

Bi-ennial Global Interlaboratory Assessment on Persistent Organic Pollutants – Third Round 2016/2017, Dioxin-like POPs and Perfluorinated Alkyl Substances

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Introduction

For the third time, the University of Örebro and the Free University Amsterdam organized the Bi-ennial Global Interlaboratory Assessment on Persistent Organic Pollutants (POPs) as part of the UN Environment Programme's capacity building projects. These international proficiency tests have been recommended as a tool to assess the performance of POPs laboratories at international level. Regular participation in such assessments is recommended in the guidance document for the Global Monitoring Plan on POPs under article 16 of the Stockholm Convention on Persistent Organic Pollutants [1]. After an initial test in 2006/2007 comprising seven laboratories from the African, Asia-Pacific, Central and Eastern European and Latin-American/Caribbean regions [2], the first round was implemented in 2010/2011 and had the initial twelve POPs to be analyzed in test solutions of POPs standards and naturally contaminated test samples; 83 laboratories participated [3,4,5]. The second round – organized in 2012/2013 - had 89 laboratories participating and included the POPs listed by the Conference of the parties to the Stockholm Convention in 2009 such as polybrominated flame retardants and perfluorinated alkyl substances (PFAS) [6]. In this third round (2016), 175 laboratories registered and 133 delivered results for at least one group of POPs in one of the test samples. The results for the organochlorine pesticides, indicator PCB, and polybrominated flame retardants are reported by van der Veen *et al.* [7]. This paper gives an overview of the results for dioxin-like POPs, *i.e.*, polychlorinated dibenzo-*p*-dioxins (PCDD), polychlorinated dibenzofurans (PCDF) and dioxin-like polychlorinated biphenyls (dl-PCB) as well as for the PFAS consisting of perfluorooctanesulfonic acid (PFOS) and precursor compounds and perfluorinated acids or amides.

Materials and methods

For the dl-POPs and PFAS, the following test samples were offered: three test solutions:

Solution K containing 17 2,3,7,8-substituted PCDD/PCDF in nonane; L: 12 dl-PCB in nonane; N: perfluoroalkyl substances (PFOS, PFCAs, PFASs, FOSAs and FOSEs) in methanol; and six naturally contaminated samples:

Sediment: from the Elbe River, fish: Mitten crab from the Netherlands; human milk from Sweden; air extract from active samplers taken in Barcelona, Spain (toluene for organochlorine and organobromine POPs analysis and methanol for PFAS analysis; spiked with native POPs); human plasma: from Sweden; surface water: from the Netherlands; the latter two samples intended for analysis of PFAS and PFOS, respectively.

The results for each of the POPs groups were to be reported electronically (MsExcel[®]). As for previous rounds of the Global Interlaboratory Assessment on POPs [3,6], the performance was assessed according to the QUASIMEME proficiency testing organisation (www.quasimeme.org). The assigned value, the between-lab CV values and the laboratory assessment using z-scores are based on the Cofino Model [8,9]. The z-scores are calculated for each participant's data for each matrix/analyte combination, which is given an assigned value. The z-scores can be interpreted as follows:

$ z < 2$	Satisfactory performance	S	$2 < z < 3$	Questionable performance	Q
$ z > 3$	Unsatisfactory performance	U	$ z > 6$	Extreme performance	U

Results and discussion

The participation of laboratories analyzing dl-POPs or PFAS according to region is shown in Table 1. Also shown is the distribution of laboratories analyzing the core matrices of the Global Monitoring Plan, *i.e.*, air and human milk and water (for PFOS only). It can be seen that the analytical capacity is located in the WEOG and the Asia-Pacific regions, whereby it should be noted that the vast majority of the Asian dioxin and PFAS laboratories is located in China or in Japan. There were 59, 56 and 29 laboratories delivering results for PCDD/PCDF, dl-PCB and PFAS, respectively. In the Asia region, there is a strong presence of dioxin laboratories whereas PFAS analysis is presently more located in the WEOG region. For all three groups of POPs, there are more laboratories analyzing the abiotic matrices (air or water) than the biotic matrix (human milk).

Table 1: Regional distribution of laboratories analyzing dl-POPs or PFAS. CEE: Central and Eastern Europe; GRULAC: Group of Latin American and Caribbean; WEOG: Western European and Other Groups

Region	PCDD/PCDF			dl-PCB			PFAS			
	Total	Air	H Milk	Total	Air	H Milk	Total	Air	Water	H Milk
Africa	2	1	1	3	3	3	2	1	2	-
Asia	30	21	13	26	17	13	10	3	6	3
CEE	5	2	2	8	4	3	2	-	2	-
GRULAC	6	2	-	4	2	-	1	1	1	-
WEOG	16	12	6	15	12	7	14	6	9	3
Total	59	38	22	56	38	26	29	11	20	6

The participants used their own methods. For dioxin-like POPs, most laboratories reported use of one GC column although two columns are described in most official methods. The major reason may be that only 2,3,7,8-substituted congeners were to be reported. In addition, it is known that human milk only these congeners are present and thus, there is no need to separate them from the more polar non-TEF congeners. Further, custom-made HRGC columns are available for dl-POPs. Only one laboratory used a more sophisticated GCxGC arrangement.

