PCB AND OCP RESULTS OF FIRST WORLDWIDE UNEP INTERLABORABORY STUDY ON PERSISTENT ORGANIC POLLUTANTS

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Introduction

The analysis of polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) is well under control in most western countries. This is, however, not true for laboratories in many other parts of the world. The Stockholm Convention requires good quality data for these compounds which are listed as persistent organic pollutants (POPs). A Global Monitoring Programme has been designed in which laboratories from all Stockholm Convention parties need to analyse POPs in human milk, human blood and ambient air samples. To assist laboratories to improve the quality of their analysis, the United Nations Environment Programme (UNEP) has organized a capacity building and training programme, which started in 2009. As part of this activity, the First Worldwide Interlaboratory Study on Persistent Organic Pollutants is being organized, which included various types of biotic and abiotic matrices. The first phase of this study was conducted in Asia; however, developed country laboratories from other regions participated as well. The intercalibration study was coordinated by IVM, Free University Amsterdam and MTM Centre, Örebro University. The POP results reported here are those of polychlorinated biphenyls (indicator PCB), DDT and metabolites, mirex, dieldrin, endrin, aldrin, chlordanes, hexachlorobenzene (HCB), heptachlor and cis-heptachlorepoxide. Of the POPs pesticides, toxaphene was not included, because only limited capacity was available among the participating laboratories. Chlorinated dibenzo-*p*-dioxin and dibenzofuran results will be presented elsewhere. Thirty-eight laboratories from thirteen countries participated in the first phase. Twenty-four laboratories originate from Asia (China, Fiji, Malaysia, India, and Vietnam) and 14 laboratories were based in OECD countries (including Japan, Republic of Korea, and Australia). In the second phase, laboratories participated from Africa (e.g. Egypt, Kenya, South-Africa, Zambia and Sudan), South-America (e.g. Argentina, Brazil, Mexico and Cuba) and other regions.

Materials and Methods

The test materials comprised the following: A sediment sample from Norway was dried at 40 °C and sieved (0.5 mm). After homogenisation, individual plastic containers, tested to be free of background contamination, were filled with sediment and stored at room temperature. A freeze dried fish sample from the Great Lakes was made available by Dr. Eric Reiner from the Ontario Ministry of Environment, Laboratory Services Branch, Ontario, Canada. The human milk test material consisted of pooled, homogenised human milk samples from the Swedish mother milk bank in the Stockholm area. Solution 1B consisted of a mixture of the marker PCB (PCB 28, 52, 101, 118, 138, 153 and 180) in the concentration range of 0.1-5 ng/ml. This standard was prepared, ampouled and labelled by Wellington Laboratories (Guelph, Ontario, Canada). Solution 1C consisted of a mixture of organochlorine pesticides (OCP) in the concentration range of 10-50 ng/ml. This standard was prepared by IVM, Amsterdam, from a standard solution obtained from Cambridge Isotope Laboratories (Andover, USA). After preparation, the aliquots were ampouled, labelled and stored at room temperature. The OCPs present in the solution were HCB, aldrin, dieldrin, endrin, p,p-DDT, p,p DDE, p,p-DDD, o,p-DDT, o,p-DDE, o,p-DDD, trans-chlordane (gamma), cis-chlordane (alpha), trans-nonachlor, cis-nonachlor, oxychlordane, heptachlor, *trans*- heptachloroepoxide (HEPO), *cis*-HEPO, mirex, α-HCH, β-HCH, γ-HCH, and δ-HCH. Although present in some test materials, the HCHs were actually not part of the study since they are not included in the list of the initial twelve POPs under the Stockholm Convention at the start of this study. In May 2009, the HCHs have been added to the Stockholm Convention POPs list.

