IVM Institute for Environmental Studies

VU UNIVERSITY AMSTERDAM

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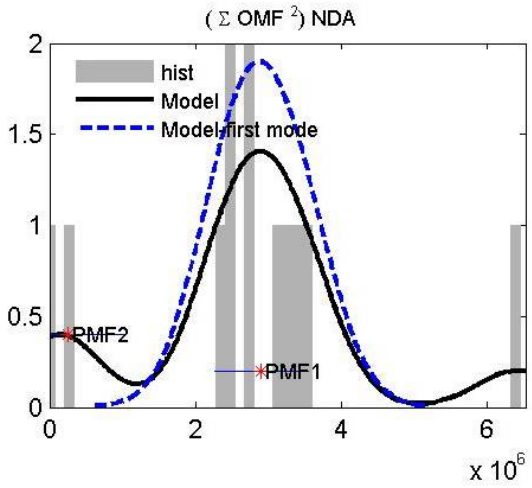
RESULTS OF SECOND WORLDWIDE UNEP INTERLABORATORY STUDY ON POPS

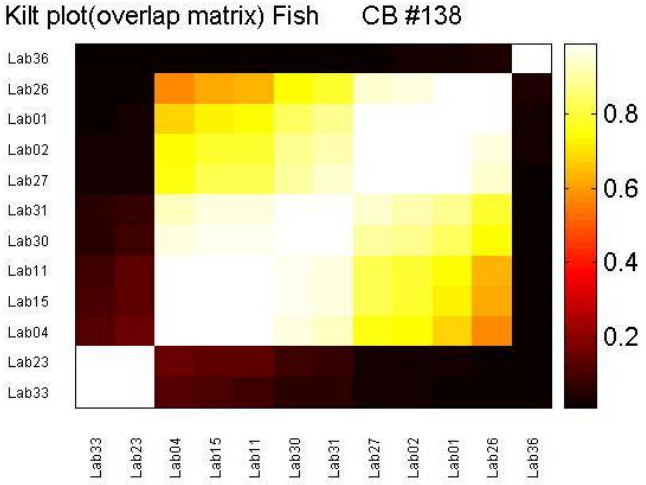
Jacob de Boer, Helena Nilsson, Ike van der Veen, Bert van Bavel, Heidi Fiedler

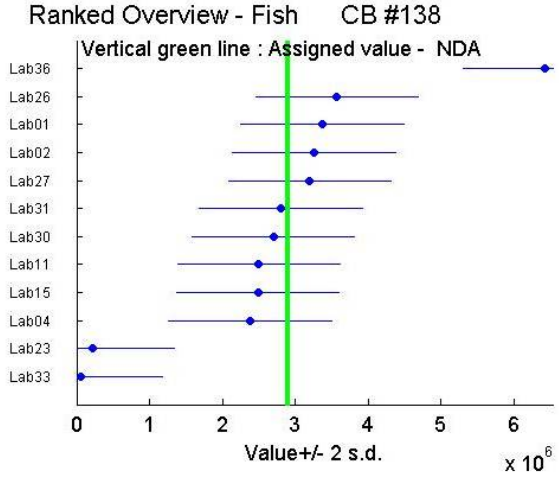
Test Materials and Target Compounds

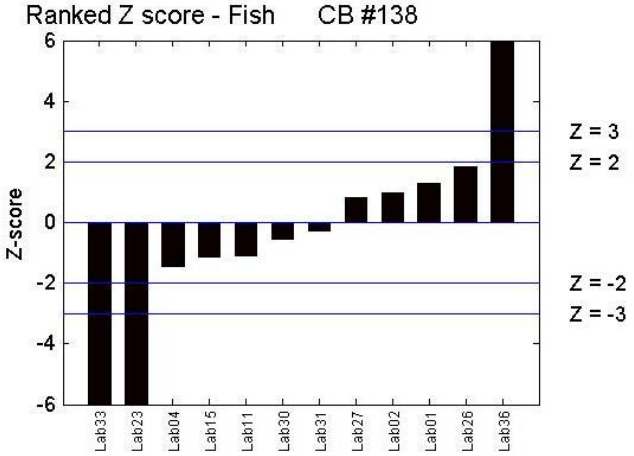
Test material	Compound class
Standard solution	OCP, dl and ndl-PCB, PCDD/Fs, PBDE/PBB, PFAS
Sediment, Netherlands	OCP, dl and ndl-PCB, PCDD/Fs, PBDE/PBB, PFAS
Pike perch fillet, Netherlands	OCP, dl and ndl-PCB, PCDD/Fs, PBDE/PBB, PFAS
Human milk, Sweden	OCP, dl and ndl-PCB, PCDD/Fs, PBDE/PBB, PFAS
Human serum, skiwax technicians, Sweden	PFAS
Air, PUF extract incinerator Sweden	dl and ndl-PCB, PCDD/Fs, PBDE/PBB, PFAS
Water, Amsterdam harbour	PFAS
Transformer oil diluted Aroclor 1254 in toluene	ndl-PCB

Statistics: Graphical presentation









Z-score

$$z\text{-score} = \frac{\text{Mean from Laboratory} - \text{Assigned Value}}{\text{Total Error}}$$

$$\text{Total Error} = \frac{\text{Assigned Value} \times \text{Proportional Error (\%)}}{100} + 0.5 \times \text{Constant Error}$$

- Constant errror: only important when close to detection limit

- Target PE: 12.5% → z=2 (PE 25%) is acceptable → labs can distinguish values that differ 50%

E.g. 10 ± 2.5 ≠ 5 ± 1.25

Constant and Proportional Error

Total error =

$$\frac{\text{Assigned value} \times \text{Proportional error (\%)}}{100} + 0.5 \times \text{Constant error}$$