The sample extraction, clean-up, separation and detection of the more polar PFAS compounds is completely different from the traditional POPs. From the 29 laboratories that submitted results for PFAS, one laboratory used a time-of-flight instrument; all others reported to use LC/MS/MS. For the separation of the analytes, the majority used HPLC columns; some used UPLC columns. C₁₈ based columns dominated over C₈-based columns. One laboratory applied GC/LRMS (DB-WAX column, 30 m x 0.25 mm x 0.25 µm) for PFOS precursors, *e.g.*, Me/EtFOSA and Me/EtFOSE.

A total of 13,255 results submitted met the statistical criteria of the assessment so that z-scores could be assigned to the results submitted by 133 laboratories; of these, 5,897 (corresponding to 44% of all) z-scores were for the dl-POPs and 630 (or 5% of all) for PFAS. Whereas across all results, 58% of the results were assigned a satisfactory z-score, the performance of the dioxin laboratories and the PFAS laboratories were above average: 69% for the dl-POPs and 73% for the PFAS (Table 2). In it can be seen that in the Asian and the WEOG regions, more laboratories submitted “S” (satisfactory) results than “U” (unsatisfactory) results. “C” and “I” are “consistent” and “inconsistent” values for values reported below the limit of quantification according to the model [6].

Table 2: Summary of z-score results for dl-POPs and PFAS in comparison to total number of z-scores

POP group	# S	# U	# Q	# C	# I	Total	% S
dl-POP	4,040	1,129	536	25	167	5,897	69
PFAS	461	89	64	8	8	630	73
Grand Total	7,737	3,570	1,207	128	613	13,255	58

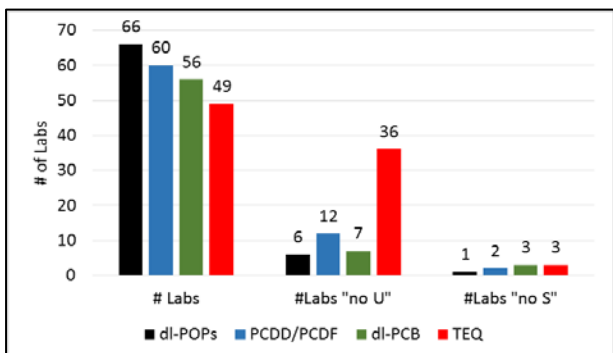


Figure 1: Number laboratories that submitted satisfactory (S) or unsatisfactory (U) results according to region

From Figure 1, it can be seen that 66 laboratories submitted results and had z-scores assigned for dl-POPs. Of these, six laboratories did not have any unsatisfactory (“U”) result, whereas one laboratory did not have any satisfactory (“S”) result. The result on TEQ basis are very promising: 2/3 of laboratories submitted satisfactory results and only three laboratories had problems and did not report any “S” data. On the other hand it can be seen that there is still a substantial number of laboratories analyzing an incomplete spectrum of dl-POPs since they were not able to report on TEQ-basis, *i.e.*, 17 PCDD/PCDF or 12 dl-PCB reported, *resp.*

With respect to dl-POPs, except for the human milk sample, the performance of laboratories for PCDD/PCDF was better than for dl-PCB (Figure 2). Highest CV values for all congeners (up to 155%) and the toxic equivalent (TEQ; as lower-bound (LB) or upper-bound (UB) value, 44% or 48%, *resp.*) were obtained for human milk (Figure 2). The concentrations and the values corresponding to 1 z or 2 z above or below the AV for each laboratory – grouped into UN regions - in the air extract are shown in Figure 3. In conclusion, the performance for the PCDD/PCDF is much better than the performance for the dl-PCB. Three of the extreme outliers for the dl-PCB were generated by PCB laboratories using ECD detector.

