Results and lessons learned from ´biennial global interlaboratory assessments´

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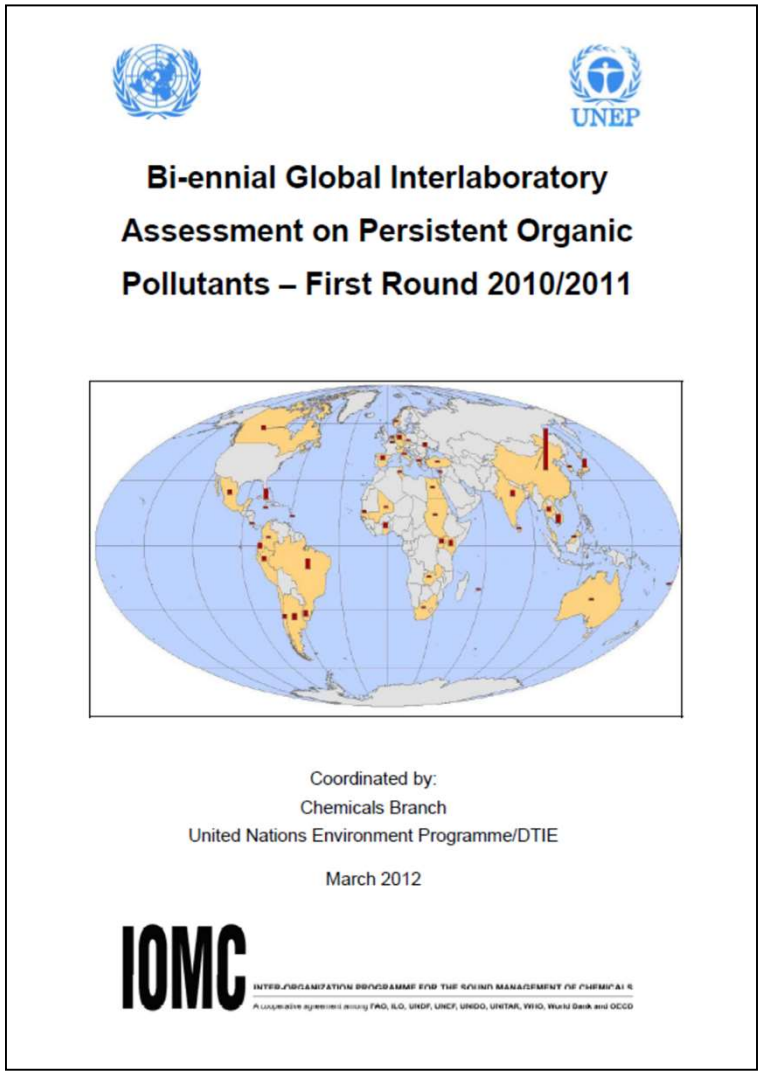
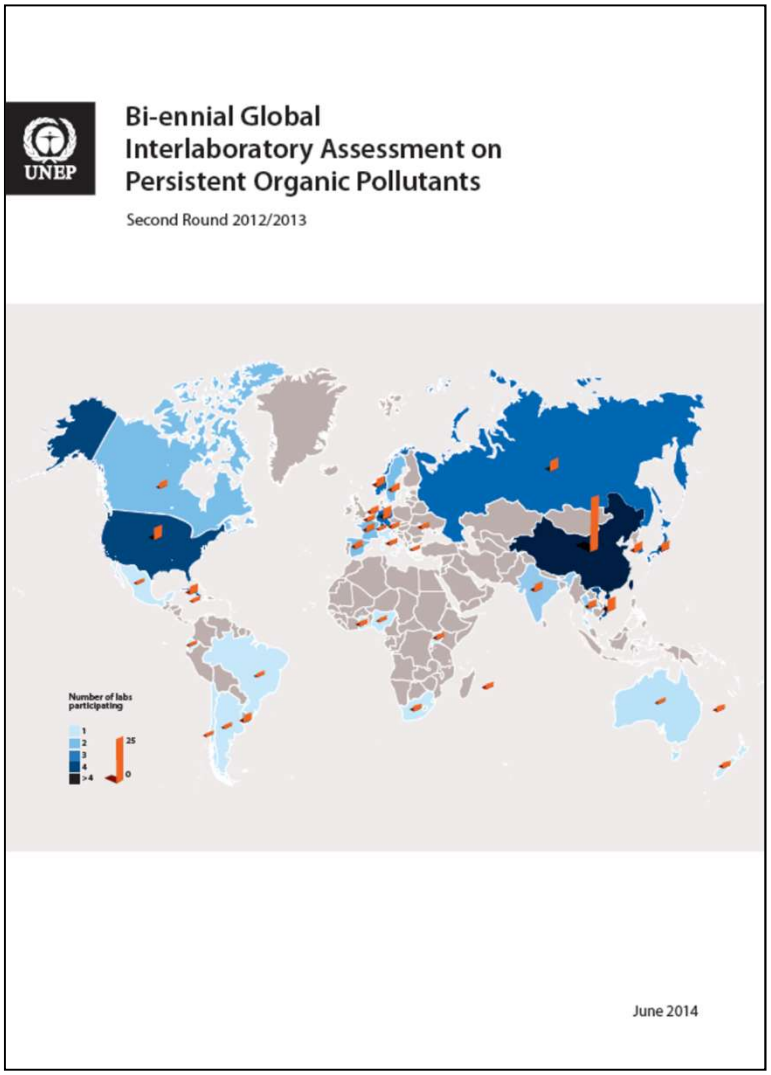
Stockholm Convention on POPs (2)