E.g.: proportional error =25%

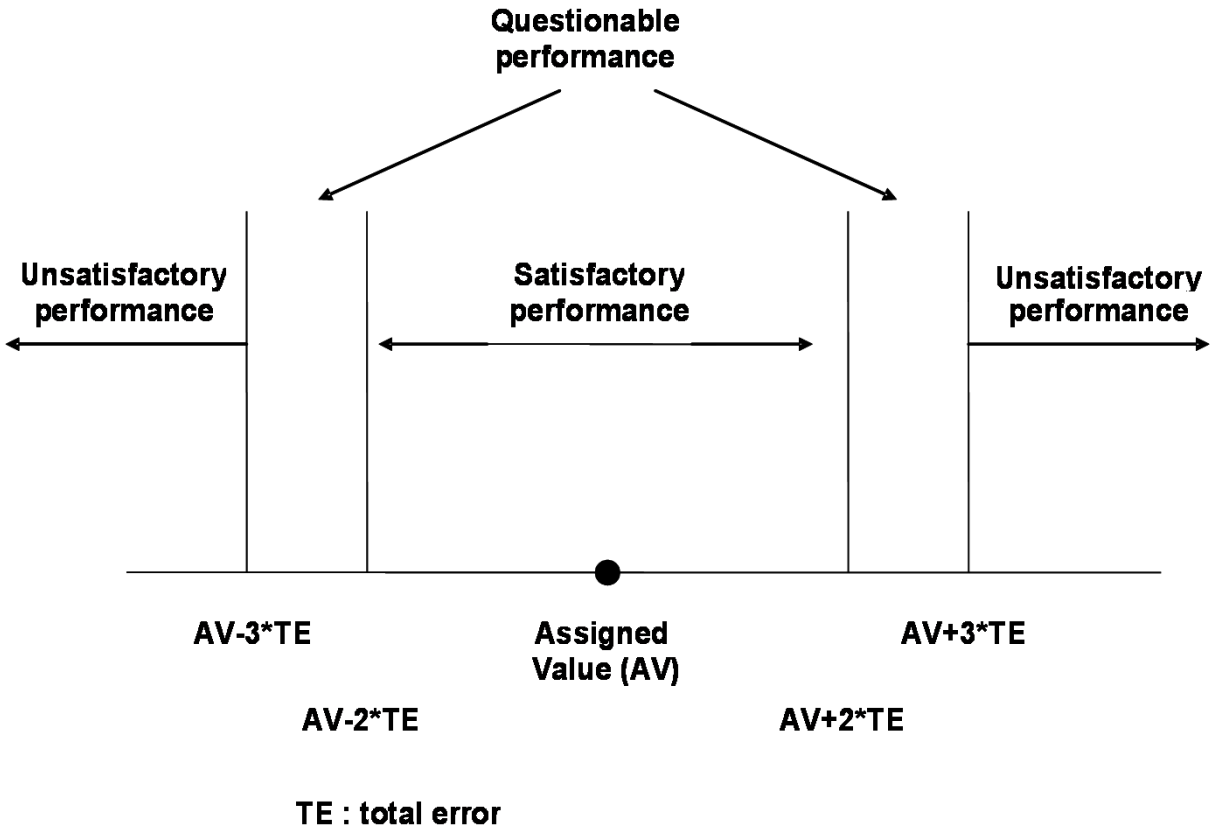
constant error = 0.05 (1/2 LOD [0.1])

Value 10: error = 10x0.25+0.5x0.1 = 2.55(CE=0.02PE)

Value 1 : error = 1x0.25+0.5x0.1 = 0.30 (CE=0.2PE)

Value 0.1:error = 0.1x0.25+0.5x0.1 =0.075 (CE=2PE)

Z-scores: satisfactory or not?



