
16	1.48	1.79	0.06	5
17	1.14	1.15	0.03	5
18	1.02	2.14	0.09	4
19	1.22	0.48	0.00	5
20	0.54	6.25	0.77	3
23	1.38	0.90	0.02	5
24	1.22	0.47	0.00	5
25	1.11	1.38	0.04	5
26	20.00*	No	score	
27	1.58	2.68	0.14	4
28	14.08	With	outliers	0
29	1.16	0.96	0.02	5
30	1.25	0.15	0.00	5
31	1.77	4.29	0.36	3
32	0.95	2.79	0.15	4

Table continued on following page

Lab	Mean	t value	C-W Distance	Score
33	1.77	4.25	0.35	3
34	1.60	2.82	0.16	4
35	50.00*	No	score	
36	1.24	0.27	0.00	5
37	1.20	0.61	0.01	5
38	0.95	2.73	0.15	4
39	0.97	2.61	0.13	4
40	1.15	1.07	0.02	5
41	0.99	2.43	0.12	4
42	1.47	1.71	0.06	5
43	1.33	0.50	0.00	5
44	1.44	1.45	0.04	5
45	1.22	0.47	0.00	5
47	1.92	5.54	0.60	3
48	1.03	2.06	0.08	4
49	1.29	0.13	0.00	5
50	1.06	1.81	0.06	5
51	1.61	2.93	0.17	4
52	0.76	4.42	0.38	3
53	1.03	2.03	0.08	4
54	4.33	With	outliers	0
55	1.06	1.81	0.06	5
56	1.37	0.88	0.02	5
57	1.30	0.25	0.00	5
58	1.28	0.08	0.00	5

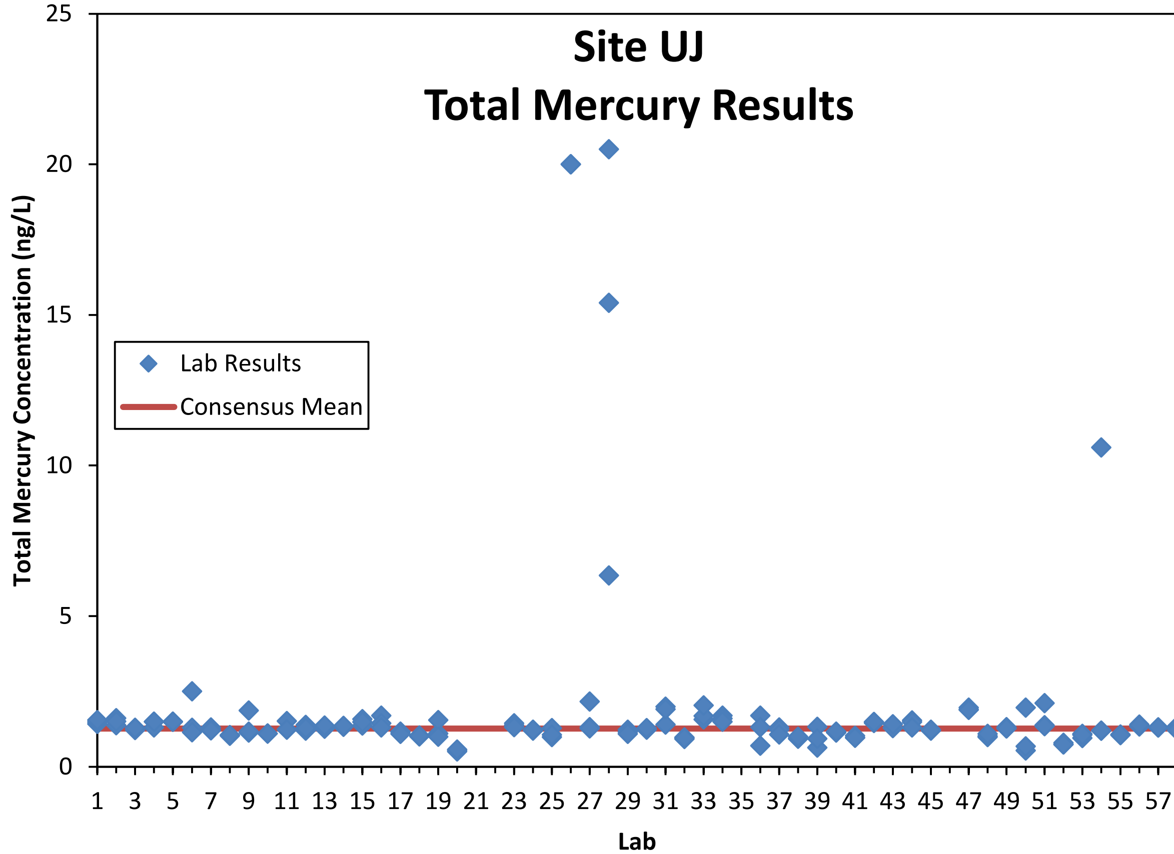

Figure 6. Total mercury results from all participating laboratories for site UJ. Not shown: three data points for Lab 35, Concentration 50 ng/L.

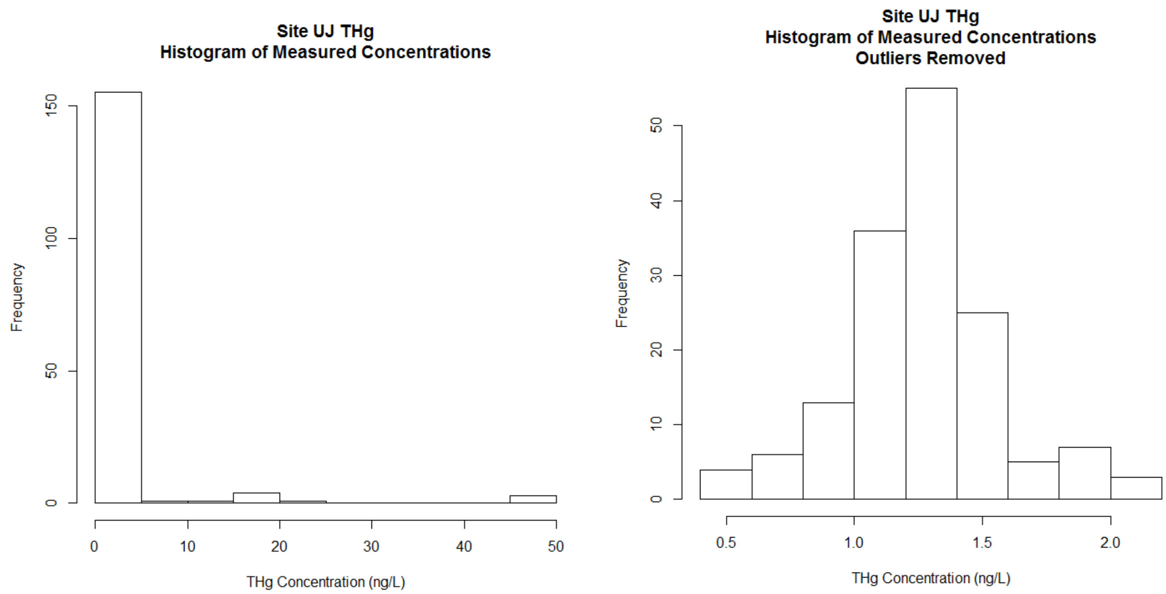

Figure 7a. Histograms of reported total mercury concentrations for site UJ. All concentrations (left); non-outlier values (right).

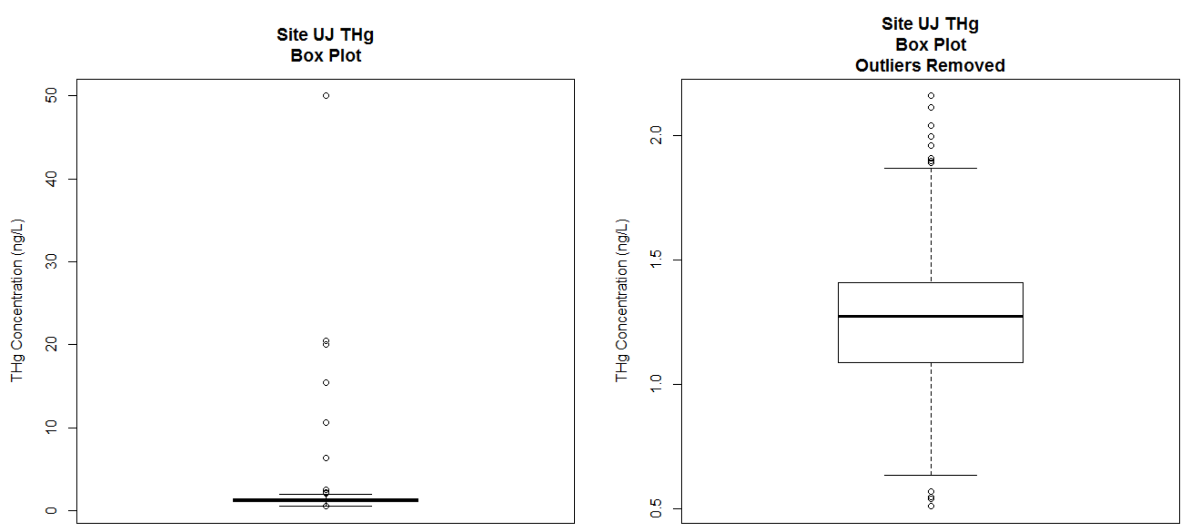

Figure 7b. Box plots of reported total mercury concentrations for site UJ. All concentrations (left); non-outlier values (right).

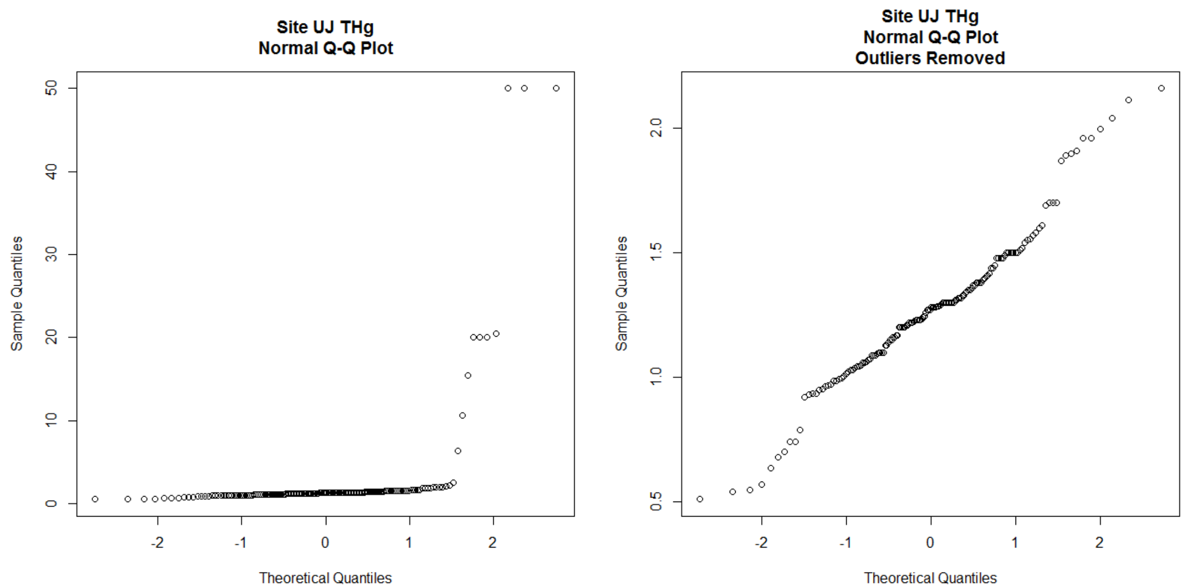

Figure 7c. Normal quantile-quantile plots of reported total mercury data for site UJ. All concentrations (left); non-outlier values (right).

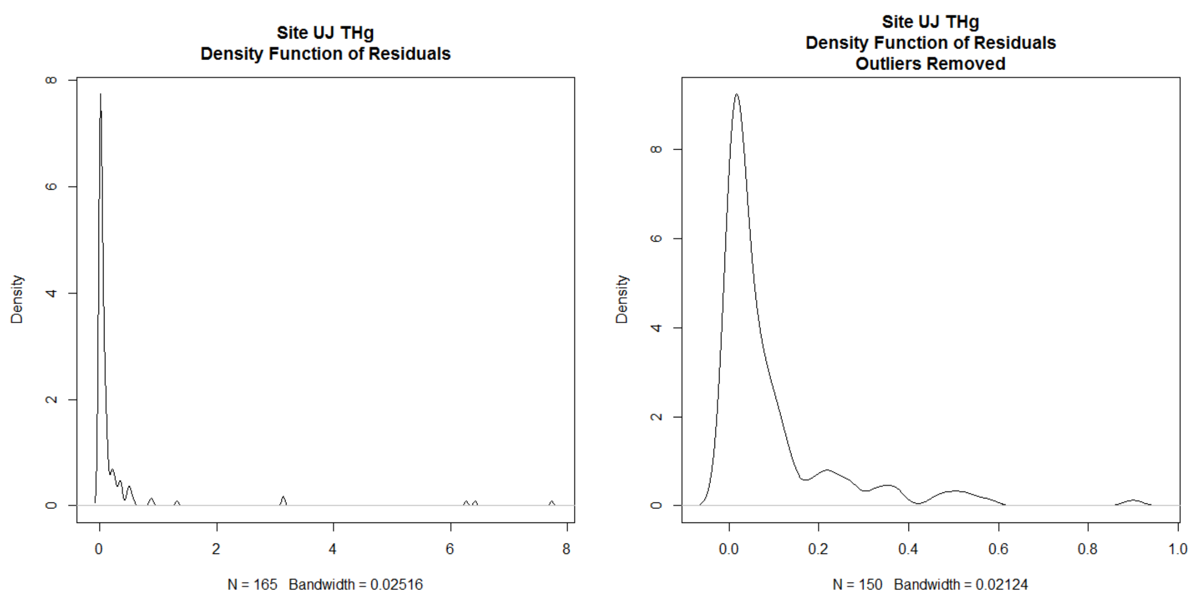

Figure 7d. Density functions of residuals (residual = individual measurement - laboratory mean) of total mercury data for site UJ. All values (left); non-outlier values (right).

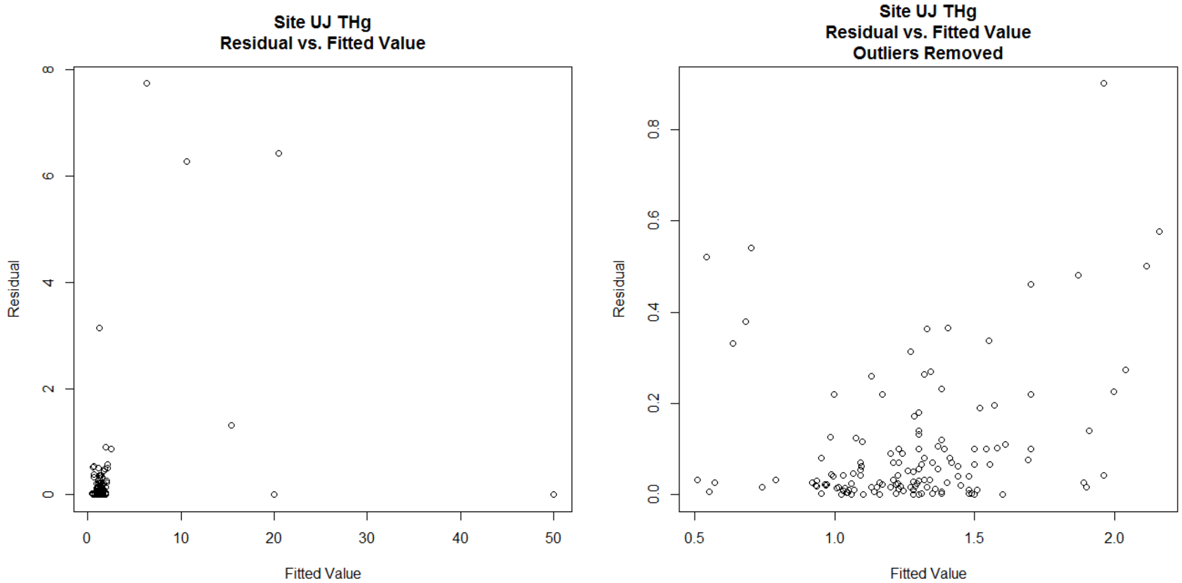

Figure 7e. Residual (residual = individual measurement - laboratory mean) vs. fitted value plots of reported total mercury concentrations for site UJ. All values (left); non-outlier values (right).

