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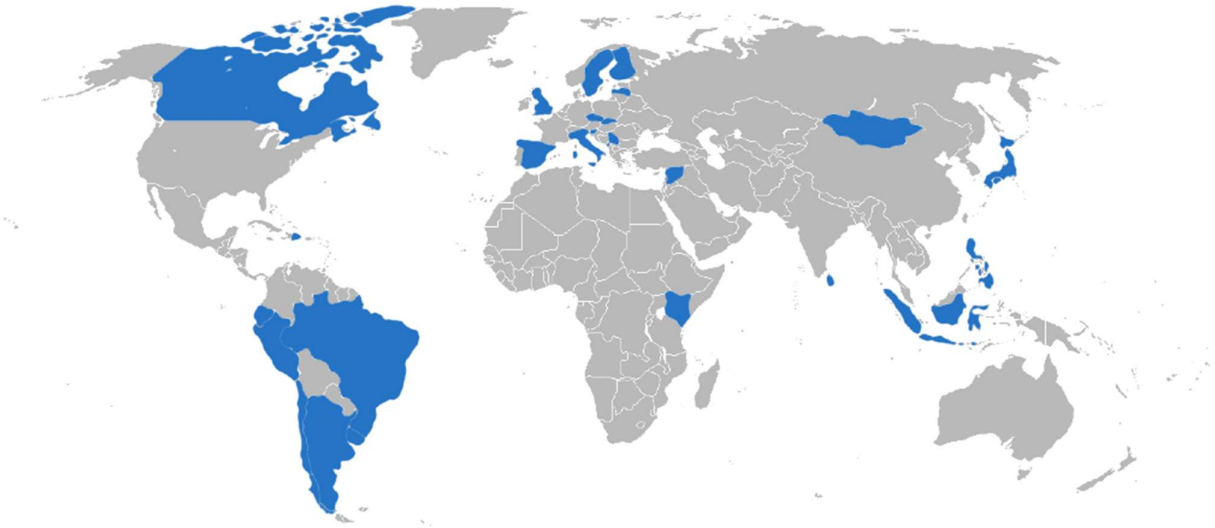
FINAL REPORT

Global Assessment of Laboratories Analysing Mercury

First Round, 2018



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This report was developed by the SCRC in the Czech Republic hosted by the Research Centre for Toxic Compounds in the Environment (RECETOX), Masaryk University, Brno, Czech Republic:

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Acronyms

GEF	Global Environmental Facility
SCRC	Stockholm Convention Regional Centre
RECETOX	Research Centre for Toxic Compounds in the Environment
UNEP	United Nations Environment Programme
UN Environment	United Nations Environment Programme
CV-AAS	Cold Vapor Atomic Absorption Spectrometry
CV-AFS	Cold Vapor Atomic Fluorescence Spectrometry
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
TD-AAS	Thermal Desorption Atomic Absorption Spectrometry
TD-GA-AAS	Thermal Desorption Atomic Absorption Spectrometry with Gold Amalgamation
XRF	X-Ray Fluorescence

1. Introduction

In 2016, the UN Environment Chemicals and Health Branch, in close cooperation with the World Health Organization and the Italian National Research Council, within the framework of the Global Environment Facility (GEF), GEF funded project "Development of a Plan for Global Monitoring of Human exposure to and Environmental Concentration of Mercury", developed a mercury laboratory survey to collect information on available capacities of laboratories analysing mercury worldwide. All countries were invited to participate in the survey through letters addressed to all SAICM focal points and Minamata Convention INC members. Participation in the survey was voluntary.

The Databank was developed in 2017 and it lists laboratories from all UN regions, including both developed and developing countries, capable of identifying and quantifying mercury species in biotic (human urine, cord blood, fish etc.) and/or abiotic (ambient air, sediment etc.) samples. The Databank is accessible online as shown in Figure 1 and is periodically updated. It currently comprises 210 laboratories from 62 countries in all five UN regions.

