

Summary of key results from 2nd round of interlaboratory assessment of POPs laboratories

Heidlore Fiedler
UNEP/DTIE Chemicals Branch
chemin des Anémones 11-13
CH-1219 Châtelaine (GE), Switzerland
e-mail: heidlore.fiedler@unep.org



Content

- Context and history
 - Stockholm Convention on POPs
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Stockholm Convention on POPs

- Interlaboratory assessments are an important part of the United Nations Environment Programme's (UNEP) capacity building programme for laboratories analysing POPs;
- Objective: Assist laboratories to improve the quality of their analysis;
- Components of the capacity building:
 - Provision of small parts and consumables to POPs laboratories;
 - Development of guidance and training materials;
 - Maintenance of a databank containing operational POPs laboratories;
 - Hands-on training courses;
 - Networking and remote assistance
- Article 16: Global Monitoring Plan (GMP) established, guidance developed
- COP decisions SC-3/16, SC-4/31, SC-5/18 and SC-6/23;
- Chapter 4, the guidance document states that “[i]nterlaboratory exercises are often used to assess the effectiveness of QA/QC practices among several participating labs and to provide a measure of interlaboratory comparability.”
- For Stockholm Convention: aims to “confirm a 50% decline in the levels of POPs within a 10 year period” → POPs laboratories must be capable – at any time – to analyse samples for POPs within a margin of $\pm 25\%$.

Global interlaboratory assessments on POPs

- Coordination:
 - UNEP/DTIE Chemicals Branch, Heidi Fiedler
- Organisers:
 - Örebro University, Man-Technology-Environment Research Center (MTM), Bert vanBavel, Helena Nilsson
 - VU University Amsterdam, Institute for Environmental Studies (IVM), Jacob de Boer, Ike van der Veen

Pilot study

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journal homepage: www.elsevier.com/locate/aca



United Nations Environment Programme Capacity Building Pilot Project—Training and interlaboratory study on persistent organic pollutant analysis under the Stockholm Convention

J. de Boer^{a,}, H. Leslie^a, S.P.J. van Leeuwen^a, J.-W. Wegener^a, B. van Bavel^b,
G. Lindström^b, N. Lahoutifard^c, H. Fiedler^d*

- 2006/2007: Pilot study with seven laboratories from five countries (Ecuador, Uruguay, Kenya, Moldova, and Fiji; for basic POPs);
- Target: Initial POPs (without toxaphene) and for dl-POPs (China);
- Test samples: Standard solutions, herring tissue, sediment.

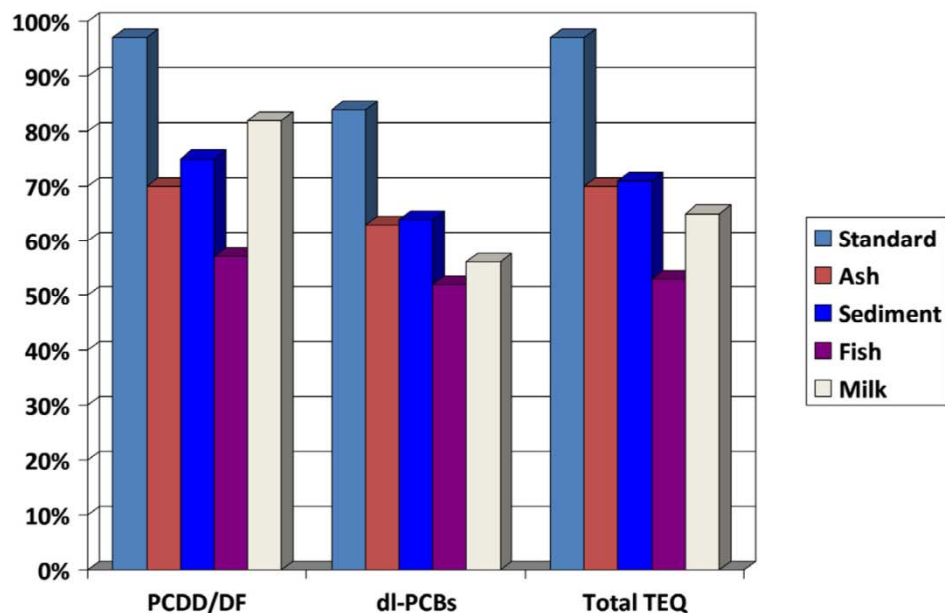
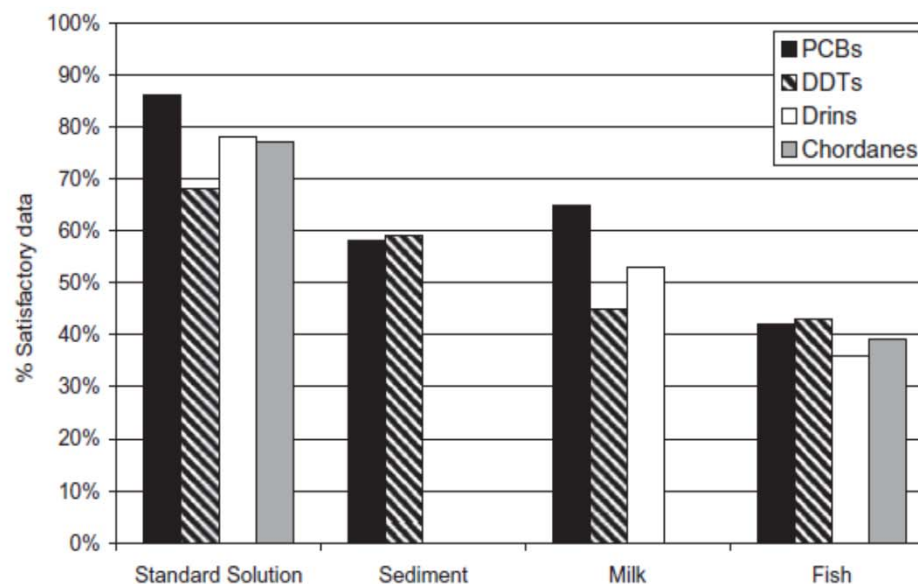
Interlaboratory assessment, 1st round

