RESULTS OF INTERCOMPARISON STUDIES AND TRAINING AS PART OF THE UNEP CAPACITY BUILDING PILOT PROJECT FOR POP ANALYSIS UNDER THE STOCKHOLM CONVENTION

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Abstract
Following an on-site training on persistent organic pollutant (POP) analysis by UNEP experts in a number of laboratories in Ecuador, Uruguay, Kenya, Moldova, and Fiji, an interlaboratory study on PCB and organochlorine pesticide (OCP) analysis was organised by the Institute for Environmental Studies (IVM). The results were discussed at a workshop in Amsterdam, in February 2007. Prior to the on-site training, laboratories had analysed two samples that had also been sent to IVM for analysis. In addition to the discussions on the results of the various comparisons, a 4-days training on POP analysis was given to the participants.
The results of the intercomparison exercise were not essentially different from those obtained in the 1980s and 1990s in European POP laboratories[1]. Only occasionally results were within ±20% of the target values. Calibrations were generally OK, and better for PCBs than for OCPs. For most of the laboratories it was the very first time they analysed PCB congeners in environmental samples. Creating an effective network of POP laboratories in different continents together with a series of interlaboratory studies is suggested to improve the measurements of POPs all through the world.

Introduction
Within the framework of the United Nations Environmental Protection (UNEP) Capacity Building project for training of laboratory staff in developing countries on POP analysis, two small-scale intercomparison exercises were organised. The parameters involved in the project were polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in environmental samples. Seven laboratories from five countries covering four continents (South-America, Africa, Oceania and Europe) participated (Table 1). The first exercise, a national sample comparison, was organised in October/November 2006, before the training sessions, and comprised shadow analyses by IVM of samples that had been selected and analysed by the participating laboratories. The second exercise was organised in December 2006/January 2007, after the training sessions, and comprised an interlaboratory study with a test solution, a sediment sample and a herring tissue.

Methods and materials
"National"samples" were analysed in the participant's laboratories and sent to IVM for shadow analysis. For the interlaboratory study, a commercially available solution (cat. no. S-1878-2X-4ML-CLP, Accustandard, New Haven, CT, USA) was distributed among the participants by IVM. No dilution was applied. The certified (by the supplier) concentrations with their standard deviations (resulting from triplicate determinations by the supplier) on a volume basis ($\mu g.ml^{-1}$) have been converted by IVM to the corresponding values to a mass basis ($\mu g.g^{-1}$) by dividing the concentration by the density of the solvent iso-octane, 0.6919 $g.ml^{-1}$. These mass fractions were used as target values.

A dried sediment sample that is being used by IVM as internal laboratory reference material was distributed to the participants. The material was acquired from the International Sediment Exchange for Tests on Organic Contaminants (SETOC) proficiency testing scheme, where it was distributed four times a year until 2002. The consensus values were calculated by SETOC as median values after two outlier rejection rounds and the median absolute deviations (MADs) were calculated. The SETOC median and MAD values for the 2002 round were used as target values in the present inter-laboratory study.
A canned herring tissue sample was distributed to the participants by IVM. The material was recently subjected to a certification as reference material for PCBs (BCR718) within the European project CHRONO. This allowed for the use of certified values with 95%-confidence interval half-widths as target values. As OCPs were not included in the certification, their target values were based upon a single determination by IVM (with the corresponding risk of erroneous values).

Results and Discussion
National samples. Five out of the seven participating laboratories had sent a total of ten ("National") samples to IVM for shadow analyses. The National samples were analysed only one time in the IVM laboratory, and therefore, errors could not be excluded. However, the conclusion of this exercise was that there are only four correct results out of 110. This conclusion includes the detectable amounts only. There were a substantial number of non-detectable amounts due to the low contamination degree of some samples. Taking the non-detects also into account, the number of correct results is substantially higher.
Interlaboratory study. Three participants submitted results on a volume basis, and these data have been converted to mass basis by IVM as well. Tables 1-4 show the results for PCBs and OCPs, in the test solution and the sediment. PCBs were determined more accurately in the test solution than OCPs: eighteen results for PCBs were within 10% from the target value against eleven results for OCPs. A number of OCPs present in the unknown solution – some of them not being official POPs – were not reported by the participants: pentachlorobenzene, hexachlorobutadiene, telodrin, isodrin, cis- and trans-heptachlorepoxide. In the sediment, again, PCBs were determined more accurately than OCPs: nine results for PCBs were within 20% from the target value against four results for OCPs.

Table 1 Results of PCB analyses in unknown solution, in µg.g^{-1}

CB	Target value[1]	Mean	Stdev	Min	Max	n
28	29 ±0.9	29.1	12.2	13.4	54.4	8
52	29 ±0.3	28.6	10.4	12.7	48.7	8
101	29 ±0.1	33.1	16.8	12.6	59.3	7
118	29 ±0.1	37.6	20.6	21.5	84.5	8
138	29 ±0.6	28.9	23.1	1.9	72.1	6
153	29 ±0.3	31.3	15.0	18.6	63.6	7
180	29 ± 1	29.0	24.9	8.1	88.4	8

[1] Concentrations with standard deviations from the certificate of the solution supplier.