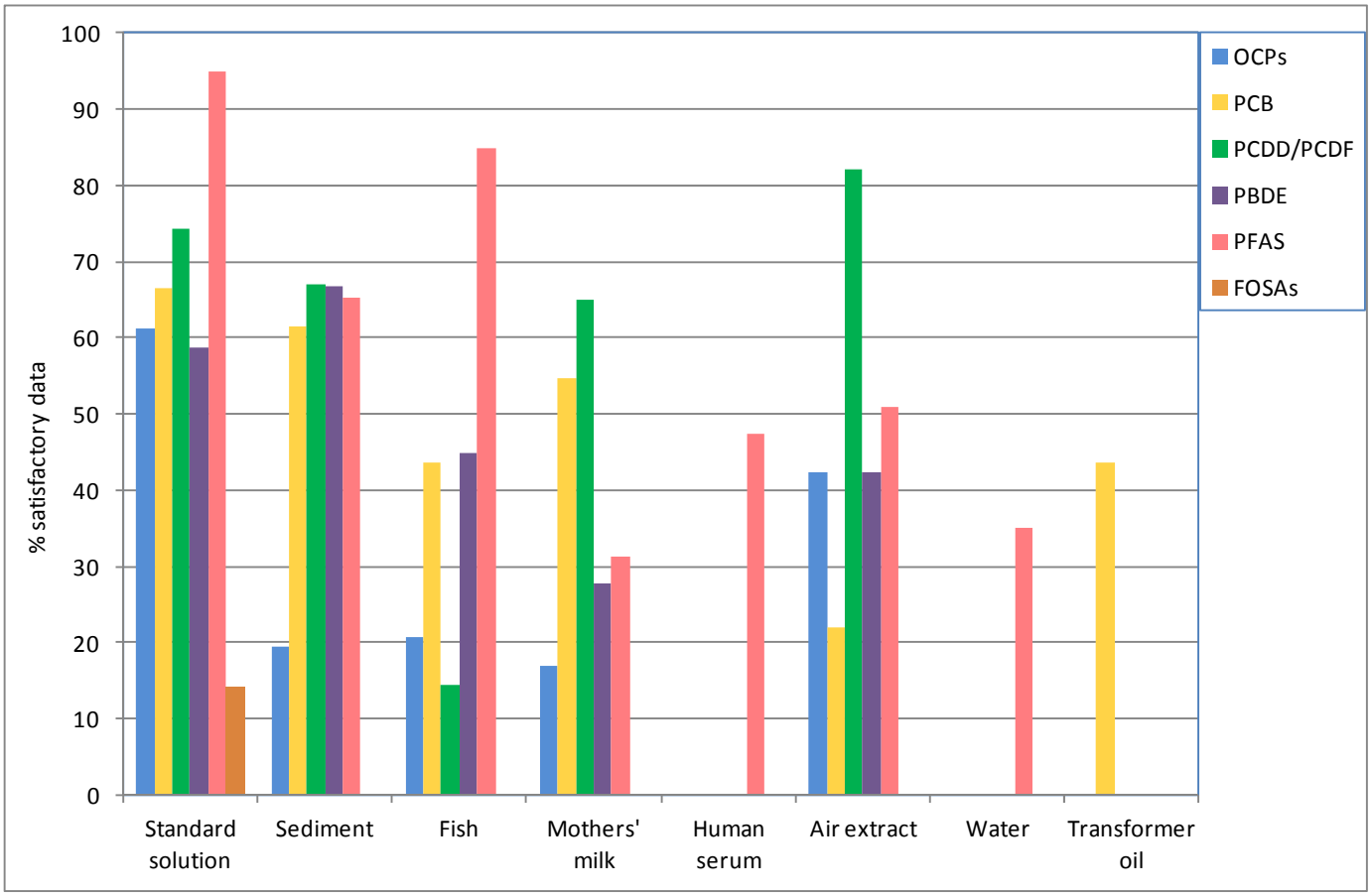
Participation Degree

Group	Standard solutions	Sedi-ment	Fish	Moth ers milk	Air	Water	Human serum	Trans-for-mer oil
OCP	50	27	36	21	23	-	-	-
PCB	47	38	43	28	25	-	-	19
dl-POPs	48	34	41	29	37	-	-	-
PBDE	42	30	34	19	21	-	-	-
PFAS	22	18	19	8	8	30	8	-

- 105 labs subscribed, 89 delivered data

Test material	Compound Class	n	Between-Lab CV (%)
Standard solution	OCPs	22-51	8-25
	PCBs	40-41	12-19
	Dioxins, Furans, dl-PCBs	31-37	6-12
Lake trout	OCPs	10-34	40-240
	PCBs	30-34	48-113
	Dioxins, Furans, dl-PCBs	13-23	21-135
Sediment	OCPs	3-38	14-451
	PCBs	25-31	31-59
	Dioxins, Furans, dl-PCBs	19-28	11-98
Human milk	OCPs	4-20	31-332
	PCBs	18-24	26-117
	Dioxins, Furans, dl-PCBs	6-21	52-76
Fly ash	PCBs	10-12	25-191
	Dioxins, Furans, dl-PCBs	20-27	13-80

