

Laboratory PT #5

October 2026

5th Round of Mercury Laboratory Proficiency Testing

Final Report

1. Objective

The main purpose of this proficiency testing (PT) programme was to evaluate the performance of mercury analyses conducted by the laboratories. It was expected to provide the individual proficiency levels of participating laboratories and the collective mercury monitoring capacity in the world.

2. Proficiency testing provider

This PT was organized by National Institute for Minamata Disease (NIMD). IDEA Consultants, Inc. prepared and distributed the test item for this PT item and collected the analytical results.

3. Implementation period

Call for participation:	December 2025 –February 2026
Test item distribution:	March 2026
Duration of test (analysis):	Until 31 July 2026

4. Participation fee

Free.

5. Test item (sample) and parameter

One (1) human hair sample was used for analysing total mercury and methylmercury concentration.

5.1. Test item preparation

The hair was collected from multiple people who was not occupationally exposed of mercury. Collected hair was cut (<1 mm) and mixed to ensure sufficient homogeneity. The test item was also sterilized by gamma-ray.

Approximately 2 g each of the prepared hair was packed in brown glass bottle. The bottles of test items were sealed in aluminium-lined laminate packs for distribution to the participants.

5.2. Homogeneity testing

The following homogeneity testing of the test item was conducted to ensure that there were no significant differences in the mercury concentrations in the test items between bottles that could affect the result of the PT.

After the preparation of the test item (packed in bottles), ten bottles were selected, and the total mercury analysis (acid digestion - aeration CVAAS measurement) and methylmercury analysis

(dithizone extraction – GC/ECD measurement) were performed three times for each test item in a bottle.

The homogeneity of the test item was then analysed from the results of the total mercury and methylmercury concentrations. Since the analytical results include the uncertainty due to the (chemical) analytical procedure, homogeneity was judged by the following criterion:

Criterion: $S_s \leqq \sqrt{F_1 \times (0.3 \times \sigma_{ep})^2 + F_2 \times {S_w}^2}$

S_s: relative standard deviation of homogeneity testing

σ_{ep}: (expected) relative standard deviation of the reported results from participants

$w_i^2 = \Sigma (x_{gm}^2 - \bar{x}_g^2) / (m-1)$ x_{gm}: result of m times analysis of the bottle

$S_w^2 = \Sigma w_i^2 / g$ $\bar{x}_g$: average of the result of each bottle

F_1 and F_2 are values which are calculated from the probability distribution. In this homogeneity testing (20 bottles testing), F_1 and F_2 were applied following numbers:

F1 = 1.88 F2 = 1.01

(Even though these values are referred from the Annex B of ISO13528:2022, they are introduced from the random variables of χ^2 distribution and F distribution.)

5.2.1. Total mercury

Analysis results of this homogeneity testing are as follows:

$S_s = 0.0205$

$S_w^2 = 0.0196$

Also, relative standard deviation of the results from the participants (used for evaluation) was as follows:

$\sigma_{ep} = 0.0741$

This standard deviation should be used the value which was used for the performance evaluation for participants. As described in 8.2, the performance of participants was evaluated from the median and normalized interquartile range (NIQR) of the results, thus relative NIQR was used for the confirmation of the criterion.

Therefore, above criterion was judged as follows:

$$\sqrt{F_1 \times (0.3 \times \sigma_{ep})^2 + F_2 \times {S_w}^2}$$

$$= \sqrt{1.88 \times (0.3 \times 0.0741)^2 + 1.01 \times 0.0196}$$

$= 0.1440 > 0.0205$ (S_s)

It was confirmed that the test item was sufficiently homogeneous to evaluate the performance of participants' results.

5.2.2. Methylmercury

Analysis results of this homogeneity testing are as follows:

S_s = 0.0136

S_w^2 = 0.0084

Also, relative standard deviation of the results from the participants (used for evaluation) was as follows:

σ_{ep} =0.0955

This standard deviation should be used the value which was used for the performance evaluation for participants. As described in9.2, the performance of participants was evaluated from the median and normalized interquartile range (NIQR) of the results, thus relative NIQR was used for the confirmation of the criterion.

Therefore, above criterion was judged as follows:

$$\sqrt{F_1 \times (0.3 \times \sigma_{ep})^2 + F_2 \times {S_w}^2}$$

$$= \sqrt{1.88 \times (0.3 \times 0.0955)^2 + 1.01 \times 0.0084}$$

= 0.1001 > 0.0136 (S_s)

It was confirmed that the test item was sufficiently homogeneous to evaluate the performance of participants' results.

5.3. Stability testing

To ensure that the concentration of the target parameter (total mercury and methylmercury) was maintained without significant changes during the PT, a following stability testing was conducted after the duration of the analysis.

Ten test items were selected from the stored (not distributed to participants), and total mercury analysis (acid digestion - aeration CVAAS measurement) and methylmercury analysis (dithizone extraction – GC/ECD measurement) was performed twice for each test item in a bottle.

The stability of the test item was then analysed by comparing the results before and after the distribution of the test item. The stability of the test item was judged by the following criterion:

Criterion: $|\bar{x} - \bar{y}| \leqq 0.3 \times \sigma_{pt} + 2 \times \sqrt{{u_{(x)}}^2 + {u_{(y)}}^2}$

$\bar{x}$: average of the item before distribution

$\bar{y}$: average of the item after proficiency testing

$u_{(x)}$: uncertainty of the item before distribution

$u_{(y)}$: uncertainty of the item after proficiency testing

σ_{pt}: standard deviation for the proficiency evaluation. In this program, NIQR was applied to evaluation of performance of the participant.