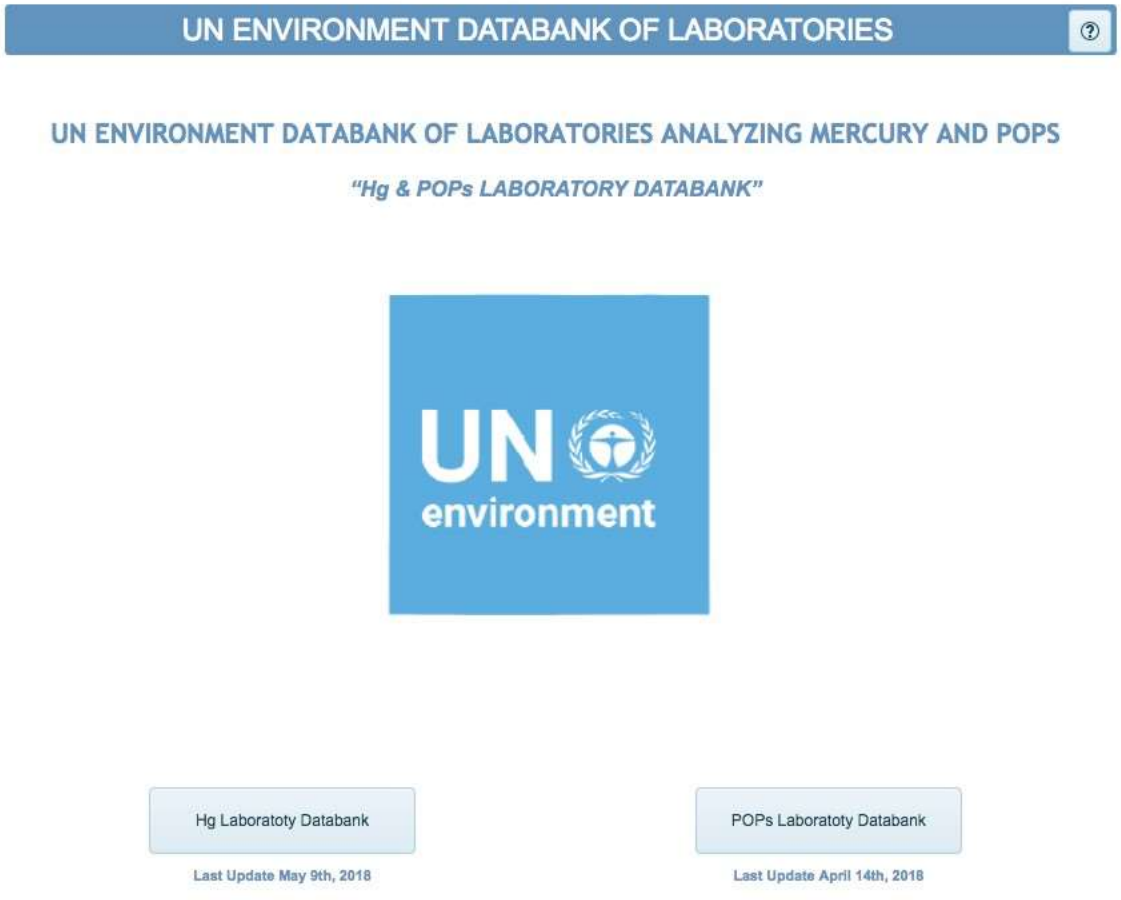

Figure 1 Print screen of the title page of Laboratory Databank at the UN Environment website (http://informea.pops.int/HgPOPsLabs/index.html), last accessed 17 November 2018.

Secondly, the Minamata Convention on Mercury requests Parties to cooperate on geographically representative monitoring of the levels of mercury in vulnerable populations and environmental media, building on existing monitoring networks and research programmes. The Convention also stipulates through Article 22 that the Conference of the Parties (COP) shall establish arrangements for obtaining comparable monitoring data for the assessment of the effectiveness of the Convention. In addition, entry into force of the Minamata Convention on Mercury and work undertaken regarding monitoring arrangements and effectiveness evaluation of the Minamata Convention between COP1 and COP2 in 2017 and 2018 resulted also in a higher request for information regarding existing laboratory capacities for mercury analyses worldwide and for the quality of such analyses.

The UN Environment has therefore asked the SCRC Czech Republic to provide support in a pilot assessment of laboratories analysing mercury and act as coordinator of the global assessment. RECETOX`s tasks were to organize a first round of a global assessment, where invited laboratories would register to analyse the same samples of three different matrices for total mercury within a limited time frame. The laboratories would report their results to the coordinator of the assessment who would evaluate all results received according to international standards.

The present report provides outcome of the assessment and shows a state-of-the-art information regarding the worldwide capacity of laboratories to analyse mercury as available in 2018.

2. Participation in the Global Laboratory Assessment

Participation in the assessment was by invitation only.

On the basis of information provided by laboratories in the mercury survey organized by UN Environment in 2016, the invitation letter "Call for expression of interest to participate in the Global Assessment of Laboratories analysing Mercury" was sent to laboratories, in the UN Environment databank, in July 2018 who had agreed to participate in the comparative studies. The invited laboratories registered via a form provided in Annex I that comprised basic information about the pilot laboratory assessment for mercury including the planned timetable.

The target participation was 50 laboratories worldwide, with a representative geographical distribution among UN regions and participation of both developing and developed countries to evaluate capacity in UN regions to gather comparable data on the levels of mercury in vulnerable populations and environmental media.

The following criteria were used for the selection of the laboratories invited:

- Laboratory is in the UN Environment databank of laboratories analysing mercury.
- Laboratory indicated "Yes" in the databank questionnaire item on participation in the intercalibration assessment
- Laboratory has Quality Controls/Quality Assurance (QC/QA) systems in place and accreditations (international and/or national)
- UN Region, laboratories from developing countries and countries with economies in transition

If more than one laboratory in one country complied with criteria above, then the following were considered:

- Capability to analyse different matrices
- Laboratory X is a public laboratory.

All participating laboratories located in developing countries participated in the first round of the global assessment free-of-charge. Developed countries participation fee was 650 USD per laboratory covering test materials, their shipment and final data processing.

In addition, the Stockholm and Basel Convention Regional Centre in Uruguay (SBCRC-Uruguay) hosted by Technological Laboratory of Uruguay (LATU) approached UN Environment and suggested a broadened participation in the Latin America and Caribbean region. This as additional activity of the GEF/UNEP projects (Minamata Initial Assessments - MIAs, GEF ID 5879 and Mercury Risk Management Approaches - GEF ID 5494) in the region and a follow up to capacity building activities for mercury analyses in laboratories of the GRULAC region supported by SBCRC-Uruguay. Therefore, SBCRC-Uruguay identified additional 11 laboratories that were invited to participate to the global laboratory assessment as shown in Table 2.

3. Organization of the assessment

The technical coordination and assessment were performed by the Research Centre for Toxic Compounds in the Environment (RECETOX), Faculty of Science, Masaryk University, Brno, Czech Republic acting as the Stockholm Convention Regional Centre in the Czech Republic.

In July 2018, UN Environment Chemicals and Health Branch identified the laboratories and invited them to register and participate in the interlaboratory assessment via the form shown in Annex 1. UN Environment also classified invited laboratories into two groups - “free of charge participation” and “pay participation fee” and communicated this to RECETOX.

Planned timetable:

- Registration: open until 10 August 2018
- Confirmation of participation and verification of shipment address: until 10 August 2018
- Distribution of test samples: from 1 August until 15 August 2018
- Reporting of results (MS Excel templates will be provided when confirming the participation): Not later than 15 October 2018.

Registration opened on 16 July 2018 and registered laboratories were contacted for confirmation of the contact person and shipment address. Due to low registration rate, two additional rounds of invitations were performed until end of July. Consequently, registrations and verification of contacts were carried out until end of August.

Shipment of samples from RECETOX by the DHL company to registered laboratories started on 20 August 2018 and the last attempt to deliver test samples (repeated attempt) occurred on 20 October 2018. Each shipment was accompanied by a letter listing the type of test samples contained in the shipment and a customs letter referring to the interlaboratory assessment and non-commercial approach. Additional certificates on non-infectiousness or non-hazardousness of the materials were provided on request. Instructions for reporting the results were sent by e-mail to all laboratories together with the link to the shipment.

Due to delays in the registration of the laboratories and verification step of their contacts, the shipment of test samples was also extended and consequently, the final deadline of providing the results was pushed back to 22 October 2018.

The first results of analyses were received on 15 September 2018 and the last results on 8 November 2018.