- 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 ±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





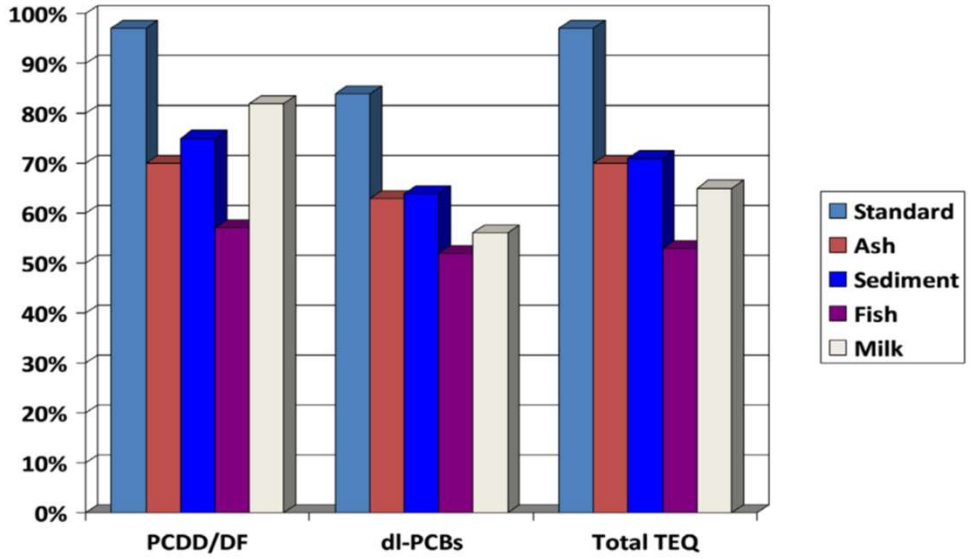
Global interlaboratory assessments on POPs

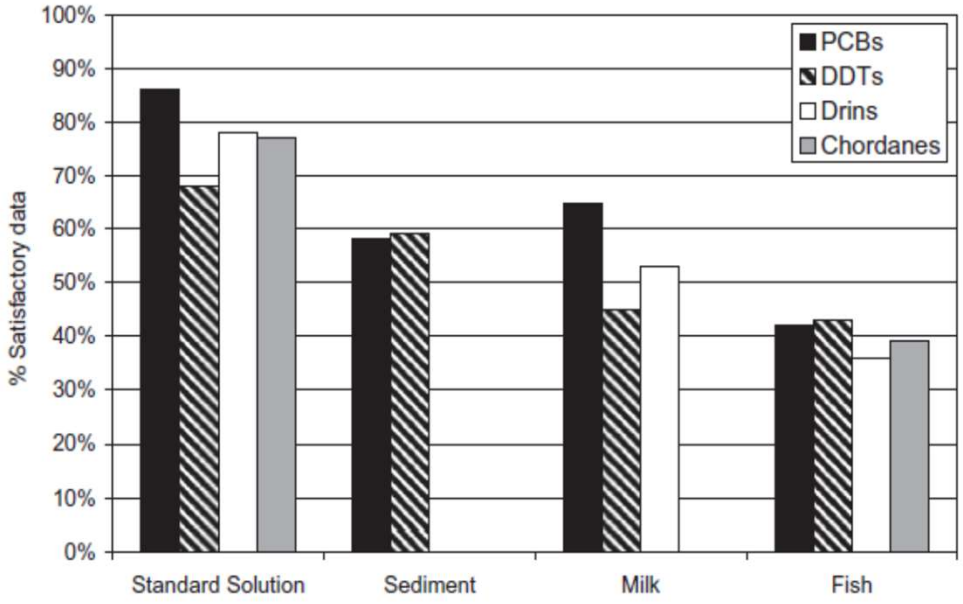
- Coordination:
  - UNEP/DTIE Chemicals Branch, Heidi Fiedler
- Organisers:
  - Örebro University, Man-Technology-Environment Research Center (MTM), Bert vanBavel, Helena Nilsson
  - VU University Amsterdam, Institute for Environmental Studies (IVM), Jacob de Boer, Ike van der Veen

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|).