Trends

Trends in Analytical Chemistry, Vol. 46, 2013

First worldwide UNEP interlaboratory study on persistent organic pollutants (POPs), with data on polychlorinated biphenyls and organochlorine pesticides

S.P.J. Van Leeuwen, B. Van Bavel, J. De Boer



Trends

Trends in Analytical Chemistry, Vol. 46, 2013

Results for PCDD/PCDF and dl-PCBs in the First Round of UNEPs Biennial Global Interlaboratory Assessment on Persistent Organic Pollutants

M. Abalos, E. Abad, S.P.J. van Leeuwen, G. Lindström, H. Fiedler, J. de Boer, B. van Bavel

Narrative summary of 1st round

dl-POPs

- 37 labs submitted data for PCDD/PCDF in standard solution, 29 labs for dl-PCB
- 26 labs submitted results for PCDD/PCDF in fly ash and sediment; 20 and 22 for dl-PCB
- 19 and 15 labs submitted for PCDD/PCDF in fish and human milk; 15 for dl-PCB
- For dl-POP unexpectedly good results,
- Best results were obtained for standard solution: $RSD(TEQ_{PCDD/PCDF}) = 8\%$
- Weakest results obtained for fly ash: $RSD(TEQ_{total}) = 20\%$

Basic POPs

- Good performance on test solution indicates satisfactory instrumental calibration
- Performance PCB>OCPs
- Σ PCB: performance Africa and GRULAC slightly worse than others
For OCPs picture is less clear.
- Generally <<50% satisfactory z-scores for naturally contaminated test samples

Test samples in 2nd round (2012-2013)

Standard solutions

1. OCPs: aldrin, dieldrin, endrin, chlordanes, heptachlors, DDTs, hexachlorobenzene, mirex, HCHs, endosulfans, chlordecone, pentachlorobenzene in the concentration range of 1 µg/kg-1,000 µg/kg
2. PCB: six indicator PCB in the concentration range of 1 µg/kg-10 µg/kg
3. PCDD/PCDF: 2,3,7,8-substituted congeners in the concentration range of 35 µg/kg-180 µg/kg
4. dl-PCB: 12 dl-PCB in the concentration range of 170 µg/kg-300 µg/kg
5. PBDE/PBB: PBDE and PBB-153 in the concentration range of 70 µg/kg -570 µg/kg
6. PFOS: polyfluoroalkyl substances (PFCAs, PFSAs, FOSA) including PFOS and FOSA in the concentration range of 125 µg/kg -320 µg/kg.
7. PFAS: mixture of perfluoroalkyl substances (Me-FOSA, Et- ME-FOSE, Et-FOSE) in the concentration range of 630 µg/kg -1,260 µg/kg

Test samples in 2nd round (2012-2013)