Preliminary data analyses of results received was performed in mid-November 2018 so that a first summary information was provided to experts participating in the Second meeting of the conference of the Parties to the Minamata Convention on Mercury. Finalization of the work took place in early December 2018.

4. Materials and Methods

4.1. Test samples

The test samples were naturally contaminated with mercury and the following three matrices were made available for the global assessment:

1. Standard solution test sample (solution)

- The samples were distributed in 30 ml dark thick glass jars with PTFE insert in the lid wrapped in the protective plastic foil (see Figure 2 below).
- Purity Test: 5 jars were filled by 2% HNO_3 + 2% HCl (about 30 ml in total) for 24 hours. Mercury concentration for four jars was lower than 1 ng/L, the fifth jar was 5 ng/L (established by ICP-MS method).
- A two litres stock solution was prepared on 9 August 2018. It contained approximately 16,5 µg/L of mercury in 2% HNO_3 + 2% HCl.
- Then 67 aliquots were prepared by pipetting on 10 August 2018. Each jar contained 20 ml of the solution
- Concentration of the stock solution was determined by AMA254 method to 15.3 ± 0,3 µg/L of mercury (RSD = 1,75 %, n = 4) on 10 August 2018.
- In addition, five aliquots were tested for homogeneity of the sample by picking random jars and establishing mercury concentration in them by AMA 254 method. The analysis yielded 15.7 ± 0.2 µg/L (RSD = 1,04 %, n = 5).
- Finally, stability test of the test samples was performed on 13 August by testing the same jars. The concentration reached was 15.7 ± 0,3 µg/L (RSD = 1,72 %, n = 5)

2. Biota test samples (fish)

- Samples were distributed in 8 ml HDPE white jars (high density polyethylene) marked with “F” letter (see Figure 2 below).
- Purity Test: 5 jars were filled by 2% HNO_3 + 2% HCl for 24 hours. Mercury concentration for all five jars was lower than 1 ng/L.
- Test sample was prepared by mixing 7 packages of certified reference material of 10g CRM ERM-BB442 each in a 250 ml polypropylene vessel. The sample was left open to be saturated by water vapours and mixed thoroughly.
- Homogeneity test of the sample was performed on 9 August 2018. Analysis was performed on AMA 254 with result of mercury level of 0.572 ± 0,007 µg/g (RSD = 1,2 %, n = 4). Reference value of the CRM was 0.601 ± 0,030 µg/g, and data were not corrected for CRM dry matter.
- Then 67 aliquots of the CRM were prepared by weighting 1 g of the test sample to the individual jars on 10 August 2018.

- Test sample homogeneity in aliquots was performed on 13 August. Five test sample jars were randomly selected for analysis. Mercury concentration analysed on AMA 254 was of 0.566 ± 0.002 µg/g (RSD = 0,3 %, n = 5).

3. Human scalp hair test samples

- Samples were distributed in 4ml HDPE white jars marked with "H" letter (see Figure 2 below).
- Purity Test: 5 jars were filled by 2% HNO_3 + 2% HCl for 24 hours. Mercury concentration for all five jars was lower than 1 ng/L.
- Test sample was prepared on 8 August 2018. Six packages of the 3.5 g certified reference material CRM ERM-DB001 each were mixed in a 250 ml polypropylene vessel. The sample was left open to be saturated by water vapours and mixed thoroughly.
- Homogeneity test was performed on 9 August 2018. Analysis was performed on AMA 354 with result of mercury level of 0,318 ± 0,007 µg/g (RSD = 2,2 %, n = 4). Reference value of the CRM was of 0,365 ± 0,028 µg/g, and data were not corrected for CRM dry matter.
- Then 67 aliquots of the test material were prepared by weighting 0.3 g of the test sample to the individual jars on 13 August 2018.
- Test sample homogeneity on aliquots was performed on 13 August. Five test sample jars were randomly selected for analysis. Mercury concentration analysed on AMA 254 was of 0,313 ± 0,005 µg/g (RSD = 1,6%, n = 5).

Figure 2 Full set of test samples ready for shipment – standard solution, fish (F), and hair (H)

4.2. Methods - Chemical analyses

Laboratories used their in-house methods for analyses of the test samples distributed. The following six methods were reported to be used, without further details or specification of the instrumentation:

CV-AAS	Cold Vapor Atomic Absorption Spectrometry (16 laboratories)
CV-AFS	Cold Vapor Atomic Fluorescence Spectrometry (3)
ICP-MS	Inductively Coupled Plasma Mass Spectrometry (5)
TD-AAS	Thermal Desorption Atomic Absorption Spectrometry (1)
TD-GA-AAS	Thermal Desorption Atomic Absorption Spectrometry with Gold Amalgamation (16)
XRF	X-Ray Fluorescence (1)

It was very difficult to interpret the results on the basis of the method employed due to the limited number of laboratories participating in the assessment overall and also to a low use of a particular chemical analysis method. There was a limited correlation between the quality of the results and analytical method used. A summary text on the outcomes of the method comparison is provided at the beginning of the result chapter 5.2. (general overview).

4.3. Methods - Data analyses

The following algorithm yields robust values of the average and standard deviation of the data to which it is applied.

Denote the p items of data, sorted into increasing order, by:

$$x_1, x_2, \dots, x_i, \dots, x_p$$

Denote the robust average and robust standard deviation of these data by x^* and s^*.

Calculate initial values for x^* and s^* as:

$$x^* = medianof\, x_i (i = 1,2, \dots, p)$$

$$s^* = 1.438 medianof |x_i - x^*| \ \ (i = 1,2, \dots, p)$$

Update the values of x^* and s^* as follows. Calculate:

$$\delta = 1.5 s^*$$

For each $x_i (i = 1,2, \dots p)$, calculate:

$$x_i^* = \begin{Bmatrix} x^* - \delta & if\, x_i < x^* - \delta \\ x^* + \delta & if\, x_i > x^* + \delta \\ x_i & otherwise \end{Bmatrix}$$

Calculate the new values of x^* and s^* from:

$$x^* = \frac{\sum x_i^*}{p}$$

$$s^* = 1.134\sqrt{\sum \left(x_i^* - x^*\right)^2/(p-1)}$$

where the summation is over i.

The robust estimates x^* and s^* may be derived by an interactive calculation, i.e. by updating the values of x^* and s^* several times using the modified data, until the process converges.