Total mercury data, Site CC

Table 4. Laboratory performance for total mercury, site CC (samples 2, 3, 8). An asterisk (*) indicates that the lab mean includes at least one undetected value that was substituted with that lab's detection limit. A dagger (†) indicates that a score is based on two results instead of three.

Consensus statistics:
Mean = 1.18 ng/L, Standard deviation = 0.28,
Median = 1.2 ng/L, Inter-quartile range = 0.29

Lab	Mean	t value	C-W Distance	Score
1	1.45	3.00	0.19	4
2	1.42	2.62	0.14	4
3	1.12	0.76	0.01	5
4	1.33	1.68	0.06	5
5	1.50*	3.56	0.26	4
6	1.23	0.55	0.01	5
7	1.20	0.18	0.00	5
8	1.10	1.00	0.02	5
9	1.09	1.06	0.02	5
10	1.03	1.70	0.06	5
11	1.22	0.37	0.00	5
12	1.17	0.16	0.00	5
13	1.30	1.30	0.04	5
14	1.33	1.68	0.06	5
15	1.45	2.95	0.18	4
16	1.36	1.98	0.08	5
17	1.04	1.61	0.05	5
18	1.06	1.40	0.04	5
19	1.23	0.50	0.01	5
20	0.58	6.80	0.96	3
23	1.27	0.93	0.02	5
24	1.23	0.55	0.01	5
25	1.11	0.82	0.01	5
26	20.00*	No	score	
27	1.20	0.21	0.00	5
28	10.33	With	outliers	0
29	1.06	1.36	0.04	5
30	1.10	0.90	0.02	5
31	2.00	With	outliers	0
32	0.90	3.20	0.21	4

Table continued on following page

Lab	Mean	t value	C-W Distance	Score
33	1.53	3.93	0.32	4
34	1.80	With	outliers	0
35	1.84	7.42	1.15	3
36	1.31	1.45	0.04	5
37	1.11	0.88	0.02	5
38	0.93	2.83	0.17	4
39	27.80	With	outliers	0
40	1.17	0.20	0.00	5
41	1.08	1.17	0.03	5
42	1.64	With	outliers	0
43	1.14	0.50	0.01	5
44	1.23	0.48	0.00	5
45	1.07	1.25	0.03	5
47	1.73	With	outliers	0
48	0.93	2.87	0.17	4
49	1.16	0.24	0.00	5
50	1.43	2.73	0.16	4
51	1.24	0.66	0.01	5
52	0.65†	6.02	0.75	3
53	0.99	2.17	0.10	4
54	15.60	With	outliers	0
55	1.00	2.04	0.09	4
56	1.36	2.02	0.08	4
57	1.20	0.18	0.00	5
58	1.40	2.46	0.13	4

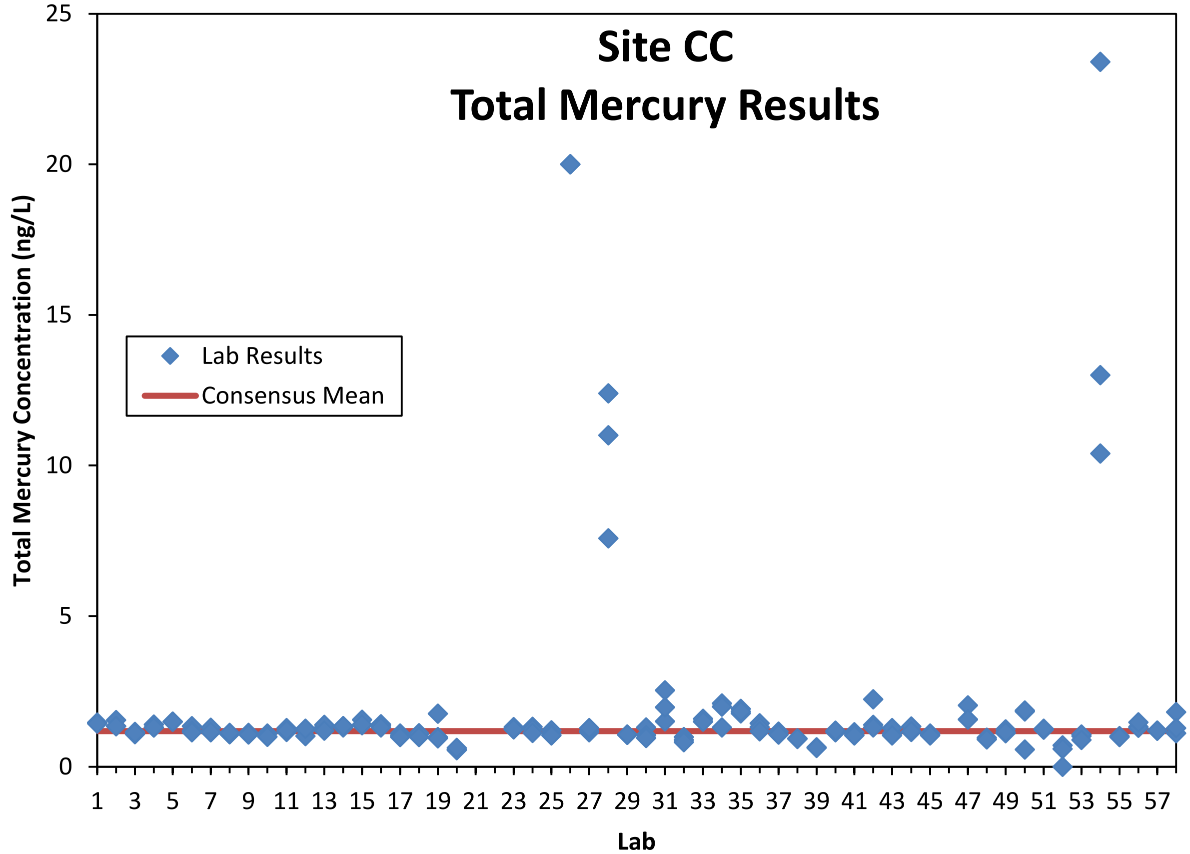

Figure 8. Total mercury results from all participating laboratories for site CC. Not shown: one data point for Lab 39, Concentration 82.14 ng/L.

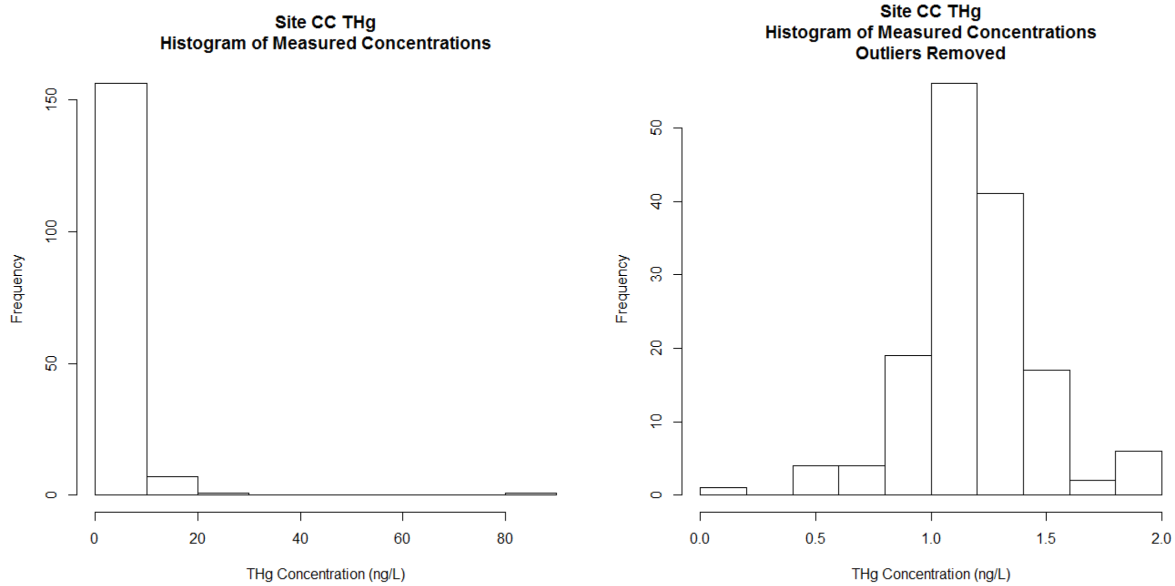

Figure 9a. Histograms of reported total mercury concentrations for site CC. All concentrations (left); non-outlier values (right).

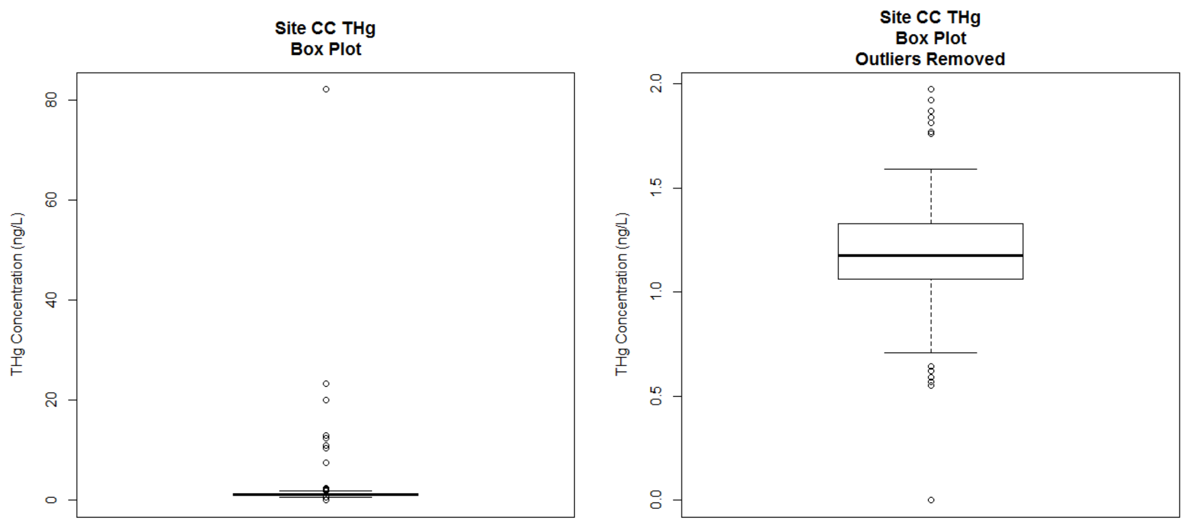

Figure 9b. Box plots of reported total mercury concentrations for site CC. All concentrations (left); non-outlier values (right).

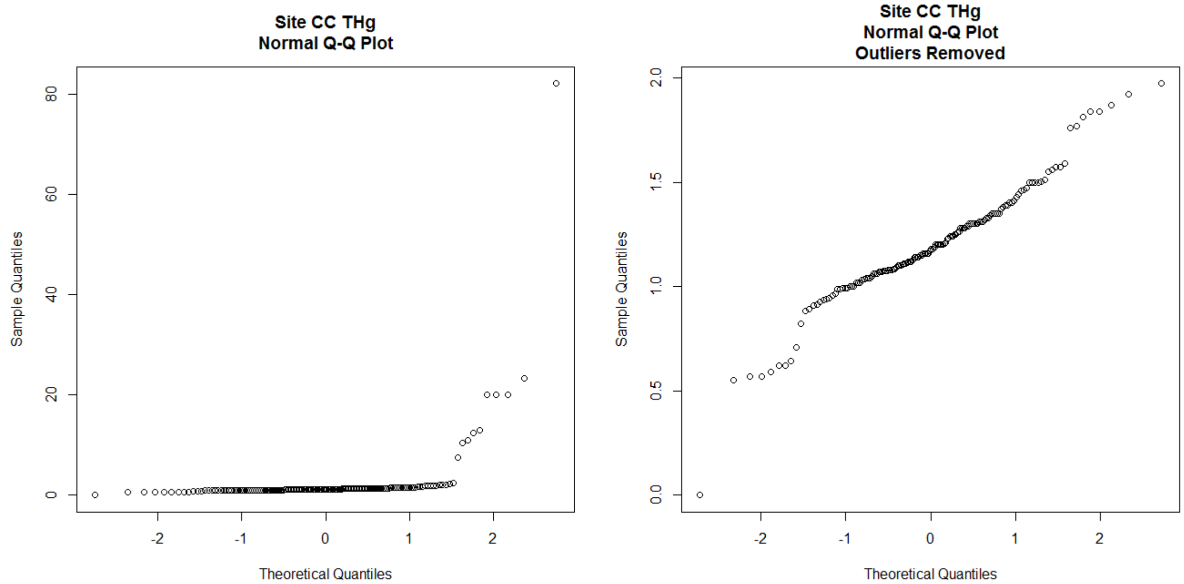

Figure 9c. Normal quantile-quantile plots of reported total mercury data for site CC. All concentrations (left); non-outlier values (right).

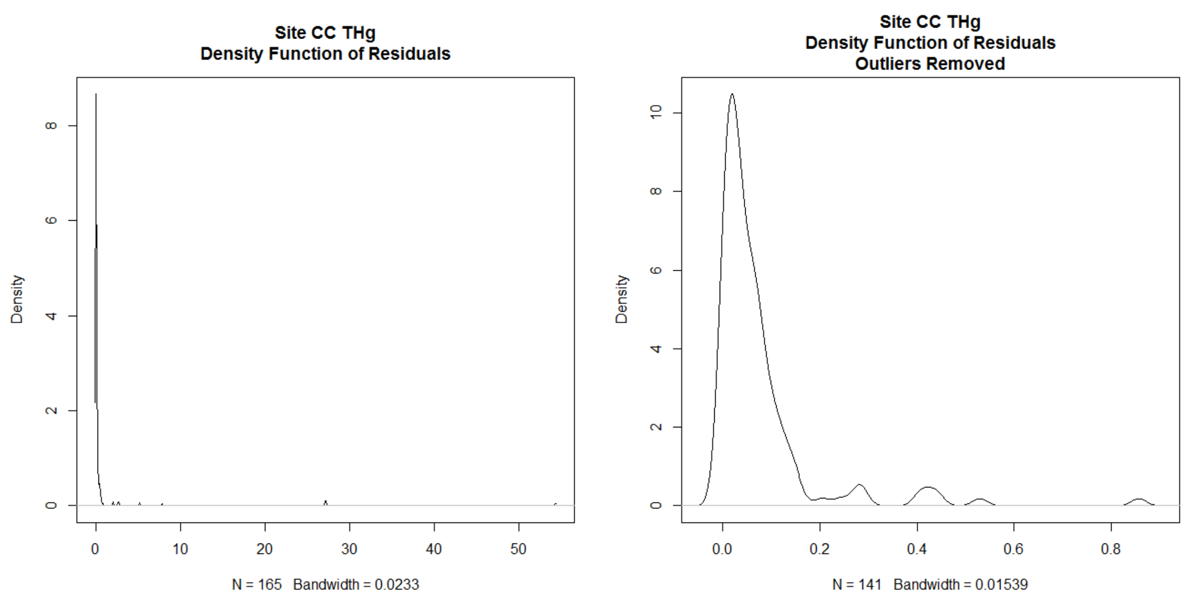

Figure 9d. Density functions of residuals (residual = individual measurement - laboratory mean) of total mercury data for site CC. All values (left); non-outlier values (right).

