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# ASSESSMENT OF RESULTS FOR THE 2ND INTERLABORATORY STUDY OF POPS LABORATORIES

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## Introduction

The results of the UNEP-coordinated 2nd interlaboratory assessment of laboratories analyzing persistent organic pollutants (POPs) have been presented at Dioxin2014 [1, 2]with the following main findings: For this second round of the interlaboratory assessment, 105 laboratories had registered and 89 delivered results for at least one POP and one test sample. Besides the 12 groups of initial POPs, ten newly listed POPs – through decisions of the Conference of the Parties in 2009 and 2011 - and "new" matrices such as air extract, water and human serum were included. Whereas for the analysis for the initial POPs covered by the Stockholm Convention, including dioxin-like POPs (dl-POPs), polychlorinated biphenyls (PCB) and organochlorine pesticides (OCPs), the improvement in performance was not as expected. Results for the PCDD/PCDF on a TEQ basis were good and within the UNEP criteria of 2 z-scores for the standard solution, the air extract and the sediment. Results for the fish sample were unsatisfactory for both the PCDD/PCDF and dl-PCB, both on TEQ basis. The results for the dl-POP for the milk sample were promising but still not within the UNEP criteria. The results for the new POPs – polybrominated diphenyl ethers (PBDE) and per-/polyfluorinated alkyl substances (PFAS) - were promising. However, it was noted that the capacity to analyze these POPs is located in the Asia-Pacific and WEOG (Western European and Other Groups) regions. The results for the PBDE were good for the standard solution (CV 31%), the air extract (CV 31%) and the sediment samples (CV 23%), and promising for the milk sample (CV 38%). The results for the fish sample were less impressive (CV 51%). The results were good for certain PFAS compounds, including perfluorooctanoic sulfonate (PFOS), but only a limited number of results were submitted for other PFAS compounds, including the precursor compounds such as N-ethyl and N-methyl sulfonamides (FOSAs) and sulfonamidoethanols (FOSEs) or PFAS of longer or shorter carbon chains. For the analysis of the group of PFAS compounds, LC/MS/MS is needed which at the moment only seems to be available in developed countries in the WEOG region and in Asia. The full report for this second bi-ennial interlaboratory assessment (IL) is available from the UNEP Website [3]. Here we assess the results in a comprehensive manner for the broader groups of POPs, test samples and on laboratory basis in terms of capacity and coverage.

## Materials and Methods

The performance of the participating laboratories followed recommendations according to ISO 17043 and z-scores have been assigned for each of the POPs (congeners or isomers) as well as for sum parameters such as toxic equivalents (TEQs) for the dioxin-like POPs or the sum of the six indicator polychlorinated biphenyls (PCB) according to the Cofino model [4].

In the 2nd round of the interlaboratory assessment, laboratories were tasked to analyze and report results for the groups of POPs that are listed in the annexes of the Stockholm Convention and the transformation products that are recommended for analysis (see chapter 2 of the guidance document for the Global Monitoring Plan of POPs [5]).

The performance was grouped as follows:

$|z| < 2$ Satisfactory performance S

$2 < |z| < 3$ Questionable performance Q

$|z| > 3$ Unsatisfactory performance U

## Results and Discussion

Table 1 shows that through the provision of test samples (standard solutions, sediment, sediment, air, water, human milk and human serum; transformer oil included to address a POPs waste issue – PCB in transformer oils - under the Stockholm Convention) and analytes to be reported, theoretically 438 z-scores should have been resulted. However, for some of the analytes in combination with their test sample