5.3.1. Total mercury

Analysis results of test items before and after the PT are as follows:

$\bar{x}$ = 3.18 $u_{(x)}$ = 0.0651

$\bar{y}$ =3.21 $u_{(y)}$ = 0.1390

Standard deviation of the result of all participants was as follows:

σ_{pt} = 0.234

This standard deviation should be used the value which was used for the performance evaluation for participants. As described in 8.2, the performance of participants was evaluated from the median and normalized interquartile range (NIQR) of the results, thus NIQR was used for the confirmation of the criterion.

Therefore, above criterion was judged as follows:

$$0.3 \times \sigma_{pt} + 2 \times \sqrt{u_{(x)}{}^2 + u_{(y)}{}^2}$$

$$= 0.3 \times 0.234 + 2 \times \sqrt{0.0651^2 + 0.1390^2}$$

$$= 0.377 > 0.03 \ (|\bar{x} - \bar{y}|)$$

It was confirmed that the concentration of total mercury in test item was not changed during the PT.

5.3.2. Methylmercury

Analysis results of test items before and after the PT are as follows:

$\bar{x}$ = 2.65 $u_{(x)}$ = 0.0359

$\bar{y}$ =2.66 $u_{(y)}$ = 0.0756

Standard deviation of the result of all participants was as follows:

σ_{pt} = 0.222

This standard deviation should be used the value which was used for the performance evaluation for participants. As described in9.2, the performance of participants was evaluated from the median

and normalized interquartile range (NIQR) of the results, thus NIQR was used for the confirmation of the criterion.

Therefore, above criterion was judged as follows:

$$0.3 \times \sigma_{pt} + 2 \times \sqrt{u_{(x)}{}^2 + u_{(y)}{}^2}$$

$$= 0.3 \times 0.222 + 2 \times \sqrt{0.0359^2 + 0.0756^2}$$

$$= 0.234 > 0.01 \ (|\bar{x} - \bar{y}|)$$

It was confirmed that the concentration of methylmercury in test item was not changed during the PT.

6. Target parameter

The target parameter of the PT was total mercury and/or methylmercury. Participants could perform analysis and report either or both of total mercury/methylmercury. Participants conducted three total mercury / methylmercury analyses and reported all results. Participants also conducted analysis of moisture in the test item. The result of moisture was used for the analysis of the reported data, however, it was not the target of the PT, and the result of total mercury was not calculated by moisture.

The moisture analysis procedure was instructed to the participants as follows:

1. Take a test item (more than 100 mg) other than it used for mercury analysis, and measure its weight correctly.
2. Dry at 85 degrees C for 4 hours.
3. Measure the item's weight after drying, and calculate the moisture from the loss of the item.

It has also been instructed that the sample used for moisture analysis should not be used for total mercury analysis.

7. Participating institutions

This PT was intended for the laboratories of public, university, or other organizations which involves mercury management and/or monitoring performing mercury analyses. The analysis was requested with a lower detection limit of less than 0.1 mg/kg for a 10 mg test item.

70 laboratories registered for the PT, and 19 registered laboratories were not able to receive the test items due to several issues such as customs clearance. Among 51 laboratories received the

samples, 44 laboratories reported their analysis results. The number of laboratories and their statuses are shown inTable 1.

Table 1 Number of participating laboratories

Category	Number of laboratories	
Registered	70	
Sample received	51	
Result delivered	Total Mercury 44	Methylmercury 12

8. PT Analysis Result: Total Mercury

In total, 44 laboratories submitted results. Reports with an insufficient number of reported results were excluded from the statistical analysis and z-score calculation. The statistical data were calculated from the average of each participant's results.

8.1. Basic statistical data of the PT result

The basic statistics of the result of PT are shown inTable 2.

Table 2 Summary of the results of the PT (total mercury)

Statistical data of the results (unit: μg/L)	Reject excluded
n	42
Mean	3.133
Median	3.159
Standard deviation:	0.342
Minimum	1.951
Maximum	3.909
25th percentile	3.005
75th percentile	3.321
Interquartile range (IQR)	0.316
Normalized IQR (NIQR)	0.234
Parameter related to distribution	
Skewness of distribution	-0.879
Kurtosis of distribution	2.886

The distribution of the average values of all results is shown in Fig. 1.

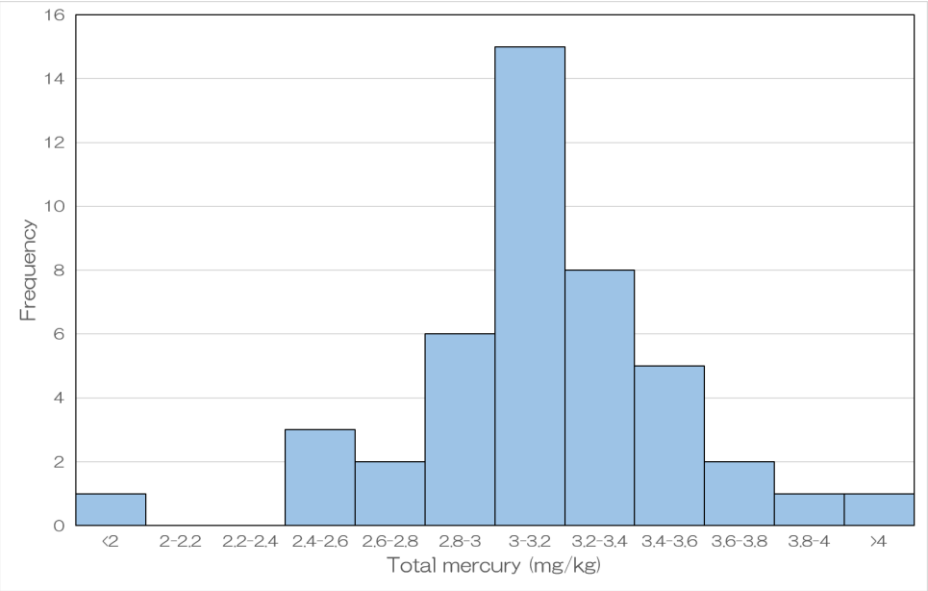


Fig. 1 Histogram of the report data (total mercury)