Naturally contaminated test samples

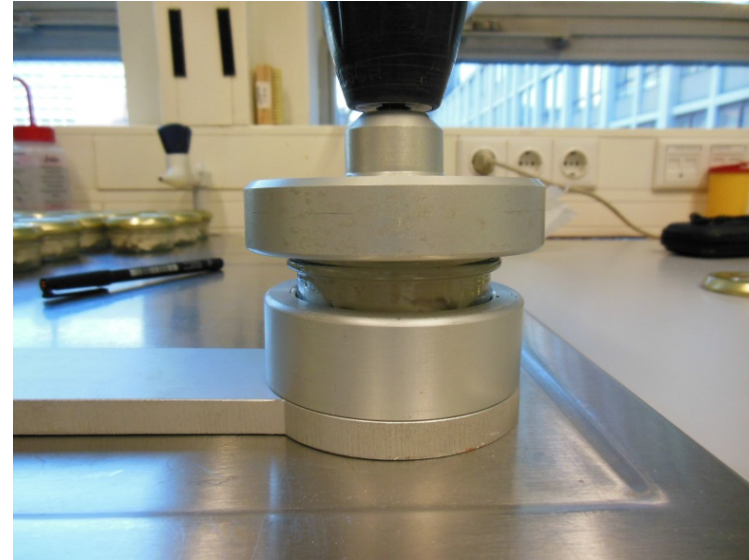
1. Sediment: Marine sediment from the Netherlands
2. Fish: Pike-perch filet from the Netherlands
3. Mother's milk: Homogenized mother's milk from the Swedish mother milk bank in the Örebro region
4. Human blood serum: Pooled human blood serum of both occupationally exposed (professional ski wax technicians) and the general population
5. Air extract: Toluene extract of polyurethane foams (PUF), taken near an hazardous waste incinerator (HWI) and fortified with OCPs, PBDE and PFAS
6. Water : Surface water taken from Amsterdam harbour ("het IJ"), the Netherlands
7. Transformer oil: Dilution of an Aroclor 1254 oil.

Preparation of water test sample



Preparation of fish test sample

Human milk test sample

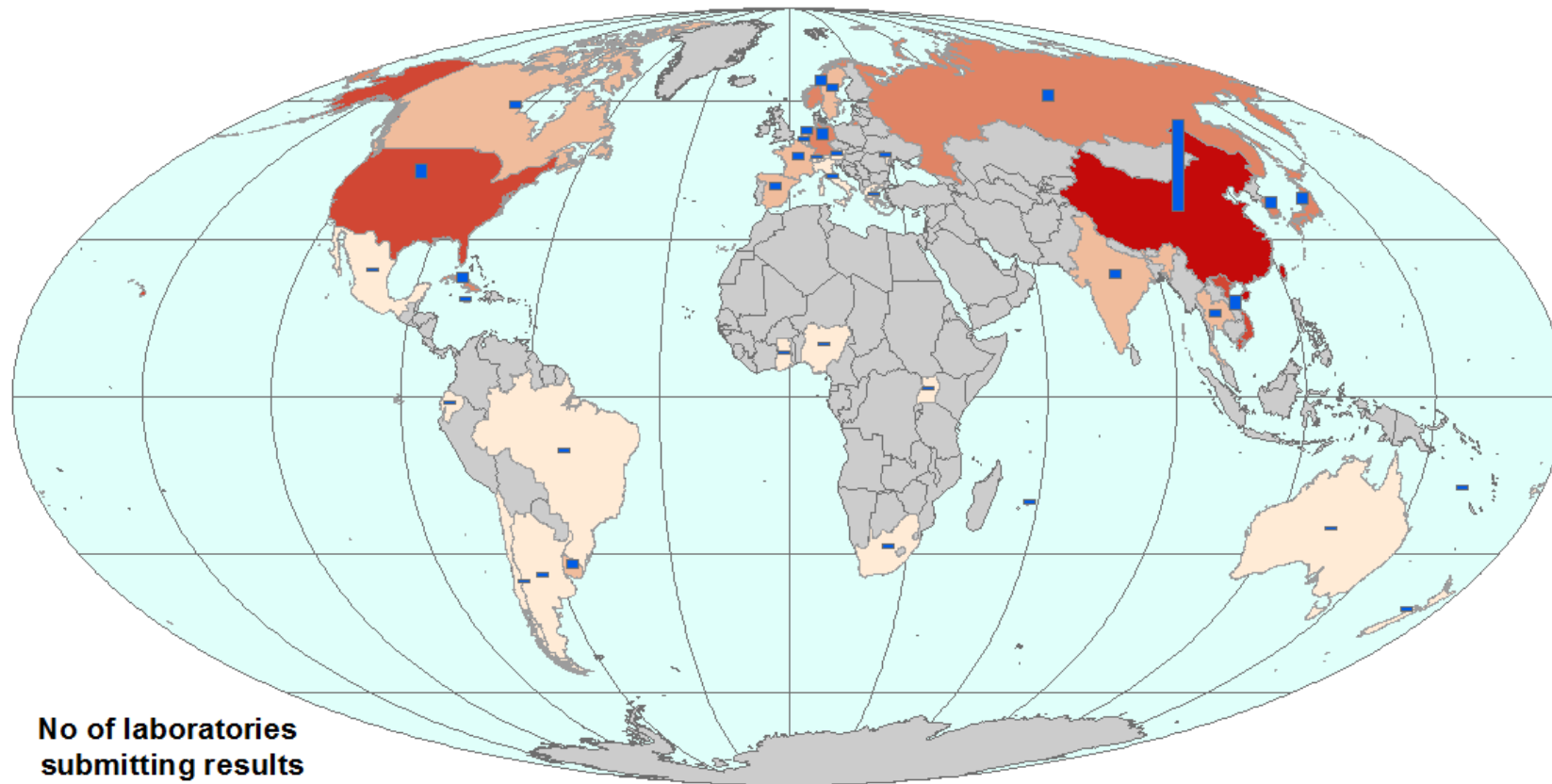


Final test vials

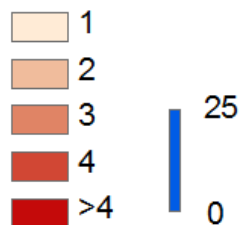


Participation of countries in interlab II

Countries and number of laboratories participating in the interlaboratory assessment



