



Results and lessons learned from the second round of the 'Biennial global interlaboratory assessment of POPs laboratories'

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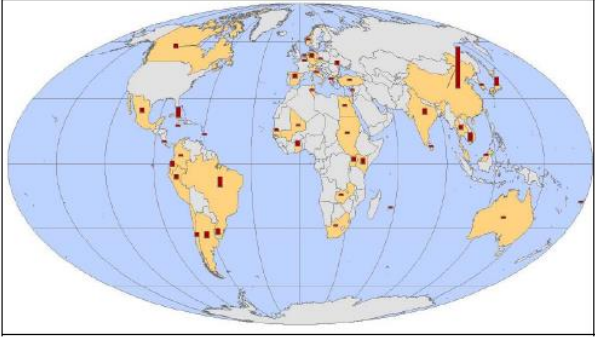
Stockholm Convention on POPs (2)

- Article 16: Global Monitoring Plan (GMP) established, guidance developed
- COP decisions SC-3/16, SC-4/31, SC-5/18 and SC-6/23;
- 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 $\pm 25\%$;
 - Harmonized data generation and assessment
- Guidance document for monitoring and list of POPs must be harmonized as new POPs – and new matrices – are added.

2 Rounds of interlaboratory assessments


Bi-ennial Global Interlaboratory Assessment on Persistent Organic Pollutants – First Round 2010/2011

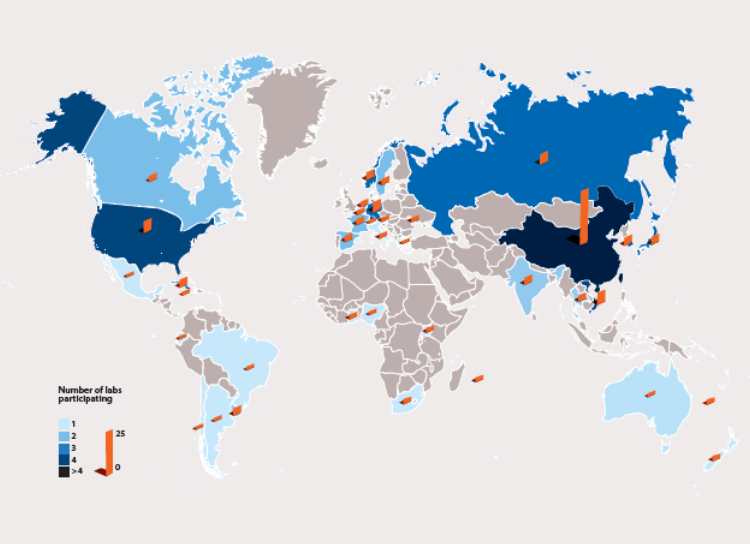


Coordinated by:
Chemicals Branch
United Nations Environment Programme/DTIE

March 2012

IOMC
INTER-ORGANIZATION PROGRAMME FOR THE SOUND MANAGEMENT OF CHEMICALS
A cooperative agreement among FAO, ILO, UNFIC, UNEP, UNIDO, UNITAR, WHO, World Bank and OECD

 **Bi-ennial Global Interlaboratory Assessment on Persistent Organic Pollutants**
Second Round 2012/2013



Number of labs participating

1 2 3 4 >4

0 25

June 2014

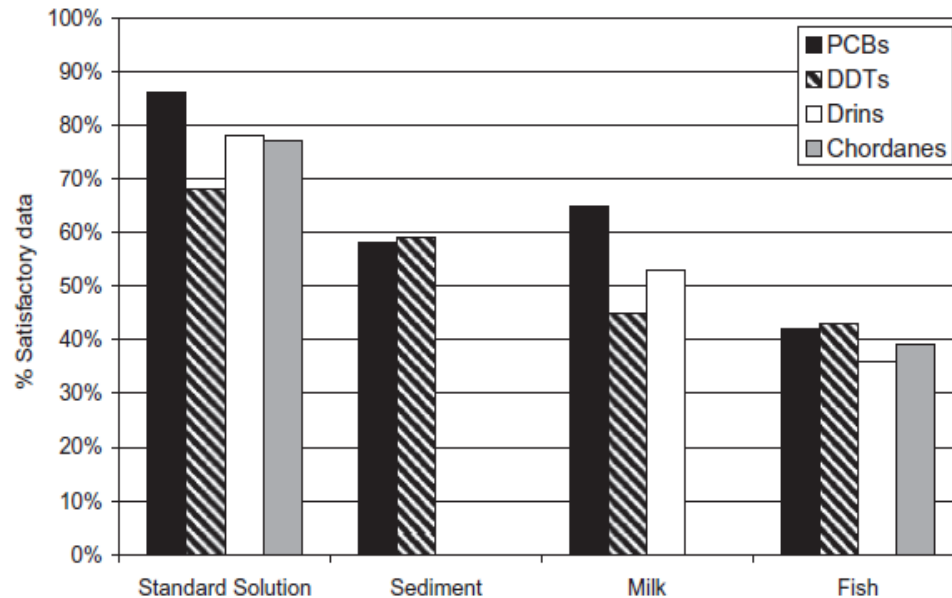
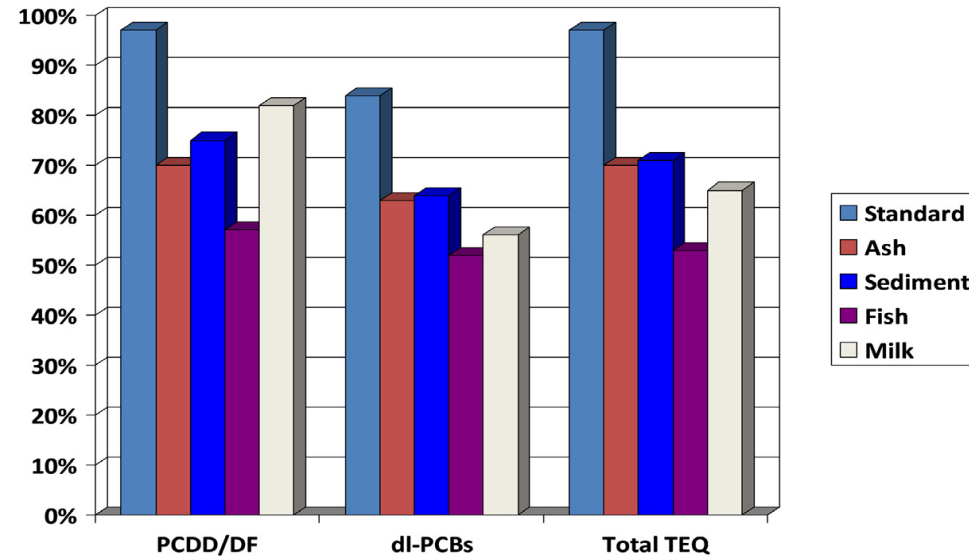
Global interlaboratory assessments on POPs

