Laboratory PT #3

June 2025

3rd 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 region.

2. Proficiency testing provider

This PT was organized by National Institute for Minamata Disease (NIMD) in collaboration with United Nations Environmental Programme (UNEP). Asian Institute of Technology Regional Resource Centre for Asia and the Pacific (AIT RRC.AP) distributed the test item and collected the analytical results. IDEA Consultants, Inc. prepared the test item for this PT.

3. Implementation period

Call for participation:	October 2023 – August 2024
Test item distribution:	September 2024
Duration of test (analysis):	Until 31 January 2025

4. Participation fee

Free.

5. Test item (sample) and parameter

One (1) dried bottom sediment sample was used for analysing total mercury concentration, methylmercury concentration or both (participating laboratories shoed the preferred option).

However, due to the limited number of participating laboratories, performance evaluation for the results of methylmercury was not conducted.

5.1. Test item preparation

The test item was made from the bottom sediment collected from one site in a bay. The gravel sand and coarse sand were removed from the bottom sediment, and dried in room temperature (lower than 40 °C). The dry sediment was ground using a ceramic ball mill. After grinding, a 75 µm sieve was used to obtain silt samples smaller than 75 µm. Then the obtained test item was sterilized using gamma-ray.

Approximately 5 g of each test item was packaged in a 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. Since the test item was collected from a single site and the ratio of total mercury and methylmercury was assumed to be stable between test items, homogeneity testing was conducted by analysing total mercury.

After the preparation of the test item (packed in bottles), twenty bottles were selected, and the total mercury analysis (acid digestion - aeration CVAAS measurement) was performed four times for each test item in a bottle.

The homogeneity of the test item was then analysed from the results of the total mercury 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 = 1.59 F2 = 0.57

(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.)

Analysis results of this homogeneity testing are as follows:

S_s = 0.0052

S_w^2 = 0.0033

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

σ_{ep} =0.0882

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:

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

$$= \sqrt{1.59 \times (0.3 \times 0.0882)^2 + 0.59 \times 0.0033}$$

$= 0.0548 > 0.0052$ (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) was maintained without significant changes during the PT, a following stability testing was conducted after the duration of the analysis. Since the test item was collected from a single site and the ratio of total mercury and methylmercury was assumed to be stable between test items, stability testing was conducted by total mercury analysis.

Ten test items were selected from the stored (not distributed to participants), and total mercury analysis (acid digestion - aeration CVAAS 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.

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

$\bar{x} = 4.672$ $\quad u_{(x)} = 0.0069$

$\bar{y} = 4.696$ $\quad u_{(y)} = 0.010$

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

σ_{pt} = 0.362

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:

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

$$= 0.3 \times 0.362 + 2 \times \sqrt{0.0069^2 + 0.010^2}$$

$$= 0.133 > 0.024 \ (|\bar{x} - \bar{y}|)$$

It was confirmed that the concentration of total mercury 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 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 and methylmercury was not calculated by moisture.

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

1. Take a test item of 100 mg or more and weigh it precisely.
2. Dry the taken test item (100 °C, 2 hours).
3. Weigh the dried test item again and calculate the moisture of the sample from the reduced mass.

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

7. Participating institutions

This PT was intended for public or university laboratories that perform mercury analysis. It was requested to perform the analysis with a lower detection limit than 0.1 mg/kg on 0.5 g test item for total mercury, and 0.001 mg/kg on 0.5 g test item for methylmercury analysis.

43 laboratories registered in the PT and 35 laboratories (total mercury) and 4 laboratories (methylmercury) respectively reported the analysis results.

The number of participants for each parameter (total mercury/methylmercury) and status are shown in Table 1.

Table 1 Number of participating laboratories for parameter and step

Category	Number of laboratories	
Registered	43	
Sample received	42	
	Total mercury	Methylmercury
Result delivered	35	4

8. Total Mercury Analysis Result

8.1. Basic statistic data of the PT result (total mercury)

The basic statistics of the result of PT are shown in Table 2.