8.2. Performance evaluation for participants

Median data of laboratories excluding rejected laboratories was applied as agreement value. Performance of the results was evaluated by the robust z score, which was calculated from the median and normalized interquartile range (NIQR).

z score of each participant was calculated from the following equation.

z = [(average of reported result) – (median of laboratories excluding rejected laboratories)] / NIQR

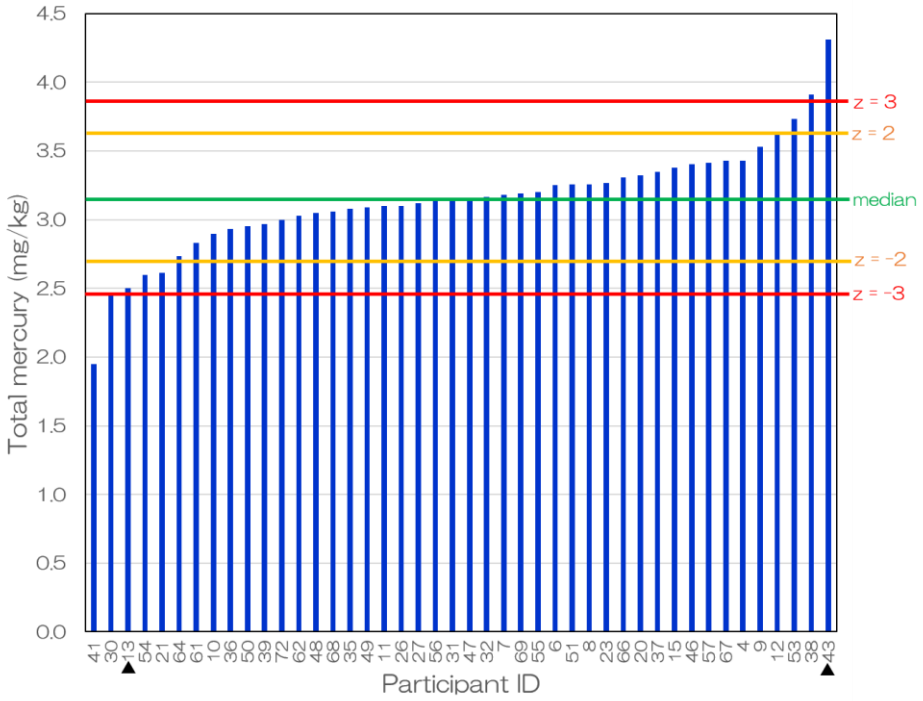
Performance of the result is classified by z score as follows:

|z| ≦2: Performance is satisfactory (satisfactory)

2 < |z| < 3: Performance is questionable (caution)

|z| ≧ 3: Performance is unsatisfactory (action)

The results and performances of laboratories are shown in Fig. 2.



(Symbols below the Participant ID denote results excluded from the Z-score calculation:

▲ = insufficient replicate.)

Fig. 2 Result of each participant (total mercury)

The numbers of laboratories disaggregated for each z score range are shown inTable 3.

Table 3 Number of the laboratories in the range of z score (total mercury)

z score	z ≦ -3	-3 <z< -2	-2 ≦z≦ 2	2 < z < 3	z ≧3
n	2	1	36	4	1

As described in Table 2, IQR of reported results were relatively small. Therefore, satisfactory range of the result (mercury concentration) was relatively close and results around 15 % difference from the median was the classified range of unsatisfactory of the result.

8.3. Types of laboratories and the performances

Number of laboratories per type (academic, government, or non-government) and the performance of the PT are shown in Fig. 3.

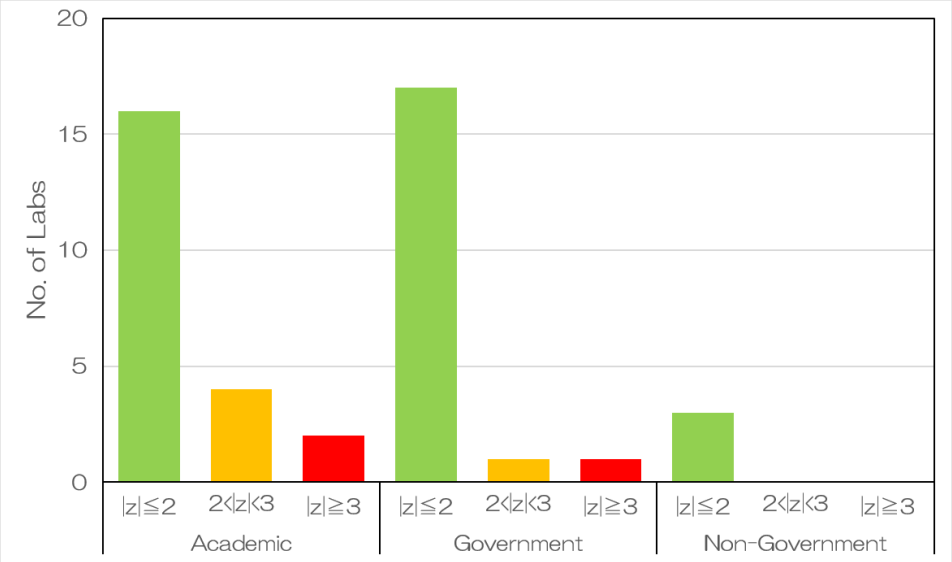


Fig. 3 Number of laboratories per types and performance (total mercury)

8.4. Analysis methods and results

The method of analysis was not specified for the PT and the participants performed analysis by the method that they usually used in their routine analysis, or they were planning to use in the future.