- 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

1st Global Interlaboratory Assessment

Performance of laboratories

The overall goal is to reach a maximum analytical variation of 25% between the participating laboratories ($z < |2|$).



z-scores can be interpreted as follows:
 $|z| < 2$: Satisfactory performance
 $2 < |z| < 3$: Questionable performance
 $|z| > 3$: Unsatisfactory performance

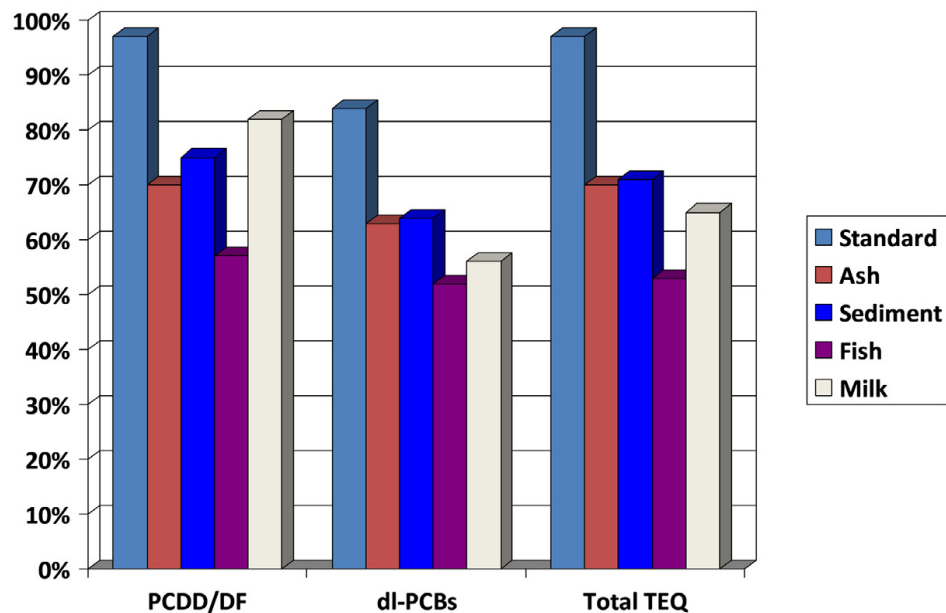
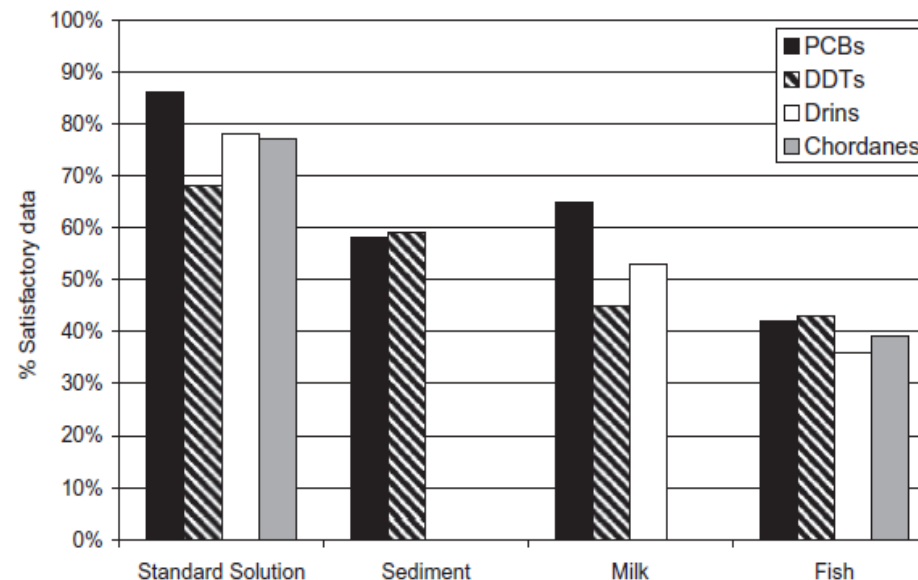
Interlaboratory assessment, 1st round

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

Registration form (2nd round)

Name of Laboratory:						Lab code*:	
Address (for shipment)							
City:		Contact person:	Name:				
Country:		E-mail:					
*: 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"/>					

Test samples in 2nd round (2012-2013)

Standard solutions

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

Test samples in 2nd round (2012-2013)

Naturally contaminated test samples

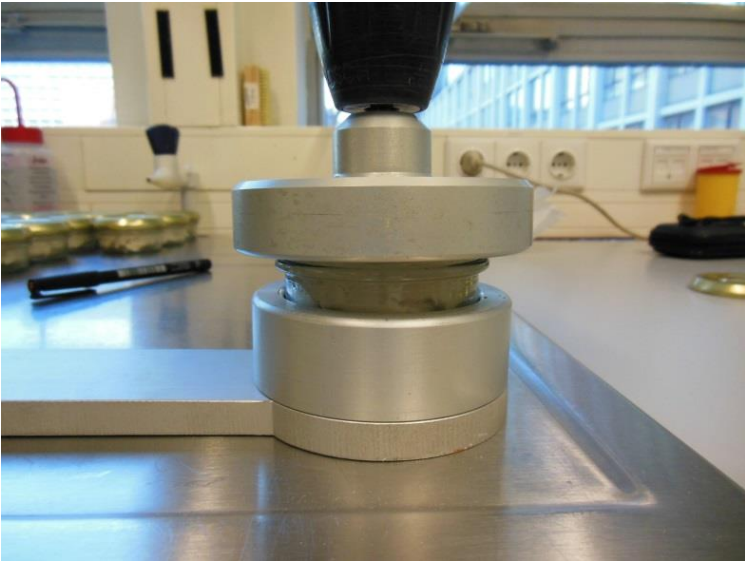
1. Sediment: Marine sediment from the Netherlands
2. Fish: Pike-perch filet from the Netherlands
3. Mother's milk: Homogenized mother's milk from the Swedish mother milk bank in the Örebro region
4. Human blood serum: Pooled human blood serum of both occupationally exposed (professional ski wax technicians) and the general population
5. Air extract: Toluene extract of polyurethane foams (PUF), taken near a 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