The participants were not restricted in the methodology used for the analysis of the target compounds in this first UNEP intercalibration study. The use of capillary GC was considered mandatory to achieve the separation needed for an accurate determination of the analytes. The laboratories used their own extraction and clean up protocols, spiking schemes, standards and internal QA/QC. Typically, the freeze dried fish sample was extracted by pressurized liquid extraction systems, Soxhlet, microwave assisted extraction (MASE) or liquid/liquid extraction (e.g. after KOH/ethanol decomposition of the sample). A large variety of extraction methods were used for the milk samples ranging from liquid/liquid to supercritical fluid extraction after mixing with an absorbent or pressurized extraction systems or again Soxhlet extraction. The sediment was analysed by low

resolution GC/MS (incl. ion trapMS), GC/HRMS and ECD. The marker PCB in the fish and the milk sample were extracted by liquid/liquid, Soxhlet, MASE and pressurized liquid extraction systems. Fat removal was achieved by multi layer silica, gel permeation or concentrated sulphuric acid (H_2SO_4). GC/ECD, GC/LRMS and GC/HRMS were used for detection. No data were acquired using a low resolution GC/MS system. The analytical procedures to analyse the pesticides included the same detection methods. A wide variety of sample extraction and clean up methods were used including Soxhlet, pressurized extraction systems, MASE, liquid/liquid, ultrasonic extraction, GPC, multilayer silica, alumina and Florisil.

The data assessment was carried out according to the principles employed in the data assessment of the QUASIMEME proficiency testing organisation (www.quasimeme.org). All data received from the participants were entered into a database and assessed using a standard procedure to allow direct comparison between participants. The approach of the assessment is based on the standard, ISO 13528 (2005), the IUPAC International Harmonised Protocol for Proficiency Testing (Advanced Draft) by Thompson et al. (1). The assigned value and the laboratory assessment using z-scores are based on the Cofino Model (2). This model uses a Normal Distribution Assumption (NDA) and the assigned value is based on the Cofino NDA model without any trimming of the data. This approach includes all data in the evaluation and no subjective truncation or trimming is made. The performance of the laboratories in this study is illustrated in the z-score histograms. When the assigned value for an analyte was indicative, the value was plotted as the originally reported concentration. The rules for confirming whether the consensus value should be an assigned value or an indicative value are given in the Assessment Rules for the Evaluation of the QUASIMEME LP Studies Data (3), with appropriate examples.

To determine if different regions in the world performed differently, the participants were grouped according to the United Nations Regional Groups system. The following groups were subdivided: Asian Group, African Group, GRULAC (Latin American and Caribbean Group), EEG (Eastern European Group) and WEOG (Western Europe and Others Group)

Results and discussion

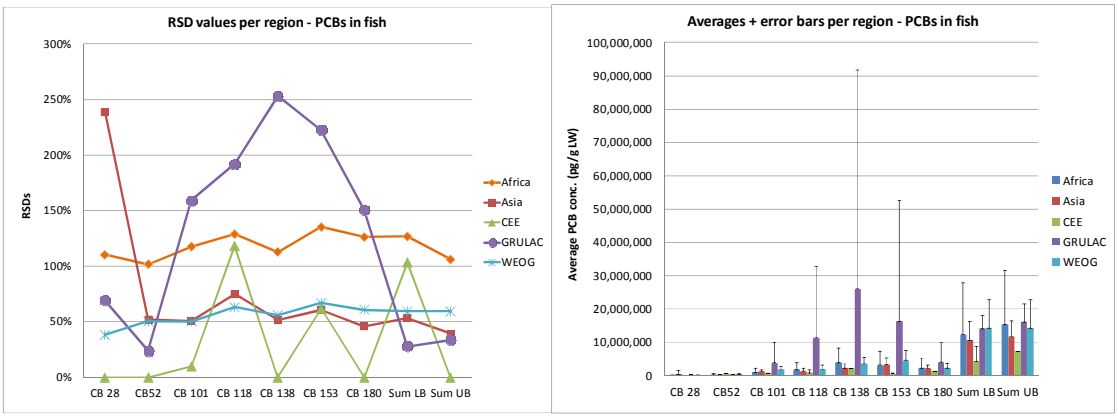

Figure 1. Performance of laboratories for PCBs in the fish sample.

Figure 1 shows that for PCBs (indicator PCBs and their upperbound (UB) and lowerbound (LB) totals). This shows that regional differences can be observed. The relative standard deviation (RSD) is very similar for the WEOG and Asian laboratories. This can be explained by the long experience in POPs analysis by the WEOG laboratories and the extensive use of GC-HRMS instruments (and 13C internal standards) by many of the Asian laboratories. The performance (RSDs) is worse for the African and GRULAC laboratories. The GRULAC laboratories severely overestimated the results for CBs 118, 138 and 153, being caused by outlying results. The EEG results are difficult to interpret as only 3 laboratories submitted data in this case.