The *z*-score is calculated as:

$$z_i = (x_i - x^*)/s^*$$

When the participant reports a result that gives rise to a *z*-score above 3.0 or below –3.0, then the result shall be considered to give an "action signal". Likewise, a *z*-score above 2.0 or below –2.0, shall be considered to give a "warning signal".

5. Results

5.1. Participation

The number of laboratories participating in the assessment was half of those invited, as shown in Table 1.

Geographical coverage in all UN regions was attained (Figure 3 and Table 2). In the GRULAC region the Basel Convention-Stockholm Convention Regional Centre for Latin America and the Caribbean (SBCRC) hosted by the technological Laboratory of Uruguay (LATU) invited and financed an additional set of 11 laboratories throughout the GEF/UNEP projects: Minamata Initial Assessments (MIAs, GEF ID 5879) and Mercury Risk Management Approaches (GEF ID 5494).

Table 1 - Summary of changes in number of laboratories per stage of the assessment

Category	N laboratories	N countries
Laboratories in the UN Environment databank - background	210	62
Laboratories invited	82	50
Laboratories registered	42	30
Laboratories receiving samples	39	28
Laboratories delivering results	38	28

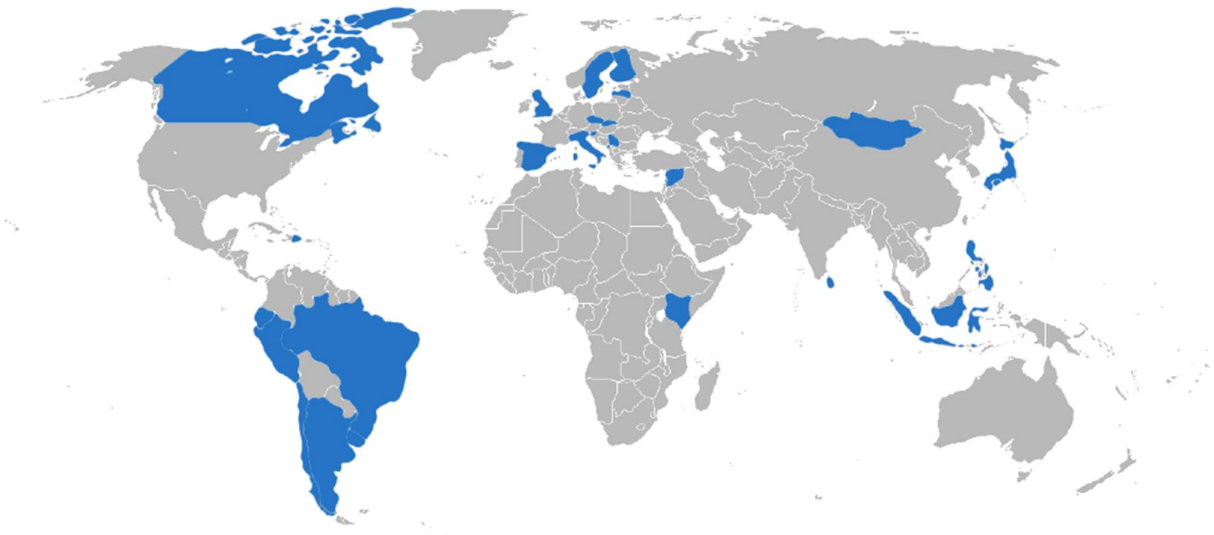

Figure 3 - Geographical distribution of laboratories delivering results in the Global Assessment of Laboratories Analysing Mercury

Table 2 Summary of countries by regions involved in the assessment (delivering results)

UN Region	Number of laboratories registered	Number of countries
Africa	1	1
Asia	7	7
CEE	6	6
GRULAC	15* (6 UNEP + 9 LATU)	8
WEOG	9	7

* detail of laboratories invited and funded thought the Global Mercury Monitoring Project (UNEP) and the through the GEF-UNEP- SBCRC-Uruguay (LATU) projects.

Table 3 Summary of Laboratories by UN regions invited to participate in the assessment

UN Region	Number of laboratories invited	Number of countries
Africa	5	5
Asia	13	12
CEE	14	12
GRULAC	18+11	15
WEOG	21	15

Differences (drop outs) between laboratories invited and those registered and delivering results is shown in tables 3 and 2 respectively. The largest drop-outs are shown in the Africa region (80%), followed by WEOG and CEE regions (almost 60%), and then by Asia and GRULAC, where it is about 50%.

As shown in the table 1, there is no major difference between the last two rows. Undelivered shipment was caused in two cases out of three by obstacles at the customs of the receiving country and in one case the laboratory registered for the assessment stopped communicating.

5.2. Results - Data analyses

General overview

No matrix was compulsory in this pilot laboratory assessment, therefore there was no full participation of registered laboratories regarding individual matrices. There were 26 out of 38 laboratories (68%) who analysed all three matrices and 19 of them (73%) did deliver satisfactory z-score[1] in all three matrices. There was only one laboratory, among the laboratories that analyses all three matrices, that did not succeed to receive a satisfactory result in any of the test samples (Table 5).

Moreover, there were five laboratories that registered for analyses two matrices (13.1%), and 7 laboratories only analysed one matrix (18.4%) - predominantly a standard solution - and five delivered satisfactory results and one provided unsatisfactory data (Table 5).

Almost 90% of all laboratories took part in analyses of the standard solution and 80% presented satisfactory z-scores (Table 6). Lower amount, 84% of all laboratories analysed biota sample (fish) and almost 85% showed satisfactory z-scores (Table 7). 73.7% laboratories analysed human scalp hair and there were 82% of satisfactory z-scores (Table 8).

Table 4 - Results received per matrix

	Number of laboratories delivering data	Share of laboratories delivering data from the total	Percentage of satisfactory z-scores > -2 and < +2
standard solution	34	89,4 %	79.4 %
fish sample	32	84,2 %	84.4 %
human scalp hair	28	73,7 %	82.1 %

Full set of all reported results (mercury concentrations in µg/litre and µg/g) is provided in Table 5 below for all laboratories delivering results. And, as shown in figures 4-7, results of the assessment are also expressed as z-scores in individual matrices and individual conclusions are drawn relevant sections.