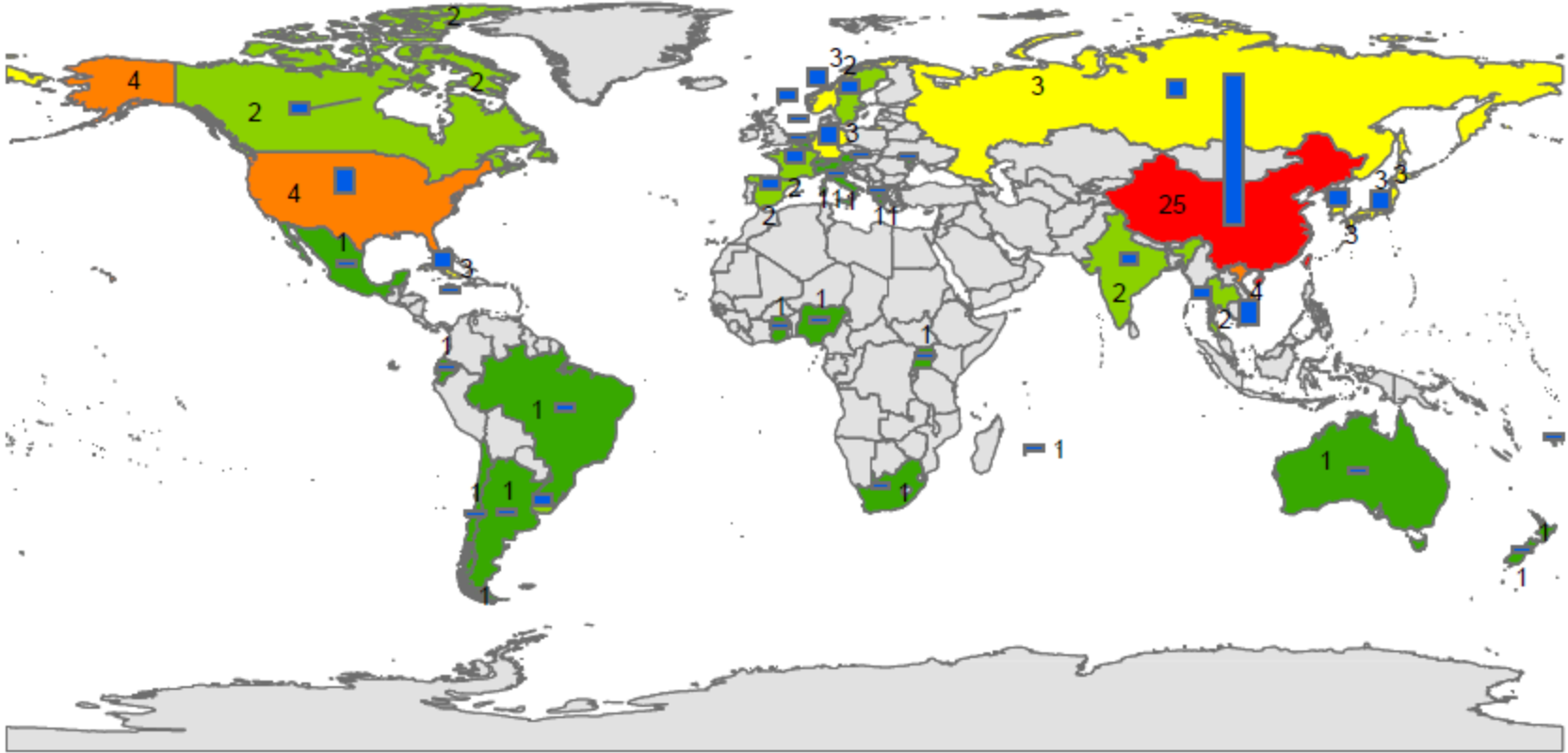
Human milk test sample



Final test vials



Laboratories in 2nd Interlaboratory Assessment 2012/2013



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

Of the Asian labs: 25 from China

2nd Global Interlaboratory Assessment

Distribution of samples according to matrix and POP for analysis (2012-2013)

Group	Standard solutions	Sediment	Fish	Human milk	Air	Water	Human serum	Transformer oil	Totals
OCP	50	27	36	21	23	-	-	-	157
PCB	47	38	43	28	25	-	-	19	200
dI-POPs	48	34	41	29	37	-	-	-	189
PBDE	42	30	34	19	21	-	-	-	146
PFAS	22	18	19	8	8	30	8	-	113
Totals	209	147	173	105	114	30	8	19	805

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

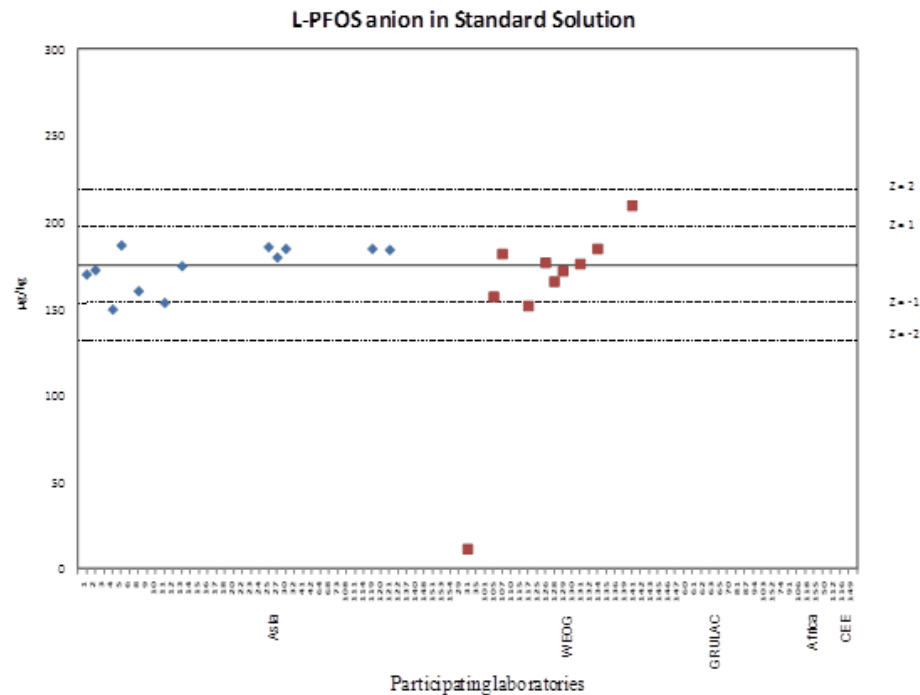
Region	Total	Standard solution	Sediment	Fish	Mothers' milk	Human serum	Air extract	Water
ASIA	16	15	13	12	6	7	7	13
WEOG	15	11	9	10	6	6	6	12
GRULAC	0	0	0	0	0	0	0	0
AFRICA	0	0	0	0	0	0	0	0
CEE	0	0	0	0	0	0	0	0
Total	31	26	22	22	12	13	13	25