No of laboratories submitting results



Region	Africa	Asia	CEE	GRULAC	WEOG	Total
No of Countries registered	9	9	2	10	16	46
No of Labs registered	12	45	4	14	31	106
No of Labs with results	5	42	4	11	27	89

Registration form (2nd round)

Name of Laboratory: <input type="checkbox"/>					Lab code*:	
Address (for shipment) <input type="checkbox"/>						
City: <input type="checkbox"/>			Contact person:		Name: <input type="checkbox"/>	
Country: <input type="checkbox"/>				E-mail: <input type="checkbox"/>		
*: Lab code from 1 st Round						
My laboratory is interested in analyzing the following matrices and POPs and provide the analytical results according to the reporting scheme and timetable (analysis within eight weeks after receipt):						
Test material	Persistent Organic Pollutants					
Standard solution	OCP <input type="checkbox"/>	PCB ₆ <input type="checkbox"/>	PCDD/PCDF <input type="checkbox"/>	dl-PCB <input type="checkbox"/>	PBDE <input type="checkbox"/>	PFOS <input type="checkbox"/>
Sediment	OCP <input type="checkbox"/>	PCB ₆ <input type="checkbox"/>	PCDD/PCDF <input type="checkbox"/>	dl-PCB <input type="checkbox"/>	PBDE <input type="checkbox"/>	PFOS <input type="checkbox"/>
Fish	OCP <input type="checkbox"/>	PCB ₆ <input type="checkbox"/>	PCDD/PCDF <input type="checkbox"/>	dl-PCB <input type="checkbox"/>	PBDE <input type="checkbox"/>	PFOS <input type="checkbox"/>
Human milk	OCP <input type="checkbox"/>	PCB ₆ <input type="checkbox"/>	PCDD/PCDF <input type="checkbox"/>	dl-PCB <input type="checkbox"/>	PBDE <input type="checkbox"/>	PFOS <input type="checkbox"/>
Human blood						PFOS <input type="checkbox"/>
Air extract	OCP <input type="checkbox"/>	PCB ₆ <input type="checkbox"/>	PCDD/PCDF <input type="checkbox"/>	dl-PCB <input type="checkbox"/>	PBDE <input type="checkbox"/>	PFOS <input type="checkbox"/>
Water						PFOS <input type="checkbox"/>
Transformer oil		PCB ₆ <input type="checkbox"/>				

Labs present in Freiburg

2	42	87	110
4	50	91	116
8	60	94	126
13	65	101	129
22	73	103	130
41	74	105	132

Laboratories present in Freiburg

Standard solution							Sediment							Fish							Transformer oil	
No.	OCP	PCB	PCDD PCDF	dI-PCB	PBDE	PFOS	No.	OCP	PCB	PCDD PCDF	dI-PCB	PBDE	PFOS	No.	OCP	PCB	PCDD PCDF	dI-PCB	PBDE	PFOS	No.	PCB
1	1		1	1	1	1	0							1	1	1	1	1	1	1	0	
1	1		1	1	1	1	1	1	1	1	1		1	1	1	1	1	1	1		0	
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1			1	1			1			1	1			1			1	1			1	
1	1	1		1	1	1	1	1	1		1	1	1	1	1	1		1	1	1	1	1
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1		1	1	1			1		1	1	1			1		1	1	1			1	1
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1	1	1			1	1	1	1	1			1	1	1	1	1			1	1	0	
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1	1	1		1	1		1	1	1		1	1		1	1	1		1	1		0	

Number of labs reporting OCPs per region

Region	Total	Standard solution	Sediment	Fish	Mothers' milk	Air extract
ASIA	25	24	17	16	10	11
WEOG	16	16	13	14	9	8
GRULAC	9	9	7	7	5	4
AFRICA	4	4	2	4	2	2
CEE	2	2	2	2	1	2
Total	56	55	41	43	27	27

CEE = Central and Eastern Europe; WEOG = Western European and Other Groups

Number of labs reporting PCB *per* region

Region	Total	Standard solution	Sediment	Fish	Mothers' milk	Air extract	Transformer oil
ASIA	28	22	18	20	14	15	10
WEOG	21	20	15	17	12	14	7
GRULAC	9	9	8	6	5	3	2
AFRICA	4	3	2	4	2	2	1
CEE	3	2	2	2	1	3	2
Total	65	56	45	49	34	37	22