matrix, no consensus value could be calculated and therefore, no z-score assigned, so that effectively 381 z-scores could be assigned to the 89 laboratories. Only within the OCPs, z-scores could be assigned for all analytes/test samples. For the ndl-PCB three z-scores could not be provided and for the dl-POPs, PBDE/PBB and PFAS the respective numbers were 32, 5 and 17, respectively.
One of the outcomes of this interlaboratory assessment is that no laboratory did report results for all of the POPs analytes and all of the test samples (see Table 5, Table 6, Table 2). Rather the laboratories were specialized on certain groups of POPs (often OCPs and non-dioxin-like PCB (ndl-PCB) vs. dl-POPs - whereby ndl-PCB were analysed in both, basic POPs laboratories or dioxin laboratories - and either biotic samples (fish, human milk) or abiotic samples (sediment, air). Since for human serum and water, only PFAS compounds were recommended and their analysis requires LC/MS-MS techniques, these laboratories form an own group.
Table 5 shows how the 381 z-scores are distributed among the groups of POPS and test samples. The majority of the z-scores can be found for dl-POPs (38% of total) but within the test samples, fewest are for the fish matrix where only 9 z-scores could be assigned (the maximum per matrix would be 35 with 19 for PCDD/PCDF, 14 for dl-PCB – including the TEQ for upper-bound (UB) and lower-bound (LB) values - and 2 for the total TEQ). For the ndl-PCB, the full number of z-scores (6 for the six congeners and in addition for the sum of the six with UB and LB) could be achieved for all test samples but the air extract.
As can be seen from Table 6, three laboratories from 61 reported results for all of the dl-POPs (corresponding to 5% of total) and two laboratories from 44 reported results for all of the PBDE and PBB-153 (5%). Further, it can be seen that even for the individual test matrices, no laboratory has reported results for all OCPs. The picture is different for the other POPs, e.g., for the ndl-PCB it seems to be common practice that laboratories analyse (and report) the six indicator PCB congeners (28, 52, 101, 138, 153, and 180) so that between 68% and 80% of the laboratories report 100% of the data. Also for dl-POPs, the matrix-specific coverage is high (between 55% and 79%); however, only 20% of the labs reported all dl-congeners in human milk. For water, all laboratories reported results for the PFOS.
In summary, the Asia-Pacific region had 42 laboratories reporting results, followed by the Group of Western Europe and Others (WEOG) with 27 laboratories. The Asia-Pacific laboratories contributed 52% or 3,691 of the satisfactory performance results, followed by WEOG laboratories, which had 2,752 satisfactory performance results (corresponding to 39% of the total) (Tale 4).

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Table 1: Summary of effective z-scores and theoretically available z-scores

| Number of z-scores | Total in IL2 | Effective in IL2 | % assigned |
|---|---|---|---|
| OCPs | 110 | 110 | 100% |
| ndl-PCB | 48 | 45 | 94% |
| dl-POPs | 175 | 143 | 82% |
| PBDE/PBB | 50 | 45 | 90% |
| PFAS | 55 | 38 | 69% |
| Total | 438 | 381 | 87% |

Table 2: Number of z-scores assigned to ndl-PCB or PFAS and test sample types that are specific to these groups of POPs (NA = not applicable)

| | Transformer oil | | Human serum | | Water | |
|---|---|---|---|---|---|---|
| | z-scores assigned | | z-scores assigned | | z-scores assigned | |
| | No. | % of total | No. | % of total | No. | % of total |
| ndl-PCB | 8 | 18% | NA | NA | NA | NA |
| PFAS | NA | NA | 11 | 29% | 1 | 5% |
| Total | 8 | 2% | 11 | 3% | 1 | 0.3% |

Table 3: Number of laboratories reporting results for ndl-PCB or PFAS and their associated test sample types (NA = not applicable)

| | Transformer oil | | | | Human serum | | | | Water | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Labs with data | | Labs with 100% data | | Labs with data | | Labs with 100% data | | Labs with data | | Labs with 100% data | |
| | No. | % | No. | % | No. | % | No. | % | No. | % | No. | % |
| ndl-PCB | 19 | 31% | 14 | 74% | NA | NA | NA | NA | NA | NA | NA | NA |
| PFAS | NA | NA | NA | NA | 9 | 33% | 4 | 44% | 20 | 74% | 20 | 100% |