Performance *per* group
of POPs and test
sample

Assessment according to ISO 17043

z-scores can be interpreted as follows:

- $|z| < 2$ Satisfactory performance
- $2 < |z| < 3$ Questionable performance
- $|z| > 3$ Unsatisfactory performance

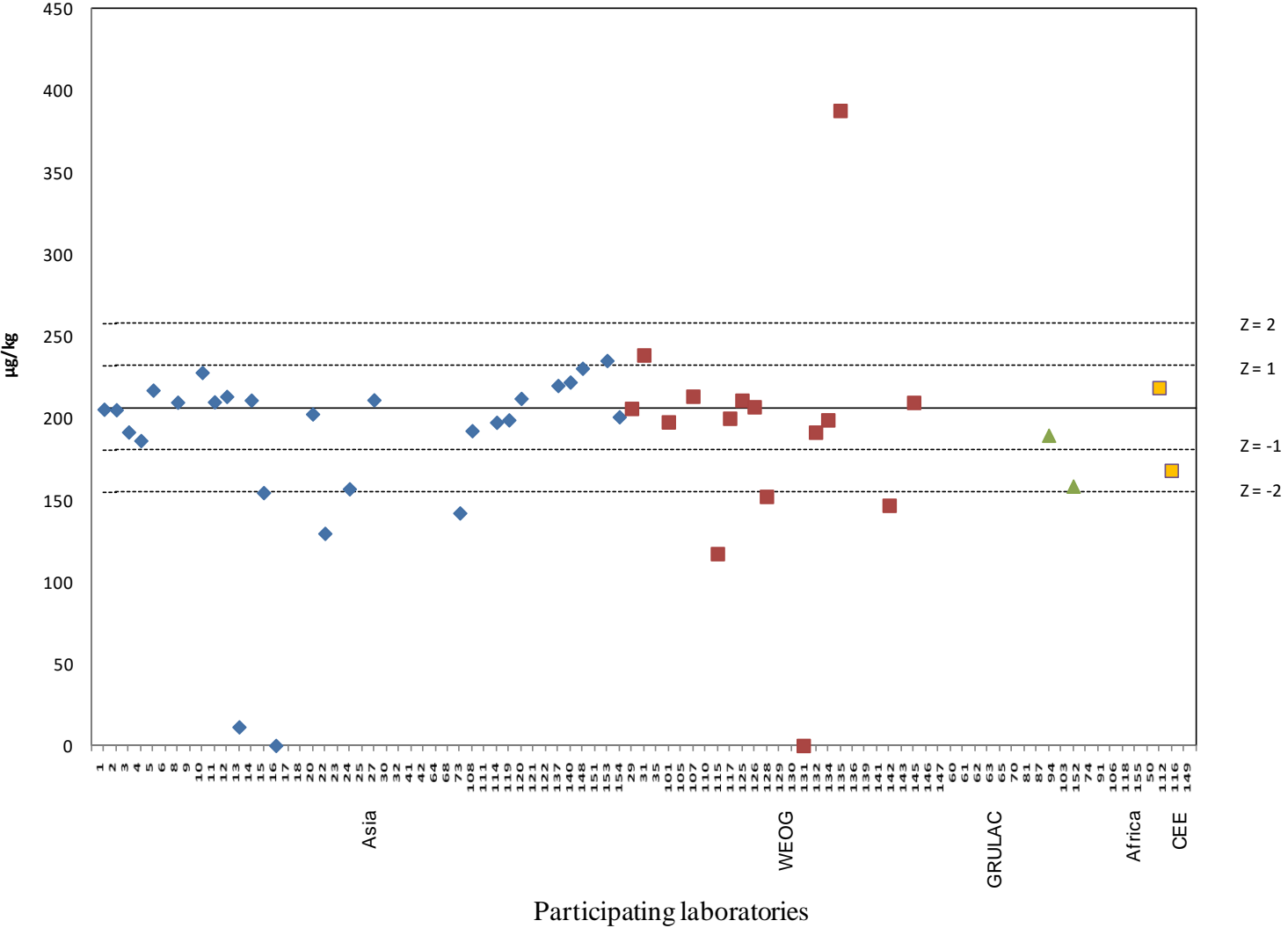


Results of concentrations per analyte and matrix presented;
⇒ z-scores available for all laboratories