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

Statistic data of the results (unit: mg/kg)	
Average:	4.147
Median:	4.105
Standard deviation:	0.751
Minimum	1.225
Maximum	5.990
25 percentiles	3.875
75 percentiles	4.364
Interquartile range (IQR)	0.488
Normalized IQR (NIQR)	0.362
Parameter related to distribution	
Skewness of distribution	-1.018
Kurtosis of distribution	6.871

The distribution of the results from the participants is shown in Fig. 1.

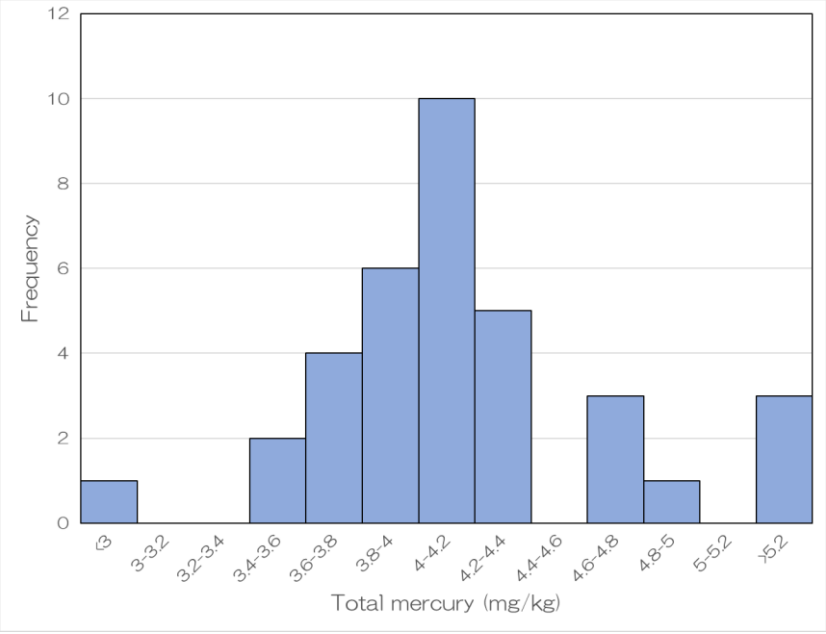

Fig. 1 Histogram of the report data (total mercury)

One registered participant was unable to receive the test item due to a customs clearance issue. There were also participants who were unable to report the results of their analyses due to problems such as trouble with the measuring instruments.

These statistical data were calculated from the average of each participant. There was one participant who did not report 3 results (2 results were reported), but all data were used for statistical analysis.

The distribution had a large kurtosis, indicating that many part of reported values were concentrated around the median, while some other values deviated from it. This means the interquartile range was relatively small compared to the standard deviation.

The skewness values were negative and the distribution of reported values was slightly skewed toward lower concentrations. However, these data did not have a major impact on the performance evaluation because the distribution was not so different from the normal distribution and the evaluation was estimated from the median and normalized interquartile range (NIQR).

8.2. Performance evaluation for participants

Median data of all 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.

$$z = [(\text{average of reported result}) - (\text{median of all participants})] / \text{NIQR}$$

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

$|z| \leqq 2$: Performance is satisfactory (satisfactory)

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

$|z| \geqq 3$: Performance is unsatisfactory (action)