Overview discussion of methods used for analysing mercury

There were six methods employed for analysing samples. In general, participating laboratories rather used a single method to analyse different matrices, but there were three laboratories that reported mercury levels determined by two different methods (for different matrices).

16 laboratories from four regions (but not from WEOG) used CV-AAS[2] method for determining mercury concentrations in three matrices. CV-AFS method was used by three laboratories (WEOG region only) for all three matrices. TD-GA-AAS was used by 16 laboratories from four regions in all three matrices and ICP-MS was employed by five laboratories from three regions. TD-AAS and XRF methods were used by one laboratory (different one for each method) from all laboratories participating in the assessment. CV-AFS (employed by 3 laboratories), TD-AAS (1 laboratory) and

[1] Were considered satisfactory z-scores if the z-scores were in the interval > -2 and < +2, questionable results between -3 and -2 or +2 and +3, and unsatisfactory results < -3 and > +3.

[2] For the full name please go to section 4.2. Methods – Chemical analyses.

TD-GA-AAS (16 laboratories) provided satisfactory results (expressed as z-score terminology) in 100%, 100%, and 98% of uses respectively.

Table 5 - Comparison of all results of mercury concentrations analysed in test samples by individual laboratories (mercury concentrations in µg/l or µg/g)

Code of the laboratory	Results of mercury analyses		
	standard solution (µg/l)	human scalp hair (µg/g)	biota/fish sample (µg/g)
9	50		
153	23	0.35	0.65
132	16.45	0.33	0.59
36	16	0.293	0.507
6	19	0.24	0.51
167	20.7	0.315	0.565
115	50.5	0.5	0.97
207			0.773
79	19.6	0.355	0.605
143	16		
37	15.5	0.289	0.536
23	17.1	0.366	0.55
44	15.3	0.279	0.531
158	18.1	0.348	0.276
14	17.2	0.311	0.589
5	16.7	0.33	0.596
46		0.3486	0.658
86	15.4		
121	17.07	0.331	0.616
110	9.66	1.01	0.64
61	34.12	0.99	0.79
111	17.5		
7	15.3	0.778	0.394
3	17.5	0.342	0.605
4		1.03	0.36
185	<LOD		0.476
112	14.9	0.263	0.5

Code of the laboratory	Results of mercury analyses		
	standard solution (µg/l)	human scalp hair (µg/g)	biota/fish sample (µg/g)
8	31.29	0.33	0.61
181	17		0.65
130	16.36	0.316	0.585
94	20.76	0.42	0.74
159	20.15		
148	9.39	0.386	0.711
95	20.1	0.38	0.66
194	18	0.38	0.69
24	17.84		
195	17	0.319	0.589
35	23.9		0.633

The colours shown in the table 5 provide a quick overview on the compliance with the desired z-scores: interval -2 and +2, blue colour - satisfactory result; z-score between -3 and -2 or +2 and +3, orange - questionable results; and with z-score either lower than -3 or higher than +3, red colour- unsatisfactory results.

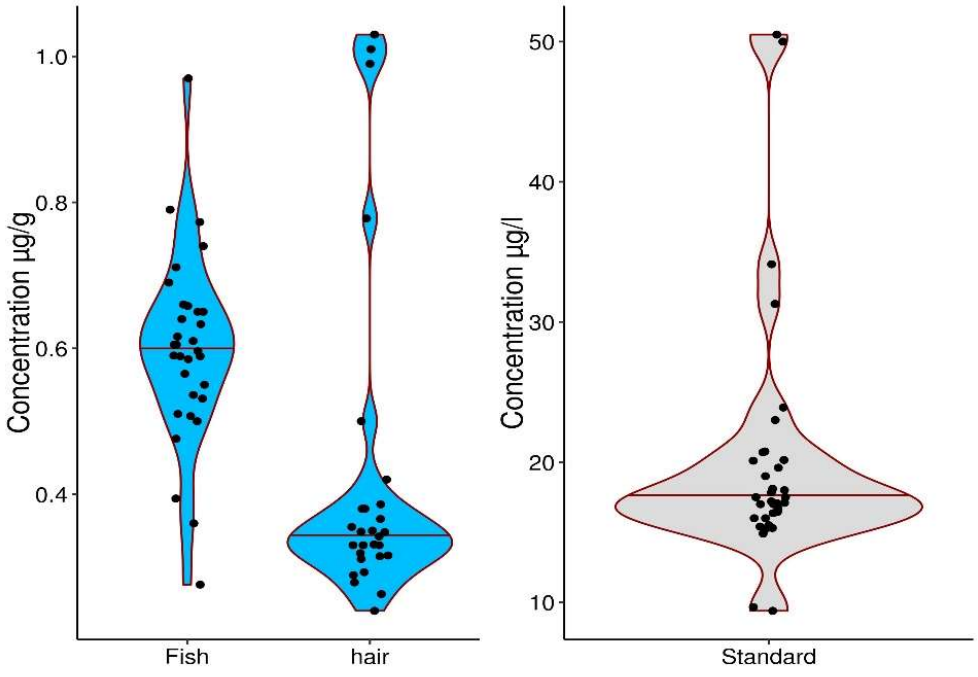

Figure 4 Violin plot showing the probability density of all results (black dots) of mercury concentrations analysed in test samples, the line in the middle represent the median value of the data.

Results for standard solution

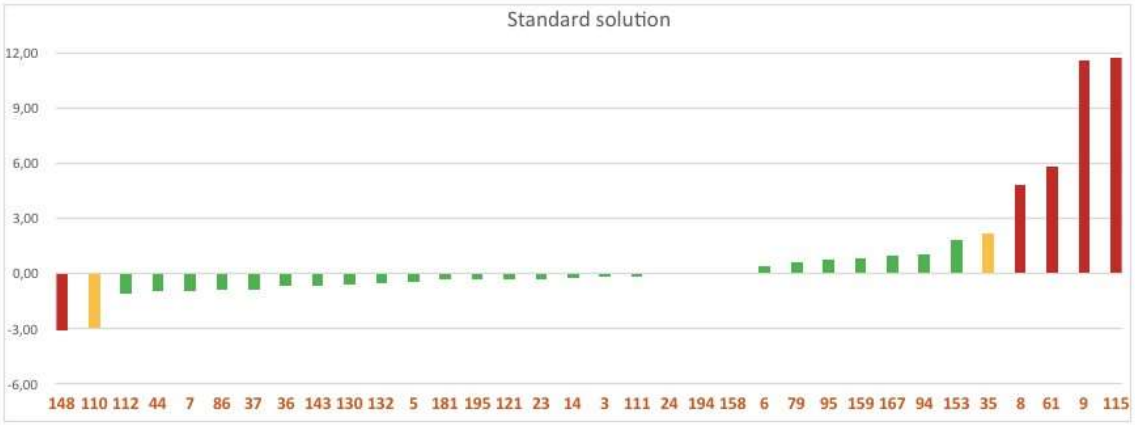

Figure 5 Results delivered for standard solution test sample expressed in z-scores for individual laboratories identified by laboratory codes.