Number of labs reporting PCDD/PCDF *per* region

Region	Total	Standard solution	Sediment	Fish	Mothers' milk	Air extract
ASIA	31	27	21	22	18	22
WEOG	18	16	12	13	10	13
GRULAC	2	2	0	2	0	1
AFRICA	0	0	0	0	0	0
CEE	3	3	3	3	1	3
Total	54	48	36	40	29	39

Number of labs reporting dl-PCB *per* region

Region	Total	Standard solution	Sediment	Fish	Mothers' milk	Air extract
ASIA	28	25	20	25	20	18
WEOG	21	18	14	15	11	13
GRULAC	2	2	0	2	0	1
AFRICA	0	0	0	0	0	0
CEE	3	3	3	3	1	3
Total	54	48	37	45	32	35

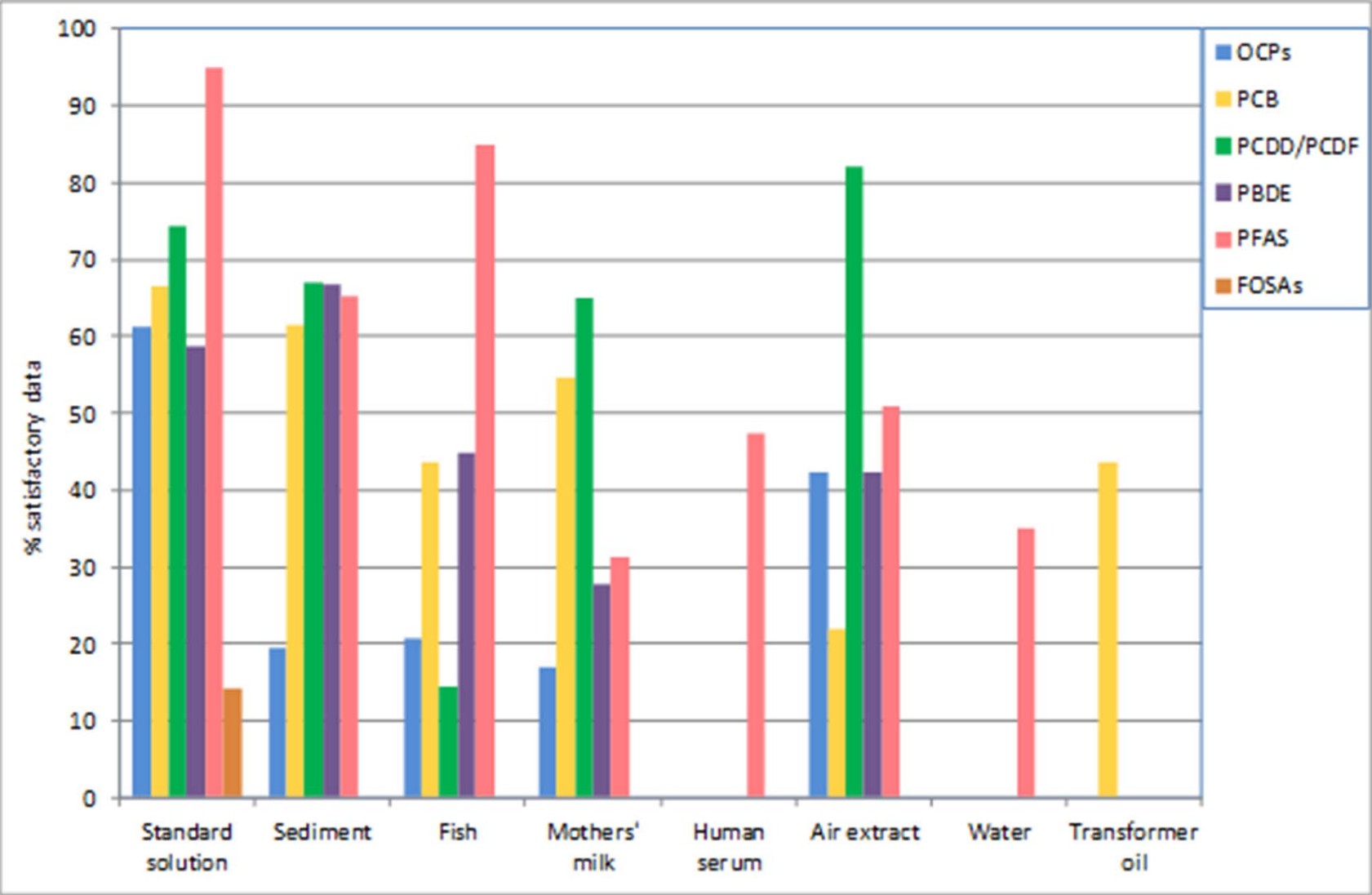
Number of labs reporting PBDE *per* region

Region	Total	Standard solution	Sediment	Fish	Mothers' milk	Air extract
ASIA	22	23	15	22	13	10
WEOG	18	16	13	14	10	10
GRULAC	1	1	1	1	1	1
AFRICA	1	1	1	1	1	0
CEE	2	2	1	1	1	1
Total	44	43	31	39	26	22

