RESULTS OF UNEP'S 2ND GLOBAL INTERLABORATORY ASSESSMENT OF THE PERSISTENT ORGANIC POLLUTANTS UNDER THE STOCKHOLM CONVENTION IN VARIOUS MATRICES

Van Der Veen I[2], Nilsson H[1], Van Bavel B[1], De Boer J[2], Fiedler H[3]

[1] Örebro University, School of Science and Technology, MTM Research Center, SE 70182 Örebro, Sweden;
[2] VU University, Institute for Environmental Studies (IVM), De Boelelaan 1087, NL-1081 HV Amsterdam, The Netherlands;
[3] UNEP Chemicals Branch, chemin des Anemones, CH-1219 Châtelaine (GE), Switzerland;

Introduction

The Stockholm Convention on Persistent Organic Pollutants (POPs) requires countries to implement a Global Monitoring Plan (GMP) and to analyze POPs in various matrices. Since persistent organic pollutants (POPs) are omnipresent in our environment and in humans it is of high importance that the concentrations are monitored throughout the world at high quality. Sine 2005, UNEP has initiated capacity building projects for laboratories in developing countries [1,2]. Within this framework the laboratory staff was trained on extraction, analysis and data validation of POPs. Many laboratories in developing countries have little or no experience of POP analysis in environmental samples. This has proved challenging, and the quality of data obtained has been a major issue of concern. Issues include the lack of high-quality mass labeled standards, background contamination in laboratories, interferences in chromatogrammes and poor recovery of standards or analytes. In addition, the analytical demands regarding limits of detection (LOD) and accurate and precise quantification have increased since the analytical sensitivity has improved significantly over the past decades pushing the LOD even lower. Forming an active network of POP laboratories at different continents together with a series of interlaboratory studies and workshops is suggested to improve the measurements of POPs in these countries.

Interlaboratory assessments are quality assurance programs used in several research areas to enable and to assess the performance of both methods and laboratories participating in such programs. UNEP has initiated such studies for the POPs on the Stockholm Convention in several matrixes with the first round taking place in 2009/10 covering the traditional POPs [3,4]. The aim of 2nd round of the UNEP study was to evaluate and improve the quality of the participants' results for the traditional POPs but also included the new POPs included in the Stockholm Convention in 2009 by providing feedback to the participants as well as to suggest general precautions that need to be taken prior to or during the analysis of Stockholm Convention POPs. It is expected that this reoccurring studies will improve the quality of the data reported in literature and the data to be submitted to the Global Monitoring Plan [5].

Materials and methods

The laboratories were offered to register for a total of eight different matrices and six different groups of compounds. The samples were distributed to the laboratories in December 2012 with a detailed instruction of required report format. The participants were encouraged to use their in-house methodology for the analysis of the target compounds in this 2nd UNEP interlaboratory study. The laboratories used their own extraction and clean up protocols, spiking schemes and QA/QC validation procedures. Upon completing the tests, each laboratory electronically submitted their data to the United Nations Environmental Programme (UNEP) ILS coordinators (MTM Research center, Örebro University, Sweden and VU University, Amsterdam, The Netherlands) for use in generating statistical summary reports. The participants received electronic data submittal forms and study instructions. The laboratories are encouraged to use their in-house methods normally conducted within their own facility to analyze the samples.

Standards consisted of the target compounds at for the participants undisclosed concentrations including OCPs (1 - 1000 µg/kg) in iso-octane, PCDD/PCDF (10-350 µg/kg in nonane), dl-PCBs (50-700 µg/kg in nonane), indicator PCBs (1-10 µg/kg in iso-octane), PBDE and PBB #153 (30-100 µg/kg in nonane), PFASs (10-65 ng/mL in methanol) and FOSAs/FOSEs (100- 2500 ng(mL in methanol). The sediment, originated from the

