June 2025

2024 Interlaboratory Study for Atmospheric Mercury Survey and Analysis

Final Report

1. Introduction and Objective

Comparability of measurement data between laboratories is very important in order to use the data for mutual or comprehensive analysis. In particular, mercury travels on a global scale in a gaseous form. Therefore, spatial comparison and analysis are necessary to evaluate the global mercury cycle. To obtain the information for the comparability of measurement data, interlaboratory comparisons between analytical laboratories provide the important information.

However, there are challenges for interlaboratory comparison for atmospheric mercury analysis, and the number of interlaboratory studies or proficiency tests were not so many, although a methodological comparison studies have been conducted. Unlike other heavy metals, most of the mercury in air is in gaseous form. The distribution of homogeneous gaseous samples for such comparison is difficult, which is one of the reasons why few interlaboratory study or proficiency tests have been conducted for atmospheric mercury. In this study, the interlaboratory study for atmospheric mercury analysis using the gold amalgamation trap method was conducted to obtain the information of the comparability of atmospheric mercury measurement data.

2. Outline of the Interlaboratory Study

To confirm the comparability of data from atmospheric mercury analysis using the gold amalgamation trap method (manual active sampling). Gold amalgamation trap cartridges that absorbed the fixed amount of gaseous elemental mercury (GEM) were distributed to 7 participating laboratories capable of measuring the cartridges. The participating laboratories measured the study items (cartridges) and reported their results; statistical analysis of the reported measurement data and discussion of the comparability of the data between laboratories were performed.

3. Study Item Preparation, Distribution and Homogeneity and Stability Test

3.1. Study Item Preparation

For the interlaboratory study item, gold amalgamation trap cartridges (4mm i.d. x 150mm quartz tube packed the gold-coated diatom particle in it) absorbed fixed amount of GEM were prepared. Gold cartridges were adopted with the glass vessel, soda lime trap and air suction pump. A fixed amount of mercury chloride ($HgCl_2$) aqueous solution was added to the glass vessel, and the gold cartridge and air pump were connected. Stannous chloride ($SnCl_2$) was added to the $HgCl_2$ solution in the glass vessel and the air in the vessel was sucked into the gold cartridge. Mercury in the glass vessel was reduced and volatilized, and it was introduced and absorbed into the gold-coated particles in the cartridge. The figure of the items to absorb gaseous mercury into the study item (cartridge) is shown in Fig. 1.