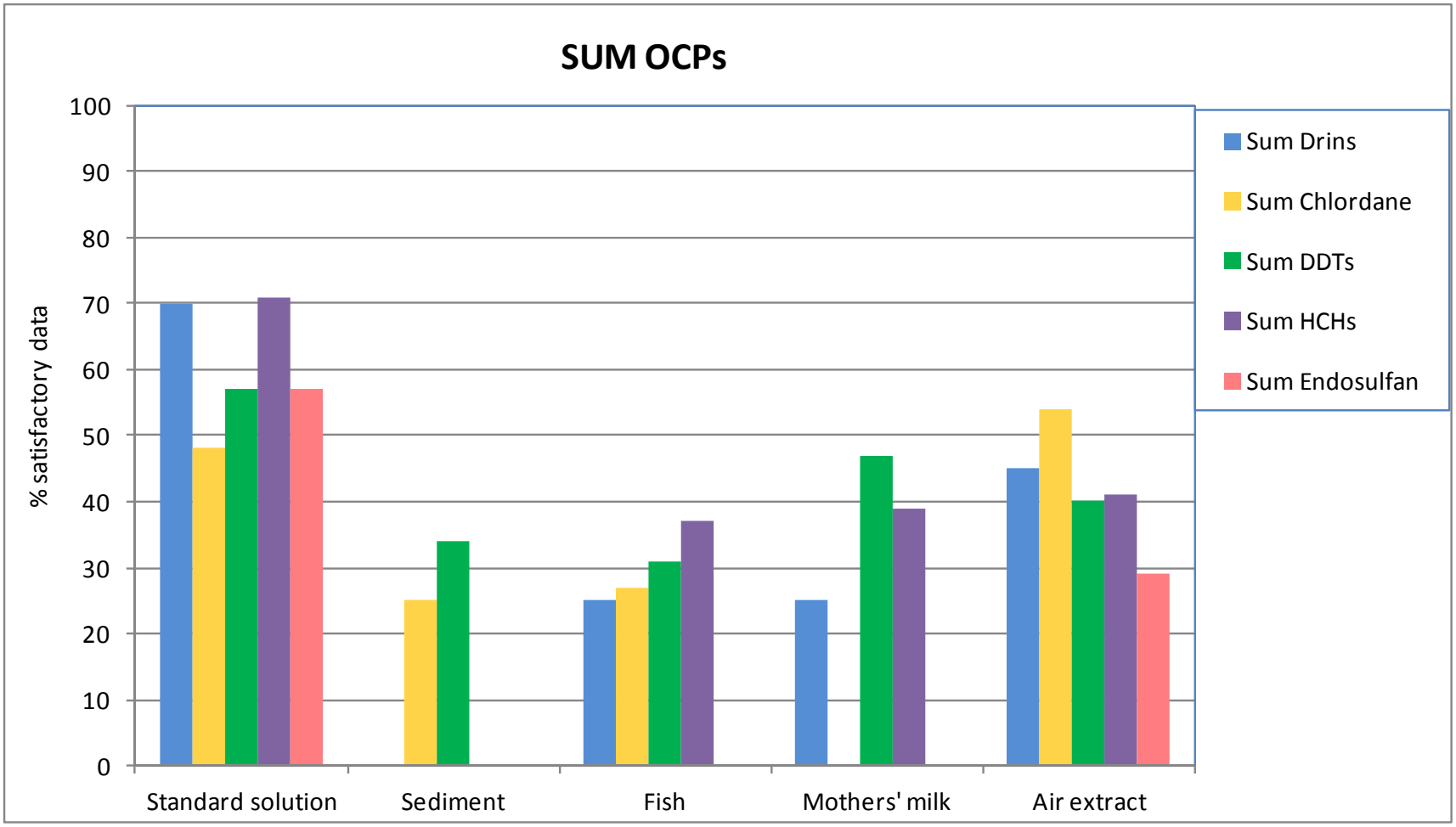
Percentage satisfactory z-scores



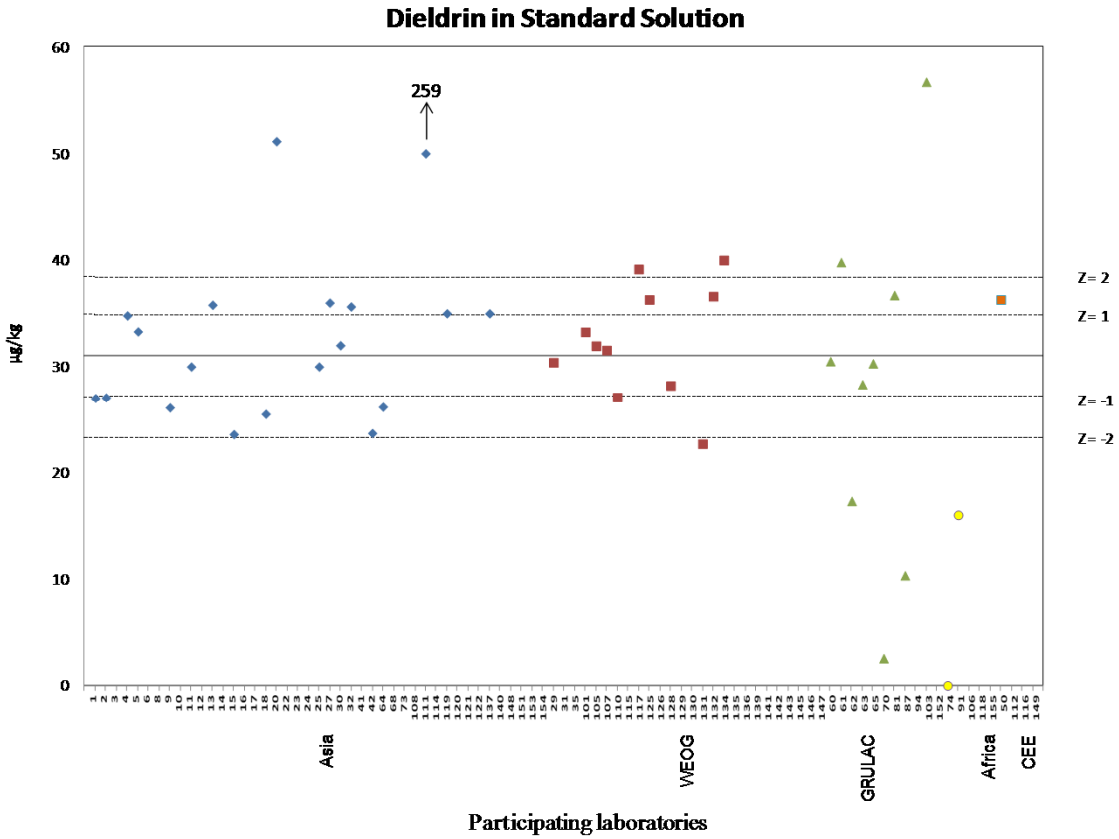
Summary Results

CV%→	St. sol.	sediment	air	fish	milk
PCB	18	21	71	28	26
Dieldrin	26	86	26	111	
DDT	22	▪ 43-79			
Chlordanes			32	▪ 40-113	
HCHs	<25	▪ >>25			