Rotterdam harbour (the Netherlands), was dried and homogenised before packed in plastic bottles. The sediment samples contained measurable amounts of OCPs, PCB, PCDD, PCDF, dl-PCB, PBDE and PFAS. The fish sample consists of a pike-perch filet from the Netherlands. After processing and homogenisation from the material was sterilized by autoclavation and packed in a glass jar. For the fish sample OCPs, PCB, PCDD, PCDF, dl-PCB, PBDE and PFASs could be reported. The human milk test material consists of homogenised human milk samples from the Swedish mother milk bank in the Örebro region. The sample contained measurable amounts of OCPs, PCB, PCDD, PCDF, dl-PCB, PBDE and PFASs. The human blood serum sample consisted of pooled human blood serum of both occupationally exposed and serum from the general population. This sample was specially included for the analysis of PFOS and the option of analysis other PFASs**.** Two different air extracts were prepared for the study. Both PUF extracts were prepared from a large number of air extracts taken outside a hazardous waste incinerator. To one of the raw PUF extracts, OCPs, PBDE and PFASs were added at a concentration of 2-35 ng/ml. The other raw extract measurable amounts of the target compounds. PCB, PCDD, PCDF, dl-PCB, were present. Two ml of the extract were shipped in sealed glass ampoules. The water sample consisted of a surface water from the canal "het IJ" in Amsterdam, The Netherlands. After bottling, the material is sterilized by irradiation. The sample was known to contain several PFAS compounds. The transformer oil was a dilution of Aroclor oil. For the oil only indicator PCB could be reported**.**

Results and discussion

In total, 106 laboratories registered for participation in the present 2nd UNEP Interlaboratory study 2013. The worldwide distribution of the participating laboratories is given in Figure 1. As can be seen from Figure 1, not only laboratories from developed countries submitted data but also a large number of laboratories were from non OECD countries.

Figure 1. Global distribution of the laboratories participating in the 2nd UNEP Interlaboratory study 2013.

A total of 90 laboratories out of the 106 registered participants submitted data before the set deadline with reporting efficiencies as shown in Table 1. This is a very good efficiency even compared with QA/QC studies with only participants from OECD countries.

Registrations can be differentiated for the different compound PCDD/PCDF, dl-PCB, OCPs, PBDE and PFAS per matrix in a Table 1.

Table 1. Number of laboratories registered for analysis of OCPs, PCBs, dl-PCBs, PCDD/DFs, PBDEs and PFAS in various matrices and the reporting efficiency in %.

		OCPs	PCB	dl-PCB	PCDD/DF	PBDE	PFAS
Standard	Registered, (*n*)	71	76	59	59	54	37
	Reported* (%)	73	63	89	87	78	59
Sediment	Registered, (*n*)	52	56	44	44	41	27
	Reported* (%)	58	68	85	87	73	67
Fish	Registered, (*n*)	57	63	39	39	47	31
	Reported* (%)	56	70	91	86	72	61
Human milk	Registered, (*n*)	41	47	33	33	34	21
	Reported* (%)	56	62	88	88	65	38
Air extract	Registered, (*n*)	40	49	44	44	31	18
	Reported* (%)	65	67	77	84	68	44
Transformer oil	Registered, (*n*)	-	28	-	-	-	-
	Reported* (%)	-	68	-	-	-	-
Water	Registered, (*n*)	-	-	-	-	-	32
	Reported* (%)	-	-	-	-	-	63
Human serum	Registered, (*n*)	-	-	-	-	-	18
	Reported* (%)	-	-	-	-	-	44

* Highest reporting rate for the any compound in the group

An example of the raw data submitted without any statistical treatment is given in Figure 2, where the results of 30 participants are given for the new POPs included in 2009, the PBDE, in the sediment sample, reported in µg/kg.