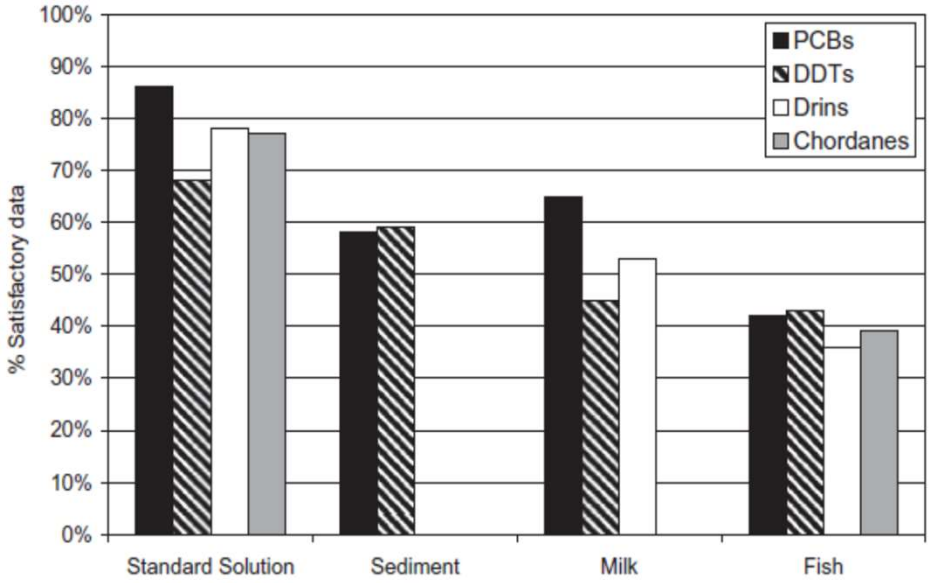
z-scores can be interpreted as follows:
|z| < 2: Satisfactory performance
2 < |z| < 3: Questionable performance
|z| > 3: Unsatisfactory performance

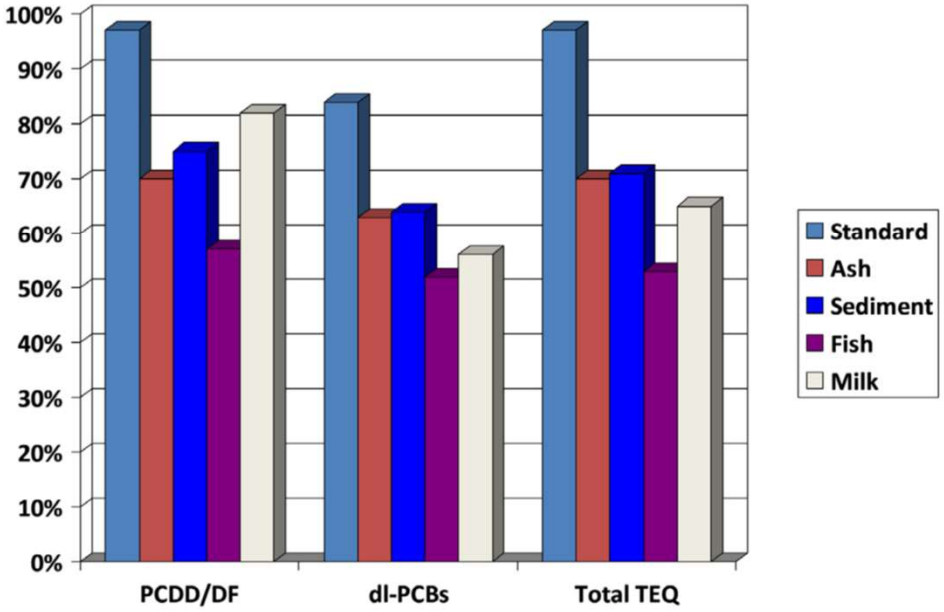
Interlaboratory assessment, 1st round

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
- ΣPCB: 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 1st 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 ☐	PCB_6 ☐	PCDD/PCDF ☐	dl-PCB ☐	PBDE ☐	PFOS ☐
Sediment	OCP ☐	PCB_6 ☐	PCDD/PCDF ☐	dl-PCB ☐	PBDE ☐	PFOS ☐
Fish	OCP ☐	PCB_6 ☐	PCDD/PCDF ☐	dl-PCB ☐	PBDE ☐	PFOS ☐
Human milk	OCP ☐	PCB_6 ☐	PCDD/PCDF ☐	dl-PCB ☐	PBDE ☐	PFOS ☐
Human blood						PFOS ☐
Air extract	OCP ☐	PCB_6 ☐	PCDD/PCDF ☐	dl-PCB ☐	PBDE ☐	PFOS ☐
Water						PFOS ☐
Transformer oil		PCB_6 ☐				

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, PFSAs, 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)

