Bi-ennial Global Interlaboratory Assessment on Persistent Organic Pollutants – Third Round 2016/2017, Organochlorine Pesticides, PCBs and Brominated Flame Retardants

I. Van der Veen[1], H. Fiedler[2], J. de Boer[1]*

[1]Vrije Universiteit, Dept. Environment & Health, 1081HZ Amsterdam, The Netherlands, [2]Örebro University, School of Science and Technology, MTM Research Centre, SE-701 82 Sweden

Introduction

The third round of the Bi-ennial Global Interlaboratory Assessment on Persistent Organic Pollutants (POPs) was organized in 2016. This interlaboratory assessment accompanies UN Environment Programme's capacity building program for laboratories analysing persistent organic pollutants (POPs) that has started in 2005 with Global Environment Facility (GEF) funding and implements the recommendations by the Conference of the Parties to the Stockholm Convention as expressed in the Guidance on the global monitoring plan for POPs in article 16 of the Convention [1]. After invitation to participate in this third round, 175 laboratories from 66 countries had registered. This is a sharp increase in comparison to the previous interlaboratory assessment where 105 laboratories had registered. The test materials included test solutions of analytical standards, the abiotic matrices sediment, air extract and water and the biotic matrices Chinese mitten crab, human milk and human plasma. The results for the 23 groups of POPs that were listed in the annexes of the Stockholm Convention until 2013 and in addition hexachlorobutadiene were assessed. This resulted in a wealth of information on POP analysis and huge datasets from which the laboratories can evaluate their own methods and performance. This paper gives an overview of the results of indicator PCBs, organochlorine pesticides (OCPs) and brominated flame retardants (BFRs).

Materials and methods

The data assessment was carried out, likewise the assessment of the previous rounds of the UN Bi-ennial Global Interlaboratory Assessment on Persistent Organic Pollutants [2], according to the principles employed in the data assessment of the QUASIMEME proficiency testing organisation (www.quasimeme.org). The assigned value, the between-lab coefficient of variation (CV) values and the laboratory assessment using z-scores are based on the Cofino Model [3,4], as is described in the report of the second round [2]. The z-scores [5] are calculated for each participant's data for each matrix/analyte combination, which is given an assigned value.

Since it is not possible to calculate a z-score for values below the limit of detection (LOD), the so-called 'left censored values' (LCVs) are used. The quality criterion used for LCVs is:

LCV/2 < (concentration corresponding to |z|=3): LCV consistent with assigned value

LCV/2 > (concentration corresponding to |z|=3): LCV inconsistent with assigned value, i.e., LCV reported by laboratory much higher than numerical values reported by other laboratories.

Results and discussion

133 laboratories from 57 countries submitted data for the test solutions, the sediment, fish, human milk, human plasma, air extracts, or water samples (Table 1). The laboratories that submitted results can be assigned to the five UN regions as follows: Africa (n=14), Asia (n=53), Central and Eastern Europe (CEE) (n=16), Latin and Central America (GRULAC) (n=25), and Western Europe and other groups (WEOG) (n=25).

The performance for the test solution went again backwards (Figure 1). Also the human milk and sediment showed poorer results compared to the two previous rounds. For the sediment it may be explained by a difficult matrix with high background, due to a polluted river from which the sediment was taken (river Elbe, Germany). The human milk sample showed lower contractions of most analytes compared to the human milk samples used in the previous rounds. The poorer performance for the test solution is most likely due to a sudden increased participation degree in this exercise. A number of unexperienced laboratories, participating for the first time may have negatively influenced the overall between-lab CV (Figure 2). This effect is stronger for the test solution and for PCBs and OCPs as many of these new labs did not analyse other matrices or other compounds. On the other hand, results for the air extract improved since the previous round. That is promising as air is one of the matrices in the UN Global Monitoring Program. The air sample was a toluene extract from polyurethane foams in an active sampler and no further clean-up was necessary.

Table 1: Participating degree per compound class (maximum number of labs is given).