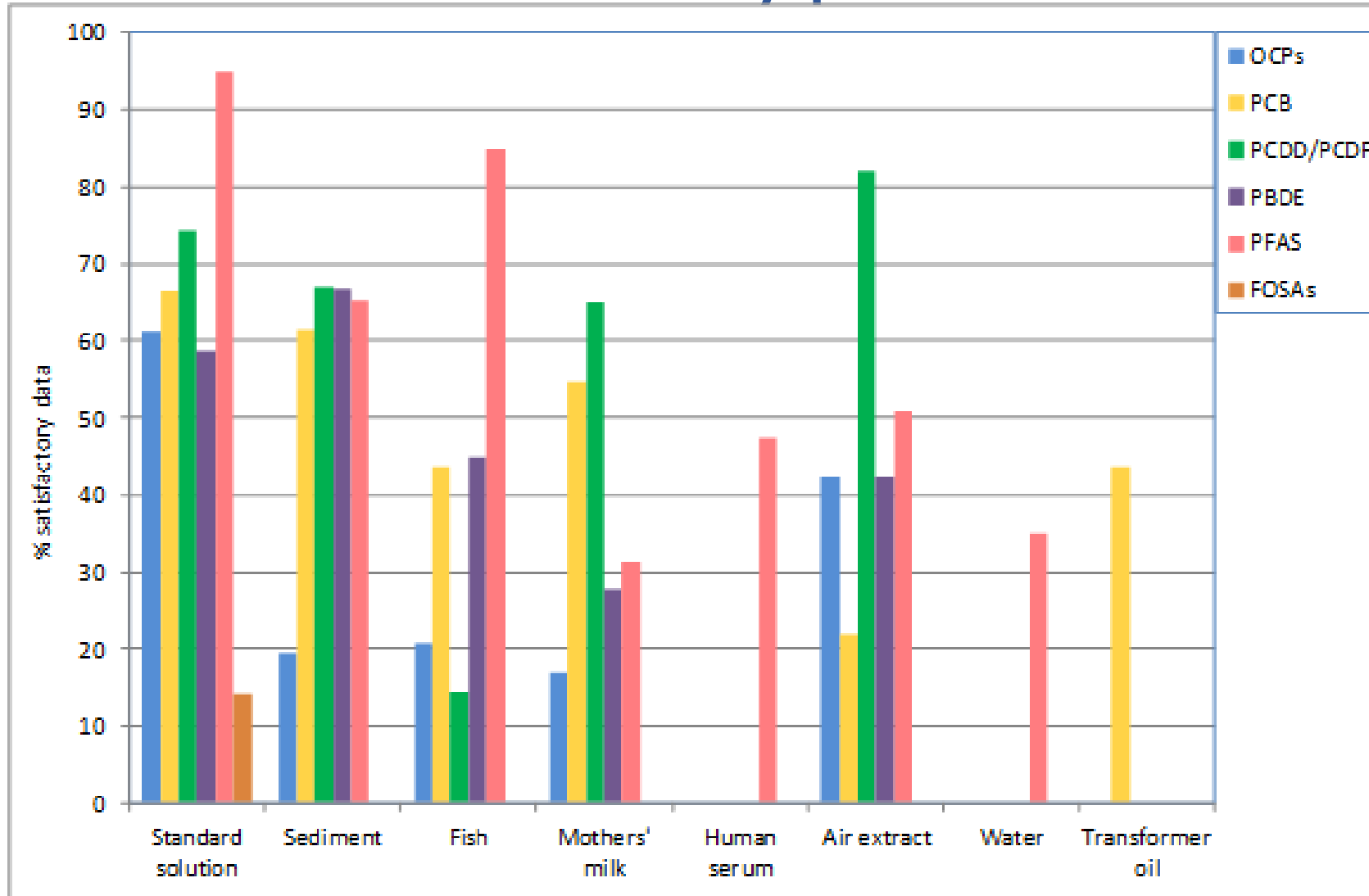
z = 12.5%

PCDD/PCDF in standard solution

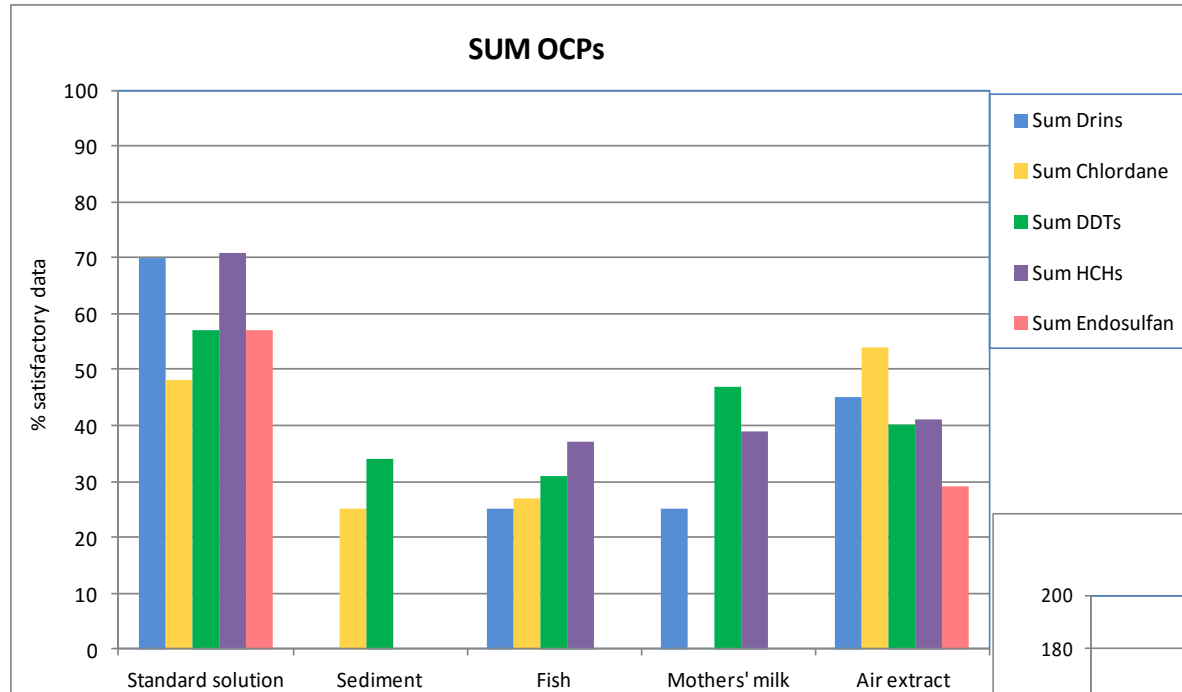
PCDD/PCDF TEQ in Standard Solution



Laboratories with satisfactory performance