The participants performed analysis of total mercury by the following methods:

- Thermal Decomposition Cold Vapour Atomic Absorption Spectrometry (TDAAS)
- Acid digestion, aeration Cold Vapour Atomic Absorption Spectrometry (CVAAS)
- Acid digestion, Cold Vapour Atomic Fluorescence Spectrometry (CVAFS)
- Acid digestion, Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

The distribution of the results from participants by analysis method is shown in Fig. 4.

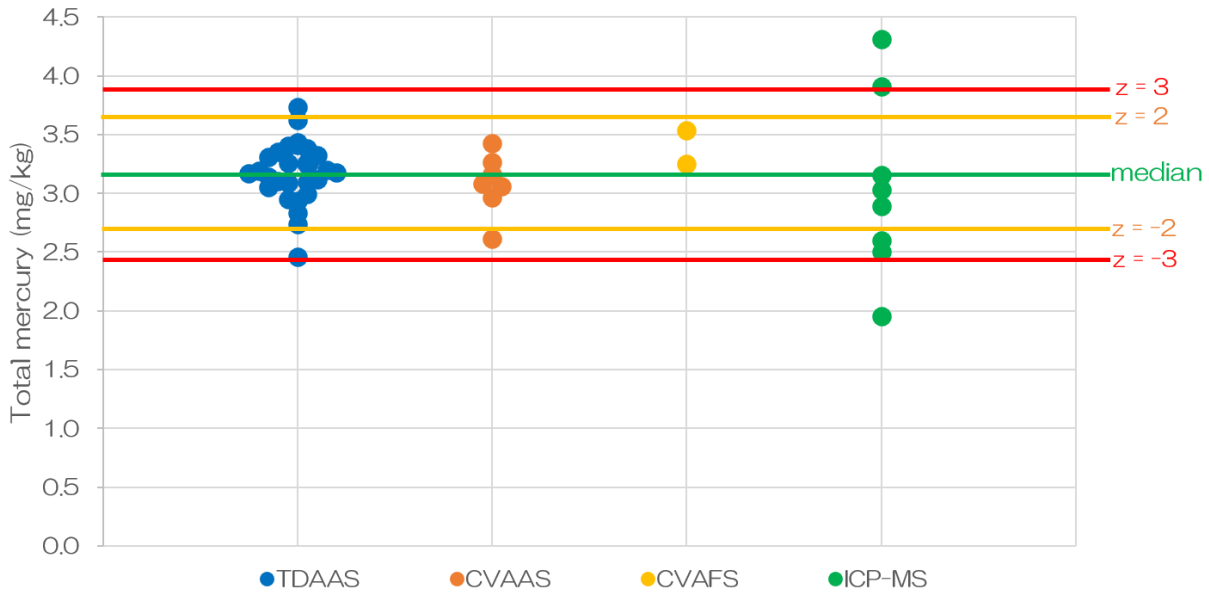


Fig. 4 Distribution of the report data by analysis method (total mercury)

No significant difference was found among the analysis methods performed. (Kruskal-Wallis one-way ANOVA on ranks, p=0.21. It does not contain excluded data.)

9. PT Analysis Result: Methylmercury

In total, 12 laboratories submitted results. Reports with an insufficient number of reported results were excluded from the statistical analysis and z-score calculation. The statistical data were calculated from the average of each participant's results.

9.1. Basic statistical data of the PT result

The basic statistics of the result of PT are shown in Table 4.

Table 4 Summary of the results of the PT (methylmercury)

Statistical data of the results (unit: μg/L)	Reject excluded
n	11
Mean	2.350
Median	2.319
Standard deviation:	0.285
Minimum	1.891
Maximum	2.885
25th percentile	2.181
75th percentile	2.480
Interquartile range (IQR)	0.299
Normalized IQR (NIQR)	0.222
Parameter related to distribution	
Skewness of distribution	0.401
Kurtosis of distribution	0.104

The distribution of the average values of all results is shown in Fig. 5.

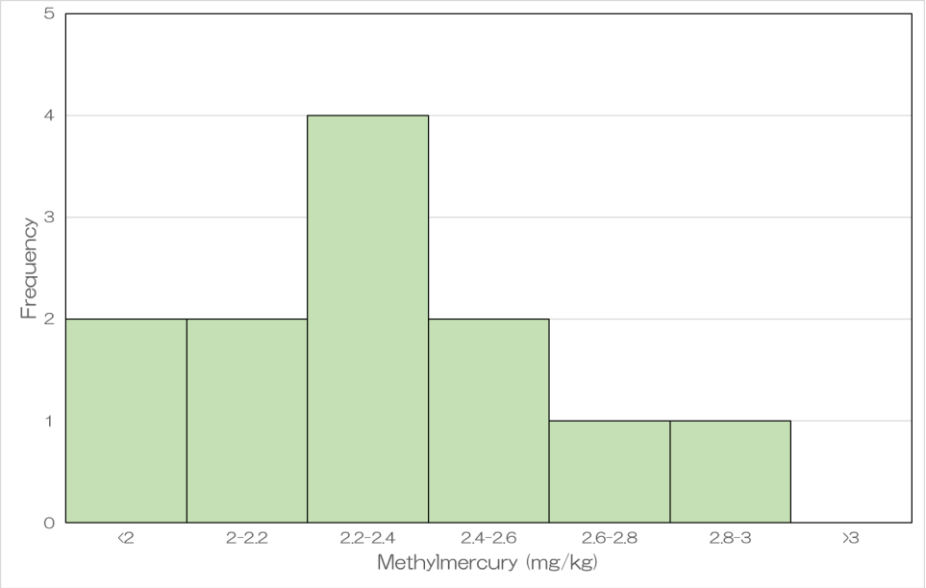


Fig. 5 Histogram of the report data (methylmercury)

9.2. Performance evaluation for participants

Median data of laboratories excluding rejected laboratories was applied as agreement value. Performance of the results was evaluated by the robust z score, which was calculated from the median and normalized interquartile range (NIQR).

z score of each participant was calculated from the following equation.