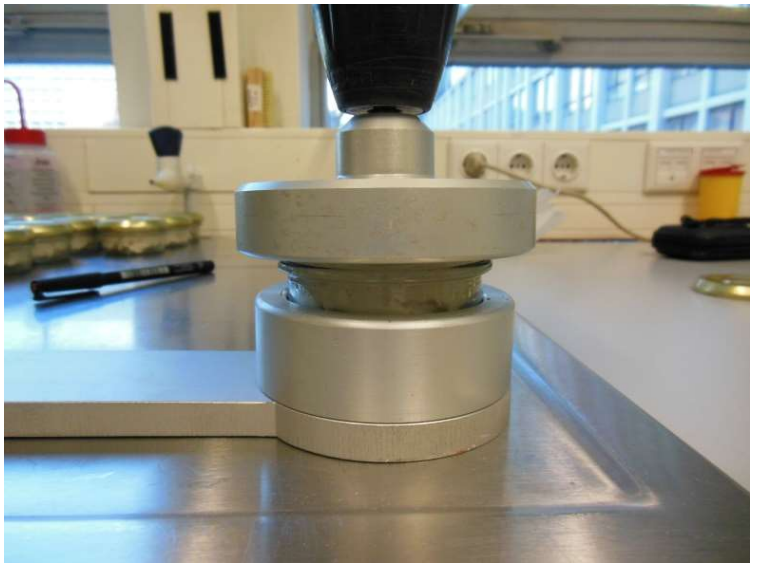
Naturally contaminated test samples

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

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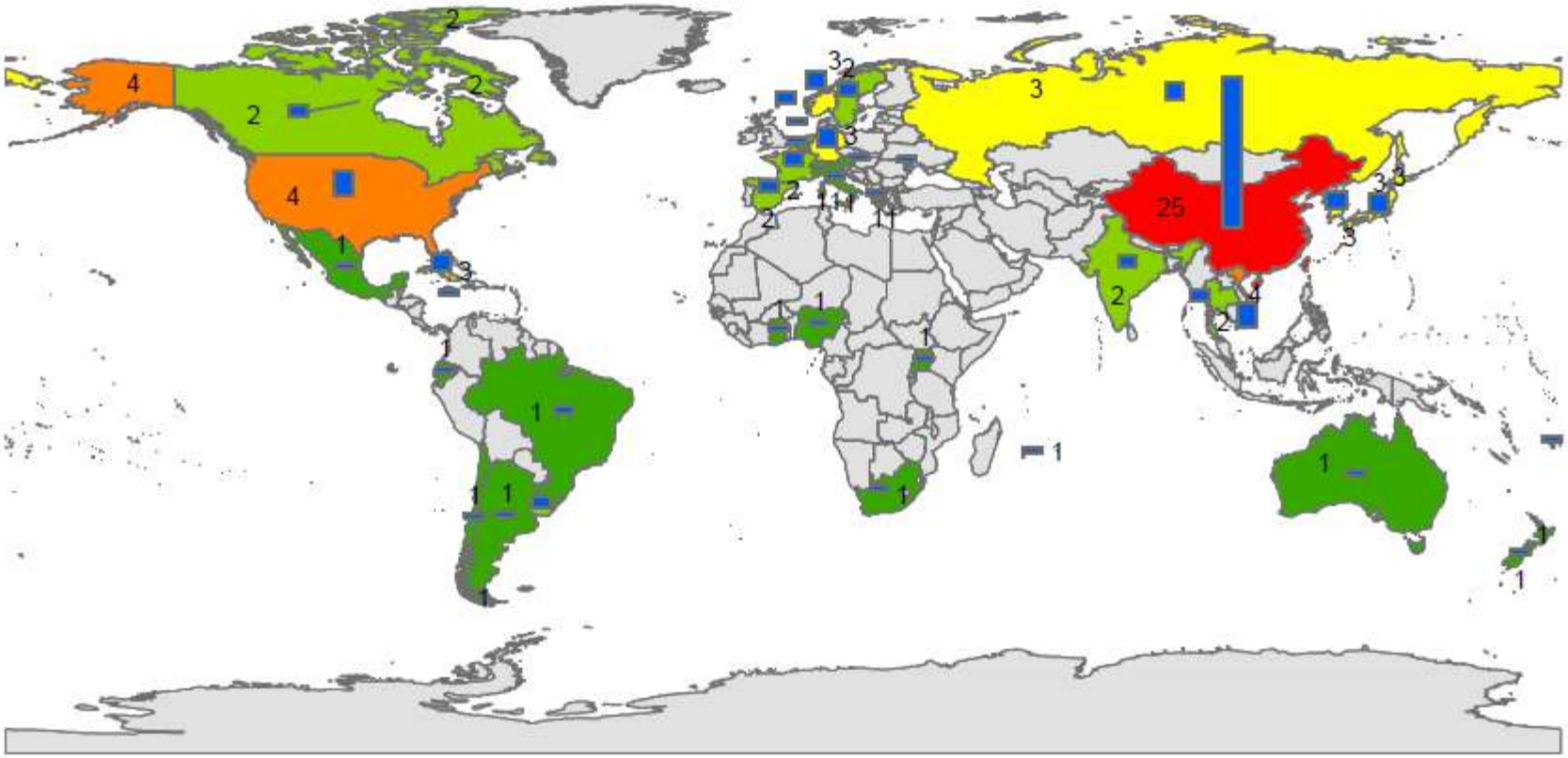
Laboratories in 2nd Interlaboratory Assessment 2012/2013



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	Trans-former oil	Totals
OCP	50	27	36	21	23	-	-	-	**157**
PCB	47	38	43	28	25	-	-	19	**200**
dl-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