Number of labs reporting PFAS *per* region

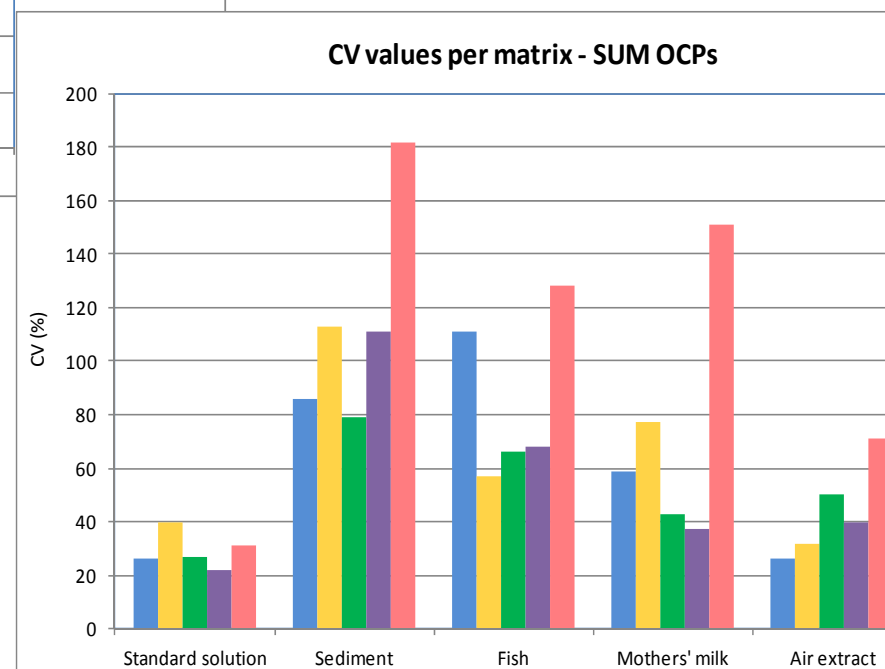
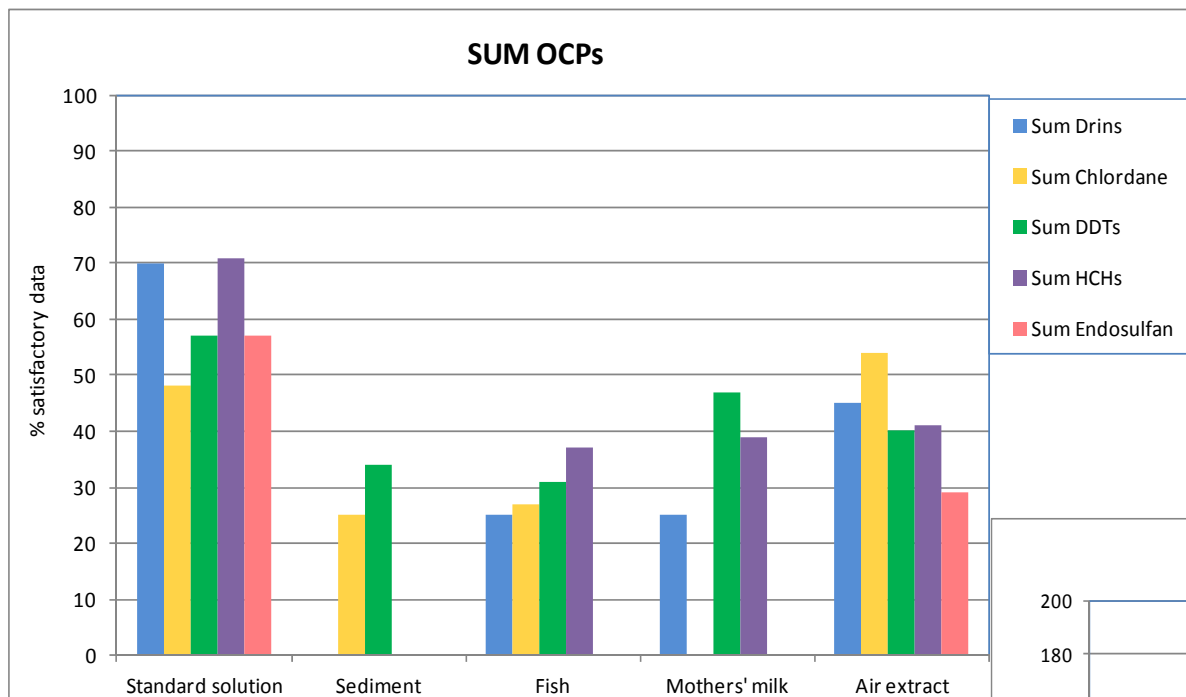
Region	Total	Standard solution	Sediment	Fish	Mothers' milk	Human serum	Air extract	Water
ASIA	16	15	13	12	6	7	7	13
WEOG	15	11	9	10	6	6	6	12
GRULAC	0	0	0	0	0	0	0	0
AFRICA	0	0	0	0	0	0	0	0
CEE	0	0	0	0	0	0	0	0
Total	31	26	22	22	12	13	13	25