z = [(average of reported result) – (median of laboratories excluding rejected laboratories)] / NIQR

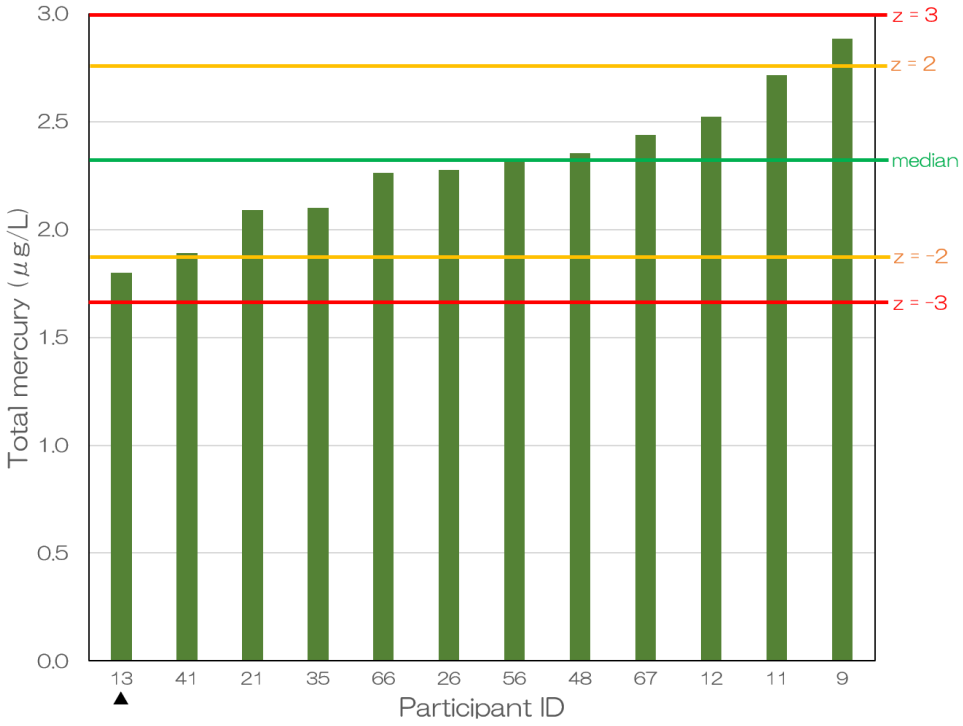
Performance of the result is classified by z score as follows:

|z| ≦2: Performance is satisfactory (satisfactory)

2 < |z| < 3: Performance is questionable (caution)

|z| ≧ 3: Performance is unsatisfactory (action)

The results and performances of laboratories are shown in Fig. 6.



(Symbols below the Participant ID denote results excluded from the Z-score calculation:

▲ = insufficient replicates)

Fig. 6 Result of each participant (methylmercury)

The numbers of laboratories disaggregated for each z score range are shown in Table 5.

Table 5 Number of the laboratories in the range of z score (methylmercury)

z score	z ≦ -3	-3 <z< -2	-2 ≦z≦ 2	2 < z < 3	z ≧3
n	0	1	10	1	0

A Although the analytical methods for methylmercury differ from those for total mercury, there was no notable difference in the NIQR ranges of the reported values between methylmercury and total mercury. Therefore, satisfactory range of the result (mercury concentration) was relatively close and results around 19 % difference from the median was the classified range of unsatisfactory of the result.

9.3. Types of laboratories and the performances

Number of laboratories per type (academic, government, or non-government) and the performance of the PT are shown in Fig. 7.

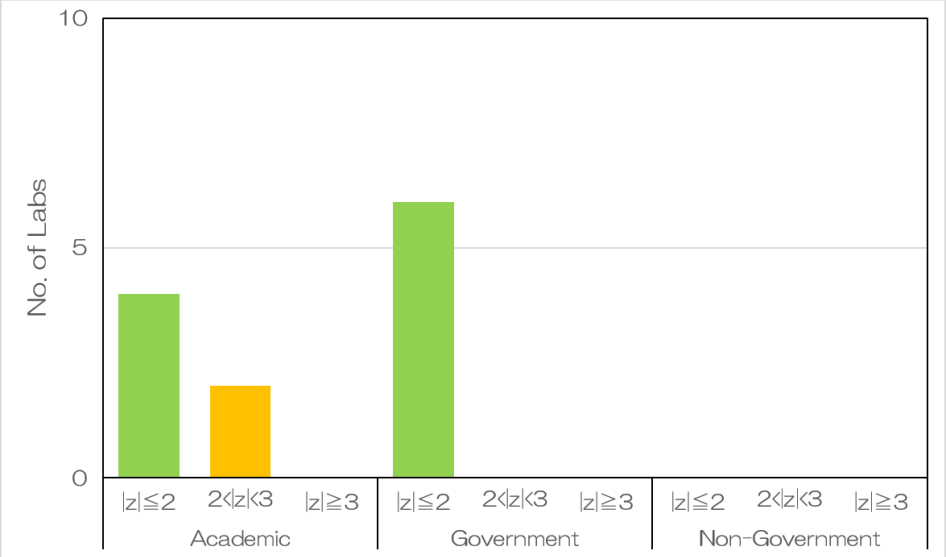


Fig. 7 Number of laboratories per types and performance (methylmercury)

9.4. Analysis methods and results

The method of analysis was not specified for the PT and the participants performed analysis by the method that they usually used in their routine analysis, or they were planning to use in the future.

The participants performed analysis of total mercury by the following methods:

- Liquid Chromatograph and Inductively Conducted Plasma Mass Spectrometer (LC/ICP-MS)
- Liquid Chromatograph and Cold Vapour Atomic Fluorescent Spectrometer (LC/CVAFS)
- Gas Chromatograph and Cold Vapour Atomic Fluorescent Spectrometer (GC/CVAFS)
- Gas Chromatograph and Electron Capture Detector (GC/ECD)
- Thermal Decomposition Cold Vapour Atomic Absorption Spectrometry (TDAAS)
- Acid digestion, aeration Cold Vapour Atomic Absorption Spectrometry (CVAAS)
- Acid digestion, Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

The distribution of the results from participants by analysis method is shown in Fig. 8.