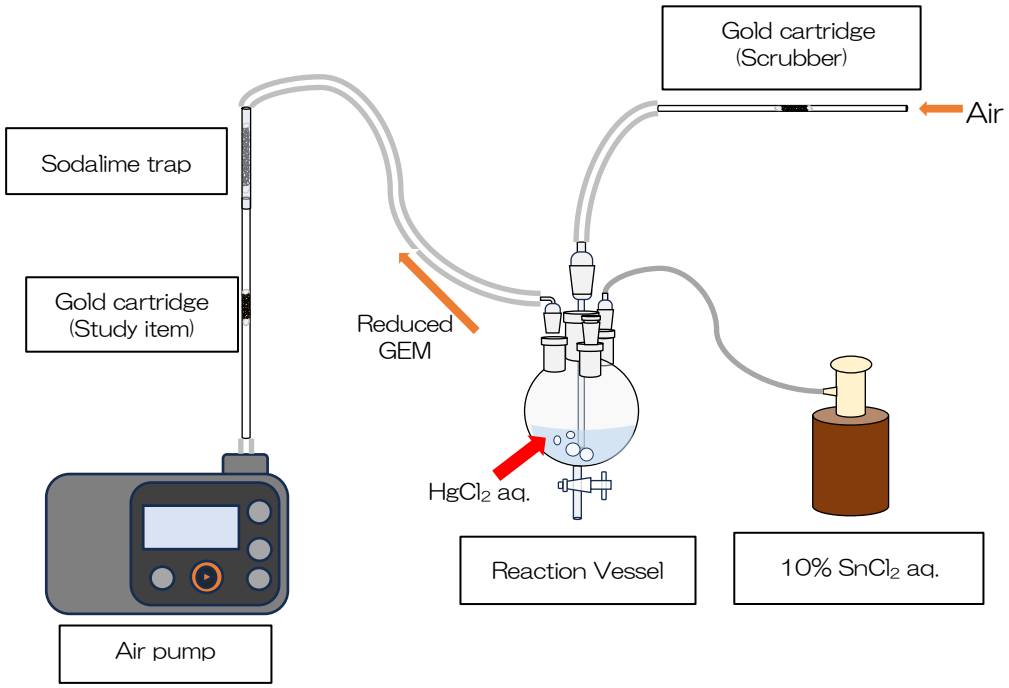

Fig. 1 Schematic diagram of the gaseous mercury absorption device

5 study items were distributed to each participating laboratory and measured the mercury amount in the item. And also, 3 cartridges that no mercury were absorbed were distributed and measured as the field blank test items.

3.2.Homogeneity testing

To evaluate the deviation among the study items, the following homogeneity testing of the test items was performed.

After the preparation of the study item (absorption of the fixed amount of GEM in the cartridge), 10 items were selected from all the prepared items, and the total gaseous mercury (TGM) was measured by thermal desorption and cold vapor atomic absorption spectrometer (CVAAS).

The relative standard deviation (RSD) of the measurement results of the homogeneity testing was 0.0096 (0.96%). Because the mercury absorbed in the gold cartridge can be measured only once, it is difficult to separate the homogeneity of the test item and the measurement uncertainty of the items in the same laboratory. Therefore, this RSD of the homogeneity testing results includes the deviation of the amount of mercury in the study items and the uncertainty of the laboratory measurement. However, as mentioned above, the maximum estimated of the difference was less than 1% RSD, it was confirmed that there was no significant difference between the study item.

3.3. Stability testing

To ensure that the amount of mercury in the study items did not change during the study, the following stability tests were performed before and after the study (measurements were completed by all participating laboratories). Stored (not distributed to participants) 10 items were selected and mercury measurement was performed, and their average amount was compared with the average measurement results measured before the study.

The average of the measurement result of the mercury amounts of the study item measured before the study item distribution was 1.216 ng, and the average of the measurement results after the study (all participants completed the measurement) was 1.233 ng. As described in Table. 2, the standard deviation of the participants' measurement results was 0.014 ng, the difference of the measurement results between before and after study results was similar to the standard deviation of the study results. The difference of the measurement results between before and after the study is also similar to the deviation of the result of each participating laboratory. Therefore, it was considered that there was no significant change in the amount of mercury in the study items during the study.

4. Measurement Results of Study Items

The basic statistics of the results from each participating laboratory are shown in Table. 1, and the basic statistics of the results from all participants' data (calculated from the average of each participant's data) are shown in Table. 2.

Table. 1 Study results (laboratory)

Laboratory	A	B	C	D	E	F	G
Average	1.189	1.167	1.199	1.199	1.263	1.377	1.289
Median	1.188	1.167	1.199	1.200	1.265	1.376	1.288
SD	0.00720	0.00270	0.00600	0.01536	0.00720	0.04261	0.00713
Min	1.179	1.162	1.1907	1.182	1.254	1.323	1.282
Max	1.198	1.169	1.2066	1.221	1.270	1.423	1.301

(unit: ng)

Table. 2 Study result (all)

Average	1.241
Median	1.199
SD	0.014
RSD	1.11%

(unit: ng)

The figure showing the mercury measurement results of each participating laboratory is shown in Fig. 2.