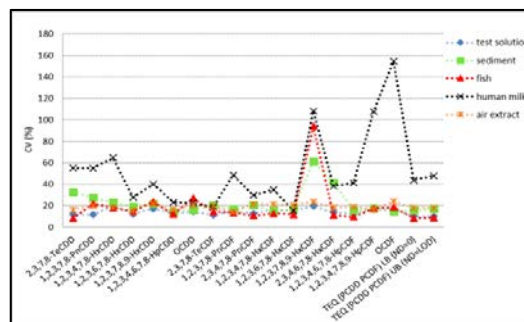
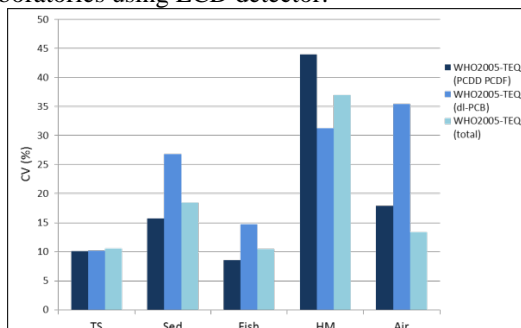


Figure2: Left: CV values (%) for WHO₂₀₀₅-TEQ; Right: CV values (%) for 17 PCDD/PCDF and WHO₂₀₀₅-TEQ

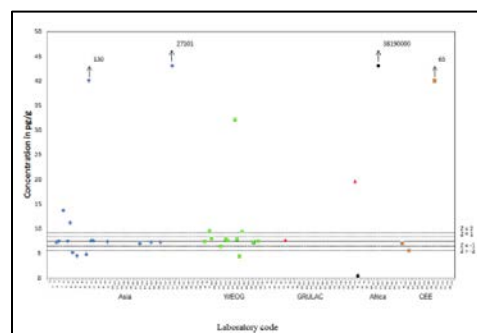
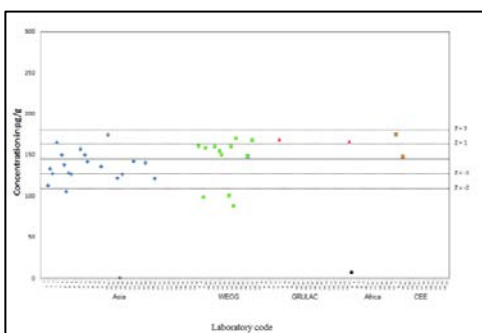


Figure 3: Concentrations for TEQ_{PCDD/PCDF} (left) and TEQ_{PCB} (right) in the toluene extract for air sample AV by straight line, $z=\pm 1$ (12.5%), $z=\pm 2$ (25%) by dotted lines. \blacklozenge Asia, \blacksquare WEOG, \blacktriangle GRULAC, \bullet Africa \blacksquare CEE

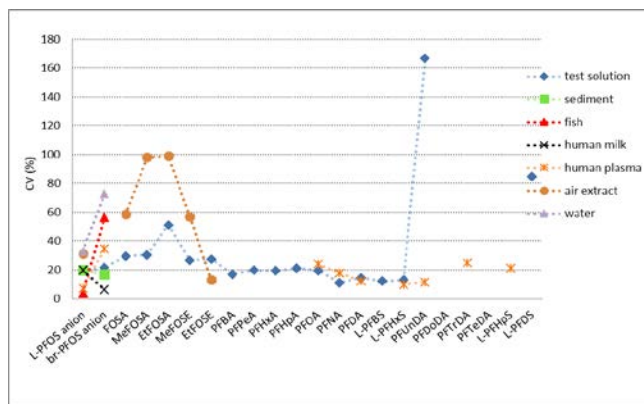


Figure 4: Performance of laboratories for PFAS according to sample type (as CV)

For the PFAS, the global picture of laboratory's performance – as percentage variation of the CV – is shown in Figure 4. It shall be noted that the broader spectrum of PFAS has been analysed for the test solution of analytical standards and human plasma only. For water, sediment, fish and human milk only the linear and branched PFOS isomers and their sum were requested. The air test sample included the precursor FOSAs and FOSEs. The standard test solution did not contain any PFUnDA, PFDoDA, PFTrDA, PFTeDA, L-PFHpS or L-PFDS. The performance of the laboratories was satisfactory for the PFOS anion in the test solution, sediment, human milk and human plasma sample.

For the fish and the water samples, difficulties were observed for the branched PFOS. The results for the air extract, and especially for the precursors compounds – Me-/Et-FOSA/-FOSE and FOSA - were less impressive. In general, the small number of laboratories reporting results for PFAS hampers the assessment of this group of POPs: for the air sample, a consensus value could be assigned for the L(inear)-PFOS only (11.8 ng/g).

This interlaboratory assessment has shown that in general, the dioxin and PFAS laboratories are advanced with respect to instrumentation (MS, MS/MS, HRMS) and experience (number of analytes reported, number of "S" results) in comparison to the laboratories that analyse (few) POPs pesticides or indicator PCB. The large number of HRMS laboratories analyzing dl-POPs in developing countries and their performance is impressive.

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