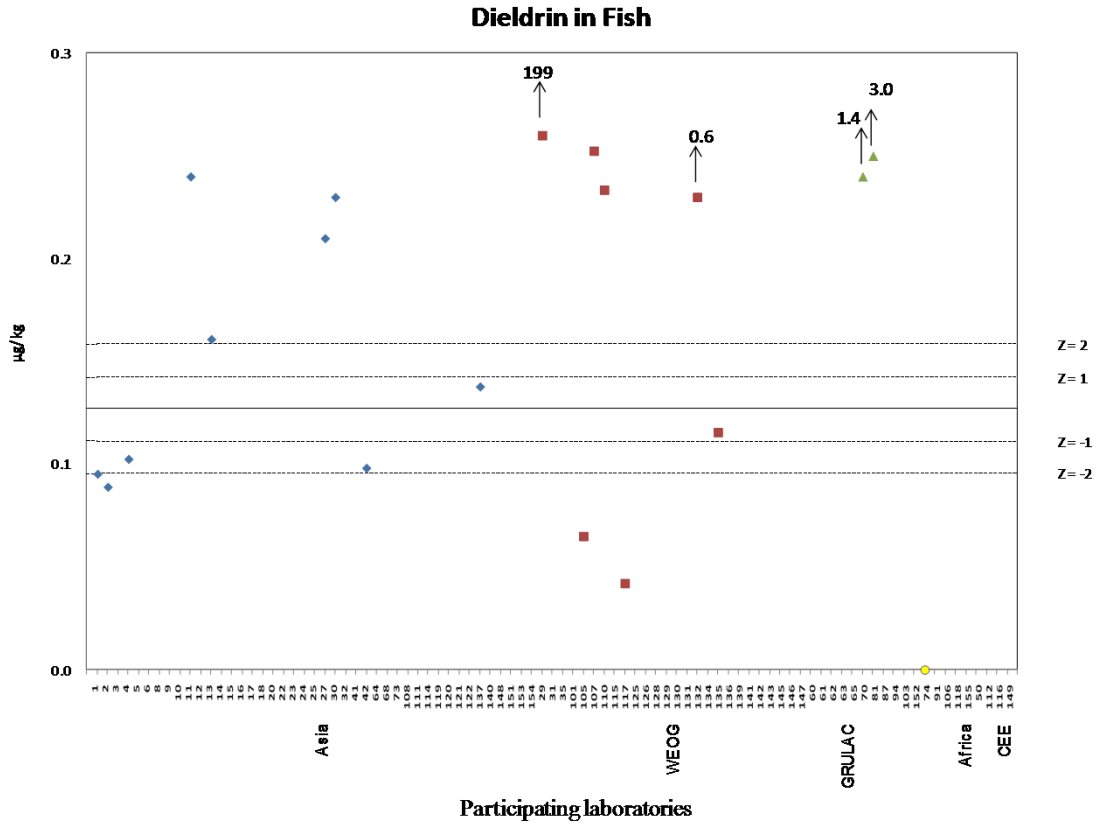
Sum OCPs in various matrices



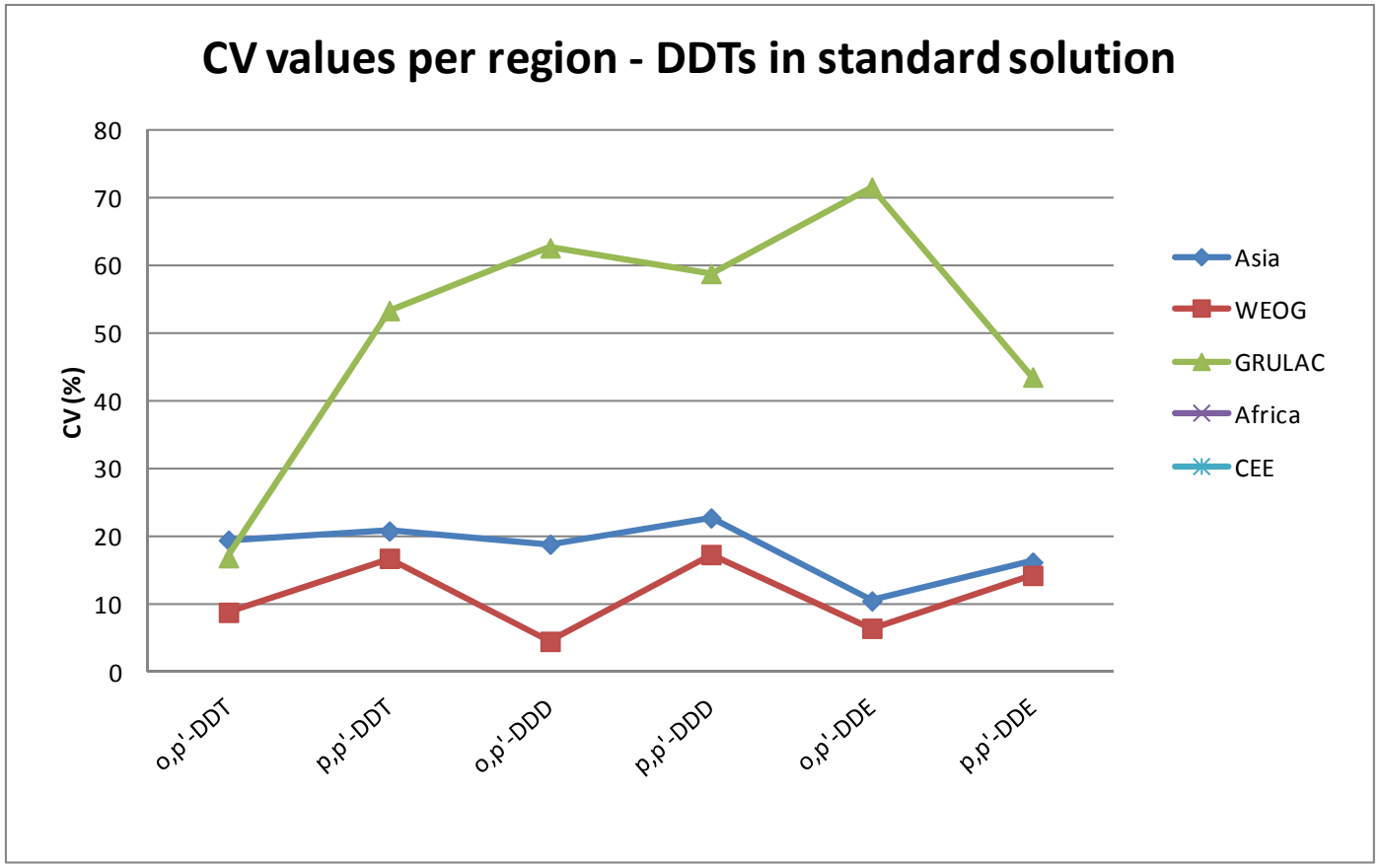
Dieldrin in standard solution



Dieldrin in fish

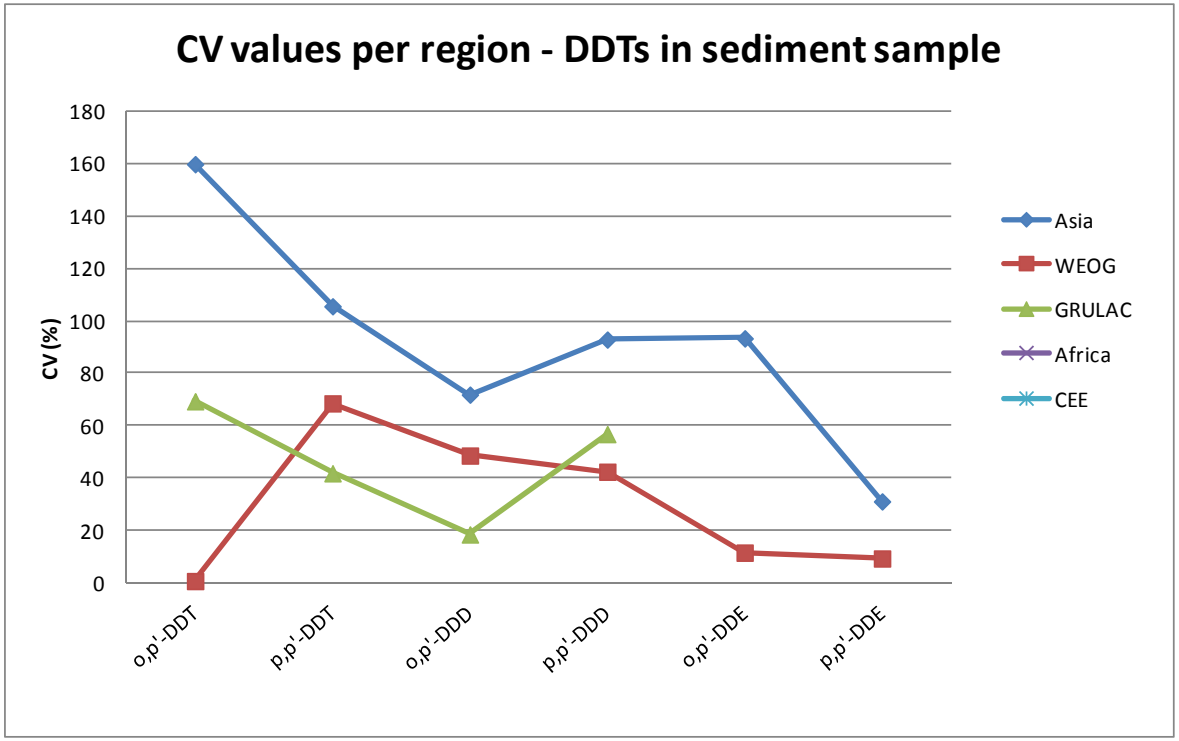