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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

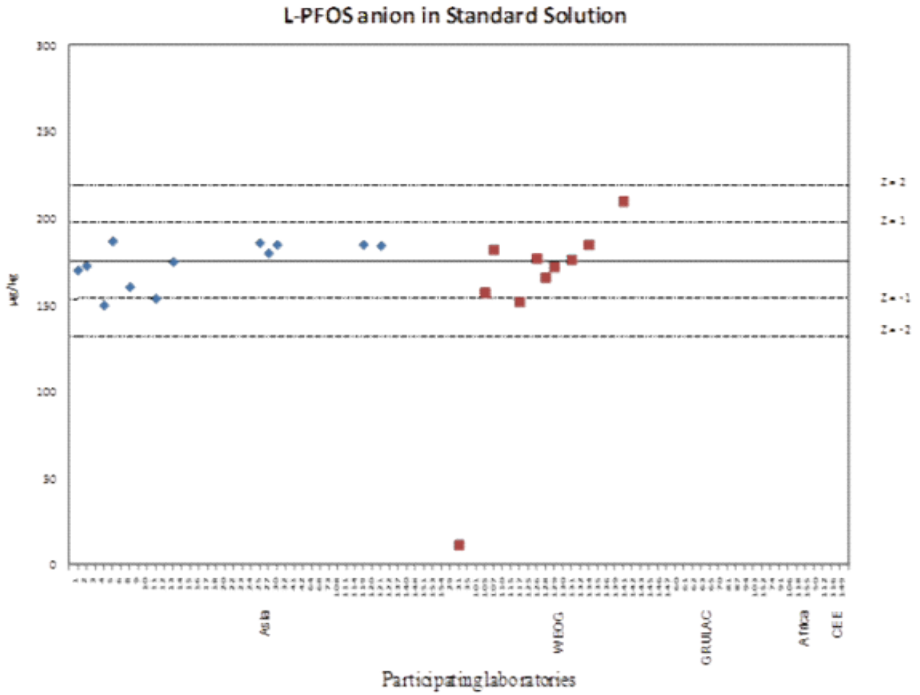
Region	Total	Standard solution	Sediment	Fish	Mothers' milk	Human serum	Air extract	Water
ASIA	16	15	13	12	6	7	7	13
WEOG	15	11	9	10	6	6	6	12
GRULAC	0	0	0	0	0	0	0	0
AFRICA	0	0	0	0	0	0	0	0
CEE	0	0	0	0	0	0	0	0
Total	31	26	22	22	12	13	13	25

Performance *per* group of POPs and test sample

Assessment according to ISO 17043

z-scores can be interpreted as follows:

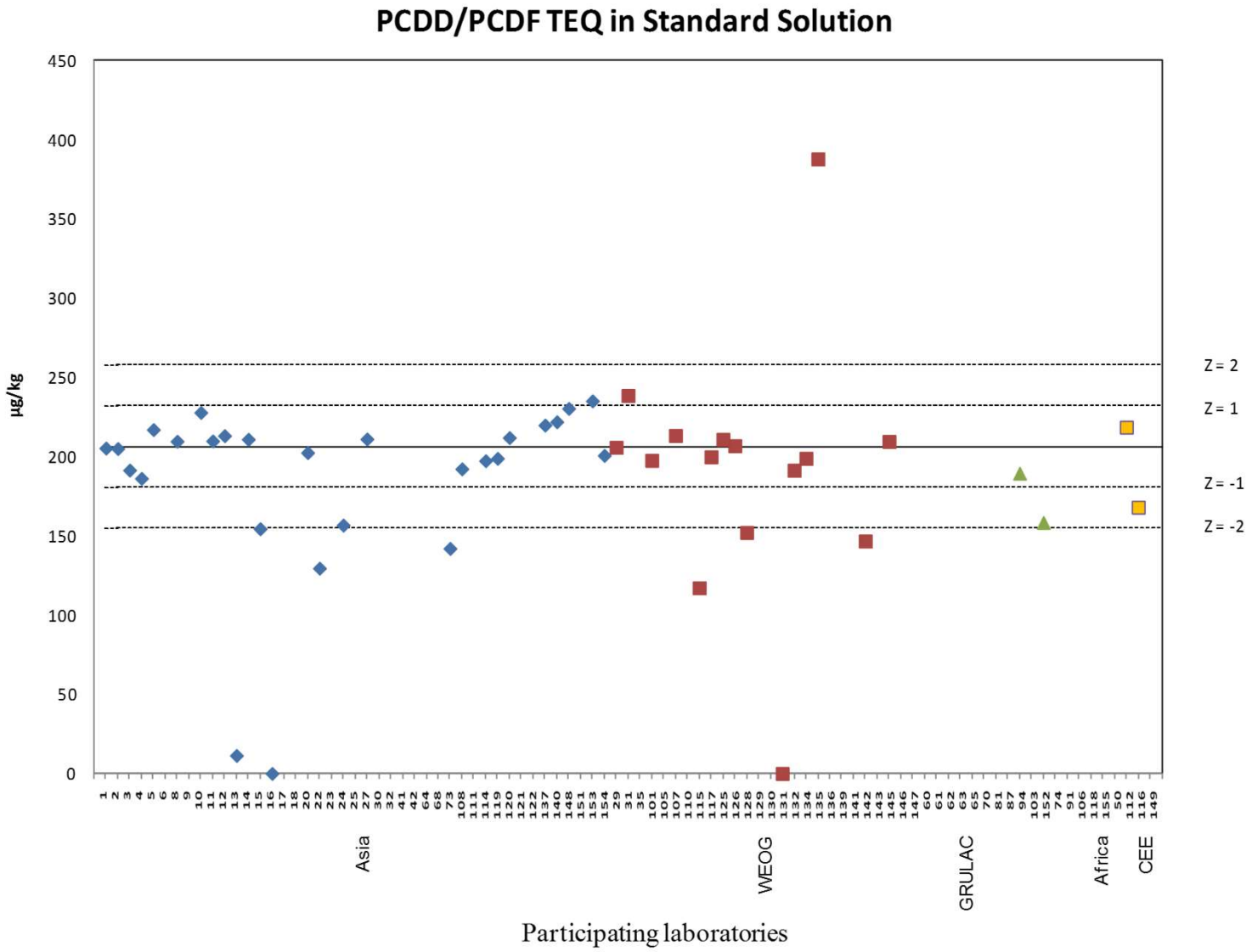
- $|z| < 2$ Satisfactory performance
- $2 < |z| < 3$ Questionable performance
- $|z| > 3$ Unsatisfactory performance