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

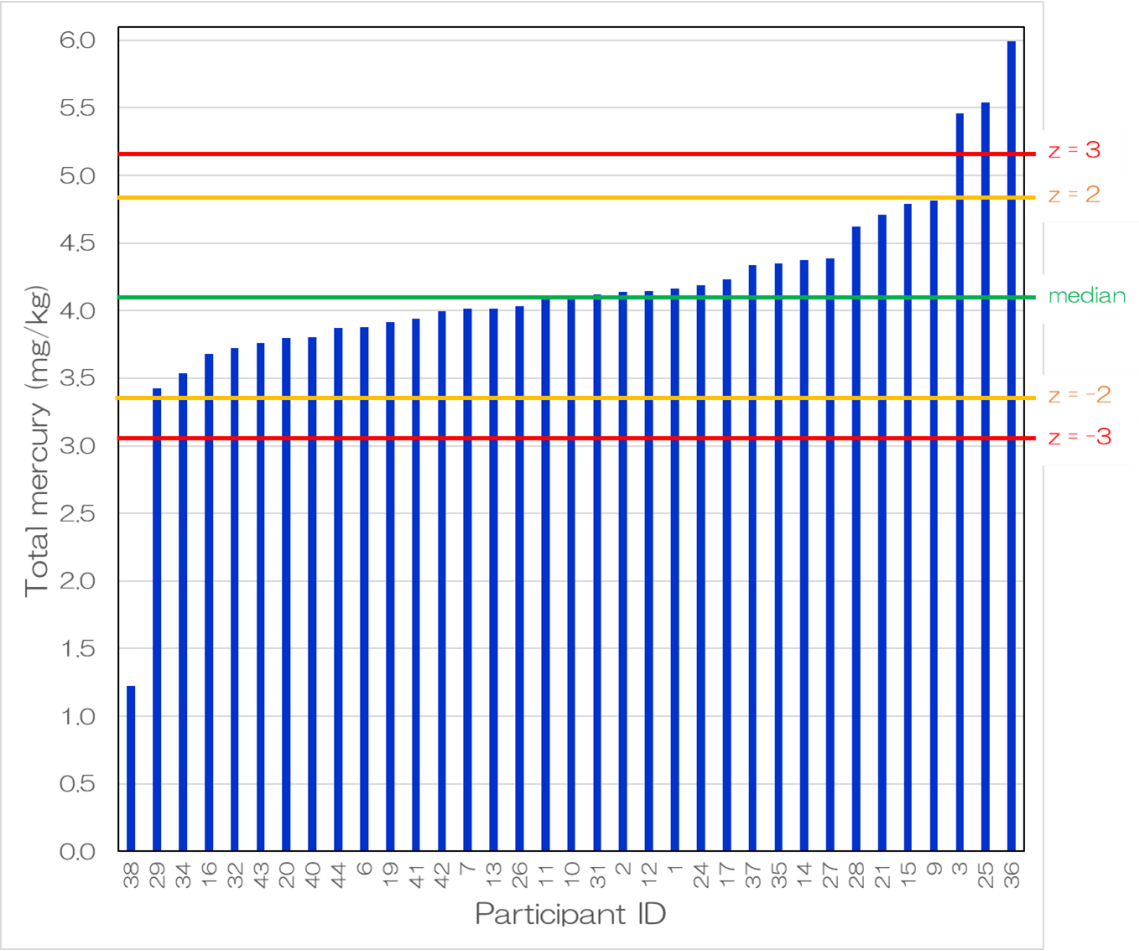

Fig. 2 Result of each participant (total mercury)

The numbers of laboratories disaggregated for each z score range are shown in Table 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	1	0	31	0	3

As described in 8.1, IQR of reported results was relatively small. Therefore, satisfactory range of the result (mercury concentration) was relatively close and results around 26 % difference from the median was the classified range of unsatisfactory result (absolute value of z-score over 3).

8.3. Regions of participating laboratories and the performances

The ratios of laboratories of each performance of the PT per region are shown in Fig. 3.