Table 1. Percentage of satisfactory z-scores (|Z|<2) obtaiuned by participants in samples provided in the study. In case no number is provided, no z-scores could be calculated.

	Standard solution	Sediment	Fish	Milk
% Lipids	NA	NA	48	65
Aldrin	83	19		
Dieldrin	76			40
Endrin	69			
Sum Drins Lower Bound (ND = 0)	73		36	47
Sum Drins Upper Bound (ND = LOD)	78		48	53
trans-Chlordane	76			
cis-Chlordane	81		36	
trans-Nonachlor	77	31	33	43
cis-Nonachlor	80			64
Oxychlordane	87		33	50
Heptachlor	74			
cis-Heptachlorepoxide	83	24	36	44
trans-Heptachlorepoxide	91			
Sum Chlordane Upper Bound (ND = LOD)	77		39	
p,p'-DDT	72	39		43
o,p'-DDT	78		36	38
p,p'-DDE	76	38	35	
o,p'-DDE	86	48		47
p,p'-DDD	63	32	39	26
o,p'-DDD	89	59	35	
Sum DDTs Lower Bound (ND = 0)	56	59		45
Sum DDTs Upper Bound (ND = LOD)	68	58	43	45
Mirex	93	33	40	41
Hexachlorobenzene	78	42		35

OCP like DDTs are easily degraded when the GC is not in optimum condition (*e.g.*, dirty liner), resulting in inaccurate results. For the DDTs, 32-59% of the labs showed an acceptable z-score. In the QUASIMEME interlaboratory studies, the general performance of laboratories analysing POPs in sediment was found to be lower for OCP than PCB (4). The authors noted that the vast majority of the participating laboratories were not able to determine OCP levels with an acceptable accuracy. This pinpoints some of the challenges encountered by several laboratories participating in the present study. The major problem with OCP analysis is in the GC/ECD analysis, which is in fact a compromise of conditions for a number of OCP.

The ECD is not specific, the baseline is rather noisy, separation of early eluting compounds is not very good, and internal standards may not compensate for all losses. The use of GC/MS, even low resolution MS, together with ^{13}C labelled standards would improve this performance substantially, as is generally seen in the analysis of PCDD/PCDF, which are normally present at much lower concentrations than the OCP.

It was mandatory for the participants to express and submit the results of the fish and milk samples on a fat weight basis. Therefore, a fat content needed to be determined, either parallel to the analytical procedure (e.g. from the crude Soxhlet extract) or as a separate fat determination. The variance in the lipid levels (RSDs 85% in fish and 109% in milk) was higher than expected, as this determination is fairly simple. It is therefore likely the variance has contributed to the variance in the analytical results of the PCBs and OCPs in fish and milk. Some laboratories performed a lipid determination for the first time, making it vulnerable for errors. Others reported the use of only non-polar solvents for the lipid determination, resulting in low lipid content results. A medium polar solvent (or solvent mixture) is recommended as it provides the highest yields.

The laboratory performance of PCB in the test solution was better (average RSD = 19-36 %) compared to a previous UNEP interlaboratory study with seven participants from South-America, Moldova, Fiji and Kenya (average RSD = 57 %) (5). An overall good performance on the test solution indicates that calibration is rather satisfactory in most laboratories. On the contrary, many laboratories performed poorly for other test materials. Various errors were encountered: one laboratory had a systematic bias for all contaminant groups, whereas many laboratories had a systematic bias for one or two contaminant groups. Furthermore, some laboratories were biased on certain samples. Specific contaminants from the OCP group (e.g. dieldrin) are vulnerable to degradation during extraction and clean up as well as to a dirty GC system. In addition, ECD detection is commonly used for detection of OCP and because of interferences, inaccurate results are obtained. Application of GC/MS would substantially improve the OCP results. Many other interlaboratory studies in OECD countries show RSD values for OCPs that are substantially higher than 25% (4).

All in all, the main causes for erroneous results are (i) limited access to high quality standards and other materials used for analysis, (ii) poor maintenance of instrumentation, (iii) lack of training of laboratory staff and technicians and (iv) problems with reporting of results (dilution factors, calculation errors). All these aspects should be controlled properly so as to arrive at high quality results in POPs analysis. This is a prerequisite for establishment of a high quality global monitoring network.

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