For the standard solution, the results were delivered by 35 laboratories. One laboratory reported too high limit of detection LOD = 35 µg/L (analytical method CV-AAS) and therefore its result is not shown in Figure 5 nor it is used in the calculations as it was impossible to calculate the relevant z-score.

On the basis of the robust analysis, robust average mercury concentration is x^* = 17.93 µg/l and robust standard deviation s^* = 2.77. A more detailed overview of results including test method used for chemical analyses is provided in Table 6 below.

The following four analytical methods were employed for determination of the standard solution. Number of laboratories using the method is in parentheses:

CV-AAS	Cold Vapor Atomic Absorption Spectrometry (14 laboratories: 12 satisfactory, 2 unsatisfactory)
CV-AFS	Cold Vapor Atomic Fluorescence Spectrometry (3 laboratories: 3 satisfactory)
ICP-MS	Inductively Coupled Plasma Mass Spectrometry (5 laboratories: 1 satisfactory, 2 questionable, 2 unsatisfactory)
TD-GA-AAS	Thermal Desorption Atomic Absorption Spectrometry with Gold Amalgamation (12 laboratories: 11 satisfactory, 1 unsatisfactory)

Table 6 Results overview for standard solution test samples expressed in z-scores and reported mercury concentrations (µg/l).

Laboratory code	Analytical method used	Calculated z-score z_i	Reported concentration value x_i (µg/l)
148	ICP-MS	-3.08	9.39
110	ICP-MS	-2.99	9.66
112	CV-AAS	-1.09	14.9
44	TD-GA-AAS	-0.95	15.3
7	CV-AAS	-0.95	15.3
86	CV-AAS	-0.91	15.4
37	TD-GA-AAS	-0.88	15.5
36	ICP-MS	-0.70	16
143	CV-AAS	-0.70	16
130	CV-AFS	-0.57	16.36
132	TD-GA-AAS	-0.53	16.45
5	TD-GA-AAS	-0.44	16.7
181	CV-AAS	-0.34	17
195	CV-AFS	-0.34	17
121	CV-AAS	-0.31	17.07
23	TD-GA-AAS	-0.30	17.1
14	CV-AAS	-0.26	17.2
3	TD-GA-AAS	-0.16	17.5
111	CV-AAS	-0.16	17.5
24	TD-GA-AAS	-0.03	17.84
194	TD-GA-AAS	0.03	18
158	CV-AAS	0.06	18.1
6	CV-AAS	0.39	19
79	TD-GA-AAS	0.60	19.6
95	TD-GA-AAS	0.78	20.1
159	CV-AFS	0.80	20.15
167	CV-AAS	1.00	20.7
94	TD-GA-AAS	1.02	20.76
153	CV-AAS	1.83	23

Laboratory code	Analytical method used	Calculated z-score z_i	Reported concentration value x_i (µg/g)
35	ICP-MS	2.16	23.9
8	TD-GA-AAS	4.82	31.29
61	CV-AAS	5.84	34.12
9	CV-AAS	11.58	50
115	ICP-MS	11.76	50.5

The colours shown in the table 5 provide a quick overview on the compliance with the desired z-scores: interval -2 +2, blue colour - satisfactory result; z-score between -3 and -2 or +2 and +3, orange - questionable results; and with z-score either lower than -3 or higher than +3, red colour-unsatisfactory results.

Results for biota (fish) test sample

Results received for biota (fish) test sample are provided in Figure 6 and Table 7.

For fish samples, the results were delivered by 32 laboratories. On the basis of the robust analysis, robust average mercury concentration is $x^* = 0.600$ µg/g and robust standard deviation $s^* = 0.093$. A more detailed overview of results including test method used for chemical analyses is provided in Table 7 below.

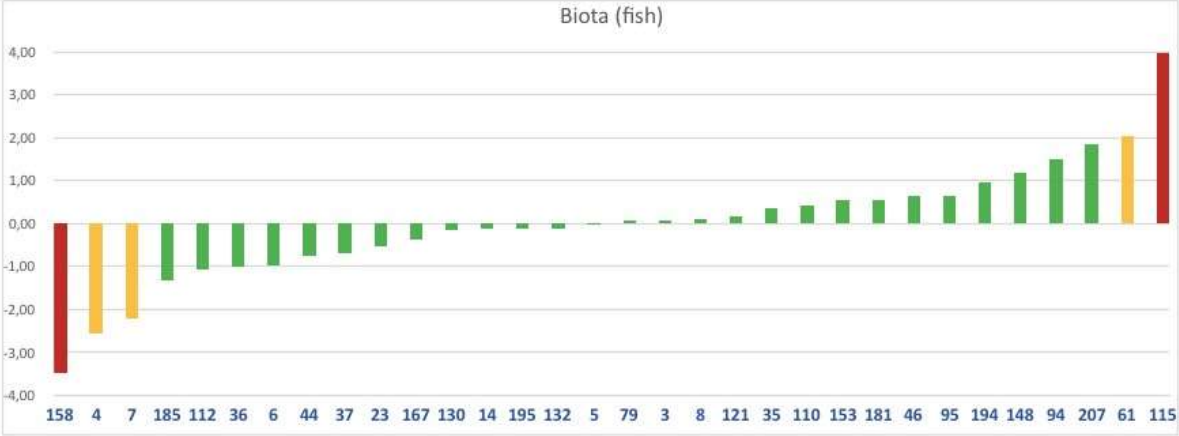

Figure 6 Results delivered for biota (fish) test sample expressed in z-scores for individual laboratories shown via laboratory codes.