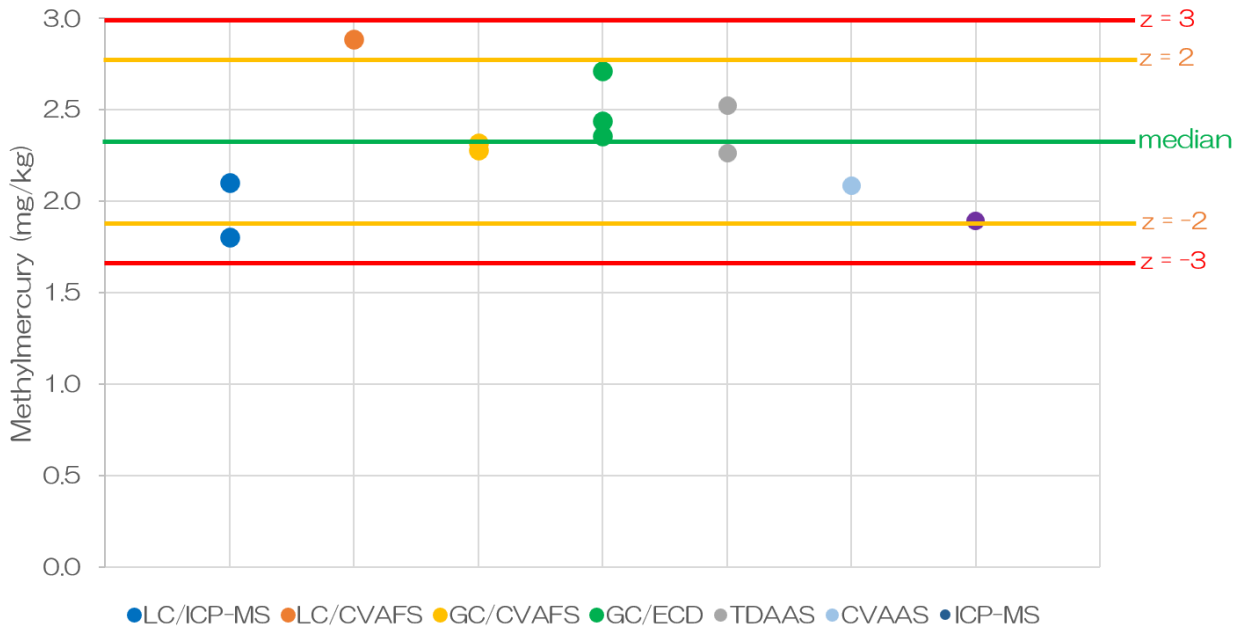


Fig. 8 Distribution of the report data by analysis method (methylmercury)

Because the number of reports for each analytical method was small, analysis of differences among analytical methods for methylmercury was not conducted.

10. Relation with total mercury and methylmercury

The plots of the relationship between total mercury and methylmercury concentration are shown in Fig. 9.

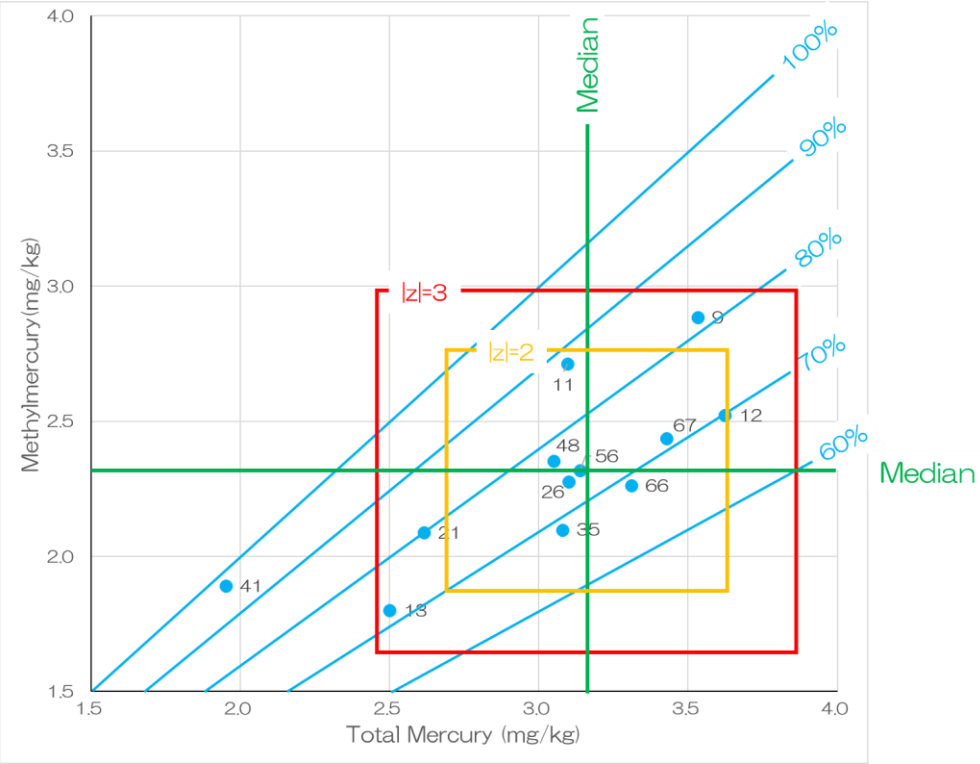


Fig. 9 Scatter plot between total mercury and methylmercury

A significant positive correlation between total mercury and methylmercury are detected (r=0.745, one-sided testing, p=0.0043. It does not contain excluded data.). The methodology used for both analysis are different. Therefore, even when analyses are conducted in the same laboratory, there is no necessarily simple correlation between the values of the results. While it is difficult to determine the exact reason for the correlation in the results, one possible factor is a difference in bias due to equipment (such as balances) used for both total mercury and methylmercury analyses. However, it is unclear whether differences in the calibration of this equipment would lead to a correlation in the results across all participating institutions. Furthermore, there is a relationship between the concentrations of total mercury and methylmercury in hair. Since participating institutions that performed both analyses were able to compare these results, it is also conceivable that this led to a positive correlation. (Of course, comparing relevant parameters in laboratory analysis is a highly appropriate procedure for ensuring the quality of results.)