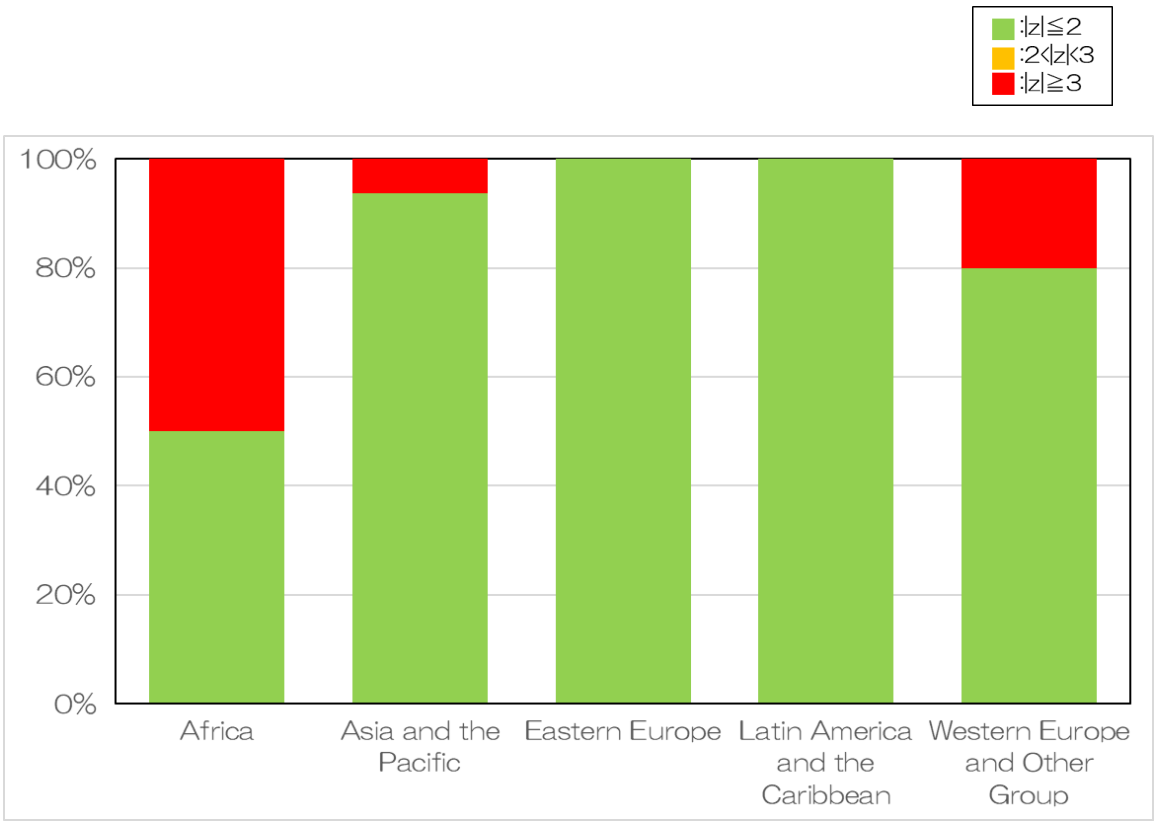

Fig. 3 Ratio of laboratories per regions and performances (total mercury)

Due to the small number of participants in certain regions, regional differences were not examined.

8.4. Types of laboratories and the performances

The ratios of laboratories of each performance of the PT per type (academic, government, or non-government) are shown in Fig. 4.