The following six analytical methods were employed for determination of the biota (fish) test sample F. Number of laboratories using the method is in parentheses:

CV-AAS	Cold Vapor Atomic Absorption Spectrometry (9 laboratories: 6 satisfactory, 2 questionable, 1 unsatisfactory)
CV-AFS	Cold Vapor Atomic Fluorescence Spectrometry (2 laboratories: 2 satisfactory)
ICP-MS	Inductively Coupled Plasma Mass Spectrometry (4 laboratories: 3 satisfactory, 1 unsatisfactory)
TD-AAS	Thermal Desorption Atomic Absorption Spectrometry (1 laboratory: 1 satisfactory)
TD-GA-AAS	Thermal Desorption Atomic Absorption Spectrometry with Gold Amalgamation (15 laboratories: 15 satisfactory)
XRF	X-Ray Fluorescence (1 laboratory: 1 questionable)

Table 7 Results overview for biota (fish) test sample expressed in z-score and reported mercury concentrations (µg/g).

Laboratory code	Analytical method used	Calculated z-score z_i	Reported concentration value x_i (µg/g)
158	CV-AAS	-3.60	0.276
4	XRF	-2.67	0.36
7	CV-AAS	-2.29	0.394
185	CV-AAS	-1.38	0.476
112	CV-AAS	-1.11	0.5
36	ICP-MS	-1.03	0.507
6	TD-AAS	-1.00	0.51
44	TD-GA-AAS	-0.77	0.531
37	TD-GA-AAS	-0.71	0.536
23	TD-GA-AAS	-0.56	0.55
167	TD-GA-AAS	-0.39	0.565
130	CV-AFS	-0.17	0.585
14	CV-AAS	-0.12	0.589
195	CV-AFS	-0.12	0.589
132	TD-GA-AAS	-0.11	0.59
5	TD-GA-AAS	-0.04	0.596
79	TD-GA-AAS	0.06	0.605
3	TD-GA-AAS	0.06	0.605
8	TD-GA-AAS	0.11	0.61
121	CV-AAS	0.18	0.616
35	ICP-MS	0.37	0.633
110	ICP-MS	0.44	0.64
153	TD-GA-AAS	0.56	0.65
181	CV-AAS	0.56	0.65
46	TD-GA-AAS	0.64	0.658
95	TD-GA-AAS	0.67	0.66
194	TD-GA-AAS	1.00	0.69
148	TD-GA-AAS	1.23	0.711
94	TD-GA-AAS	1.56	0.74

Laboratory code	Analytical method used	Calculated z-score z_i	Reported concentration value x_i (µg/g)
207	CV-AAS	1.92	0.773
61	CV-AAS	2.11	0.79
115	ICP-MS	4.11	0.97

The colours shown in the table 5 provide a quick overview on the compliance with the desired z-scores: interval -2 +2, blue colour - satisfactory result; z-score between -3 and -2 or +2 and +3, orange - questionable results; and with z-score either lower than -3 or higher than +3, red colour-unsatisfactory results.

Results for human scalp hair test sample

Results received for human scalp hair test samples are provided in Figure 7 and Table 8.

For test samples, the results were delivered by 28 laboratories. On the basis of the robust analysis, robust average mercury concentration is $x^* = 0.349$ µg/g and robust standard deviation $s^* = 0.056$. A more detailed overview of results including test method used for chemical analyses is provided in Table 8 below.

Figure 7 Results delivered for human scalp hair test sample expressed in z-scores for individual laboratories shown via laboratory codes.

The following six analytical methods were employed for determination of the human scalp hair test sample H. Number of laboratories using the method is in parentheses:

CV-AAS	Cold Vapor Atomic Absorption Spectrometry (9 laboratories: 7 satisfactory, 2 unsatisfactory)
CV-AFS	Cold Vapor Atomic Fluorescence Spectrometry (2 laboratories: 2 satisfactory)
ICP-MS	Inductively Coupled Plasma Mass Spectrometry (4 laboratories: 2 satisfactory, 1 questionable, 1 unsatisfactory)
TD-AAS	Thermal Desorption Atomic Absorption Spectrometry (1 laboratory: 1 satisfactory)
TD-GA-AAS	Thermal Desorption Atomic Absorption Spectrometry with Gold Amalgamation (15 laboratories: 15 satisfactory)
XRF	X-Ray Fluorescence (1 laboratory: 1 unsatisfactory)

Table 8 Results overview for human scalp hair test sample expressed in z-score and reported mercury concentrations (µg/g).

Laboratory code	Analytical method used	Calculated z-score z_i	Reported concentration value x_i (µg/g)
6	TD-AAS	-1.94	0.24
112	CV-AAS	-1.53	0.263
44	TD-GA-AAS	-1.24	0.279
37	TD-GA-AAS	-1.07	0.289
36	ICP-MS	-0.99	0.293
14	CV-AAS	-0.67	0.311
167	TD-GA-AAS	-0.60	0.315
130	CV-AFS	-0.58	0.316
195	CV-AFS	-0.53	0.319
132	TD-GA-AAS	-0.33	0.33
5	TD-GA-AAS	-0.33	0.33
8	TD-GA-AAS	-0.33	0.33
121	CV-AAS	-0.32	0.331
3	TD-GA-AAS	-0.12	0.342
158	CV-AAS	-0.01	0.348
46	TD-GA-AAS	0.00	0.3486
153	TD-GA-AAS	0.02	0.35
79	TD-GA-AAS	0.11	0.355
23	TD-GA-AAS	0.31	0.366
194	TD-GA-AAS	0.56	0.38
95	TD-GA-AAS	0.56	0.38
148	TD-GA-AAS	0.67	0.386
94	TD-GA-AAS	1.27	0.42
115	ICP-MS	2.70	0.5
7	CV-AAS	7.67	0.778
61	CV-AAS	11.45	0.99
110	ICP-MS	11.81	1.01
4	XRF	12.17	1.03

The colours shown in the table 8 provide a quick overview on the compliance with the desired z-scores (interval -2 +2, blue colour - satisfactory result, questionable results (orange, z-score between -3 and -2 or +2 and +3) and unsatisfactory results (red) with z-score either lower than -3 or higher than +3.

6. Conclusions

The pilot Global Assessment of Laboratories Analysing Mercury was organized in summer 2018 (August-October) as a first round of the global proficiency test. Participation was by invitation only and invitees were selected from the Mercury Laboratory Databank organized by UN Environment, Chemicals and Health Branch. There were 80 laboratories invited, 42 laboratories from 29 countries had registered for the global assessment and 38 laboratories from 28 countries worldwide delivered results.