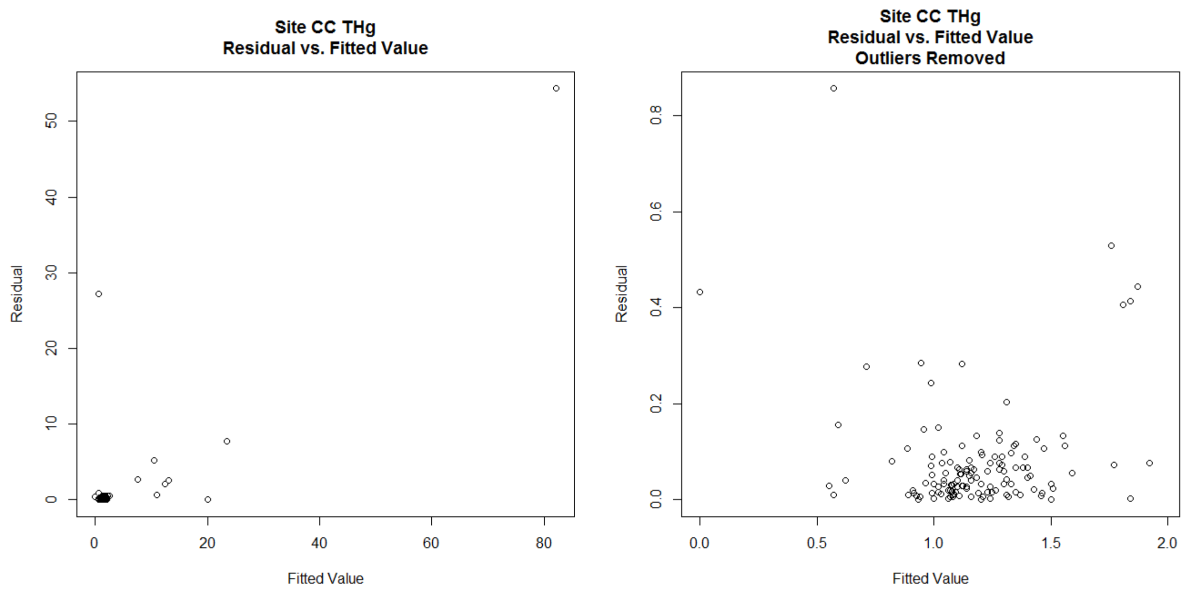

Figure 9e. Residual (residual = individual measurement - laboratory mean) vs. fitted value plots of reported total mercury concentrations for site CC. All values (left); non-outlier values (right).

Total mercury data, Site LS

Table 5. Laboratory performance for total mercury, site LS (samples 4, 5, 6). An asterisk (*) indicates that the lab mean includes at least one undetected value that was substituted with that lab's detection limit.

Consensus statistics:
Mean = 2.19 ng/L, Standard deviation = 0.30,
Median = 2.23 ng/L, Inter-quartile range = 0.43

Lab	Mean	t value	C-W Distance	Score
1	2.20	0.08	0.00	5
2	2.73	7.61	1.21	3
3	1.62	8.42	1.48	3
4	2.53	4.77	0.47	3
5	1.50*	10.14	2.14	3
6	2.27	1.02	0.02	5
7	2.23	0.34	0.00	5
8	2.41	3.04	0.19	4
9	2.25	0.68	0.01	5
10	2.10	1.48	0.05	5
11	2.28	1.16	0.03	5
12	2.27	0.97	0.02	5
13	2.33	1.79	0.07	5
14	2.36	2.27	0.11	4
15	2.46	3.66	0.28	4
16	2.42	3.13	0.20	4
17	2.29	1.23	0.03	5
18	1.93	3.90	0.32	4
19	1.62	With	outliers	0
20	1.04	With	outliers	0
23	2.25	0.68	0.01	5
24	2.03	2.49	0.13	4
25	1.98	3.16	0.21	4
26	20.00*	No	score	1
27	2.09	1.68	0.06	5
28	16.03	With	outliers	0
29	2.30	1.45	0.04	5
30	2.11	1.28	0.03	5
31	7.41	With	outliers	0
32	1.96	3.51	0.26	4

Table continued on following page

Lab	Mean	t value	C-W Distance	Score
33	2.47	3.85	0.31	4
34	2.50	4.29	0.38	3
35	2.30	1.40	0.04	5
36	1.13	With	outliers	0
37	2.08	1.73	0.06	5
38	1.90	4.32	0.39	3
39	1.86	4.92	0.50	3
40	2.25	0.63	0.01	5
41	1.80	5.86	0.72	3
42	2.72	7.51	1.17	3
43	2.31	1.55	0.05	5
44	2.16	0.62	0.01	5
45	2.28	1.06	0.02	5
47	2.37	2.46	0.13	4
48	2.34	1.98	0.08	5
49	2.55	4.96	0.51	3
50	0.94	With	outliers	0
51	2.41	3.02	0.19	4
52	1.73	6.87	0.98	3
53	1.96	3.51	0.26	4
54	20.81	With	outliers	0
55	1.83	5.43	0.61	3
56	2.48	4.05	0.34	3
57	2.30	1.40	0.04	5
58	2.03	2.55	0.14	4

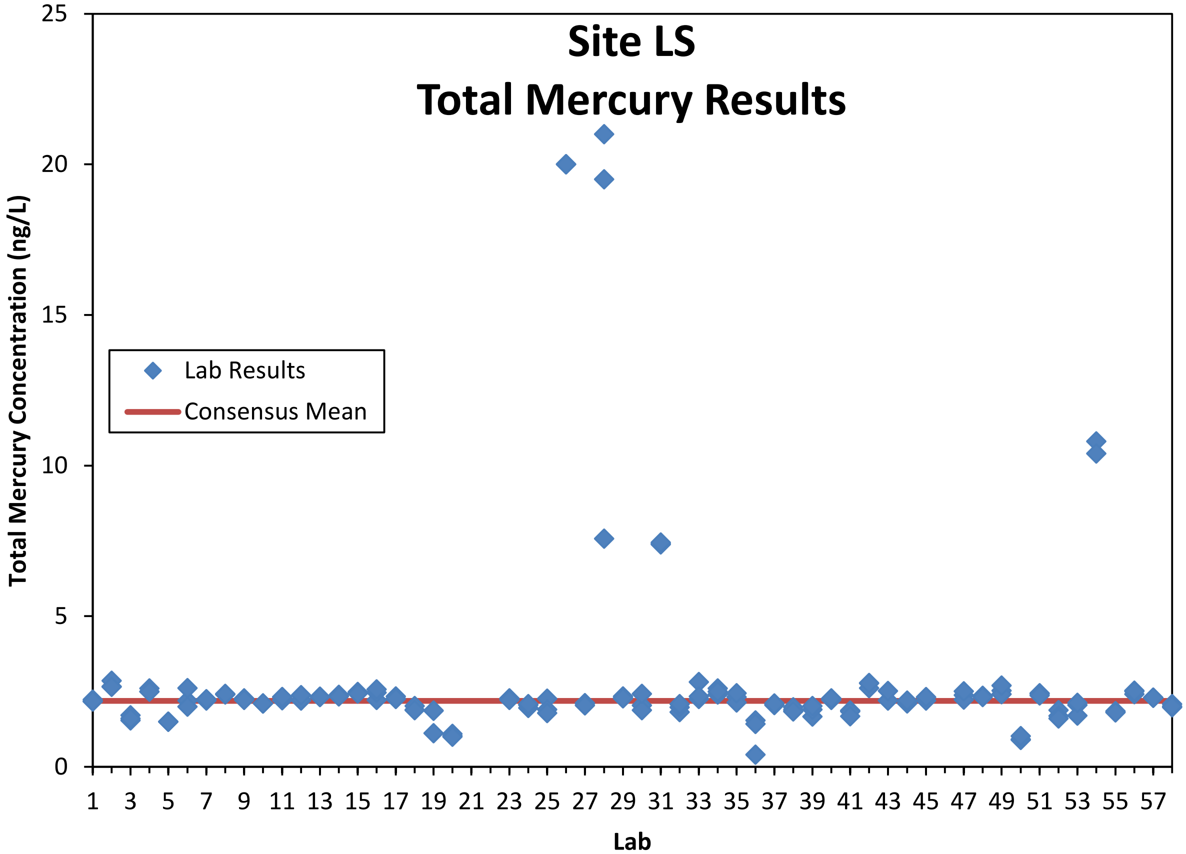

Figure 10. Total mercury results from all participating laboratories for site LS. Not shown: one data point for Lab 54, Concentration 41.23 ng/L.

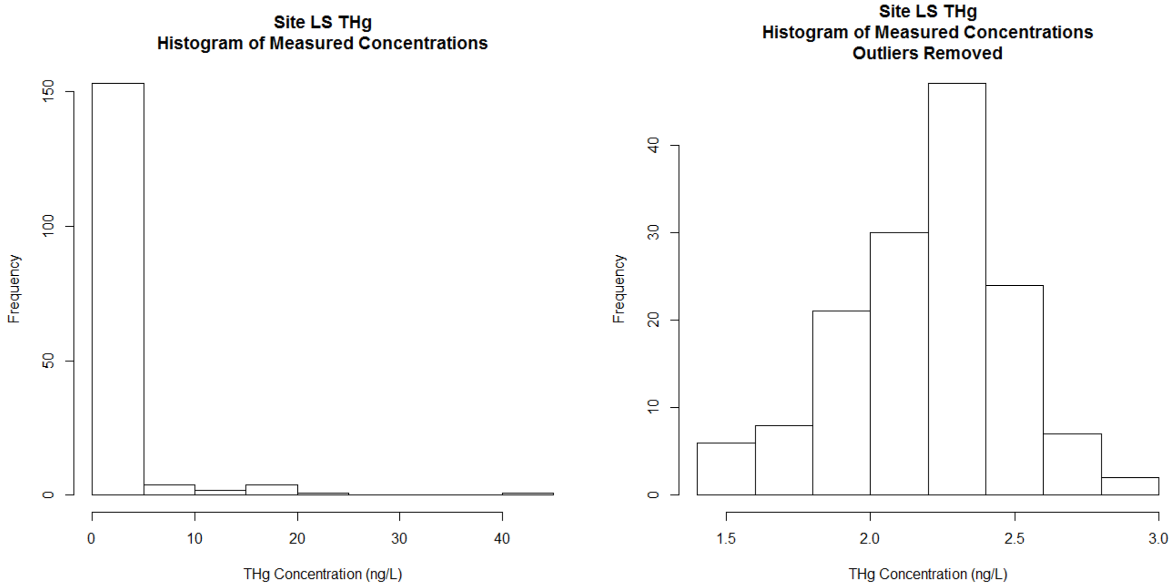

Figure 11a. Histograms of reported total mercury concentrations for site LS. All concentrations (left); non-outlier values (right).

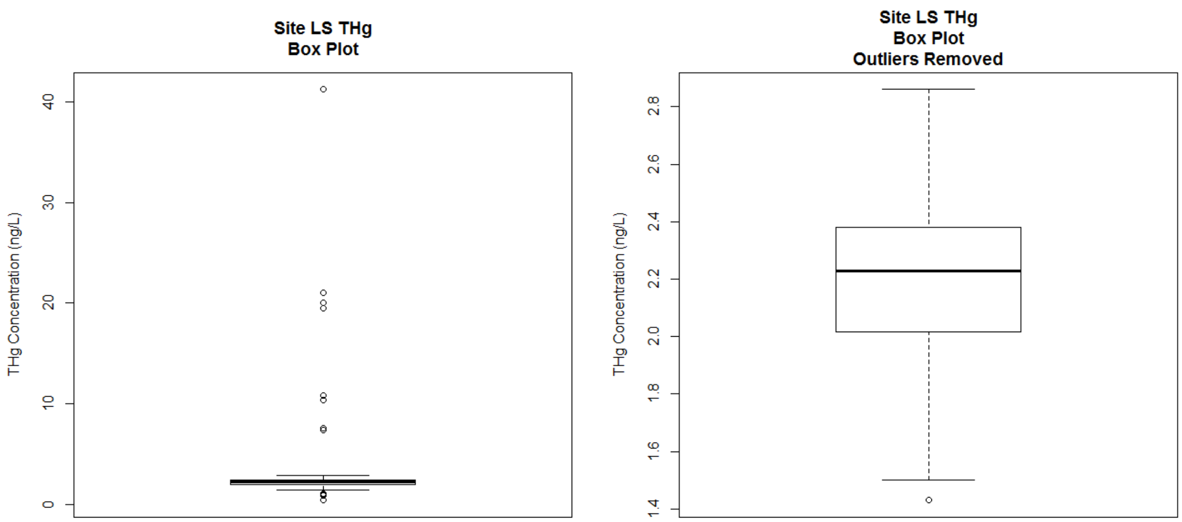

Figure 11b. Box plots of reported total mercury concentrations for site LS. All concentrations (left); non-outlier values (right).

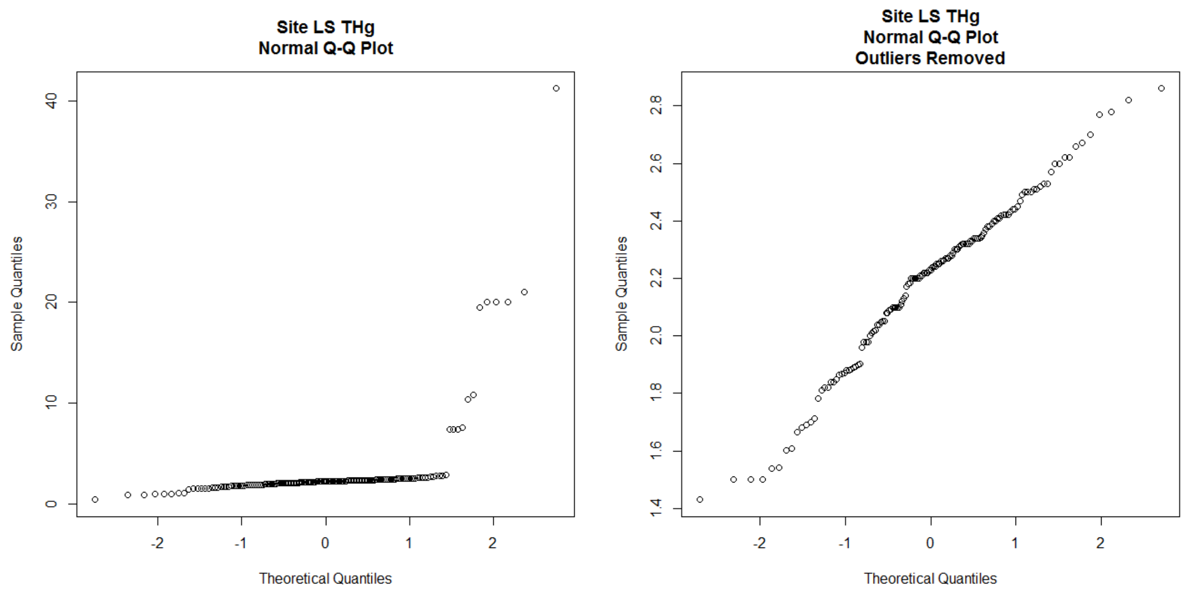

Figure 11c. Normal quantile-quantile plots of reported total mercury data for site LS. All concentrations (left); non-outlier values (right).