Laboratories with satisfactory performance



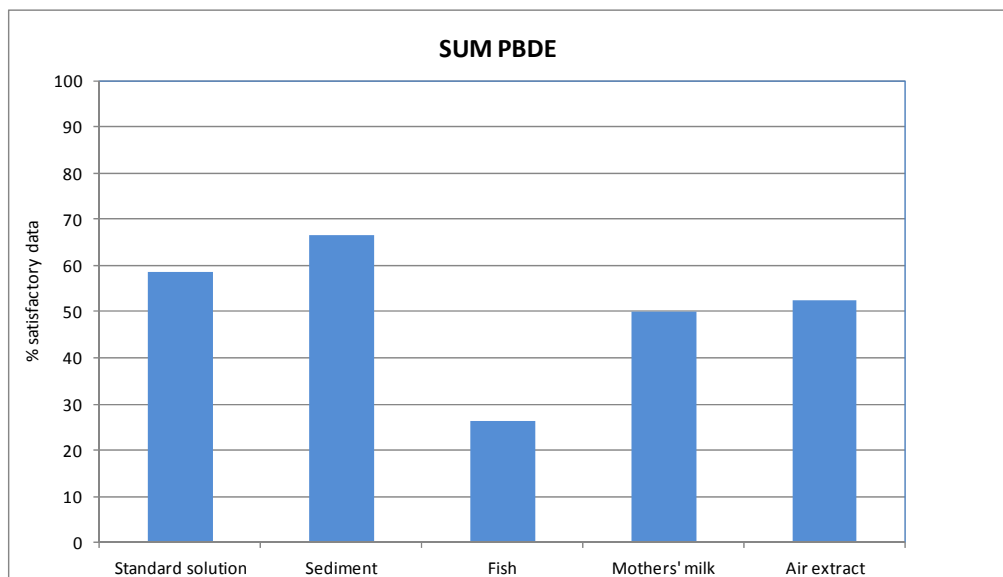
Performance *per*
group of POPs and
test sample

Laboratories with satisfactory performance



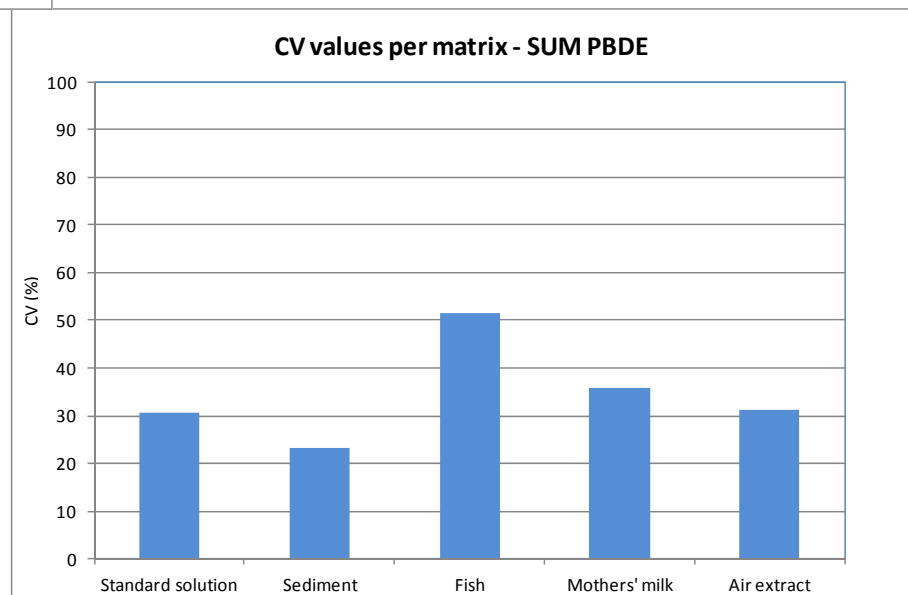
Real samples still a problem for the majority of laboratories;
New POP = endosulfans worse

Performance on sum parameters



Best performance was for sediment sample where 64% of the participants achieved satisfactory z-scores

The performance of laboratories was relatively good for the sediment sample (CVs 18%-42%)



OCPs in mothers' milk

Analyte	n	Between Lab CV (%)	Inclusion rate (%)
Sum Drins	10	59	68
Sum Chlordanes	16	77	75
Sum DDTs	17	43	63
Sum HCHs	14	37	64
Sum Endosulfans	4	151	67

Analyte	% of the	% of z-scores	% of z-scores	% of z-scores	% of z-scores
	data received	$ z < 2$	$3 > z > 2$	$6 > z > 3$	$ z > 6$
		Satisfactory	Questionable	Unsatisfactory	Extreme
Sum Drins	15	25	0	19	19
Sum Chlordanes	16	0	0	0	0
Sum DDTs	16	47	12	12	29
Sum HCHs	17	39	6	11	22
Sum Endosulfans	13	0	0	0	0