Test materials for total mercury analyses used included three matrices: (i) test solution of analytical standards and (ii) naturally contaminated samples of biota: (a) fish samples, and (b) human scalp hair samples.

Total mercury was analysed in all test samples and results provided by laboratories are shown in this report. No matrix was compulsory in this pilot laboratory assessment, therefore there was no full participation in analyses of individual matrices. Almost 90% of all laboratories analysed the standard solution and 80% of the delivered results presented satisfactory z-score. Lower amount, 84% of all laboratories analysed biota sample (fish) and almost 85% were with satisfactory z-scores outcome. 73.7% laboratories analysed human scalp hair and there were 82% of satisfactory z-scores outcome.

In addition, there were 26 out of 38 laboratories (68%) who analysed all three matrices and 19 of them (73%) did deliver satisfactory z score in all three test matrices.

Moreover, there were five laboratories that registered for analyses of two matrices (13.1%) and delivered satisfactory z-scores results for fish sample and 7 laboratories who only analysed one matrix (18.4%) - predominantly a standard solution - with five delivering satisfactory z-scores results and one provided unsatisfactory z-score.

It is quite encouraging to see a good agreement of reported data with reference values for the individual test samples provided by both developed and developing countries.

Regarding instrumentation used, there were six methods of analyses. Most laboratories used a single method to analyse different matrices, but there were three laboratories that reported mercury levels determined by two different methods (for different matrices). Most frequently used methods were CV-AAS (16 laboratories) and TD-GA-AAS (16 laboratories). On the other hand, TD-AAS and XRF methods were employed only by one laboratory from all participating (a different laboratory for each method). CV-AFS, TD-AAS and TD-GA-AAS provided satisfactory results in 100%, 100% and 98% and of uses.

Results of this pilot assessment serve as information background for stakeholders, including governments, seeking to identify laboratories capable of identifying mercury in relevant matrices for the Minamata Convention on Mercury, provide state of the art information regarding the worldwide capacity of laboratories to analyse mercury and also assess the effectiveness of Quality Assurance/Quality Control (QA/QC) practices in place in individual laboratories.

7. References

Cofino, W.P., Wells,D. E., Ariese, F., van Stokkum, I. H. M., Wegener, J.-W., Peerboom R.J.(2000). Chemometrics and Intelligent Laboratory Systems,53, 37-55.

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Annex I:

Call for expression of Interest to Participate in the Global Assessment of Laboratories Analysing Mercury First Round, 2018

UN Environment is inviting selected laboratories, who have pre-indicated their interest and are registered in the UN Environment Mercury Laboratory Databank, to confirm their interested in participating in a Global Pilot Assessment of Laboratories Analysing Mercury.

In late 2016, the UN Environment Chemicals and Health Branch, within the framework of the project "Development of a plan for Global Monitoring of Human exposure to and Environmental Concentration of Mercury", funded by the Global Environment Facility, developed a Mercury Laboratory Databank[1] comprising laboratories that analyse mercury around the globe. As a next step, UN Environment, is launching a Global Assessment of Laboratories Analysing Mercury. This activity is a global pilot assessment to evaluate capacity in the UN Regions to undertake analysis of mercury and it is an important component of the capacity building programme of UN Environment for laboratories in developing countries and in countries with economy in transition.

Results of this pilot assessment aims at providing information to stakeholders, including governments, seeking to better understand worldwide capacities to analyse mercury. The aggregated results will be presented to the Second Conference of the Parties to the Minamata Convention on Mercury, taking place from 19 to 23 November 2018 at the International Conference Centre in Geneva, Switzerland.

The assessment will also provide state of the art information with regard to the worldwide capacity of laboratories to analyse mercury, and would assess the effectiveness of Quality Assurance/Quality Control (QA/QC) practices, providing a measure of interlaboratory comparability.

The technical coordination and assessment will be performed by the Research Centre for Toxic Compounds in the Environment (RECETOX), Faculty of Science, Masaryk University, Brno, Czech Republic acting as the Stockholm Convention Regional Centre in the Czech Republic.

Laboratories interested in participating are invited to register by filling in the form attached to this note.

Key dates:

- **Registration is open until 10 August 2018.**
- **Confirmation of participation and verification of shipment address is required before 16 August 2018.**
- **Distribution of samples will be done from 10-31 August 2018.**
- **Results of the analyses from participating laboratories are expected from 15 to 30 of September.**

Note: Participation in the assessment is by invitation only. All laboratories invited to the assessment located in developing countries or countries with economies in transitions can participate in this global assessment free-of-charge. This include the test materials, shipment costs, provision of results and data evaluation. Developed countries participation fee is 650 USD per laboratory. This fee covers test materials and shipment costs, the provision of results and data evaluation are free-of-charge.

[1] The Laboratory Databank is work in progress, please use the following link for the beta version: http://informea.pops.int/HgPOPsLabs/index.html

Test materials will include (i) test solutions of analytical standards and (ii) naturally contaminated samples: (a) biota samples, and (b) Human Hair samples. Total mercury will be analysed in test samples.

Global Pilot Assessment of Laboratories Analysing Mercury, First Round 2018

Registration form

To express your interest, kindly fill in the form below and return it to: boruvkova@recetox.muni.cz, sebkova@recetox.muni.cz and to science.chemicals@un.org

Laboratory information

Name of Laboratory:			
Contact	Name		
	E-mail:		
	Telephone:		
Address (for shipment)			
Street No.			
City		ZIP	
Country:			

Test Samples

My laboratory is interested in analysing the following matrices and provide the analytical results for total mercury content according to the reporting scheme and timetable identified (latest submission of results on **30 September 2018, MS Excel template**). Please mark "X" into the cells below if you wish to analyse this test sample:

Standard solution	Hair	Biota

Contacts for technical matters:

Dr. Jana Boruvkova, RECETOX, Faculty of Science, Masaryk University, Brno, Czech Republic, e-mail: boruvkova@recetox.muni.cz
Dr. Rostislav Červenka, RECETOX, Faculty of Science, Masaryk University, Brno, Czech Republic, e-mail: cervenka@recetox.muni.cz