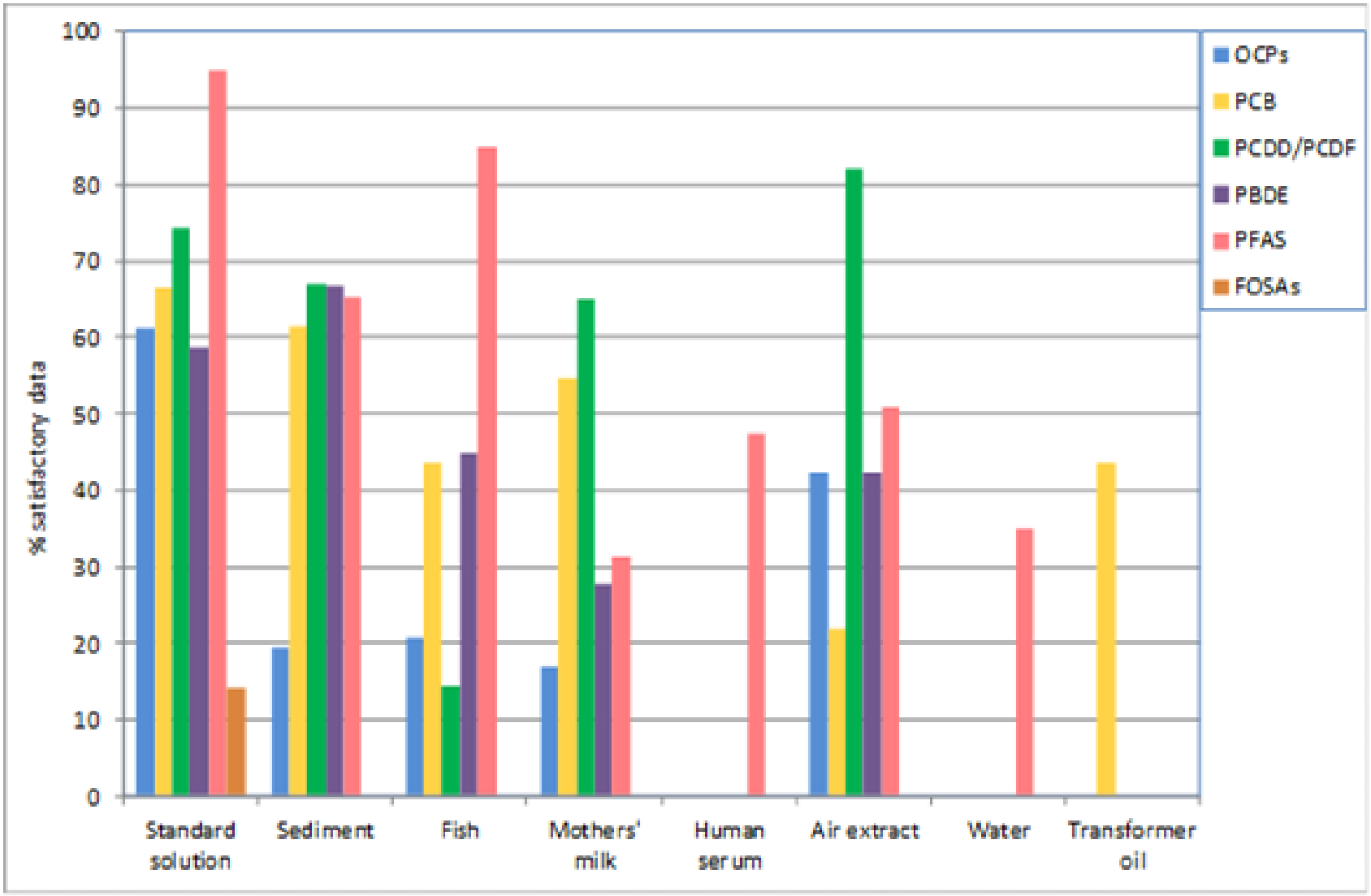
Results of concentrations per analyte and matrix presented;
$\Rightarrow$ z-scores available for all laboratories