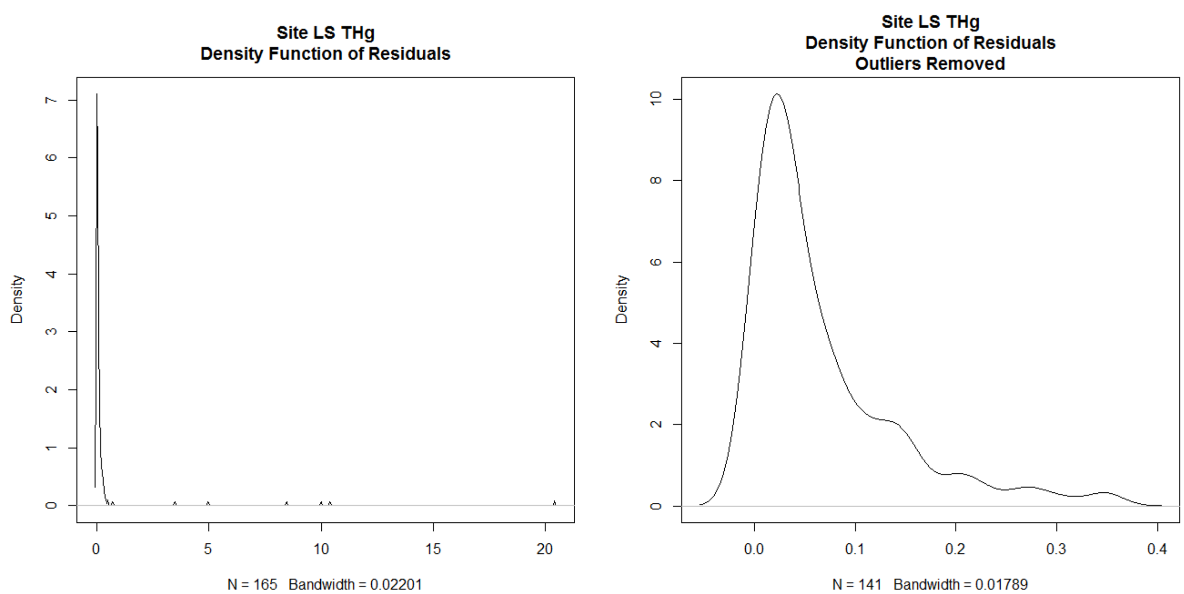

Figure 11d. Density functions of residuals (residual = individual measurement - laboratory mean) of total mercury data for site LS. All values (left); non-outlier values (right).

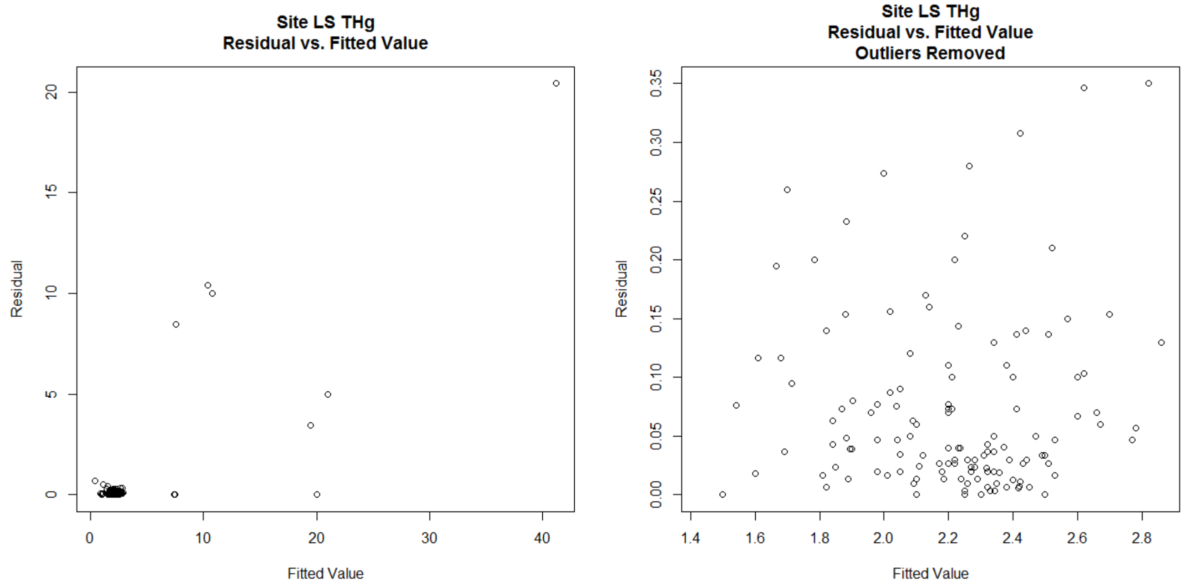

Figure 11e. Residual (residual = individual measurement - laboratory mean) vs. fitted value plots of reported total mercury concentrations for site LS. All values (left); non-outlier values (right).

Summary of total mercury scores

Table 6. Summary of total mercury scores. Scores range from 0 (unacceptable) to 5 (very good). An asterisk (*) indicates that the score is based on at least one result that was below the reported detection limit and was replaced by the detection limit. A dagger (†) indicates that a score is based on two results instead of three.

Lab	Site UJ	Site CC	Site LS	Mean
1	5	4	5	4.67
2	5	4	3	4
3	5	5	3	4.33
4	5	5	3	4.33
5	5*	4*	3*	4
6	0	5	5	3.33
7	5	5	5	5
8	5	5	4	4.67
9	5	5	5	5
10	5	5	5	5
11	5	5	5	5
12	5	5	5	5
13	5	5	5	5
14	5	5	4	4.67
15	5	4	4	4.33
16	5	5	4	4.67
17	5	5	5	5
18	4	5	4	4.33
19	5	5	0	3.33
20	3	3	0	2
23	5	5	5	5
24	5	5	4	4.67
25	5	5	4	4.67
26	*	*	*	
27	4	5	5	4.67
28	0	0	0	0
29	5	5	5	5
30	5	5	5	5
31	3	0	0	1
32	4	4	4	4
33	3	4	4	3.67

Table continued on following page

Lab	Site UJ	Site CC	Site LS	Mean
34	4	0	3	2.33
35	*	3	5	4.00
36	5	5	0	3.33
37	5	5	5	5
38	4	4	3	3.67
39	4	0	3	2.33
40	5	5	5	5
41	4	5	3	4
42	5	0	3	2.67
43	5	5	5	5
44	5	5	5	5
45	5	5	5	5
47	3	0	4	2.33
48	4	4	5	4.33
49	5	5	3	4.33
50	5	4	0	3
51	4	5	4	4.33
52	3	3†	3	3
53	4	4	4	4
54	0	0	0	0
55	5	4	3	4
56	5	4	3	4
57	5	5	5	5
58	5	4	4	4.33

Methylmercury data, Site UJ

Table 7. Laboratory performance for methylmercury, site UJ (samples 1, 7, 9). An asterisk (*) indicates that the lab mean includes at least one undetected value that was substituted with that lab's detection limit.

Consensus statistics:
Mean = 0.043 ng/L, Standard deviation = 0.011,
Median = 0.043 ng/L, Inter-quartile range = 0.013

Lab	Mean	t value	C-W Distance	Score
1	0.045	0.378	0.004	5
3	0.065	With	outliers	0
6	0.062	5.073	0.756	3
8	0.053	2.581	0.196	4
9	0.037	1.748	0.090	5
11	0.043	0.065	0.000	5
12	0.047	0.972	0.028	5
13	0.045	0.555	0.009	5
15	0.042	0.419	0.005	5
17	0.046	0.773	0.018	5
18	0.043	0.024	0.000	5
20	0.047	0.998	0.029	5
22	0.037	1.571	0.072	5
23	0.038	1.482	0.065	5
26	0.038	1.305	0.050	5
27	0.054	2.947	0.255	4
28	0.058	3.850	0.436	4
29	0.041	0.596	0.010	5
31	0.106	With	outliers	0
32	0.052	2.238	0.147	4
33	0.043	0.065	0.000	5
36	0.044	0.307	0.003	5
38	0.027	4.414	0.573	3
39	0.504	With	outliers	0
40	0.078	With	outliers	0
41	0.049*	1.415	0.059	5
42	0.041	0.508	0.008	5
43	0.030	3.652	0.392	4
44	0.053	2.610	0.200	4
45	0.038	1.491	0.065	5

Table continued on following page

Lab	Mean	t value	C-W Distance	Score
46	0.039	1.181	0.041	5
47	0.009	With	outliers	0
49	0.028	4.051	0.482	3
50	0.046*	With	outliers	0
51	0.037	1.651	0.080	5
52	0.038	1.393	0.057	5
55	0.042	0.242	0.002	5
56	0.047	0.910	0.024	5
58	0.044	0.201	0.001	5

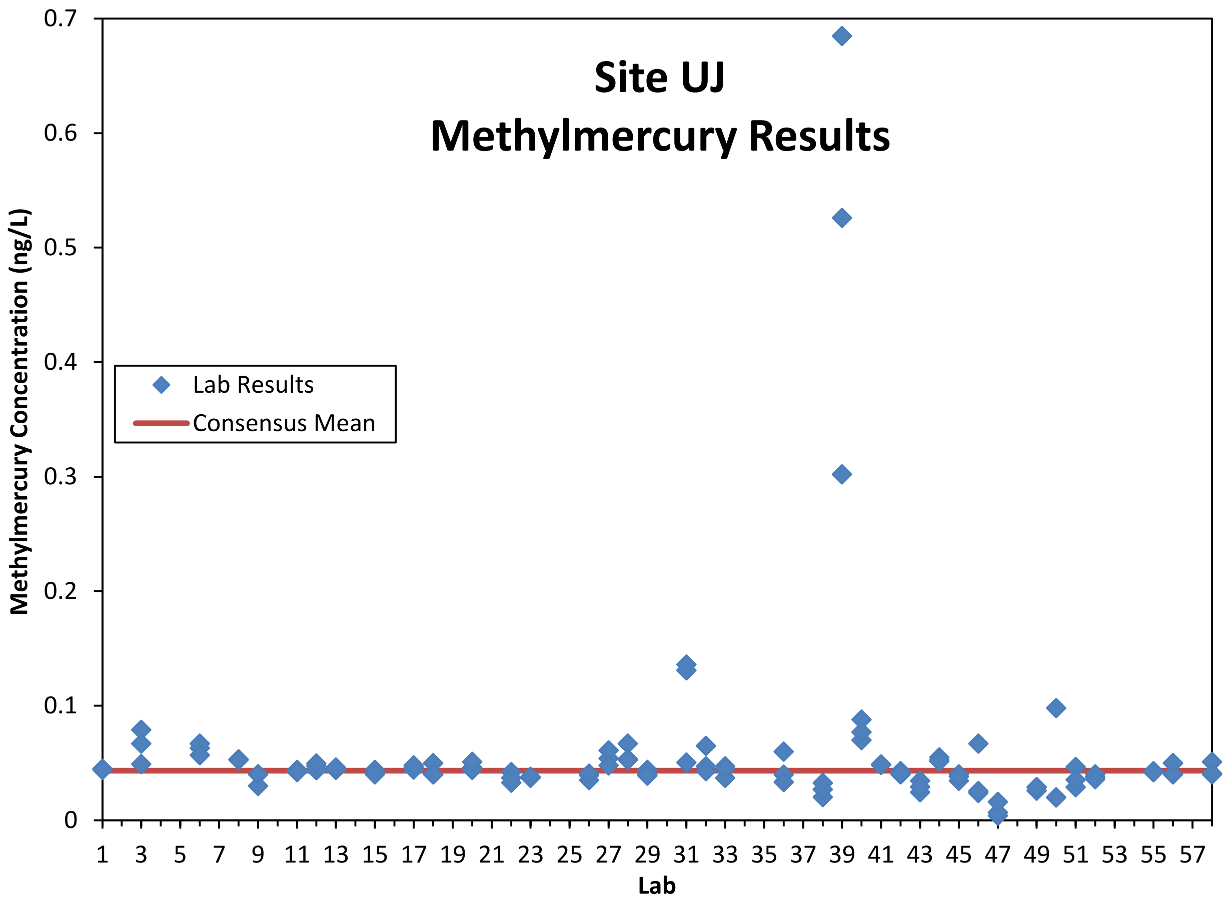

Figure 12. Methylmercury results from all participating laboratories for site UJ.

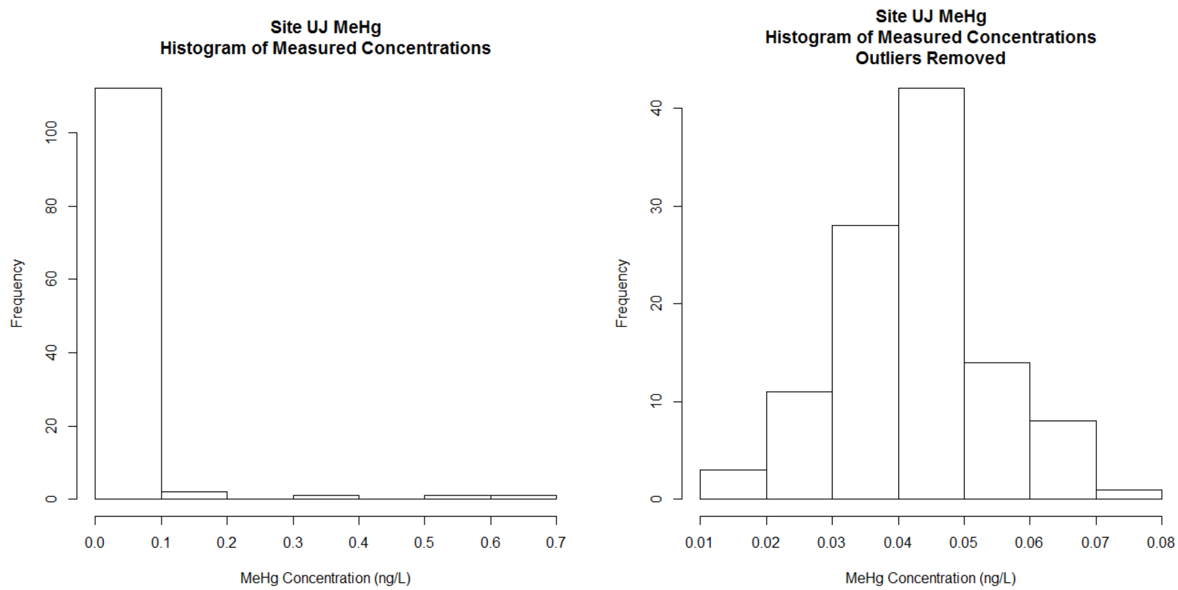

Figure 13a. Histograms of reported methylmercury concentrations for site UJ. All concentrations (left); non-outlier values (right).

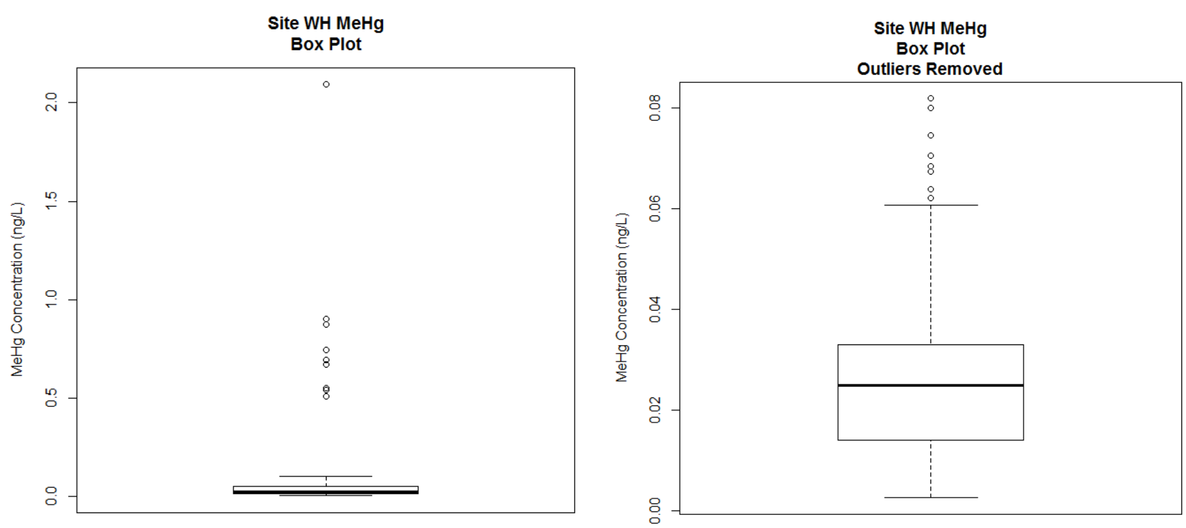

Figure 13b. Box plots of reported methylmercury concentrations for site UJ. All concentrations (left); non-outlier values (right).