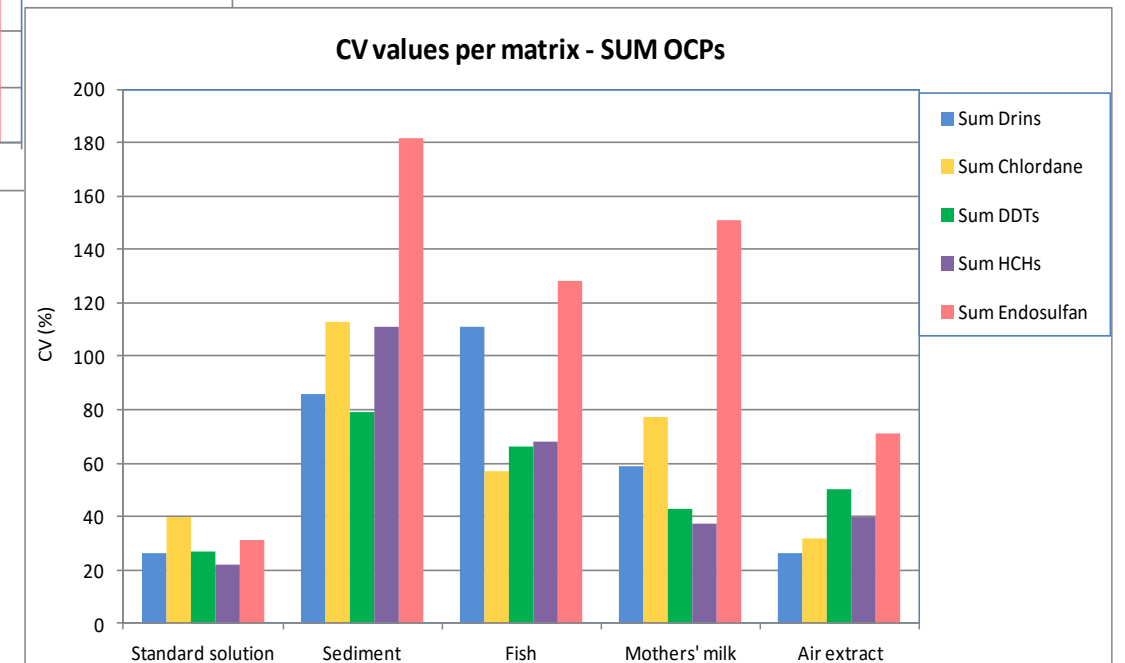


Laboratories with satisfactory performance



2nd round

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

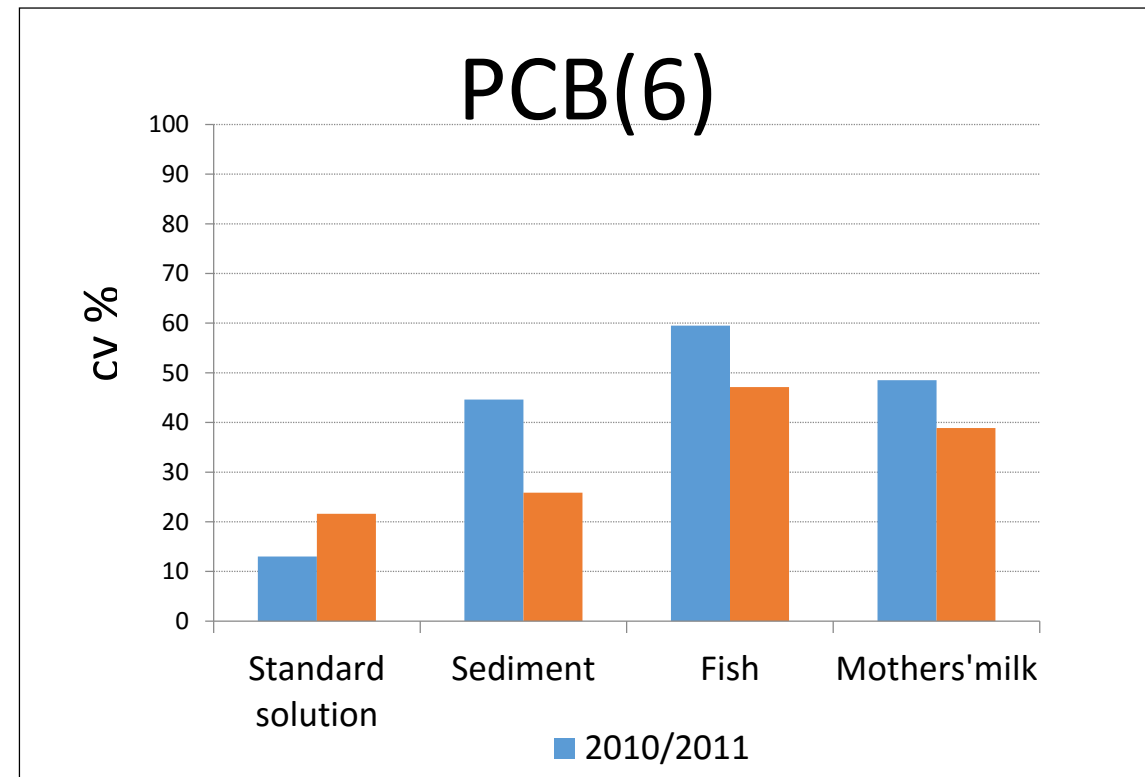
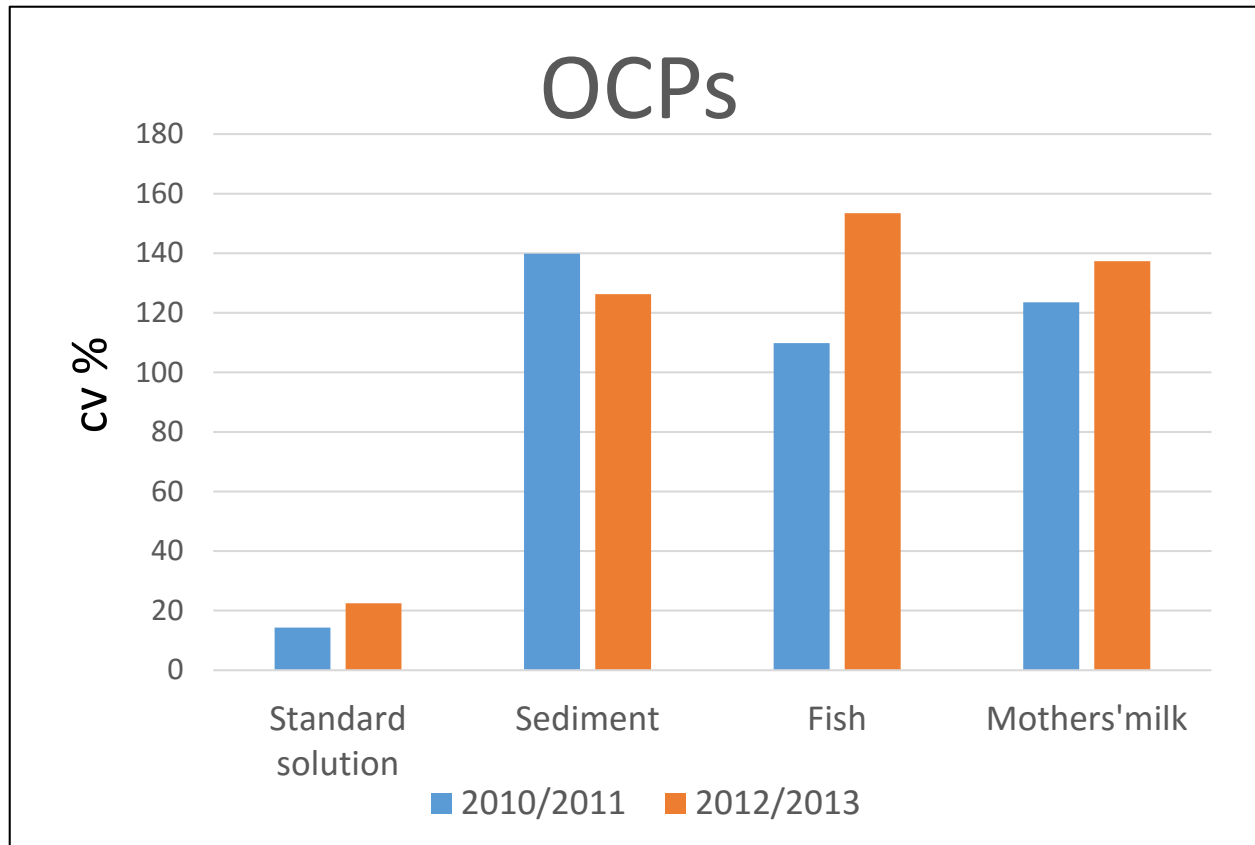