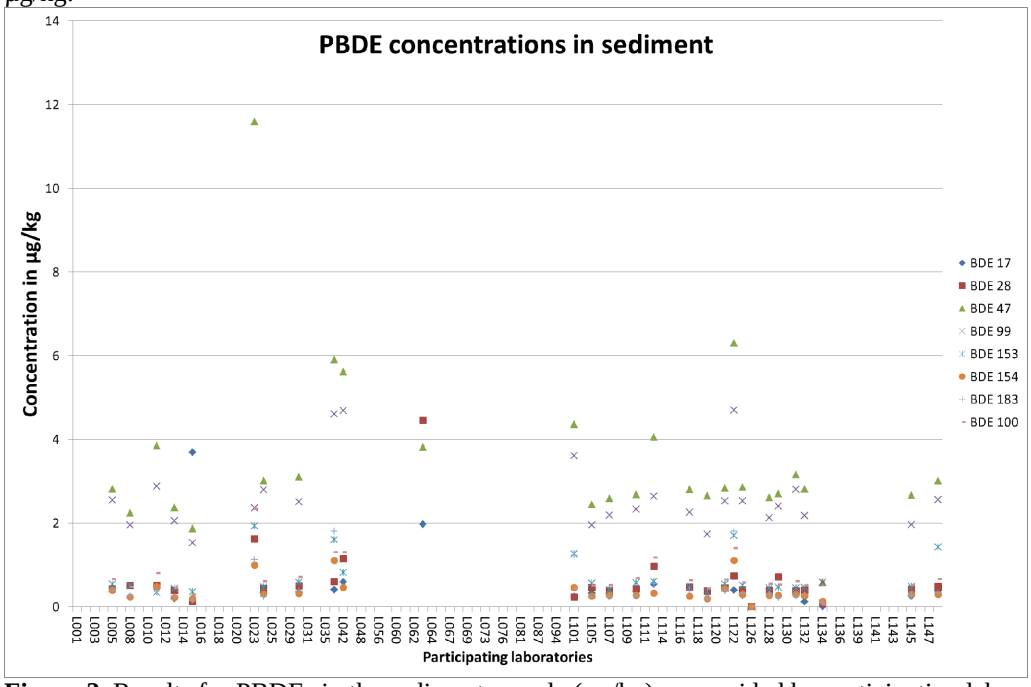

Figure 2. Results for PBDEs in the sediment sample (µg/kg) as provided by participating laboratories.

The assessment report will be provided in electronic format, containing:

- Each participating laboratory's test results (coded for confidentiality)
- Statistical analysis of test data
- Charts plotting test results versus laboratory code
- Other relevant information

The final statistical summary reports will help the laboratories to:

- Monitor strengths and weaknesses of the laboratory's performance
- Periodically compare test results and calculated statistical parameters with other laboratories worldwide
- Demonstrate proficiency in the specific analysis to meet data quality requirements

Acknowledgements
Financial support to UNEP has been provided through grants from the Global Environment Facility (GEF) and the European Union (ENRTP). The authors Prof.dr. Wim Cofino (Alterra, The Netherlands) for assisting in the statistical analysis of the data.

References

1) de Boer J, Leslie H, van Leeuwen SPJ, Wegener J-W, van Bavel B, Lindström G, Lahoutifard N, Fiedler H (2008), United Nations Environment Programme Capacity Building Pilot Project—Training and interlaboratory study on persistent organic pollutant analysis under the Stockholm Convention. Anal Chim Acta 617:208–215
2) van Leeuwen SPJ, van Bavel B, Abad E, Leslie HA, Fiedler H, de Boer J (2013) POPs analysis reveals issues in bringing laboratories in developing countries to a higher quality level. TrAC 46: 198-206
3) Abalos M, Abad E, van Leeuwen SPJ, Lindström G, Fiedler H, de Boer J, van Bavel B (2013) Results for PCDD/PCDF and dl-PCBs in the First Round of UNEPs Biennial Global Interlaboratory Assessment on Persistent Organic Pollutants. TrAC 46: 98-109
4) van Leeuwen SPJ, van Bavel B, de Boer J (2013) First worldwide UNEP interlaboratory study on persistent organic pollutants (POPs), with data on polychlorinated biphenyls and organochlorine pesticides. TrAC 46: 110-117
5) H. Fiedler H, Abad E, van Bavel B, de Boer J, Bogdal C, Malisch R (2013) The need for capacity building and first results for the Stockholm Convention Global Monitoring Plan. TrAC 46: 72-84