Group	Test solutions	Sediment	Crab	Human milk	Human plasma	Air extract	Water
OCP	75	60	44	29	-	29	-
PCB	79	66	51	38	-	45	-
PCDD/PCDF	49	40	31	22	-	38	-
dl-PCB	46	37	34	26		38	
PBDE	39	28	23	17	-	25	-
HxBB	13	16	10	9	-	13	-
Toxaphene	14	13	9	6	-	7	-
HBCD	16	7	10	9	-	7	-
PFAS	27	17	15	6	12	11	20

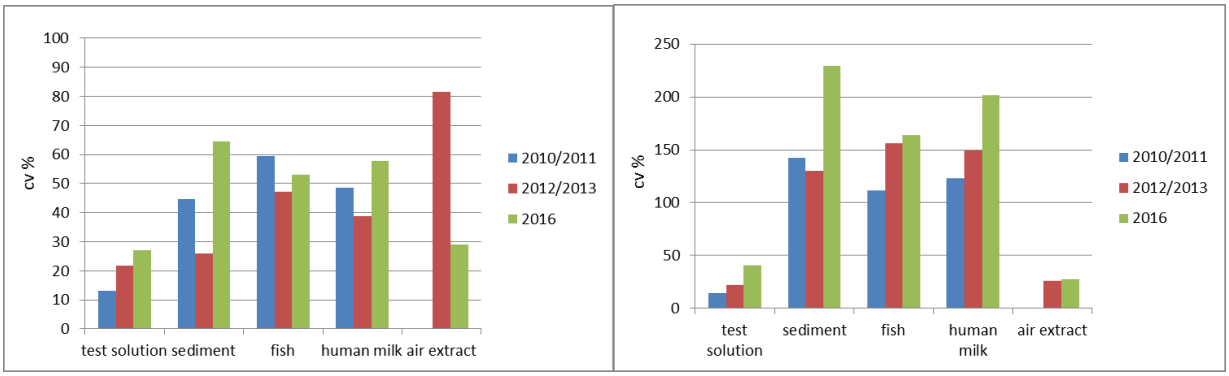

Figure 1. Comparison of performances between interlaboratory assessments for the indicator PCB (left) and OCP (right) analyses.

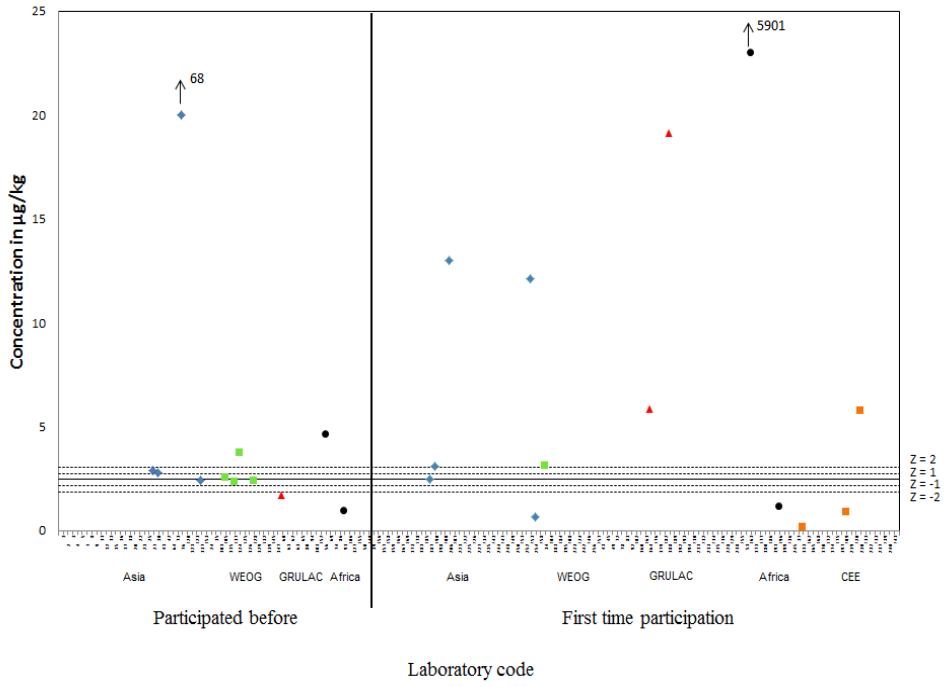

Figure 2. Dieldrin results in fish per region and according to first or multiple participation.