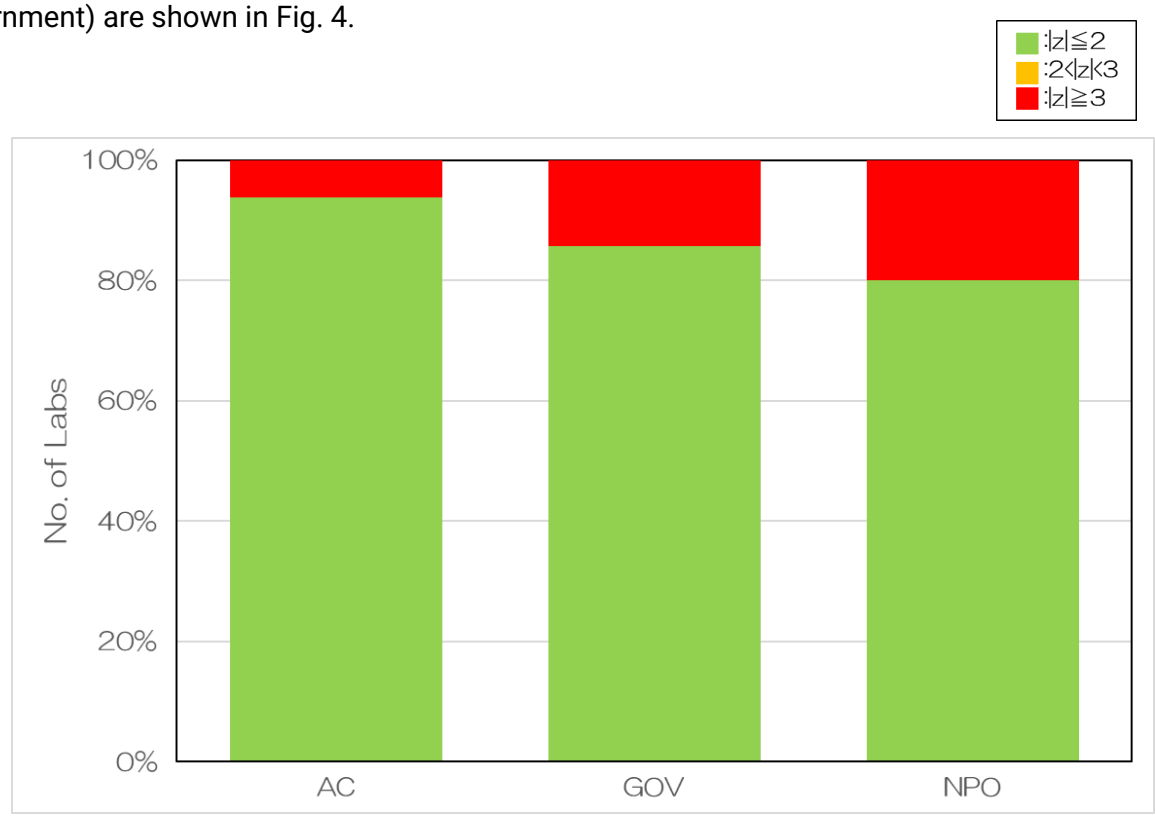

Fig. 4 Ratio of laboratories per types and performance (total mercury)

Statistical differences among the types of laboratories were not detected from the reported results (Kruskal-Wallis one-way ANOVA on ranks, p=0.38).

8.5. 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)

Additionally, one participant reported the method as "other," but did not provide details about it. Therefore, the data from this participant were not included in the following figures and analyses of differences between methods. The result from the participant who reported the method as "other" was not used only for the analysis of differences between methods; the data were used for other analyses (total statistical analysis and performance evaluation).

The distribution of the results from participants by analysis method is shown in Fig. 5.