OCPs in air extract

Analyte	n	Between Lab CV (%)	Inclusion rate (%)
Sum Drins	16	26	62
Sum Chlordanes	22	32	66
Sum DDTs	22	50	73
Sum HCHs	18	40	65
Sum Endosulfans	12	71	65

Analyte	% of the	% of z-scores	% of z-scores	% of z-scores	% of z-scores
	data received	$ z < 2$	$3 > z > 2$	$6 > z > 3$	$ z > 6$
		Satisfactory	Questionable	Unsatisfactory	Extreme
Sum Drins	19	45	5	15	15
Sum Chlordanes	23	54	4	13	21
Sum DDTs	24	40	8	20	20
Sum HCHs	21	41	9	14	18
Sum Endosulfans	13	29	0	21	36

Performance for sum parameter PCB₆

Analyte	n	Between lab CV (%)	Inclusion rate (%)
Standard solution			
PCB ₆ LB (ND=0)	41	18	67
PCB ₆ UB (ND=LOD)	38	18	66
Sediment			
PCB ₆ LB (ND=0)	34	21	70
PCB ₆ UB (ND=LOD)	31	20	71
Fish			
PCB ₆ LB (ND=0)	37	28	65
PCB ₆ UB (ND=LOD)	36	32	68
Mothers' milk			
PCB ₆ LB (ND=0)	24	26	75
PCB ₆ UB (ND=LOD)	23	26	75
Air extract			
PCB ₆ LB (ND=0)	23	71	64
PCB ₆ UB (ND=LOD)	25	83	69
Transformer oil			
PCB ₆ LB (ND=0)	15	36	80
PCB ₆ UB (ND=LOD)	15	36	74

z-scores for PCB₆

	% of the	% of z-scores	% of z-scores	% of z-scores	% of z-scores
	data received	$ z < 2$	$3 > z > 2$	$6 > z > 3$	$ z > 6$
		Satisfactory	Questionable	Unsatisfactory	Extreme
Standard solution					
PCB ₆ LB (ND=0)	39	66	17	7	10
PCB ₆ UB (ND=LOD)	36	66	16	8	11
Sediment					
PCB ₆ LB (ND=0)	32	71	9	12	9
PCB ₆ UB (ND=LOD)	30	77	3	13	6
Fish					
PCB ₆ LB (ND=0)	35	62	8	11	19
PCB ₆ UB (ND=LOD)	34	56	14	11	19
Mothers' milk					
PCB ₆ LB (ND=0)	23	71	13	8	8
PCB ₆ UB (ND=LOD)	22	70	13	13	4
Air extract					
PCB ₆ LB (ND=0)	24	36	12	8	36
PCB ₆ UB (ND=LOD)	25	0	0	0	0
Transformer oil					
PCB ₆ LB (ND=0)	14	47	33	13	7
PCB ₆ UB (ND=LOD)	14	60	13	13	13

Summary results PBDE

Matrix	n	Between lab CV (%)	Inclusion rate (%)
Standard solution	41	31	66
Sediment	30	23	65
Fish	34	51	73
Mothers' milk	20	36	73
Air extract	21	31	61

Matrix	% of the data received	% of z-scores	% of z-scores	% of z-scores	% of z-scores
		$ z < 2$	$3 > z > 2$	$6 > z > 3$	$ z > 6$
		Satisfactory	Questionable	Unsatisfactory	Extreme
Standard solution	39	59	7	15	20
Sediment	29	67	3	10	20
Fish	32	26	32	26	15
Mothers' milk	21	50	14	14	14
Air extract	20	52	10	10	29

Summary results PFAS

Matrix	n	Between lab CV (%)	Inclusion rate (%)
Standard solution	15	40	70
Human serum	7	3	62
Air extract	7	175	55

Matrix	% of the	% of z-scores	% of z-scores	% of z-scores	% of z-scores
	data received	$ z < 2$	$3 > z > 2$	$6 > z > 3$	$ z > 6$
		Satisfactory	Questionable	Unsatisfactory	Extreme
Standard solution	14	73	0	0	27
Human serum	7	86	14	0	0
Air extract	7	0	0	0	0

Regional summary results for PFAS

Human serum	Asia-Pacific group			WEOG		
Analyte	n	Between lab CV (%)	Inclusion rate (%)	n	Between lab CV (%)	Inclusion rate (%)
L-PFOS anion	4	37	80	4	25	81
FOSA	0	NA	NA	0	NA	NA

Air extract	Asia-Pacific group			WEOG		
Analyte	n	Between lab CV (%)	Inclusion rate (%)	n	Between lab CV (%)	Inclusion rate (%)
L-PFOS anion	3	55	81	5	13	46
FOSA	2	NA	NA	5	98	86

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