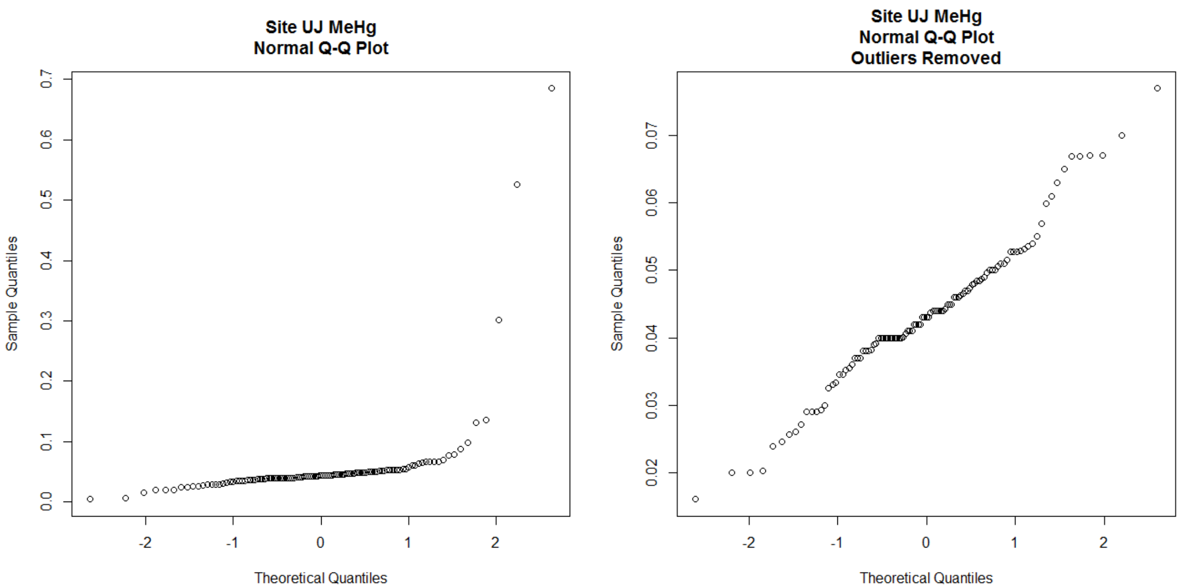

Figure 13c. Normal quantile-quantile plots of reported methylmercury data for site UJ. All concentrations (left); non-outlier values (right).

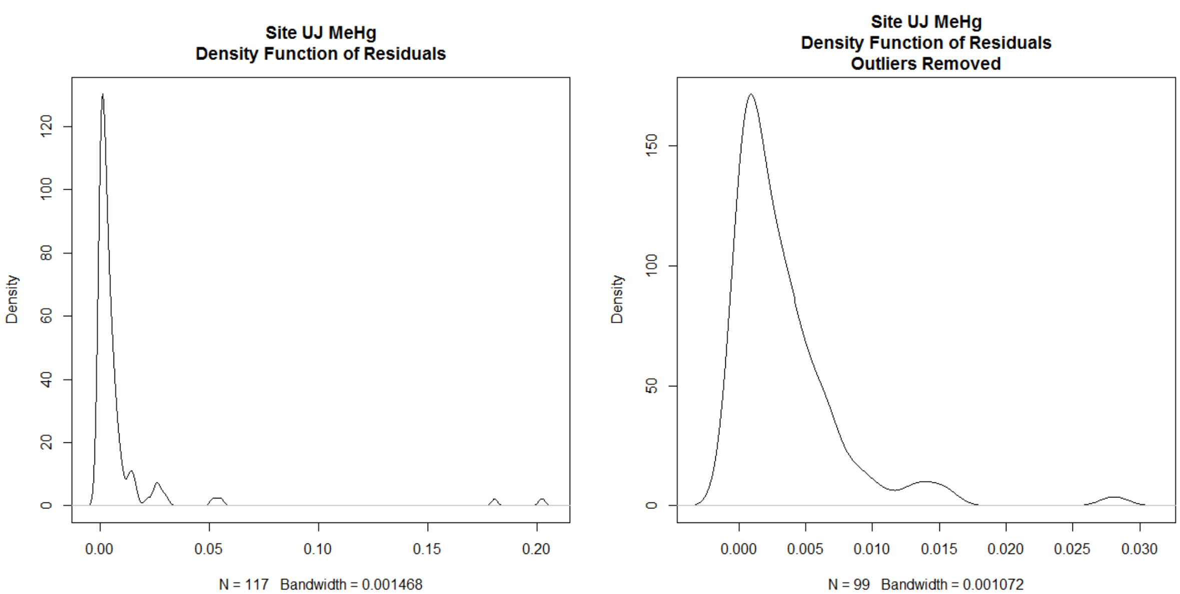

Figure 13d. Density functions of residuals (residual = individual measurement - laboratory mean) of methylmercury data for site UJ. All values (left); non-outlier values (right).

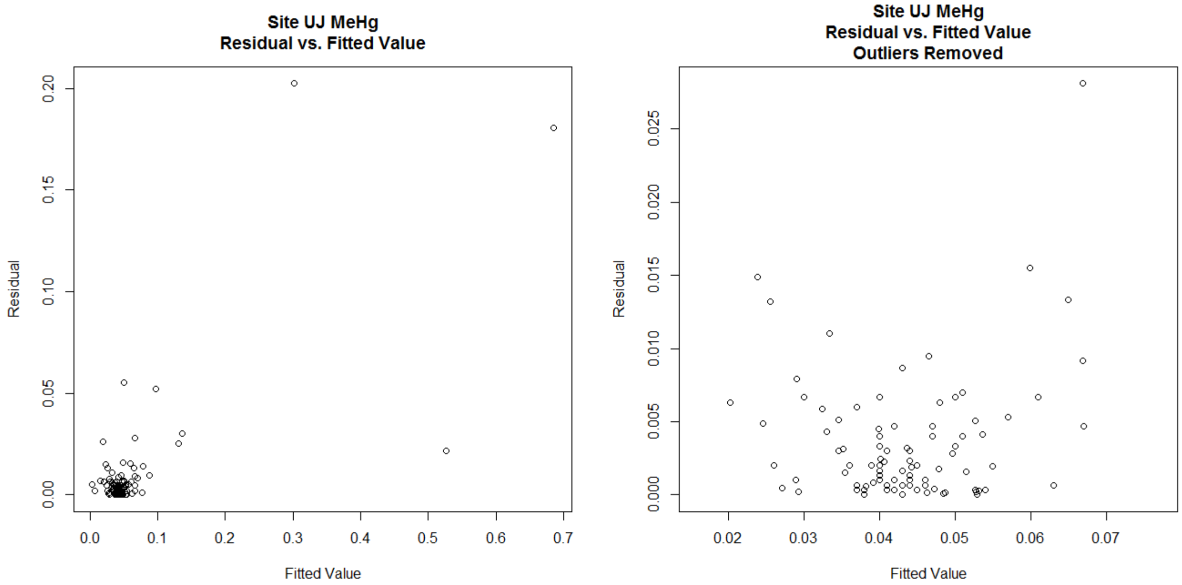

Figure 13e. Residual (residual = individual measurement - laboratory mean) vs. fitted value plots of reported methylmercury concentrations for site UJ. All values (left); non-outlier values (right).

Methylmercury data, Site CC

Table 8. Laboratory performance for methylmercury, site CC (samples 2, 3, 8). An asterisk (*) indicates that the lab mean includes at least one undetected value that was substituted with that lab's detection limit. A dagger (†) indicates that a score is based on two results instead of three.

Consensus statistics:
Mean = 0.049 ng/L, Standard deviation = 0.011,
Median = 0.049 ng/L, Inter-quartile range = 0.014

Lab	Mean	t value	C-W Distance	Score
1	0.044	0.930	0.026	5
3	0.054	1.322	0.053	5
6	0.077	With	outliers	0
8	0.061	3.049	0.281	4
9	0.050	0.437	0.006	5
11	0.047	0.287	0.002	5
12	0.046	0.568	0.010	5
13	0.049	0.196	0.001	5
15	0.051	0.598	0.011	5
17	0.045	0.819	0.020	5
18	0.040†	1.976	0.118	5
20	0.061	3.011	0.274	4
22	0.047	0.287	0.002	5
23	0.048	0.046	0.000	5
26	0.045	0.890	0.024	5
27	0.058	2.367	0.170	4
28	0.059	2.609	0.206	4
29	0.046	0.528	0.008	5
31	0.080	With	outliers	0
32	0.042	1.413	0.060	5
33	0.046	0.609	0.011	5
36	0.062	3.437	0.358	4
38	0.042	1.566	0.074	5
39	0.527	With	outliers	0
40	0.106	With	outliers	0
41	0.055*	1.635	0.081	5
42	0.051	0.759	0.017	5
43	0.043	1.156	0.040	5
44	0.058	2.408	0.175	4
45	0.045	0.802	0.019	5

Table continued on following page

Lab	Mean	t value	C-W Distance	Score
46	0.050	0.445	0.006	5
47		Not	reported	
49	0.029	4.550	0.627	3
50	0.079*	With	outliers	0
51	0.049	0.242	0.002	5
52	0.041	1.654	0.083	5
55	0.049	0.196	0.001	5
56	0.080	With	outliers	0
58	0.042	1.413	0.060	5

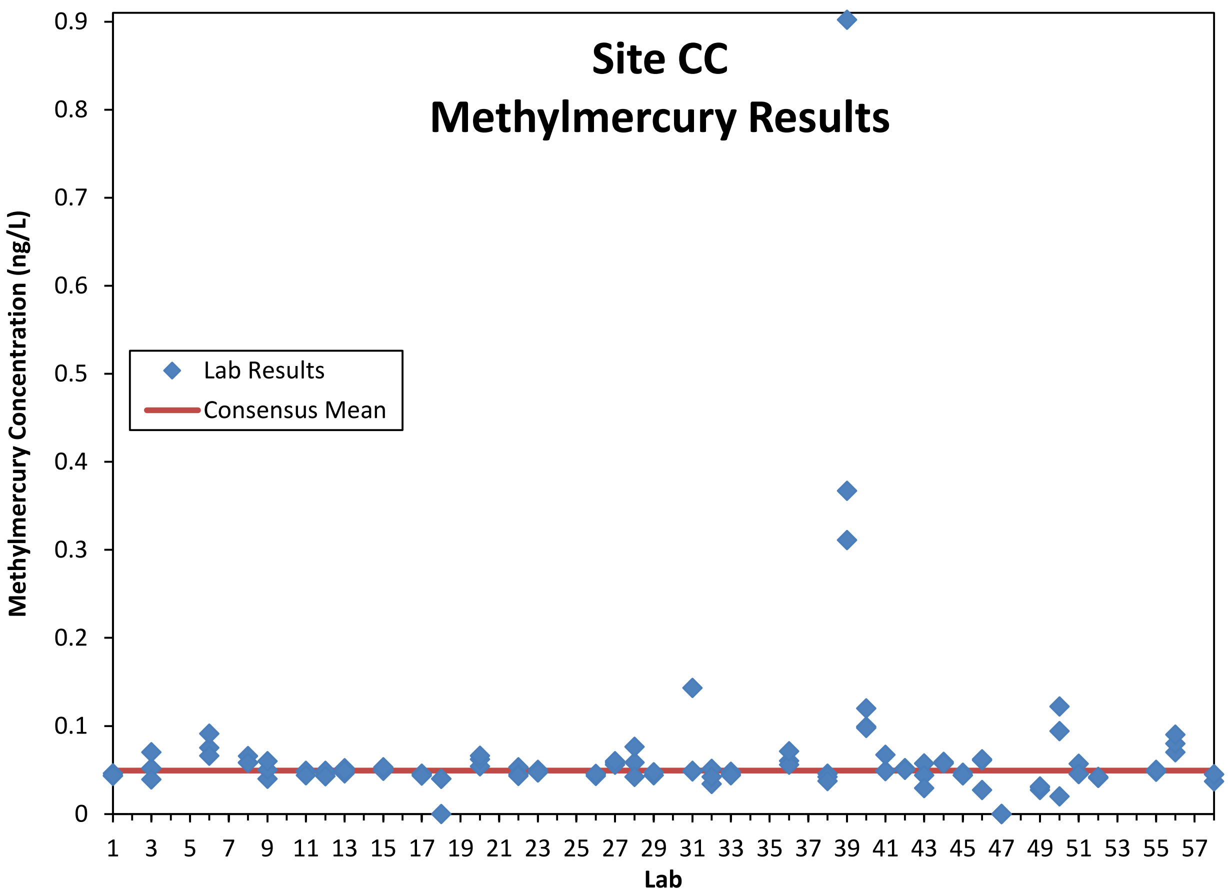

Figure 14. Methylmercury results from all participating laboratories for site CC.

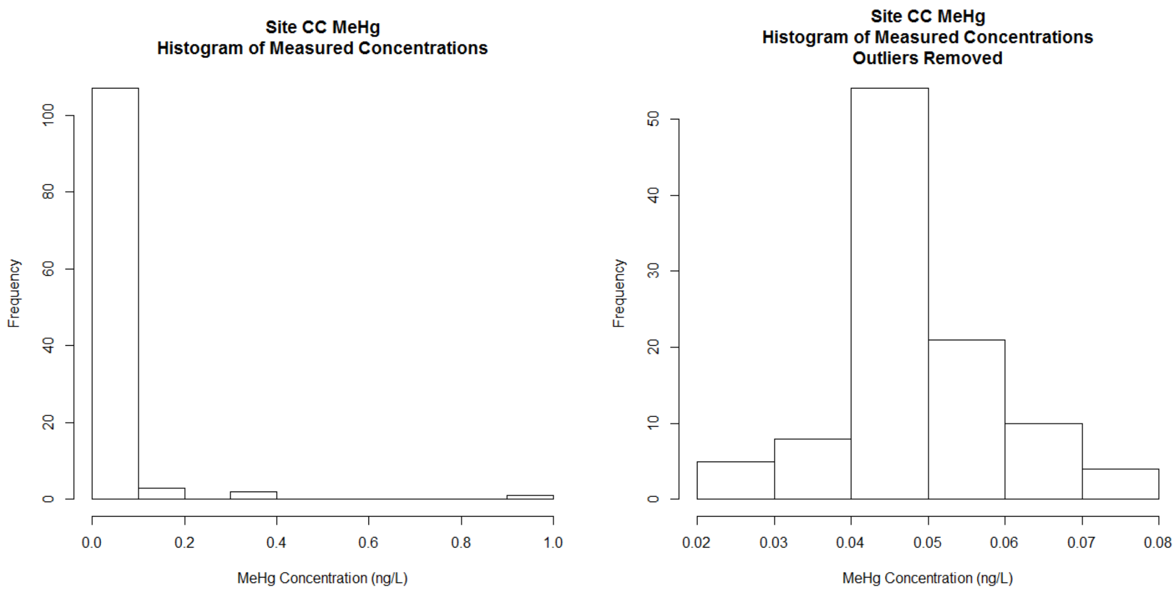

Figure 15a. Histograms of reported methylmercury concentrations for site CC. All concentrations (left); non-outlier values (right).