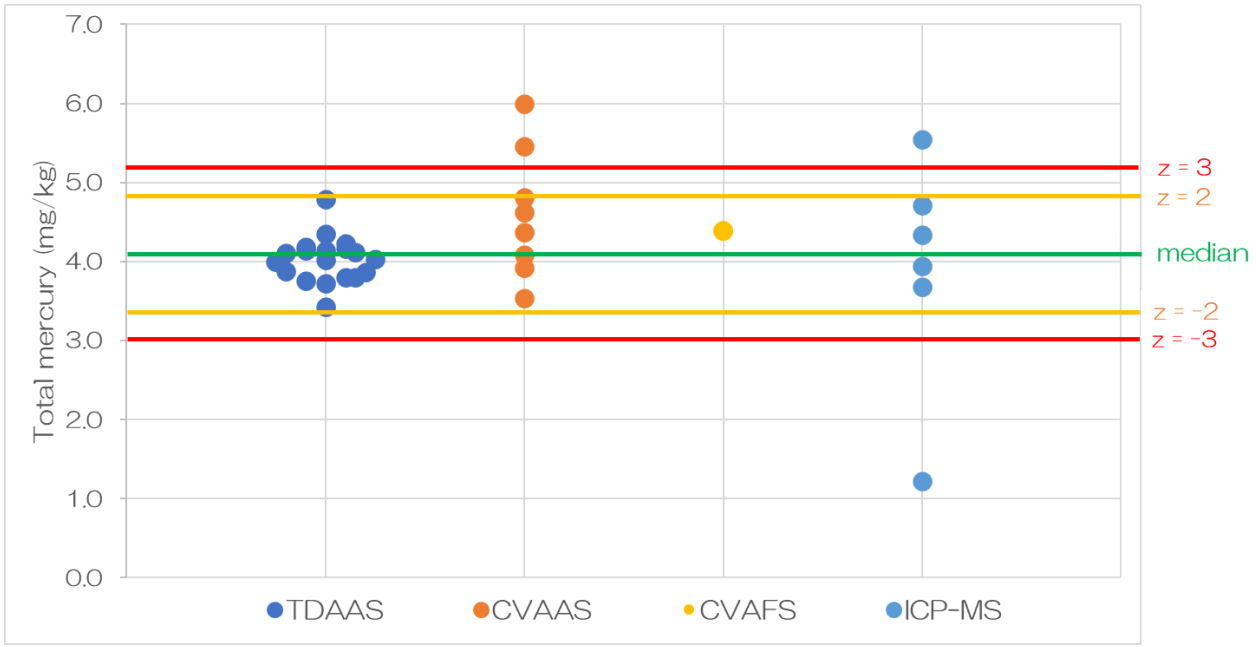

Fig. 5 Distribution of the report data by analysis method (total mercury)

No significant difference was found among the analysis methods employed (Kruskal-Wallis one-way ANOVA on ranks, p=0.22).

9. Methylmercury Analysis Result

9.1. Basic statistic data of the PT result (Methylmercury)

The basic statistics of the methylmercury result of PT are shown in Table 4.
Since the reported data on methylmercury was limited (from four participants), the statistical analysis is limited as well. Additionally, the performance evaluation of participating laboratories for methylmercury analysis was not performed due to the limited number of available data.

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

Statistic data of the results (unit: mg/kg)	
Average	0.001825
Median	0.001729
Minimum	0.001030
Maximum	0.002813

The distribution of the results from the participants is shown in Fig. 6.

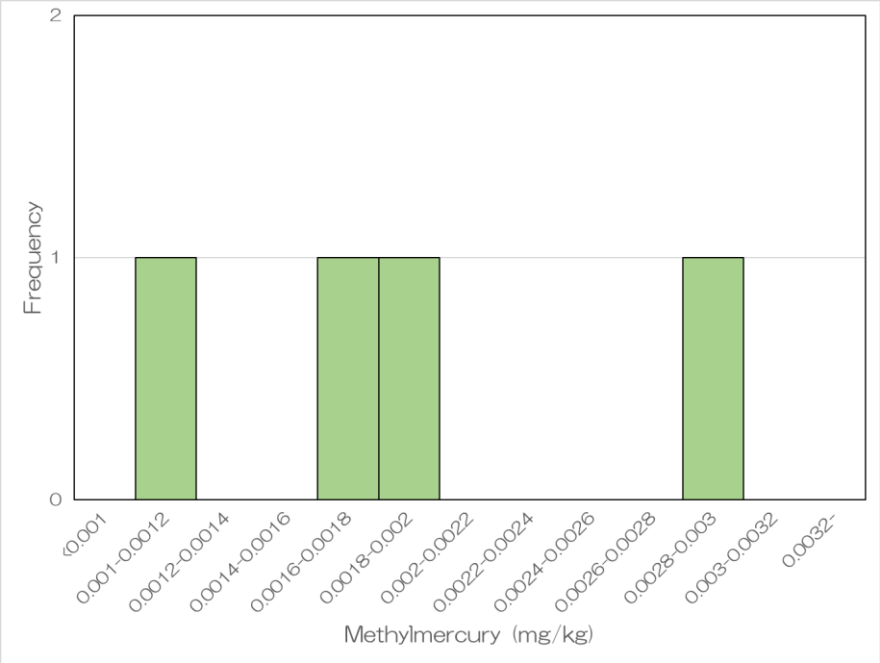

Fig. 6 Histogram of the report data (methylmercury)

10. Moisture

The basic statistics of the reported moisture of test item is shown in Table 5.