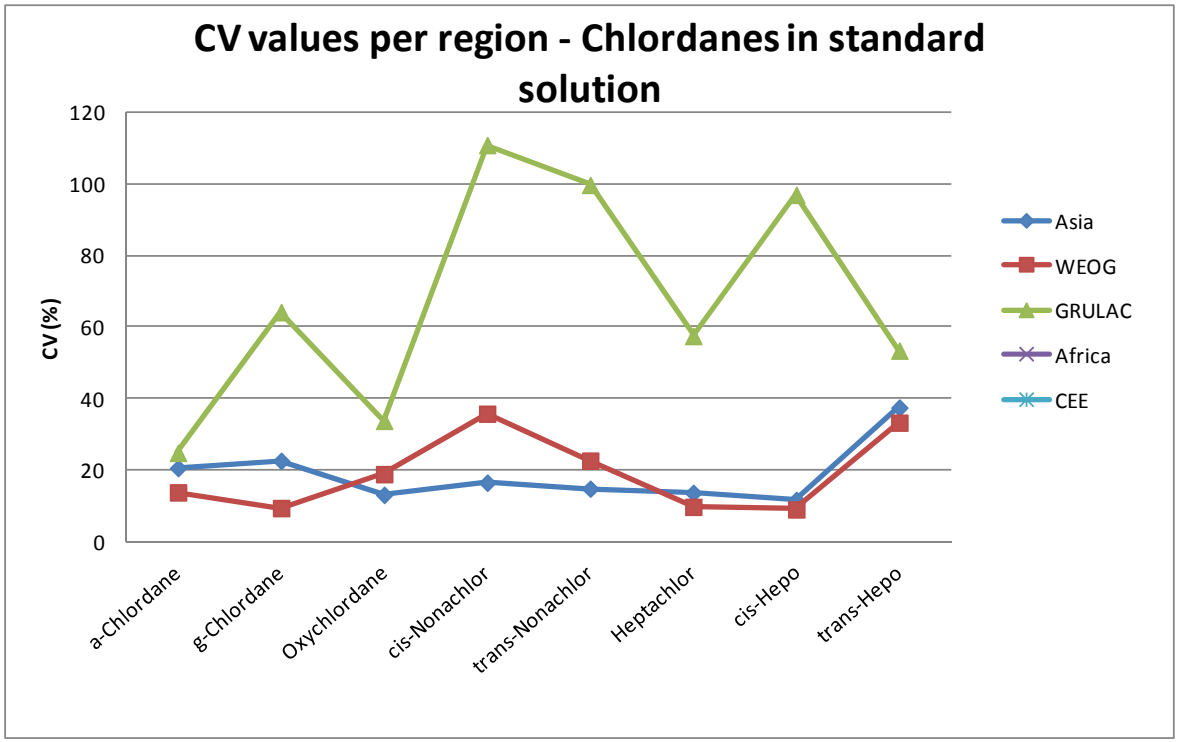
DDT per Region – Standard Solution



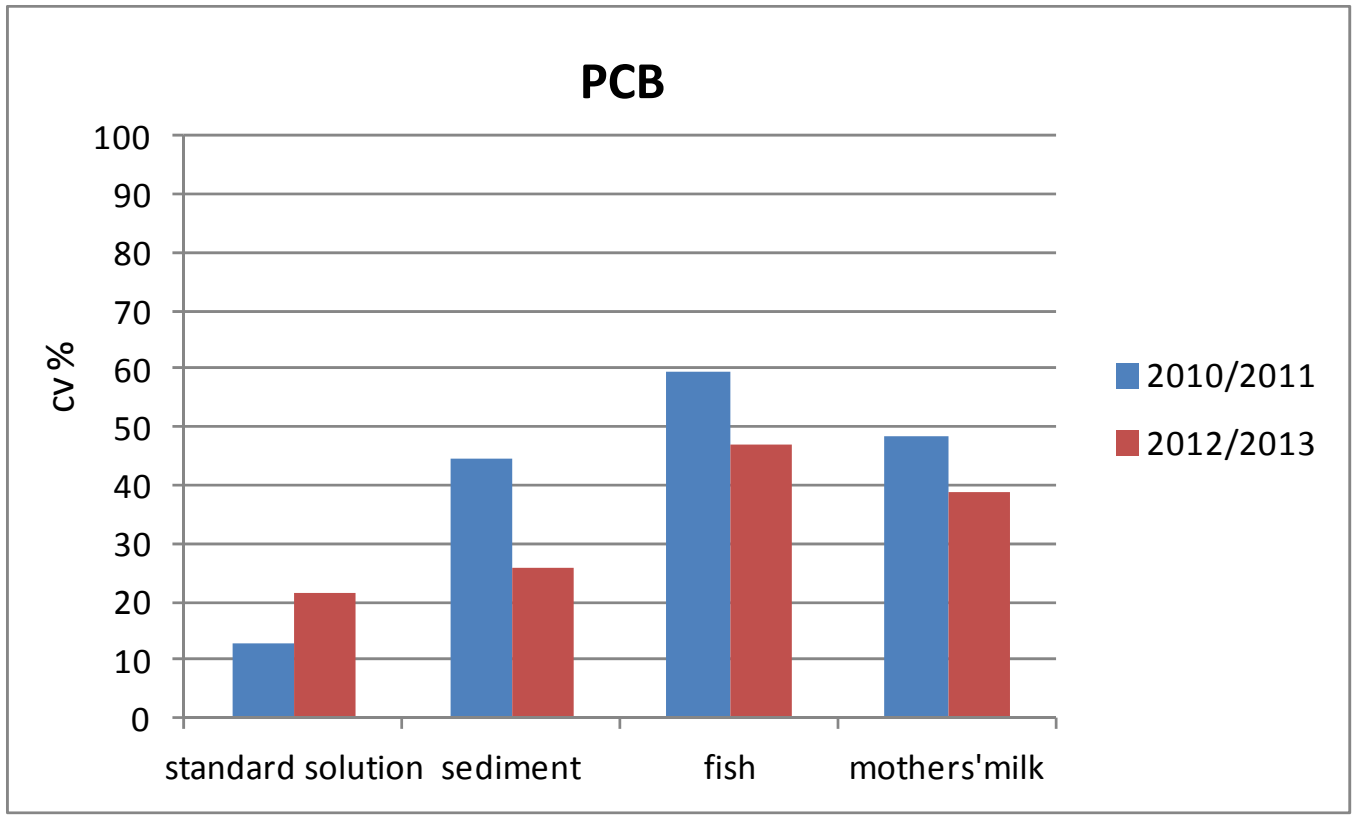
→ GRULAC: problems with GC analysis

DDT per region - Sediment

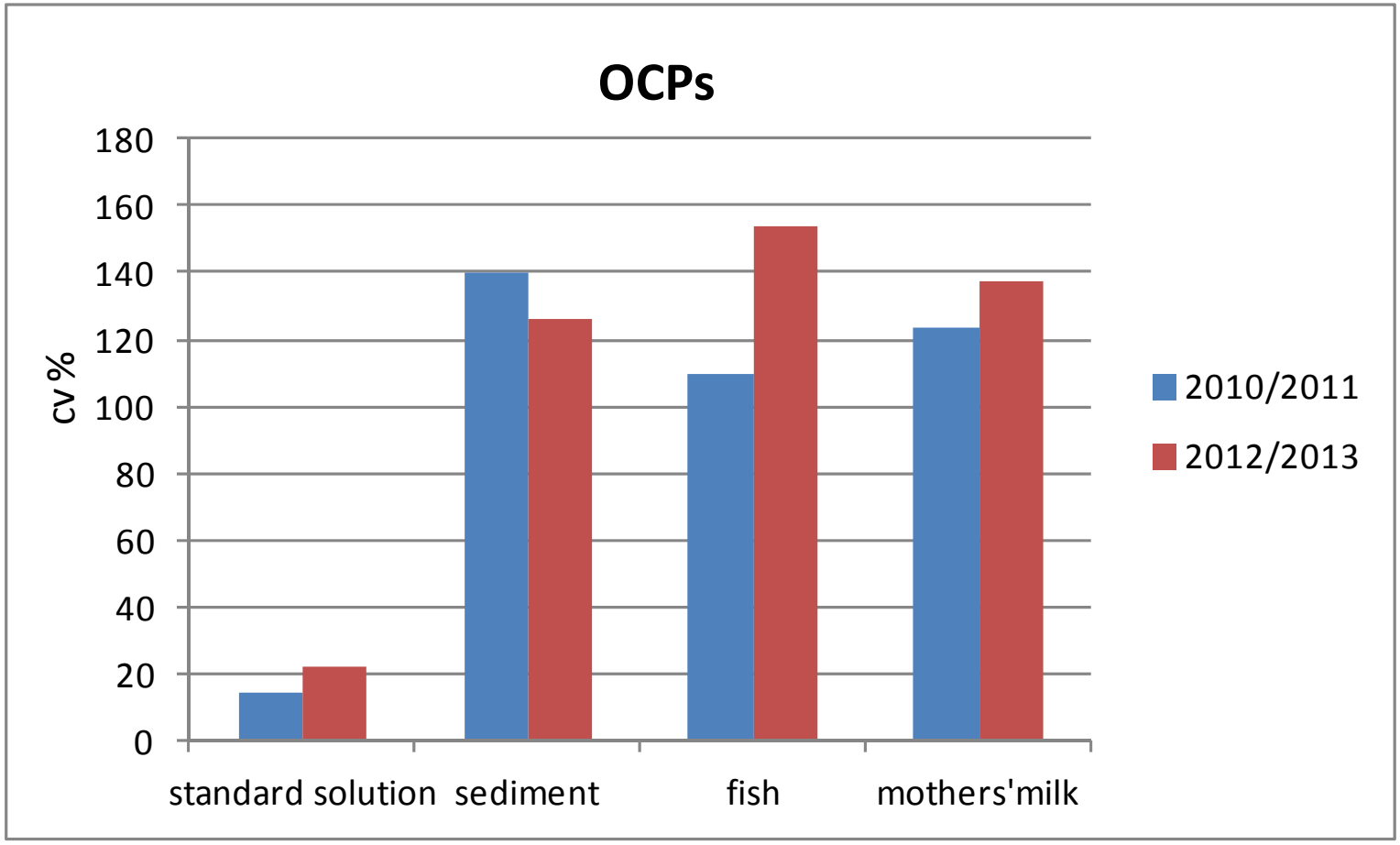



CV values per region - Chlordanes in standard solution
CV (%)
120
100
80
60
40
20
0
a-Chlordane
g-Chlordane
Oxychlordane
cis-Nonachlor
trans-Nonachlor
Heptachlor
cis-Hepo
trans-Hepo
Asia
WEOG
GRULAC
Africa
CEE