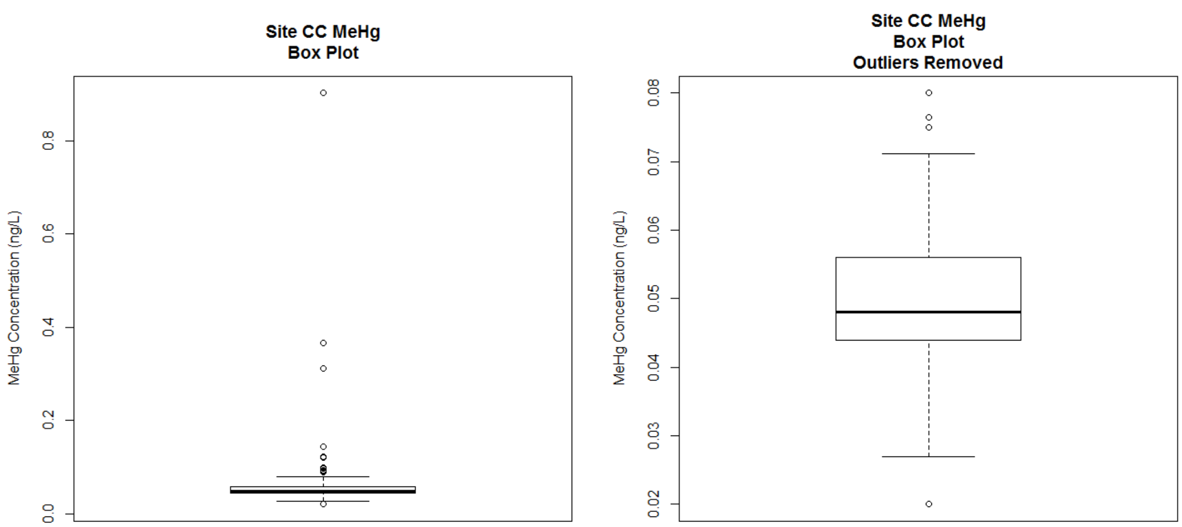

Figure 15b. Box plots of reported methylmercury concentrations for site CC. All concentrations (left); non-outlier values (right).

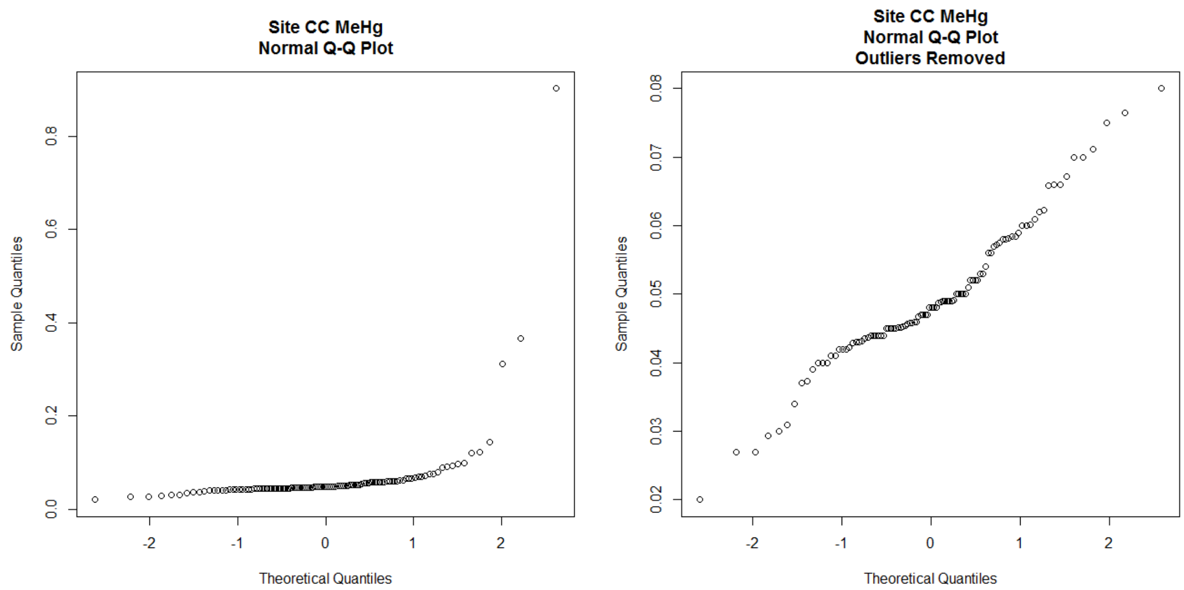

Figure 15c. Normal quantile-quantile plots of reported methylmercury data for site CC. All concentrations (left); non-outlier values (right).

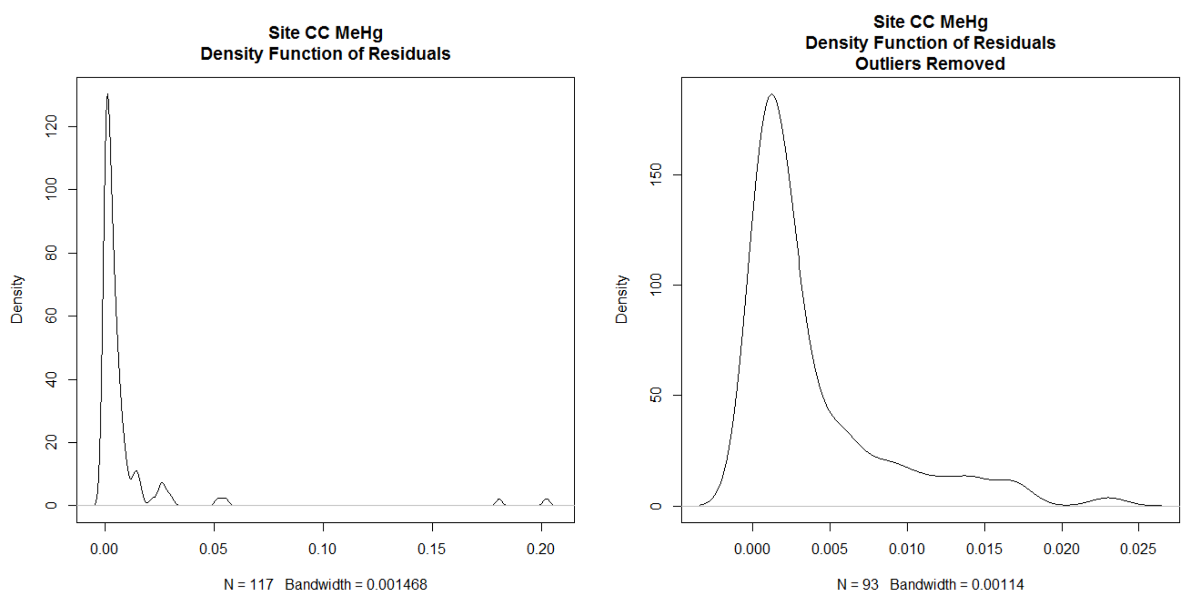

Figure 15d. Density functions of residuals (residual = individual measurement - laboratory mean) of methylmercury data for site CC. All values (left); non-outlier values (right).

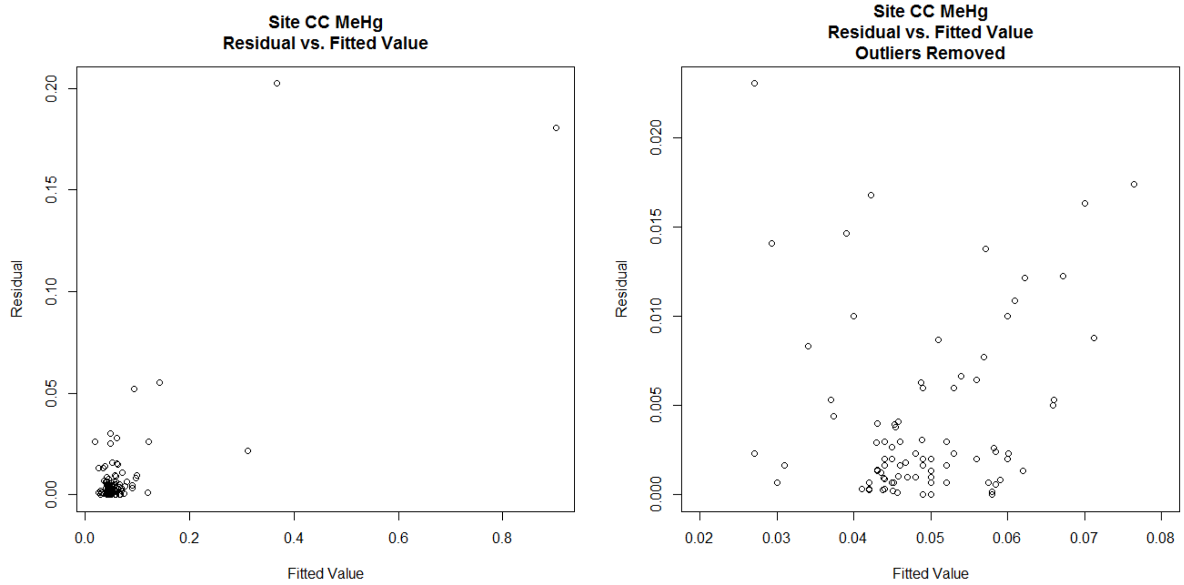

Figure 15e. Residual (residual = individual measurement - laboratory mean) vs. fitted value plots of reported methylmercury concentrations for site CC. All values (left); non-outlier values (right).

Methylmercury data, Site LS

Table 9. Laboratory performance for methylmercury, site LS (samples 4, 5, 6). An asterisk (*) indicates that the lab mean includes at least one undetected value that was substituted with that lab's detection limit.

Consensus statistics:
Mean = 0.22 ng/L, Standard deviation = 0.087,
Median = 0.24 ng/L, Inter-quartile range = 0.098

Lab	Mean	t value	C-W Distance	Score
1	0.127	6.351	1.034	3
3	0.243	1.641	0.069	5
6	0.053	11.479	3.376	2
8	0.268	3.414	0.299	4
9	0.280	4.228	0.458	3
11	0.205	0.946	0.023	5
12	0.305	5.983	0.917	3
13	0.279	4.159	0.443	3
15	0.193	1.778	0.081	5
17	0.247	1.953	0.098	5
18	0.133	5.935	0.903	3
20	0.301	5.683	0.828	3
22	0.123	6.674	1.141	3
23	0.226	0.509	0.007	5
26	0.232	0.902	0.021	5
27	0.265	3.165	0.257	4
28	0.151	4.711	0.569	3
29	0.225	0.440	0.005	5
31	0.170	3.395	0.295	4
32	0.030	13.096	4.394	2
33	0.256	2.542	0.166	4
36	0.281	4.309	0.476	3
38	0.313	6.492	1.080	3
39	0.390	With	Outliers	0
40	0.308	6.168	0.975	3
41	0.049*	11.779	3.555	2
42	0.252	2.311	0.137	4
43	0.241	1.502	0.058	5
44	0.263	3.027	0.235	4
45	0.172	3.279	0.275	4

Table continued on following page

Lab	Mean	t value	C-W Distance	Score
46	0.301	5.660	0.821	3
47	0.384	11.435	3.350	2
49	0.194	1.708	0.075	5
50	0.241	1.525	0.060	5
51	0.152*	4.628	0.549	3
52	0.240	1.433	0.053	5
55	0.244	1.756	0.079	5
56	0.337	8.155	1.704	3
58	0.037	12.634	4.090	2

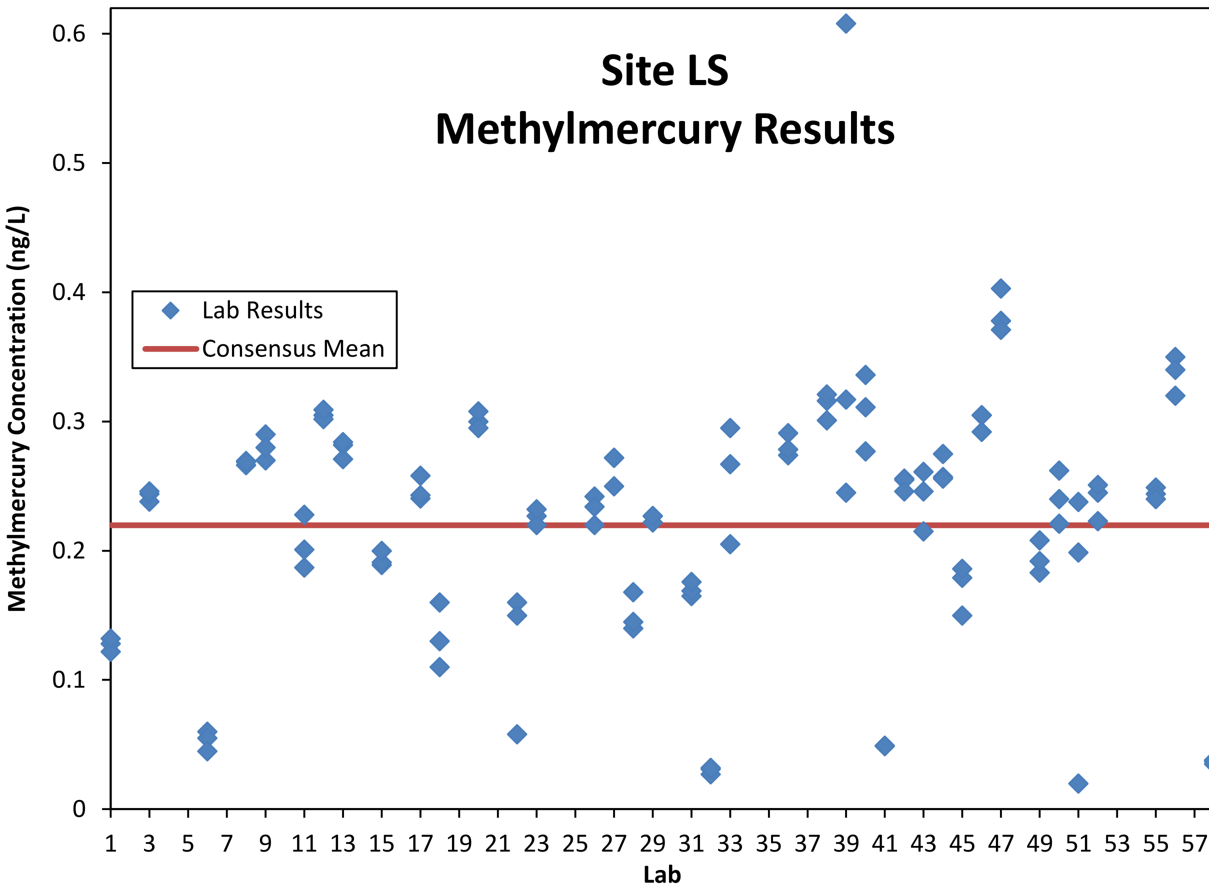

Figure 16. Methylmercury results from all participating laboratories for site LS.

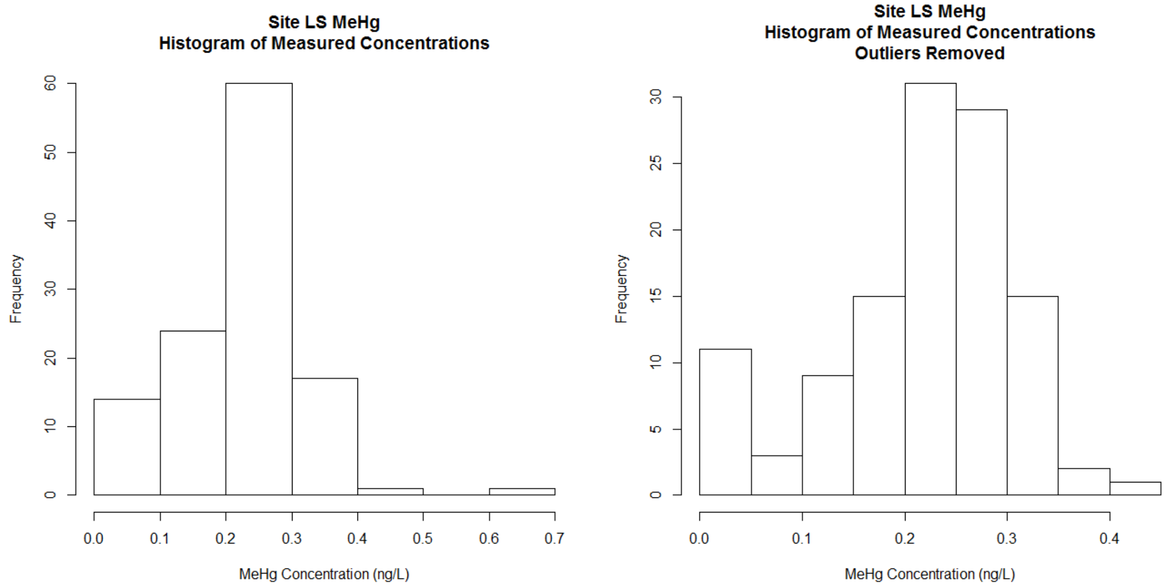

Figure 17a. Histograms of reported methylmercury concentrations for site LS. All concentrations (left); non-outlier values (right).