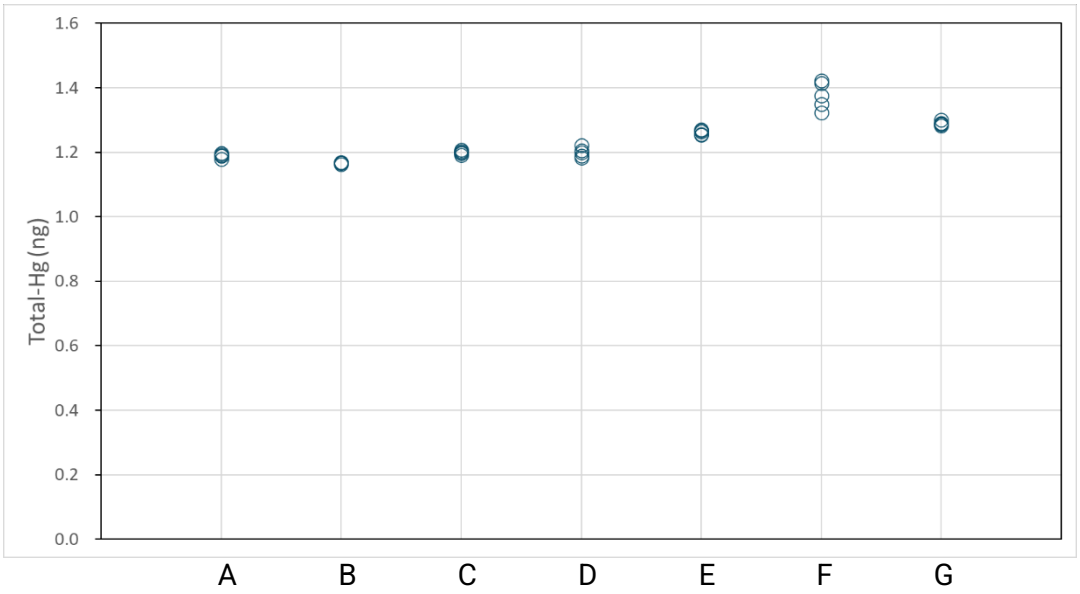

Fig. 2 Measurement results of the laboratories

Both the within-laboratory and between-laboratory deviations were very close, about 1% RSD. The item of this study was that only GEM were absorbed, and no other substances that also collected with mercury on the actual sample collection and interfere with the measurement (e.g., moisture, halogenated or organic substances) was not contained in the item. Thus, even though the deviations of the measurement of the actual air collected sample may be larger, these measurement results indicated that the method of gold amalgamation trap can be carried out in good accuracy on the atmospheric mercury survey.

5. Statistical Analysis and Discussions

The measurement results of this study were very close in both within laboratory and interlaboratory, and the RSD of the average results of the participating laboratories was about 1%. The RSD of the interlaboratory results is not so different from the RSD of each laboratory, an analysis of variance (ANOVA) was performed on the interlaboratory results. The summary of the result of ANOVA is shown in Table. 3.

Table. 3 Summary of ANOVA

	Df	Sum of Square (SOS)	Mean SOS	F	P
Group (Laboratory)	6	0.16527	0.027545	85.74	1×10^{-16}
Residuals	28	0.00899	0.000321		

The P value estimated from the F value indicated that there was a significant difference between the results of the laboratories compared with the deviation of each laboratory's result. However, the results of some laboratories were very similar. Therefore, to estimate the difference between each laboratory result, Tukey's Honestly Significant Difference (HSD) test was performed on the results. Groups of pairs that were not significantly different between laboratories ($p < 0.05$) are shown in Table. 4.

Table. 4 Group of pairs that were not significantly difference

Laboratories group
A, B, C, D
E, G
F

There are no significant differences between the data from laboratories A, B, C, and D. These data are significantly different from those of laboratories E, F, and G. Similarly, there are no significant differences between the data from E and G; they differ significantly from those of A, B, C, D, and F. The data from F differ significantly from the others. However, the difference of the result from the average of all laboratory's result is about 11%, it is not so large difference compared with the uncertainty of many kinds of chemical analysis and other factor of environmental survey.

6. Conclusion

In this study, the data of atmospheric mercury survey by gold amalgamation trap had very small difference between laboratories. Although the study item did not contain the interfering matrix that exists in the actual atmospheric sample, it is considered that the data collected by the different laboratories has a good comparability. Gold amalgamation trap method is very simple and easy to operate, so it is available in the various sites and situations. As mentioned above, information of atmospheric mercury is very important for the analysis of global mercury cycle, therefore, good comparability monitoring data contributes for the more accurate analysis for the global cycle.

7. Project Information

This interlaboratory study was conducted under the framework of the Japan-funded UNEP project “Promoting Minamata Convention on Mercury by making the most of Japan’s knowledge and experiences”.