z = 12.5%

PCDD/PCDF in standard solution



Laboratories with satisfactory performance



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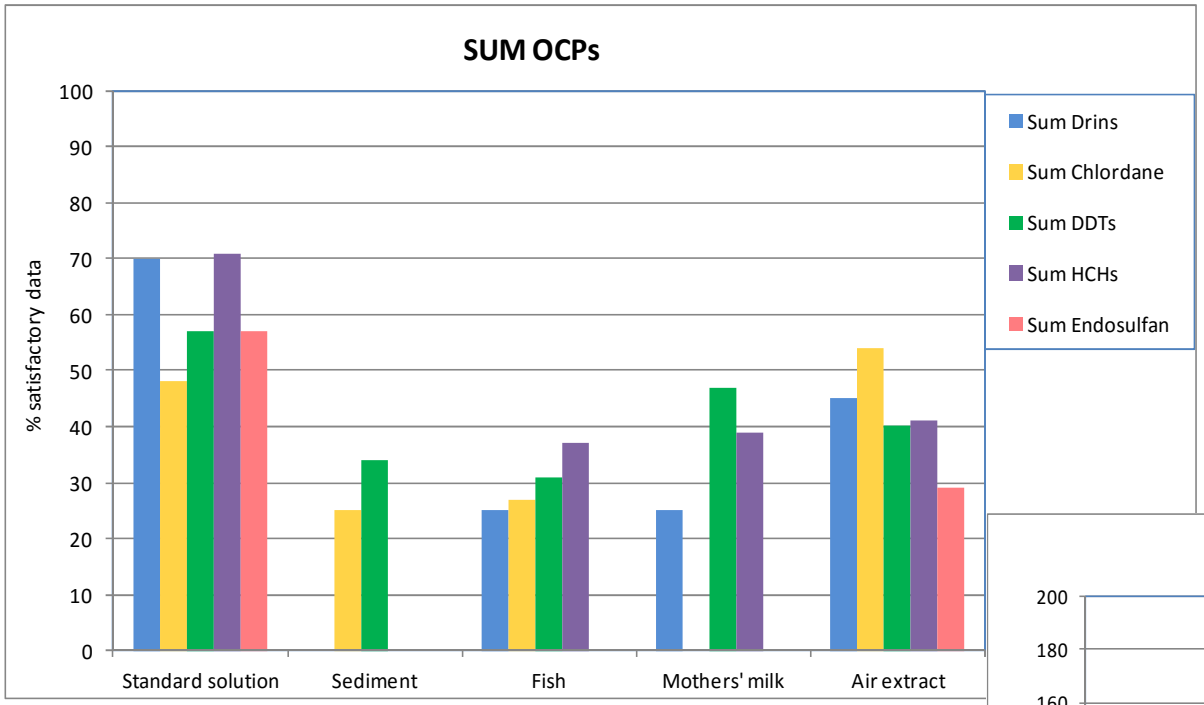
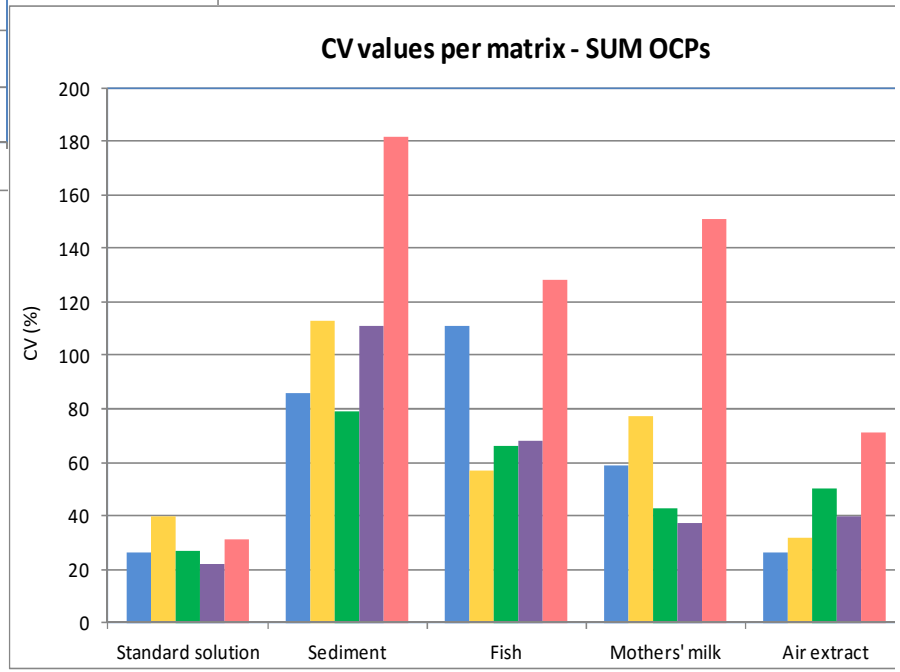
Laboratories with satisfactory performance