11. Moisture

The basic statistics of the reported moisture of test item is shown in Table 6.

Table 6 Summary of the result of moisture

	Moisture (%)
Average	8.49
Median	9.00
Standard deviation	4.54
Minimum	0.011
Maximum	22.5

The distribution of the results of moistures is shown in Fig. 10.

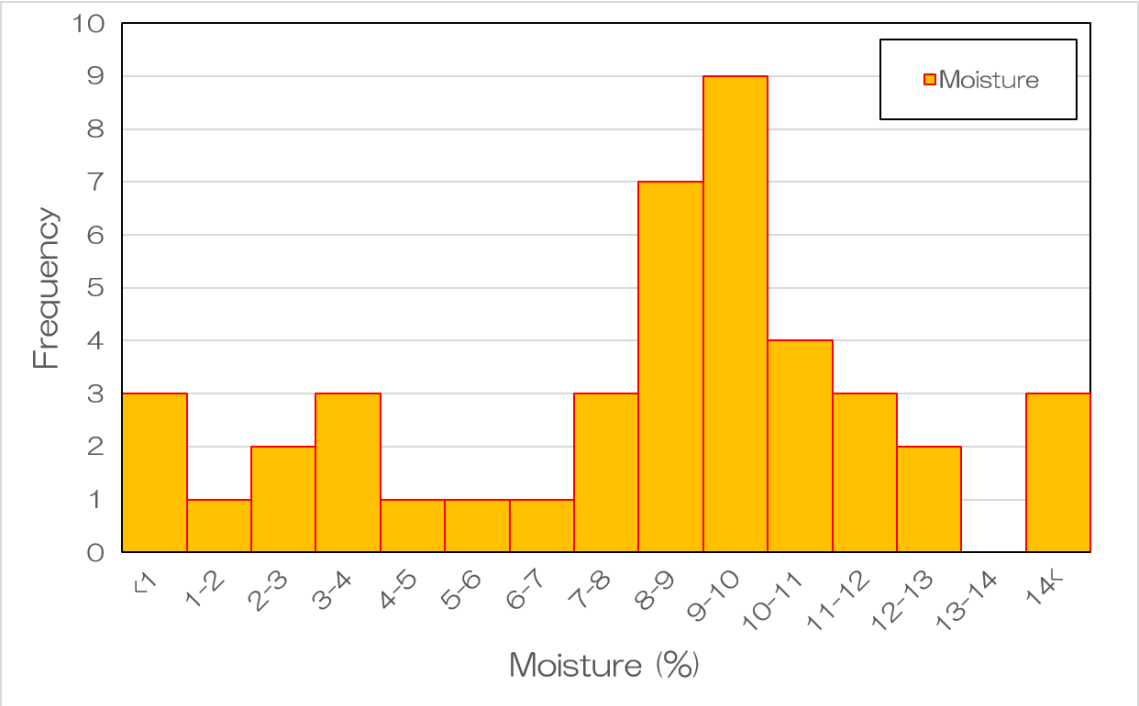


Fig. 10 Histogram of the result of moisture

The plots of the relations of moisture and total mercury concentration are shown in Fig. 11.

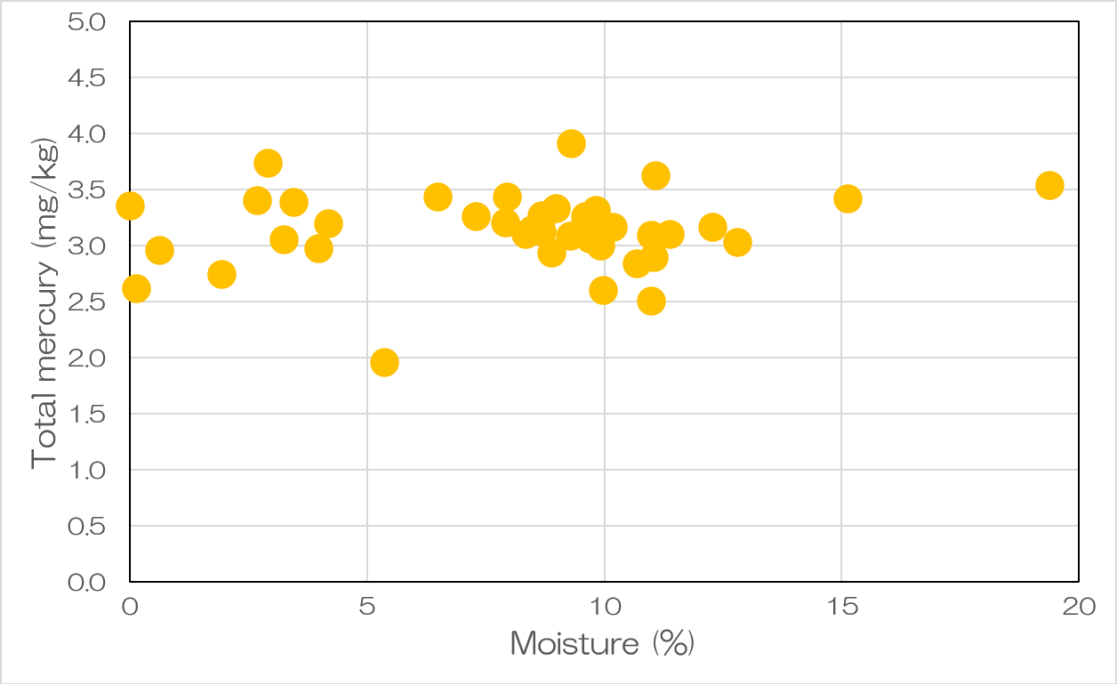


Fig. 11 Total mercury and moisture

The plots of the relations of moisture and methylmercury concentration are shown in Fig. 12.