Table 4: Distribution of laboratories across regions and performance

| Region | No of Labs | Sum of S (%) | Sum of Q | Sum of U |
|---|---|---|---|---|
| Africa | 6 | 20 (0.3%) | 17 | 109 |
| Asia-Pacific | 42 | 3,691 (52%) | 474 | 878 |
| Central and Eastern Europe | 4 | 296 (4.2%) | 57 | 89 |
| Latin America and Caribbean | 10 | 287 (4.1%) | 60 | 164 |
| Western Europe and Others | 27 | 2,752 (39%) | 420 | 535 |
| **Total** | **89** | **7,046** | **1,028** | **1,775** |

Table 5: Number of z-scores assigned to groups of POPs analytes and test sample types

| | All | | Standard solution | | Sediment | | Fish | | Human milk | | Air | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | z-scores assigned | | z-scores assigned | | z-scores assigned | | z-scores assigned | | z-scores assigned | | z-scores assigned | |
| | No. | % of total | No. | % of total | No. | % of total | No. | % of total | No. | % of total | No. | % of total |
| OCPs | 110 | 29% | 31 | 28% | 15 | 14% | 19 | 17% | 15 | 14% | 30 | 27% |
| ndl-PCB | 45 | 12% | 8 | 18% | 8 | 18% | 8 | 18% | 8 | 18% | 5 | 11% |
| dl-POPs | 143 | 38% | 35 | 24% | 34 | 24% | 9 | 6% | 31 | 22% | 34 | 24% |
| PBDE+PBB | 45 | 12% | 10 | 22% | 10 | 22% | 9 | 20% | 7 | 16% | 9 | 20% |
| PFAS | 38 | 10% | 19 | 50% | 2 | 5% | 2 | 5% | 1 | 3% | 2 | 5% |
| **Total** | **381** | **100%** | **103** | **27%** | **69** | **18%** | **47** | **12%** | **62** | **16%** | **80** | **21%** |

Table 6: Number of laboratories reporting results according to groups of POPs analytes and test sample types

| | All | | | | Standard solution | | | | Sediment | | | | Fish | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Labs with data | | Labs with 100% data | | Labs with data | | Labs with 100% data | | Labs with data | | Labs with 100% data | | Labs with data | | Labs with 100% data | |
| | No. | % | No. | % | No. | % | No. | % | No. | % | No. | % | No. | % | No. | % |
| OCPs | 55 | 100% | 0 | 0% | 52 | 95% | 3 | 6% | 37 | 67% | 4 | 11% | 38 | 69% | 3 | 8% |
| ndl-PCB | 61 | 100% | 0 | 0% | 53 | 87% | 36 | 68% | 40 | 66% | 30 | 75% | 44 | 72% | 35 | 80% |
| dl-POPs | 61 | 100% | 3 | 5% | 53 | 87% | 39 | 74% | 40 | 66% | 22 | 55% | 42 | 69% | 33 | 79% |
| PBDE+PBB | 44 | 100% | 2 | 5% | 42 | 95% | 8 | 19% | 30 | 68% | 6 | 20% | 33 | 75% | 6 | 18% |
| PFAS | 27 | 100% | 0 | 0% | 22 | 81% | 2 | 9% | 18 | 67% | 10 | 56% | 19 | 70% | 13 | 68% |

Table 6 cont´d.

| | Human milk | | | | Air | | | |
|---|---|---|---|---|---|---|---|---|
| | Labs with data | | Labs with 100% data | | Labs with data | | Labs with 100% data | |
| | No. | % | No. | % | No. | % | No. | % |
| OCPs | 23 | 42% | 3 | 13% | 27 | 49% | 0 | 0% |
| ndl-PCB | 28 | 46% | 20 | 71% | 28 | 46% | 20 | 71% |
| dl-POPs | 30 | 49% | 6 | 20% | 40 | 66% | 22 | 55% |
| PBDE+PBB | 23 | 52% | 13 | 57% | 21 | 48% | 13 | 62% |
| PFAS | 8 | 30% | 8 | 100% | 9 | 33% | 6 | 67% |