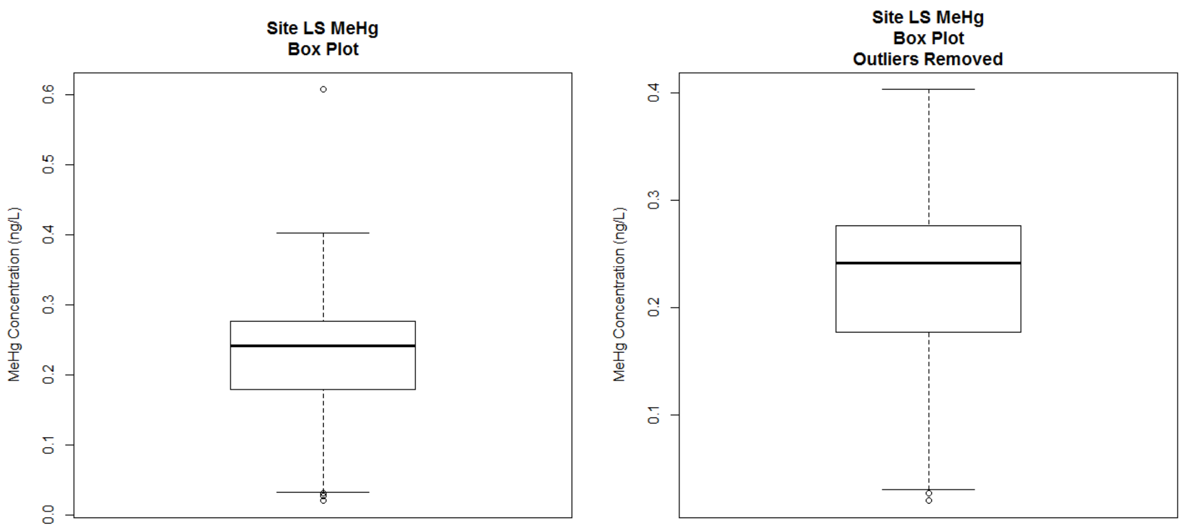

Figure 17b. Box plots of reported methylmercury concentrations for site LS. All concentrations (left); non-outlier values (right).

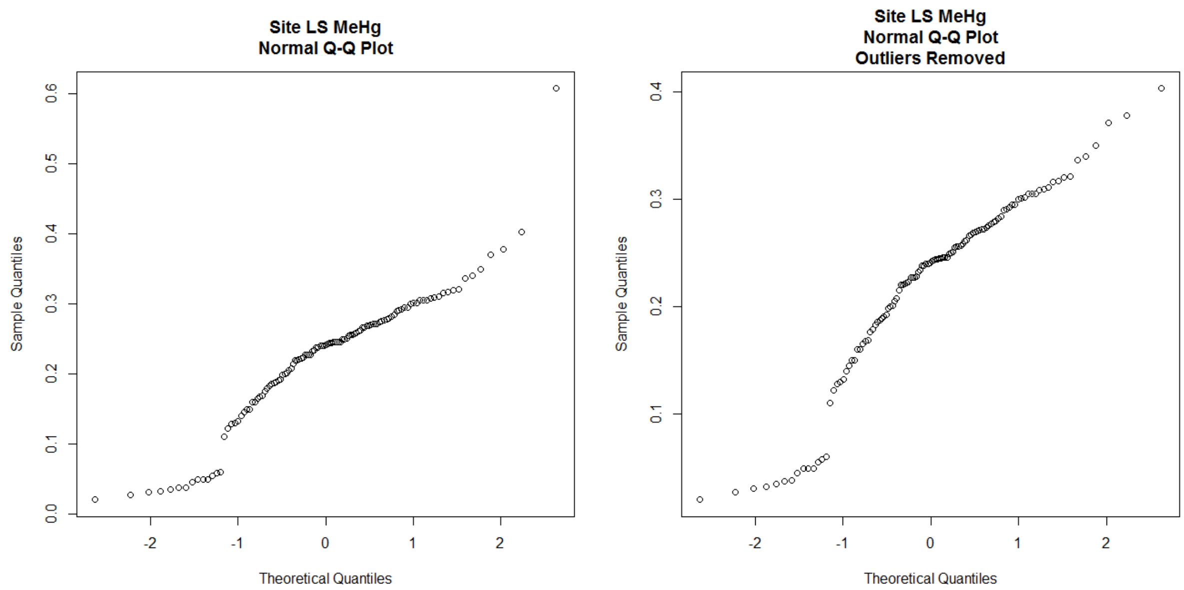

Figure 17c. Normal quantile-quantile plots of reported methylmercury data for site LS. All concentrations (left); non-outlier values (right).

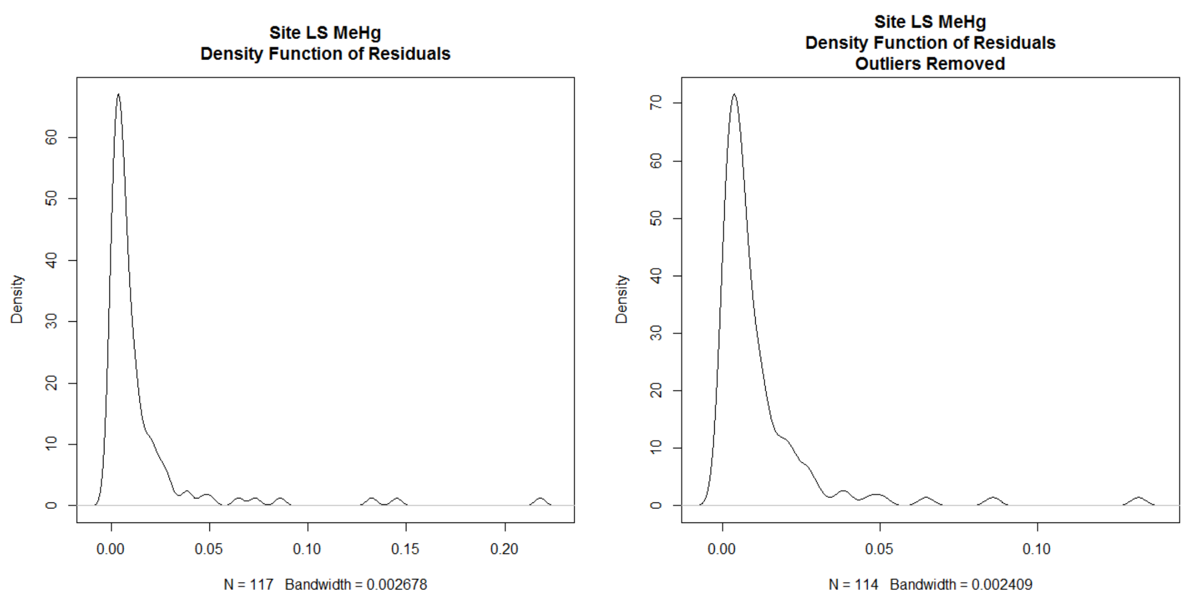

Figure 17d. Density functions of residuals (residual = individual measurement - laboratory mean) of methylmercury data for site LS. All values (left); non-outlier values (right).

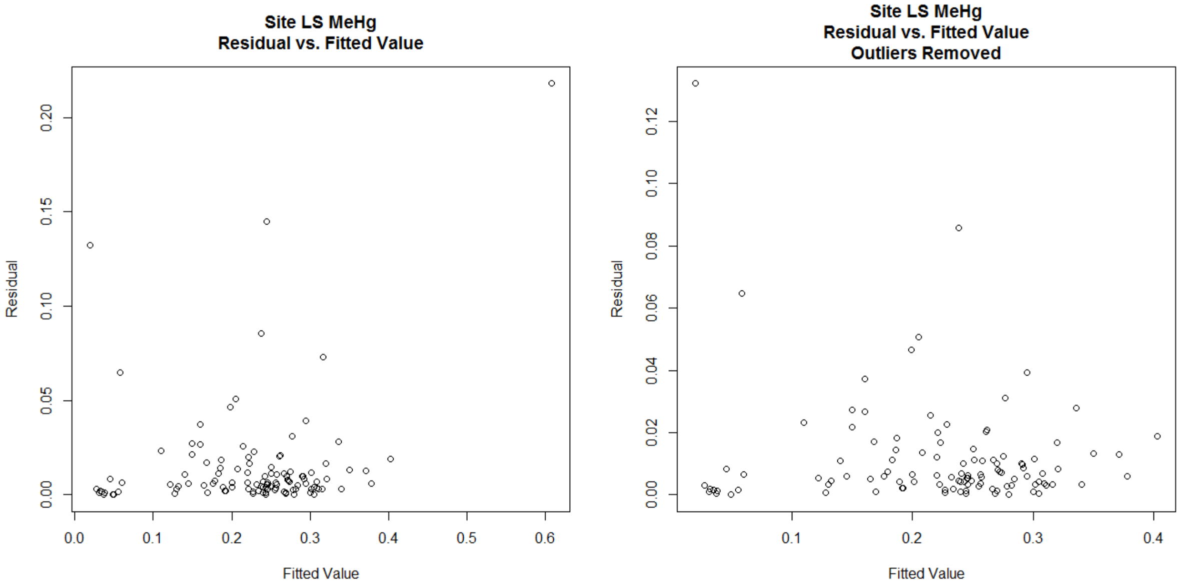

Figure 17e. Residual (residual = individual measurement - laboratory mean) vs. fitted value plots of reported methylmercury concentrations for site LS. All values (left); non-outlier values (right).

Summary of methylmercury scores

Table 10. Summary of methylmercury scores. Scores range from 0 (unacceptable) to 5 (very good). An asterisk (*) indicates that the score is based on at least one result that was below the reported detection limit and was replaced by the detection limit. A dagger (†) indicates that a score is based on two results instead of three.

Lab	Site UJ	Site CC	Site LS	Mean
1	5	5	3	4.33
3	0	5	5	3.33
6	3	0	2	1.67
8	4	4	4	4
9	5	5	3	4.33
11	5	5	5	5
12	5	5	3	4.33
13	5	5	3	4.33
15	5	5	5	5
17	5	5	5	5
18	5	5†	3	4.33
20	5	4	3	4
22	5	5	3	4.33
23	5	5	5	5
26	5	5	5	5
27	4	4	4	4
28	4	4	3	3.67
29	5	5	5	5
31	0	0	4	1.33
32	4	5	2	3.67
33	5	5	4	4.67
36	5	4	3	4
38	3	5	3	3.67
39	0	0	0	0
40	0	0	3	1
41	5*	5*	2*	4
42	5	5	4	4.67
43	4	5	5	4.67
44	4	4	4	4
45	5	5	4	4.67
46	5	5	3	4.33

Table continued on following page

Lab	Site UJ	Site CC	Site LS	Mean
47	0		2	1
49	3	3	5	3.67
50	0*	0*	5	1.67
51	5	5	3*	4.33
52	5	5	5	5
55	5	5	5	5
56	5	0	3	2.67
58	5	5	2	4

Table 11. List of the 64 participating laboratories to which samples were sent.

Laboratory Name	**Country**
ACZ Laboratories Inc.	USA
Alpha Analytical Laboratories, Inc.	USA
ALS Canada Ltd - Burnaby Environmental	Canada
ALS Environmental - Vancouver	Canada
ALS Environmental (Winnipeg)	Canada
ALS Life Sciences Division	Malaysia
American Assay Laboratories	USA
Analytical and Waste Services, Kinectrics, Inc.	Canada
Basic Laboratory	USA
Battelle Marine Sciences Laboratory	USA
Biogeochemical Analytical Service Laboratory, University of Alberta	Canada
Biotron Analytical Services Laboratory, Western University	Canada
Brooks Rand Labs	USA
BYU Mercury Lab	USA
Caltest Analytical Laboratory	USA
City of San Jose ESD Laboratory	USA
Dartmouth Trace Element Analysts Laboratory	USA
Dolan Chemical Laboratory, American Electric Power	USA
Dr Holsen's Mercury Lab, Clarkson University	USA
Dr. Danny Reible, Texas Tech University	USA
Environment Canada Burlington 1	Canada
Environment Canada Burlington 2	Canada
Environment Canada, PYLET	Canada
Environmental Analytical Laboratories, SK Research Council	Canada
Flett Research Ltd	Canada
Geoscience Laboratories	Canada
Hebei Food Inspection and Research Institute	China
IAEA MESL	Monaco
IVL Swedish Environmental Research Institute	Sweden

Laboratory Name	Country
Johnson Mercury Lab, University of Utah	USA
Jozef Stefan Institute	Slovenia
Kentucky Environmental Services	USA
Laboratoire des essais environnementaux du Québec	Canada
We Energies Laboratory Services	USA
Lakehead University Environmental Laboratory	Canada
Marine Pollutions Studies Laboratory, Moss Landing	USA
Microbac Laboratories, Inc. - Chicagoland Division	USA
NIVA (Norwegian Institute for Water Research)	Norway
North Carolina DENR Laboratory	USA
Oak Ridge National Lab	USA
Ontario Ministry of the Environment and Climate Change	Canada
P S Analytical	UK
Pace Analytical Services	USA
Sacramento Area Sewer District	USA
Science and Ecosystem Support Division	USA
South China Institute of Environmental Sciences	China
Southeast Laboratory San Francisco PUC	USA
UC Santa Cruz, Flegal Lab	USA
UIUC-NRES Mercury Lab	USA
UNCG Ecotoxicology and Biogeochemistry Laboratory	USA
University of Ottawa Mercury Laboratory	Canada
US Dept. of Energy (URS)	USA
US EPA Region 10 Laboratory	USA
US EPA Region 9 Laboratory	USA
USGS Menlo Park	USA
USGS Mercury Lab	USA
Water Pollution Control Laboratory	USA
Water Quality Lab, Clean Water Services	USA
Wisconsin State Laboratory of Hygiene	USA

Discussion

The performance of most laboratories was satisfactory (mean score of 3) or better. Of the 55 labs that submitted total mercury results, 46 (84%) received average scores of 3 or higher, 39 labs (71%) received average scores of 4 or higher, and 16 labs (29%) received the maximum average score of 5 (Figure 18). Of the 39 labs that submitted methylmercury results, 32 labs (82%) received average scores of 3 or higher, 27 labs (69%) received average scores of 4 or higher, and 8 labs (21%) received the maximum average score of 5. The percentage of labs receiving THg scores equal to or greater than 3 (satisfactory) has increased from 79% in 2014 and is near the all-time peak of 85% in 2013. The percentage of labs receiving MeHg scores equal to or greater than 3 has decreased since 2014. Because individual labs are not identifiable in these results, it is impossible to know if a change in the percentage of labs achieving a given score is due to improvements or declines in performance, differences in the participant pool from one year to the next, or differences in the samples being analyzed. It is important to note that sample variability can have a significant effect on the number of labs receiving satisfactory scores. If a sample has high natural variability in one analyte, it will create a wide range of satisfactory concentrations, driving up scores for that site.