The other encouraging achievement is that for the first time there is some data on toxaphene. The results for the test solution were very reasonable. Unfortunately, the other test materials contained very little toxaphene. For a next round test materials with substantial levels of toxaphene should be used. Another observation is the relatively poor performance of many labs for OCPs, related to the use of the electron capture detector (ECD). Labs using mass spectrometric detection and ^{13}C labeled standards produced better results for OCPs.

A mixed picture was found for laboratories that had participated in previous rounds. Some laboratories that received training before, have not improved. Lack of daily routine is probably decisive here. Laboratories that carry out POP analyses on a daily basis, and with better instrumentation, such as the WEOG group do show better results. The challenge of this program is of course to bring the laboratories in continents such as Africa or the GRULAC at that level. This is possible but only when governments support their laboratories and let them carry out monitoring programs and analyses on a regular basis.

The BFR results (PBDEs, HBCD and HxBB) were overall very reasonable. Figure 3 shows results for PBDEs in crab. Most laboratories able to analyze PBDEs have an MS available. Figure 4 shows indeed that only one African lab participated for this analysis, with deviating results. MS instruments are not often available in Africa and GRULAC and when they are, they are often not working due to lack of service. This is a serious area of attention. HBCD results were generally good for the dominating congener, so α-HBCD in crab (CV 21%) and γ-HBCD in sediment (CV 36%).

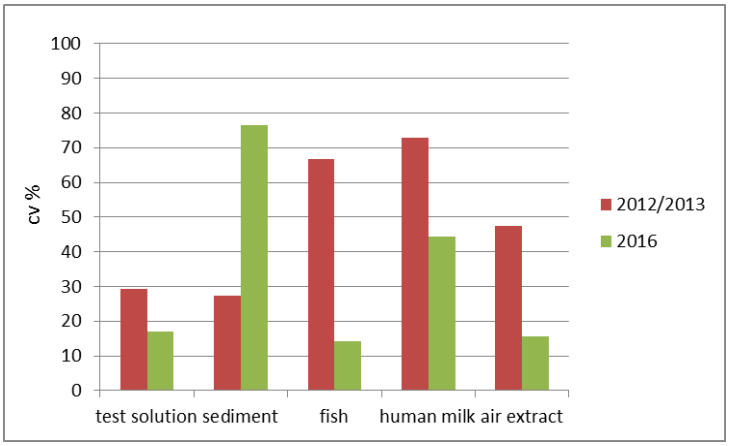

Figure 3. Comparison of performances between interlaboratory assessments for the PBDE analyses.

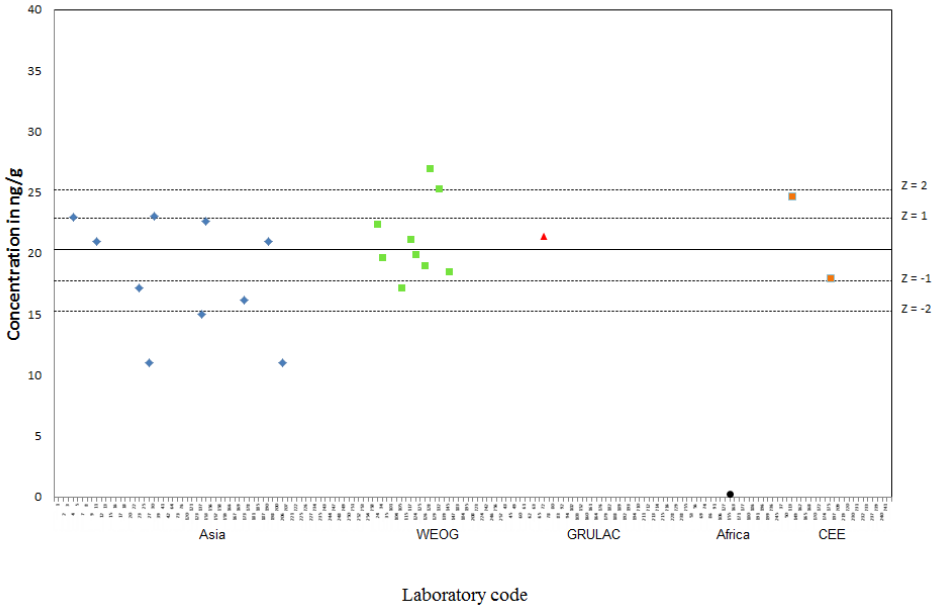

Figure 4. PBDE results in fish per region.

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