OCPs in air extract

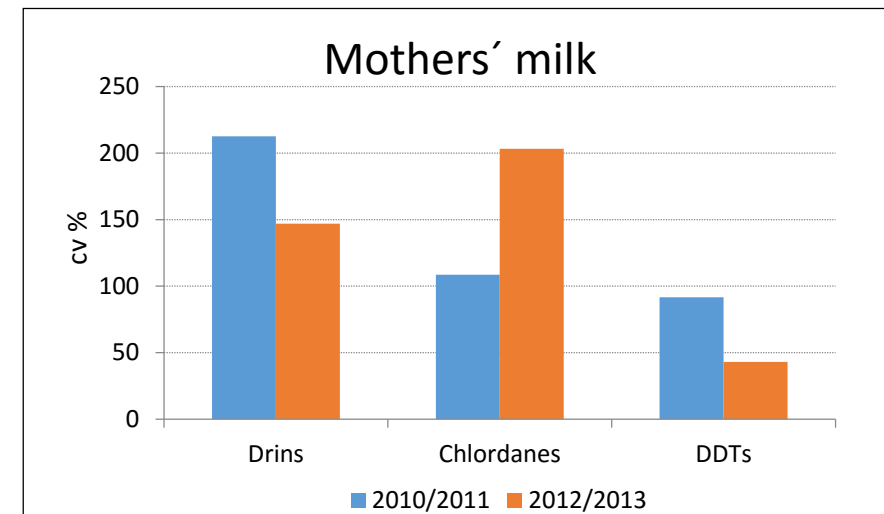
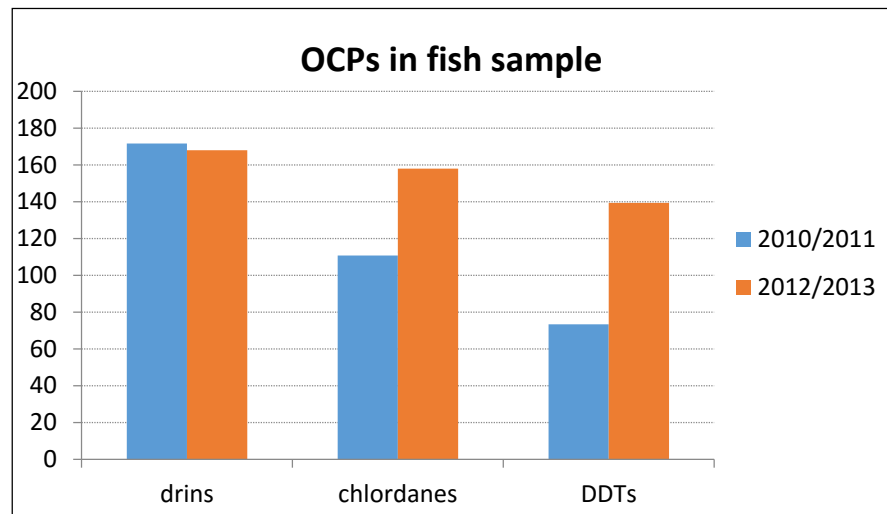
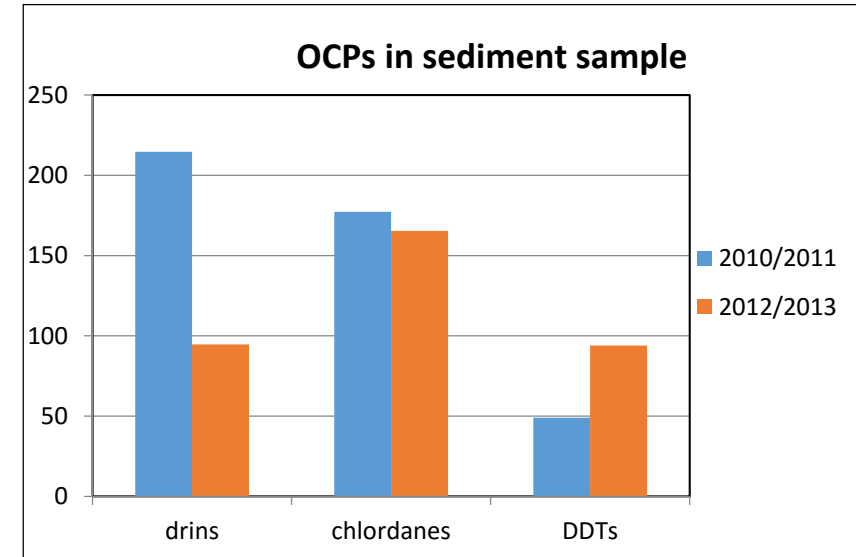
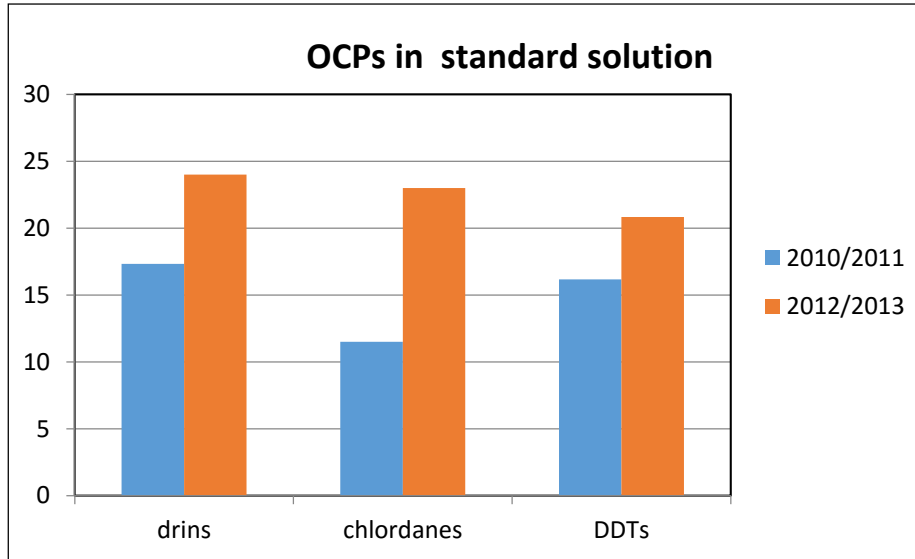
Analyte	n	Between Lab CV (%)	Inclusion rate (%)
Sum Drins	16	26	62
Sum Chlordanes	22	32	66
Sum DDTs	22	50	73
Sum HCHs	18	40	65
Sum Endosulfans	12	71	65