Table 2 Results of OCP analyses in unknown solution, in µg.g^{-1}

OCP	Target value[1]	Mean	Stdev	Min	Max	n
o,p'-DDT	29 ± 0.1	16.2				1
p,p'-DDT	29 ± 0.7	25.6	14.1	15.1	56.3	7
o,p'-DDD	29 ± 0.1	14.8	3.0	12.7	17.0	2
p,p'-DDD	29 ± 0.1	27.3	15.1	12.5	50.6	7
o,p'-DDE	29 ± 0.7	14.7				1
p,p'-DDE	29 ± 0.1	21.2	6.5	13.1	29.4	7
HCB	29 ± 0.1	22.7	6.1	14.6	29.5	5
Aldrin	29 ± 0.1	24.7	14.3	15.1	41.2	3
Dieldrin	29 ± 0.1	20.7	8.0	11.1	30.5	7
Endrin	29 ± 0.1	29.9	26.7	11.7	60.5	3
Heptachlor	29 ± 0.3	22.2	14.9	13.0	39.4	3
α-Endosulfan	29 ± 0.7	30.1				1
β-Endosulfan	29 ± 0.3	19.2	10.2	12.1	30.8	3
α-HCH	29 ± 0.1	26.5	15.6	14.9	57.3	6
β-HCH	29 ± 0.9	24.2	12.5	12.6	43.5	5
γ-HCH	29 ± 0.1	22.5	14.3	7.2	51.1	7
δ-HCH	30 ± 0.6	23.0	27.1	0.2	52.9	3

[1] Concentrations with standard deviations from the certificate of the solution supplier.

Table 3 Results of PCB analyses in sediment sample, in µg.g^{-1}dry weight

CB	Target value[1]	Mean	Stdev	Min	Max	n
28	3.4 ± 0.6 (121)	24.5	52.1	1.6	153	8
52	2.6 ± 0.3 (122)	14.9	34.6	0.74	93	7
101	5.9 ± 0.9 (144)	28.8	72.7	0.42	223	9
118	5.0 ± 0.5 (117)	11.1	13.0	3.4	42	8
153	11 ± 1.0 (146)	14.6	14.4	2.3	51	9
138	10 ± 1.9 (146)	47.2	73.3	0.44	156	4
180	6.1 ± 0.5 (127)	12.0	17.0	3.6	57	9
105	2.0 ± 0.1 (23)	3.0	2.4	1.2	7.0	5
156	1.1 ± 0.1 (17)	1.6	0.9	0.74	3.0	4

[1] Median values ± median absolute deviations and - between brackets - number of individual values in the SETOC proficiency testing scheme.

In herring, nine values for PCBs were within 20% of the target value (data not shown). For the few OCPs with target values that are reasonably high (over 1 µg.g^{-1} fresh weight: p,p'-DDE, HCB and dieldrin) seven cases of reported values within 20% of the target value can be discerned, four of them concern p,p'-DDE. There are at best two correct results per participants (out of eight).
The results of the national sample analysis, as well as the intercomparison results were discussed at a workshop at IVM in Amsterdam. This part of the workshop was held together with the discussion of the dioxin intercomparison results that was organised by the Örebro University (Sweden), and in which laboratories from China and Vietnam had participated. The training that followed this workshop was a continuation of the on-site training sessions that had taken place in each of the countries. Emphasis was placed on parts that for practical reasons could not be trained

Table 4 Results of OCP analyes in sediment sample, in µg.g^{-1}dry weight

OCP	Target value[1]	Mean	Stdev	Min	Max	n
HCB	15 ± 1.0 (59)	10.5	8.3	0.3	23	5
p,p'-DDE	125 ± 10 (58)	112	157	1.5	489	8
p,p'-DDD	8.5 ± 2.5 (65)	15.5	19.0	3.6	57	7
p,p'-DDT	68 ± 12 (57)	64.1	53.3	25	171	6
Dieldrin	0.6 ± 0.6 (8)	10.0	18.4	0.22	47	6
Aldrin	n.d. (4)	47.9				1
Endrin	1.3 ± 1.3 (8)	18.8	25.0	1.1	37	2
Heptachlor	0 (4)	24.5	42.0	0.2	73	3
α-Endosulfan	0.2 ± 0.2 (5)	1.4	0.5	1.04	1.7	2
β-Endosulfan	4.0 ± 3.0 (7)	1.2	1.1	0.41	1.9	2
Heptachl.epoxide	n.d. (4)	0.4				1
α-HCH	n.d. (4)	1.5	2.0	0.39	5.5	6
β-HCH	n.d. (4)	10.2	18.8	0.03	38	4
γ-HCH	0.3 ± 0.3 (11)	19.8	48.2	0.29	129	7

[1] Median values ± median absolute deviations and - between brackets - number of individual values in the SETOC proficiency testing scheme.

on-site or could not be completed. A part of the training was focused on the interpretation of chromatograms. Also, the use of internal standards and syringe standards was outlined, as well as the various ways of recovery determination and use of the recovery values. One returning element in the discussion was the earlier experiences of European laboratories in similar exercises on PCB and OCP analyses in the Marine Chemistry Working group if the International Council on Exploration of the Sea (ICES) and in the earlier years of QUASIMEME. The idea of bringing technicians and scientists together and create a sort of 'family' feeling and network in which an open exchange of experiences helped to improve the methods and to avoid errors made already by others seemed also very attractive for the UNEP laboratories. The results of the intercomparison exercise that was held after the on-site training could easily be considered disappointing by an outsider. However, compared to comparable starting situations in PCB and OCP analysis held in Europe in the 1980s and 1990s, and given the status of the participating laboratories and the working conditions, the results achieved are certainly encouraging. The combination and order of on-site training, intercomparison, discussion and continued training was definitely successful. However, building-up experience is something, which costs time.

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