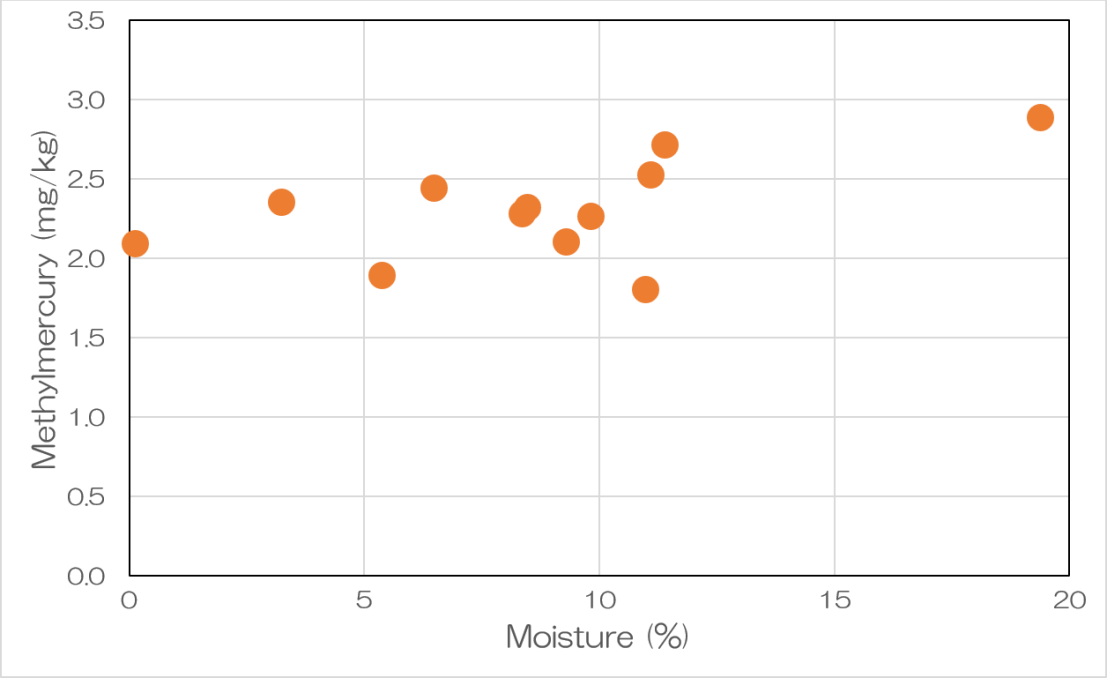


Fig. 12 Methylmercury and moisture

The reported moisture deviation was larger than the mercury deviation of the target parameter analysis (total mercury/methylmercury), but no noticeable relationship between moisture and both parameters of mercury concentration was found. The method used to measure moisture was to subtract the weight measured after drying from the weight measured before drying. Since the moisture was relatively small (median: 9.00%), it was considered that the uncertainty of the moisture analysis was larger than the change in moisture during the PT analysis period.

12. Conclusion

In both of the results of total mercury and methylmercury analysis, many of the reported results from the participants were concentrated around the median value and IQRs of the results were relatively close. The NIQR range of total mercury is around 7.4%, and methylmercury is around 9.6% respectively. Significant differences (bias) among the analytical methods were not detected in total mercury (Because the number of reports for each analytical method was small, analysis of differences among analytical methods for methylmercury was not conducted.).

The range of moisture reported from the participants were larger than the deviation of the target parameters even it was not the target of the PT. Also, the correlation between the target parameters (total mercury and methylmercury) and moisture was not detected. In addition, the result of stability testing indicates that there was not a significant change of testing item during the PT, it can be considered that differences in moisture content had little effect on the PT results.

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Appendix: List of participating laboratories (Non exhaustive)

Australian Institute of Marine Science	Laboratorio Tecnologico del Uruguay (LATU)
Australian Nuclear Science and Technology Organisation (ANSTO)	Lumex Analytics GmbH
Balai Besar Biomedis dan Genomika Kesehatan, Indonesia	National Central University, Taiwan
Biodiversity Research Institute	National Institute for Minamata Disease, Japan
Center for Ecotoxicological Research Podgorica	Peruvian Amazon Research Institute (IIAP)
Center for Environmental Management Facility, Indonesia	Qa3 Ltd.
Centre Régional de Recherches en Écotoxicologie et Sécurité Environnementale (CERES-Locustox), Senegal	Siberian Branch of Russian Academy of Sciences
Centro de Excelencia en Productos y Procesos (CEPROCOR), Gobierno de Córdoba, Argentina	Sri Lanka Standard Institute, Chemical Laboratory
Climate change and Environmental Research Center, Thailand	Universidad de la Republica, Uruguay
Environmental Management Bureau Central Office, Philippines	Universidad de Panamà
Esslingen University	Universidad Nacional Autónoma de Nicaragua
Federal Institute of Metrology (METAS), Switzerland	Universidad Nacional del Litoral
GEOMAR Helmholtz Center for Ocean Research Kiel	Universidat Autónoma de San Luis Potosi
Georgetown University	Universitas Trisakti
Hokkaido University	University of West Attica
Jozef Stefan Institute	Vietnam Academy of Science and Technology
Kagoshima University	