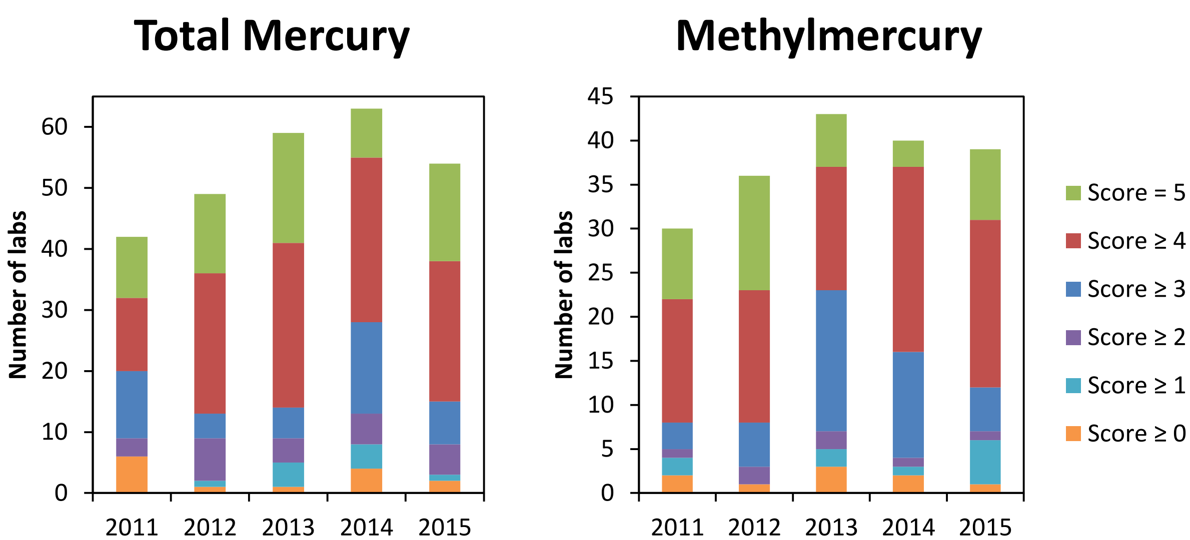

Figure 18. Total mercury and methylmercury performance scores for the five years of the Brooks Rand Instruments Interlaboratory Comparison Study.

The fact that the majority of laboratories participating in this study achieved a satisfactory score for total mercury and methylmercury suggests that the intercomparability of data among the majority of the participants is good. One of the aims of this study is to help participants identify their analytical problems so that they can isolate the causes and eliminate them. Labs with scores less than three have significant issues affecting the accuracy of their results. Labs with scores greater than three but less than five (i.e. smaller differences from the consensus mean) may be able to improve their scores by assessing different sample digestion/preparation methods, renewing their analytical standards, or cleaning/servicing their analytical system, but likely do not have significant problems.

Method Data

By collecting information on the methodology and equipment each laboratory used to analyze the samples, we attempted to assess the effectiveness of different analytical approaches. We compared methods using t-tests on mean performance scores from each lab (we only compared groups with $n \geq 4$, and used $\alpha = 0.05$). In Intercomp 2015, we observed only one significant difference between methods – a difference between THg analysis with dual gold amalgamation and no amalgamation (Table 13). The reason for the lack of significant differences in performance is likely due primarily to the size of the study. Although the study involved a large number of participants, the wide variety of methods in use and inconsistencies in the reporting of method characteristics often resulted in very small groupings of results for any one method attribute. In many cases, robust comparisons of performance between methods will require a more targeted study. However, another conclusion that can be drawn from the lack of significant differences between methods is that a wide variety of methods and equipment are capable of producing acceptable data. Participants must assess for themselves whether their score indicates a method problem or other analytical issue.

We found no significant difference between total mercury and methylmercury analysis using an automated system ("automated" was defined as having an autosampler) vs. a manual system (Table 12). The proportion of labs performing automated analysis for THg and MeHg has increased with each year of the study (Figure 19).

Table 12. Comparison of automated and manual systems. Automated systems are defined as those with an autosampler. Manual systems are defined as all others. n = number of labs.

	THg Median Score	THg n	MeHg Median Score	MeHg n
Automated	4.33	44	4.00	30
Manual	4.33	11	4.33	9

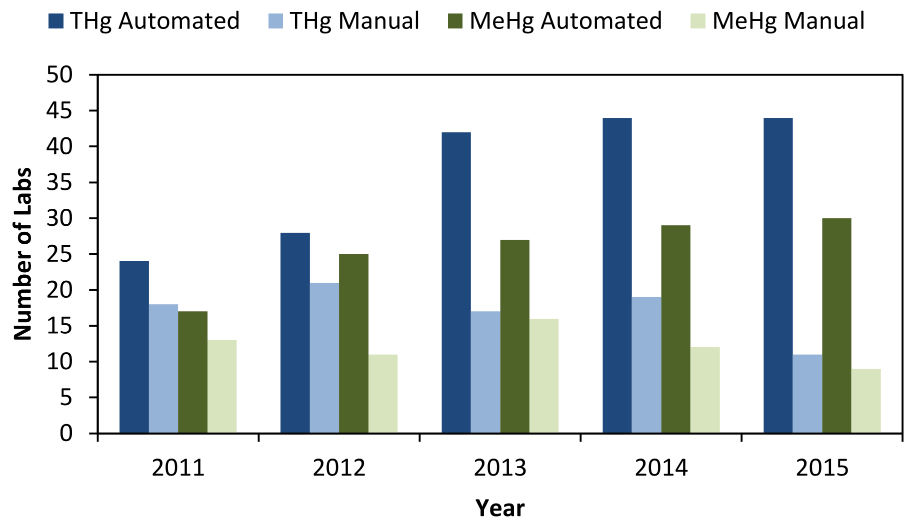

Figure 19. Number of labs performing automated and manual analysis, by year.

There was a significant difference between total mercury analysis with dual gold amalgamation and no amalgamation ($p = 0.02$; Table 13) but not between single gold amalgamation and no amalgamation. THg analysis with no amalgamation received a significantly lower score than gold amalgamation-based methods in the Intercomps in 2012 and 2013, but not 2014.

Table 13. Comparison of total mercury amalgamation methods. n = number of labs.

	Median Score	n
Dual Gold	4.33	34
Single Gold	4.33	10
No Amalgamation	4.00	10

There were no significant differences between sample preparation methods for methylmercury analysis (Table 14). As in previous years, the vast majority of labs continue to use distillation, following EPA Method 1630, however a steady fraction of participants every year use non-distillation methods. As indicated in Table 14, both distillation and non-distillation methods are capable of producing acceptable recoveries.

Table 14. Comparison of methylmercury sample preparation procedures and reagents. n = number of labs.

	Median Score	n
DCM Extraction	3.00	2
All Distillation	4.33	31
Distillation / APDC	4.33	14
Distillation / $CuSO_4$	3.67	4
Distillation / KCl/H_2SO_4	4.33	3
Distillation / L-cysteine	4.50	6
Distillation / No reagents	4.00	3
Distillation / Other	5.00	1
Direct Ethylation	3.67	4
Other Non-Distillation	4.50	2

The majority of labs performing methylmercury analysis use packed GC columns (74%; Table 15). Every lab that reported their packing material is using 15% OV-3 on Chromosorb W/AW, the material specified in EPA Method 1630. One lab reported using a packed column but did not report their packing material. Of the labs using capillary columns, the majority are using the DB-1, the standard column in a Tekran automated methylmercury system. The other capillary column type reported was HP-5. One lab reported using a capillary GC column but did not describe it. One lab is using ion chromatography (liquid chromatography) to separate mercury species. There were no significant differences between packed and capillary GC columns, or between any specific column types.

Table 15. Comparison of methylmercury separation methods. n = number of labs.

	Median Score	n
All Capillary Column	4.00	9
DB-1	4.33	7
HP-5	1.00	1
All Packed Column	4.33	29
15% OV-3 on Chromosorb W/AW	4.33	28
Ion Chromatography (Dionex CG-5A)	5.00	1

To investigate possible links between storage conditions and measured total mercury results, we collected data on the length of time and storage temperature between when BrCl was added to total mercury samples and analysis. There were effectively no correlations between storage time and measured concentrations for all three sites (Figure 20). The correlation coefficients were small and insignificant at the 95% level. There were also no significant correlations between storage temperature and measured concentrations (Figure 21). Some sample types have been shown to require more rigorous oxidation than others in order to achieve complete recovery of total mercury [*Olson et al.*, 1997; *Pyhtilä et al.*, 2012]. However either these samples are not sufficiently complex to require extra oxidation or they require a stronger digestion than that provided by added time or temperature.

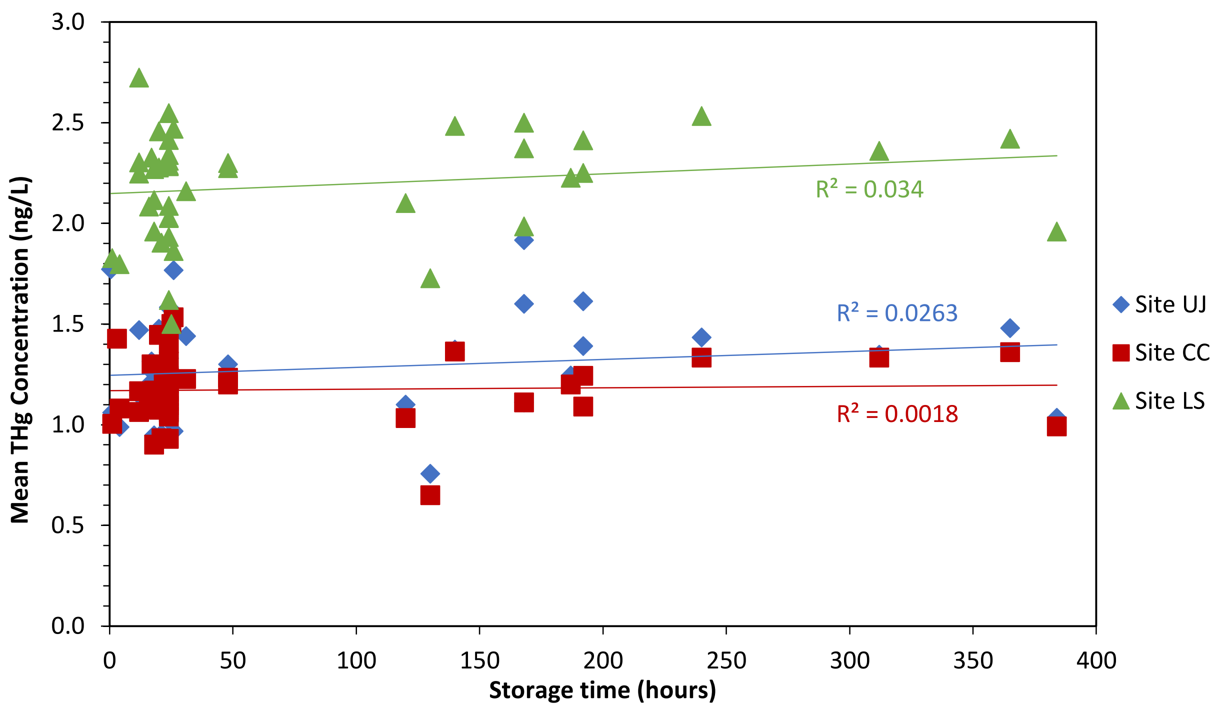

Figure 20. Plot of measured total mercury concentrations (lab means) vs. storage time after BrCl addition to the samples. Holding times reported as > x were substituted with x hours (the minimum time). Where a range of values was reported (e.g. 8-12 hours), the mid-point was used.

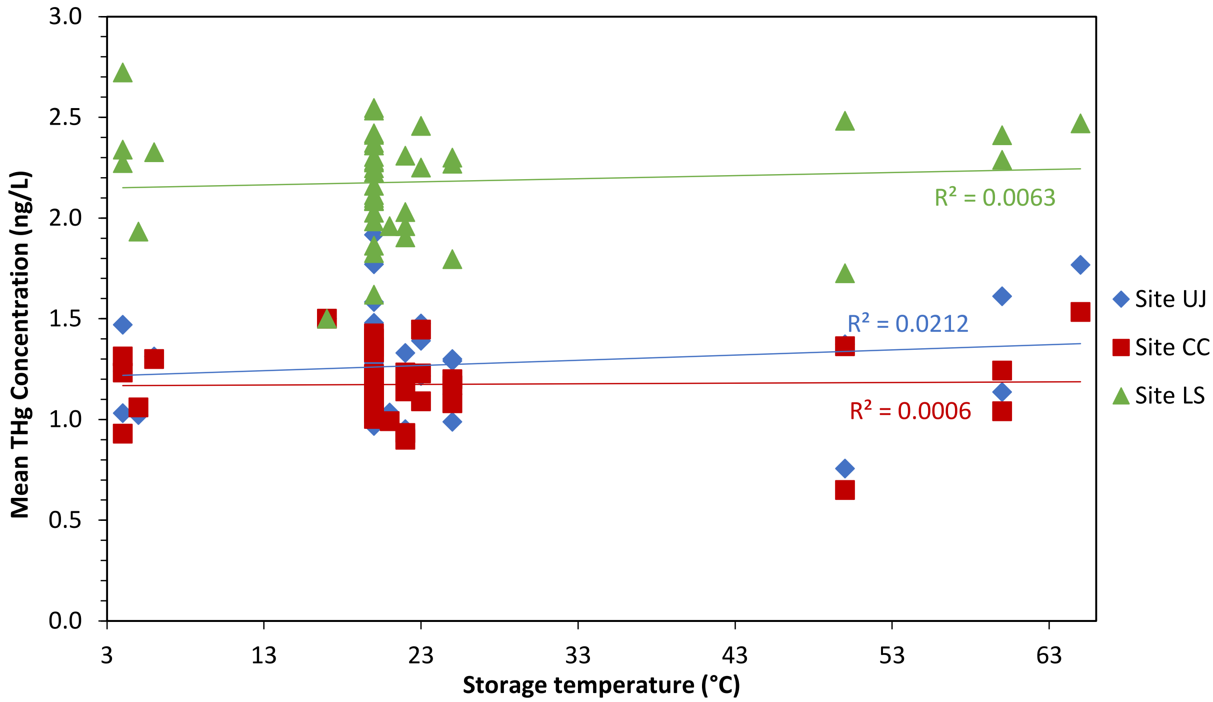

Figure 21. Plot of measured total mercury concentrations (lab means) vs. sample storage temperature after BrCl addition. Room temperature was assumed to be 20 °C. Where a range of temperatures was given, the midpoint was used. If samples were held at a higher temperature for several hours, followed by a lower temperature, they are plotted at the higher temperature.

Additional method data beyond what we include in the report did not reveal any significant differences and were omitted for brevity.

Future Studies

Brooks Rand Instruments conducts this study on an annual basis. Any feedback on this year's study or interest in participating in future studies should be directed to bri@brooksrandinc.com.

Acknowledgements

This study was made possible by the dedicated effort and input of many people. Chris Ransom at EcoChem, Inc. received, organized, anonymized, and archived all of the data. Vesna Fajon and Milena Horvat at the Jožef Stefan Institute and John DeWild at the U.S. Geological Survey Wisconsin Mercury Research Lab generously performed extra analysis for the holding time study. The Hg Group at Brooks Rand Labs performed holding time analysis and analyzed site screening samples. Virginia Engel cleaned the field sampling carboys and mixing drums and helped with sample bottling. James FrederickLindenfelser, Jennie Kim, Candace Kittleson, and Lisa Nichols packed and shipped sample bottles to participants. Brittany Nelson, Nathan Andersen, and Frank McFarland provided insight and advice into the statistical analysis. In addition to the participation fees, additional funding for this study was provided by Brooks Rand Instruments. We thank everyone involved, especially the participants, for helping make this study possible.

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