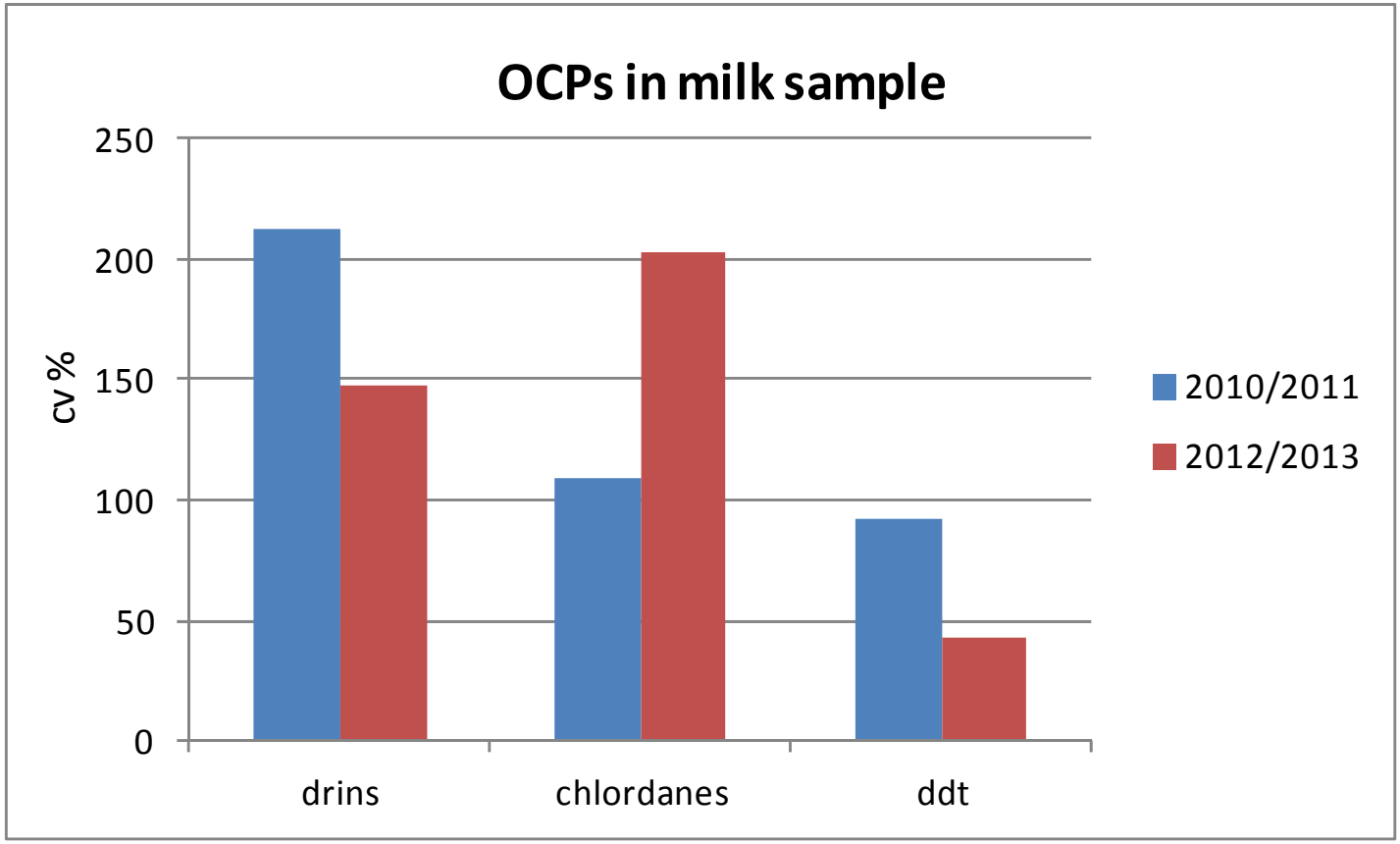
First vs. second UNEP Interlab, PCBs



First vs. second UNEP Interlab, OCPs



OCPs mother's milk 1st and 2nd ILS



Conclusions

- Regular inter laboratory studies are needed to monitor and improve the overall level of performance of POPs
- More laboratories should receive training, either in their own laboratory or in an expert laboratory
- The poor results for the fish samples need to be investigated in more detail.
- The results for the air extract in this round of this inter laboratory assessment was good for all compounds except PFAS and PCB
- Participating laboratories are encouraged to train their own technicians by repeatedly analysing certified reference materials and internal laboratory reference materials
- Laboratories analysing OCPs are encouraged to use GC-MS and ^{13}C labelled standards to improve their analysis
- The new POPs, such as PBDEs and PFOS require additional training and instrumentation
- Interactive workshops – through Webinars or on-site with the participating laboratories – might be an easy and cost effective way to improve understanding and interpretation of the results and to dissimilate the lessons learned.

Conclusions (II)

- The first results on several of the new POPS were promising for HCHs, PBDE and PFAS. However only limited data was acquired for endosulfan and hexabrominated biphenyl and the PFAS precursors, and no data for chlordecone. Special efforts have to be taken to improve and increase the data for these classes of compounds.
- **All** laboratories to pay more attention to quality assurance (QA) and method development