Table 5 Summary of the result of moisture

	Moisture (%)
Average	2.85
Median	2.69
Standard deviation	1.87
Minimum	0.0002
Maximum	10.2

The distribution of the results of moistures are shown in Fig. 7.

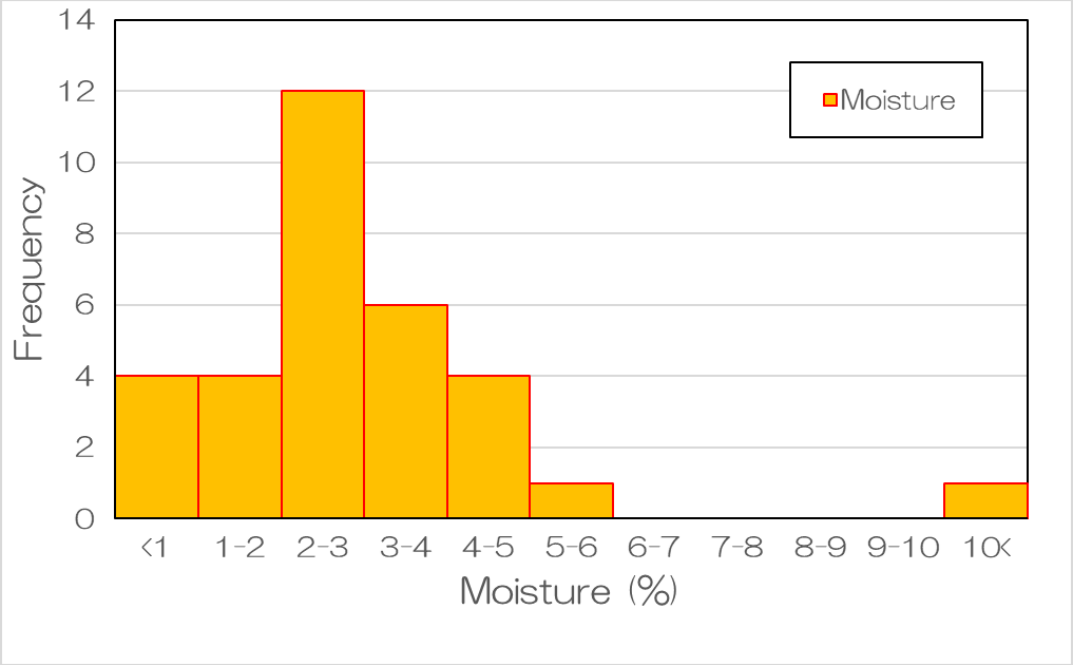

Fig. 7 Histogram of the result of moisture

The plots of the relations of moisture and total mercury concentration are shown in Fig. 8.