Analyte	% of the data received	% of z-scores $ z < 2$ Satisfactory	% of z-scores $3 > z > 2$ Questionable	% of z-scores $6 > z > 3$ Unsatisfactory	% of z-scores $ z > 6$ Extreme
	Sum Drins	19	45	5	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

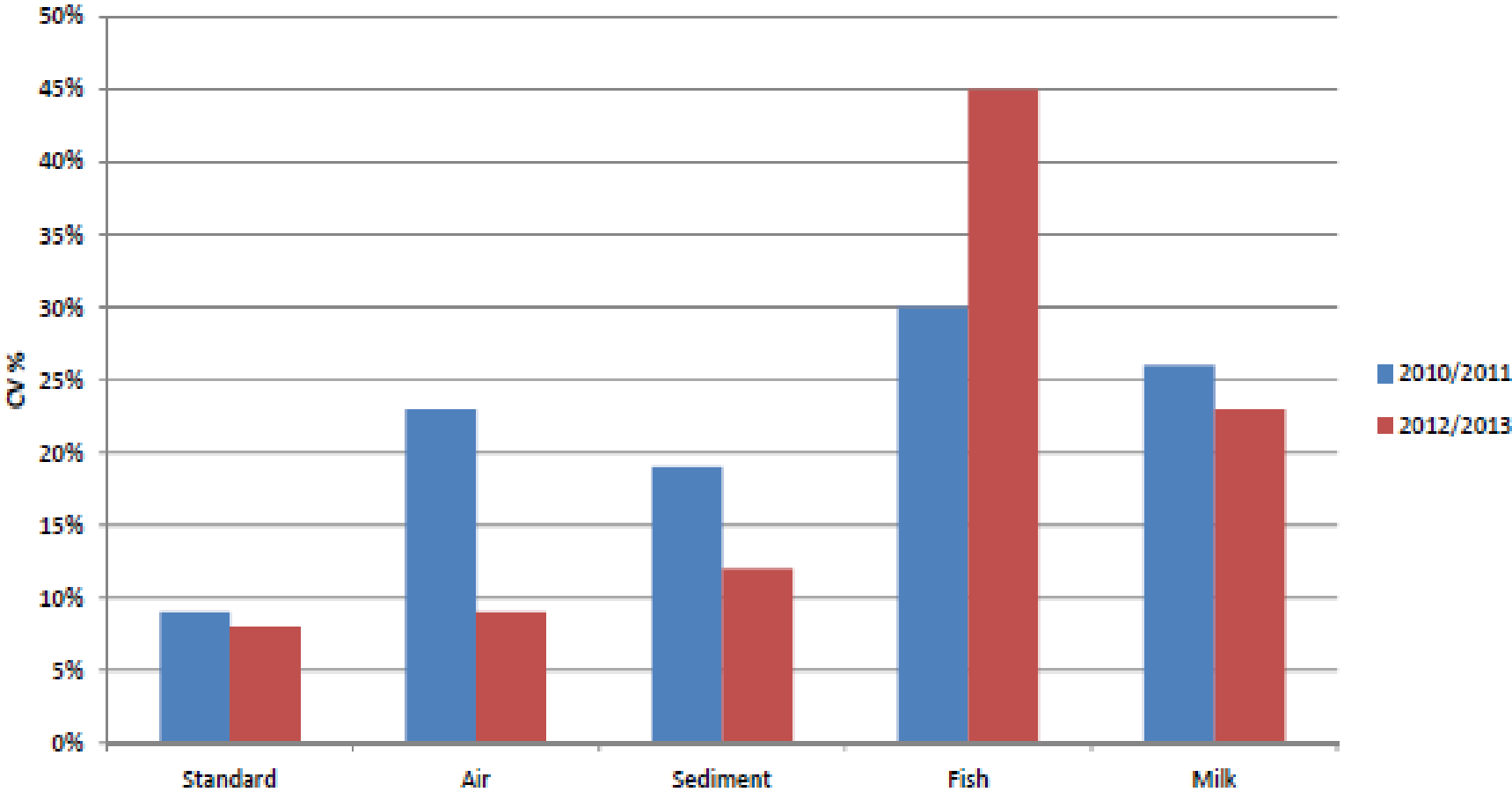
Comparison 1st round vs. 2nd round



Comparison 1st round vs. 2nd round



Comparison PCDD/PCDF analysis: 1st round vs. 2nd round



Regional performance
per group of POPs and
test sample

2nd Interlaboratory assessment on POPs

Region	# Labs	Results S	% S	Results Q	Results U
Africa	5	11	0.3 %	13	67
Asia-Pacific	42	3,691	52 %	474	878
Central + Eastern Europe	4	296	4.2 %	57	89
Latin America and Caribbean	10	287	4.1 %	60	164
Western Europe and Others	27	2,752	39 %	420	535
Total	89	7,035		1,024	1,801

Approx. 10,000 z-scores generated

$ z < 2$	Satisfactory performance	S
$2 < z < 3$	Questionable performance	Q
$ z > 3$	Unsatisfactory performance	U

African laboratories' performance

Lab	Total reported	Satisfactory	Questionable	Unsatisfactory	Empty cells
L074	68	1	-	67	79
L091	34	5	7	22	62
L106	4	1	-	3	46
L118	28	-	-	28	22
L155	25	4	6	15	1

African laboratories (GHA, MUS, NGA, UGA, ZAF) reported for OCPs (4 labs), indicator PCB (4 labs) and 1 lab for PBDE

Conclusions from 2nd interlaboratory assessment

- The degree of participation (105 laboratories from 48 countries) showed high interest of laboratories to participate in this assessment;
- New POPs added to the scheme of the initial twelve groups of POPs, and new matrices;
- High interest for capacity-building resulted in a wealth of information on POP analysis and huge data set from which the laboratories can evaluate their performance;
- Improvement in performance of initial POPs not satisfactory for UNEP criteria;
- Results for new POPs – PBDE, PFAS - were promising although limited participation;
- Capacity for analysis of new POPs is located in Asian and WEOG regions;
- For the analysis of the group of PFAS compounds, LC/MS/MS is needed;
- None of the 105 participating laboratories were able to carry out all analyses that were offered in this assessment.

Acknowledgement

UNEP thanks

- All laboratories participating in this interlaboratory assessment;
- Wellington Laboratories (Guelph, ON, Canada) and Cambridge Isotope Laboratories (Andover, MA, U.S.A.) for preparing the test solutions;
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- Secretariat of Basel, Rotterdam, and Stockholm conventions for fruitful cooperation;
- MTM Center, Örebro University (Sweden) and IVM VU University, Amsterdam (the Netherlands) for coordinating the assessment;
- CVUA, EURL and UNEP/WHO Reference Laboratory, Freiburg (Germany) for organizing the workshop and the training;
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