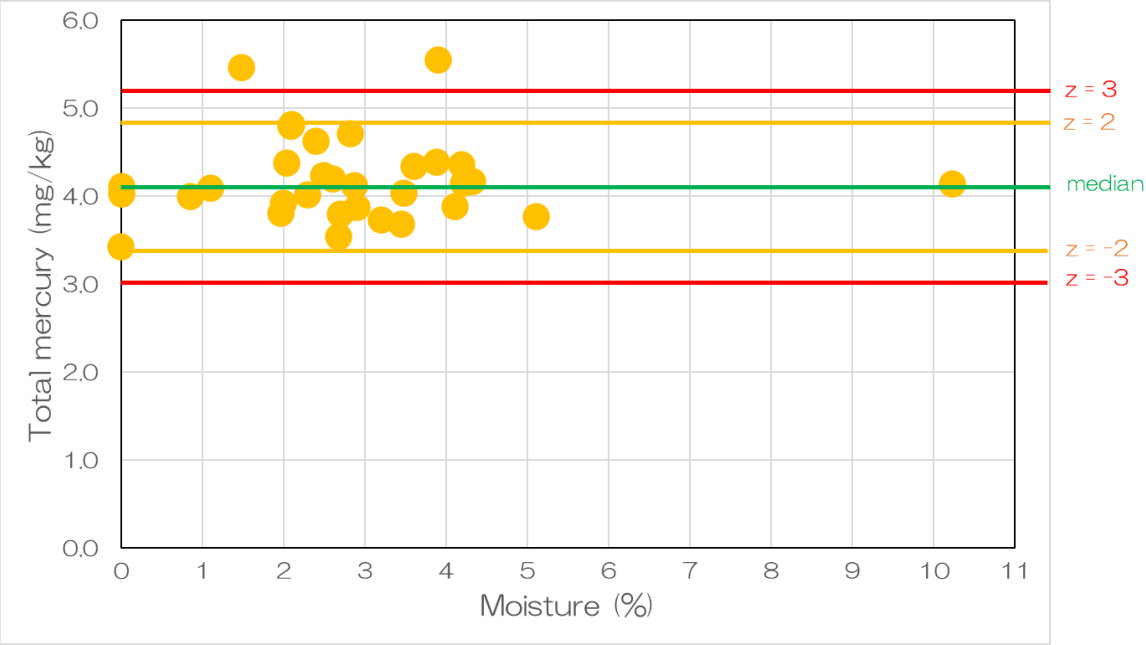

Fig. 8 Total mercury and moisture

The reported moisture deviation was larger than the total mercury deviation that were reported from participants, but no noticeable relationship between moisture and total mercury concentration was found. (Since the number of the data was few, the relationship between moisture and methylmercury was not analysed.) 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 was about 2-3%), it was considered that the uncertainty of the moisture analysis was larger than the change in moisture during the PT analysis period.

11. Conclusion

In total mercury analysis, many of the reported results from the participants were concentrated around the median value and IQRs of the results were relatively close. Thus, it was considered that the difference among many mercury analysis laboratories were relatively small. Some analysis methods were performed on the total mercury analysis, significant difference between the method was not detected. Because of the limited number of the report of methylmercury analysis, detailed analysis and performance evaluation to the participating laboratories were 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 mercury and moisture was not detected. Because the result of stability testing indicates that there was not a significant change of testing item during the PT, it can be considered that the difference of moisture affects the results of the PT because the deviations of the analysis results were small.

Appendix: List of participating laboratories (Non exhaustive)

Balai Besar Biomedis dan Genomika Kesehatan	Ministerio de Producción, Ciencia e Innovación Tecnológica, Gobierno de Córdoba, Argentina
Centre for Mineral Technology of Brazil	Ministry of Natural Resources and Environment of Thailand
Cheng Shiu University	National Central University of Taiwan
Council for Scientific and Industrial Research of South Africa	National Institute for Minamata Disease
Department of Environment and Natural Resources of Philippines	National Institute of Industrial Technology of Argentina
Dirección Nacional de Calidad y Evaluación Ambiental, Uruguay	Philippine Nuclear Research Institute
Esslingen University of Applied Sciences	Prefectural University of Kumamoto
Georgetown University	Universidad Nacional Autónoma de Nicaragua
Ghana Standards Authority	Università degli Studi dell'Insubria
Hokkaido University	Universitas Trisakti
Instituto de Toxicología de la Defensa de España	University of Pretoria
Instituto Nacional de Tecnología Industrial, Argentina	Vietnam Academy of Science and Technology
Instituto Polo Tecnológico de Pando	Vietnam Environment Administration