2nd round



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

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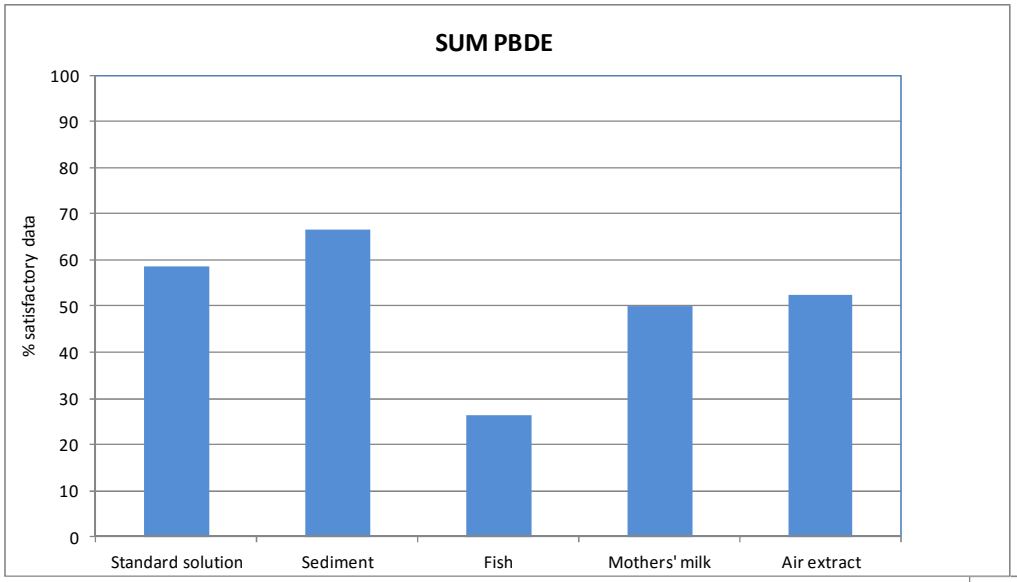
OCPs in mothers' milk

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

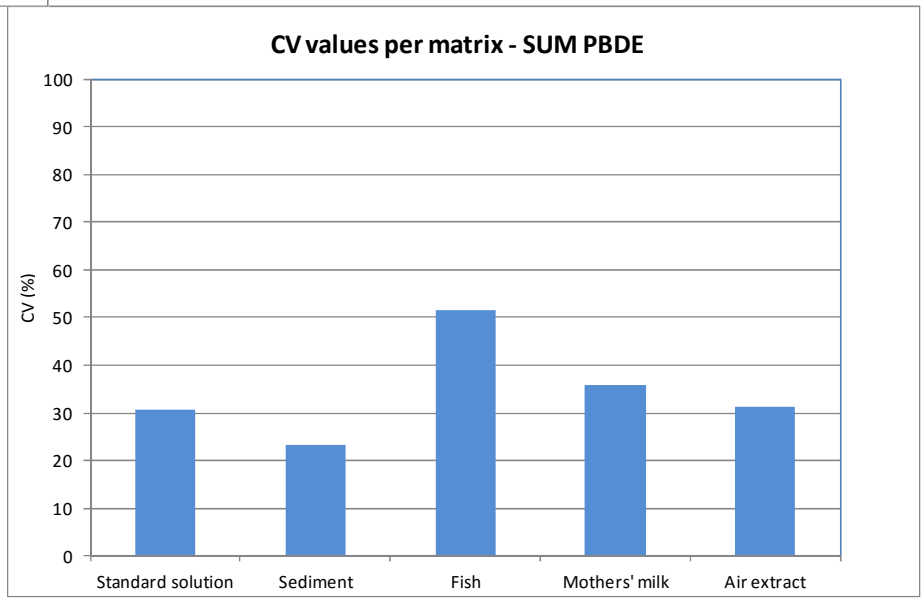
Analyte	% of the data received	% of z-scores |z|<2 Satisfactory	% of z-scores 3>|z|>2 Questionable	% of z-scores 6>|z|>3 Unsatisfactory	% of z-scores |z|>6 Extreme
Sum Drins	15	25	0	19	19
Sum Chlordanes	16	0	0	0	0
Sum DDTs	16	47	12	12	29
Sum HCHs	17	39	6	11	22
Sum Endosulfans	13	0	0	0	0

Performance on sum parameters (PBDE)



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 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	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

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Performance for sum parameter PCB_6

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 PCB_6

	% 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
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 |z|<2 Satisfactory	% of z-scores 3>|z|>2 Questionable	% of z-scores 6>|z|>3 Unsatisfactory	% of z-scores |z|>6 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

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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

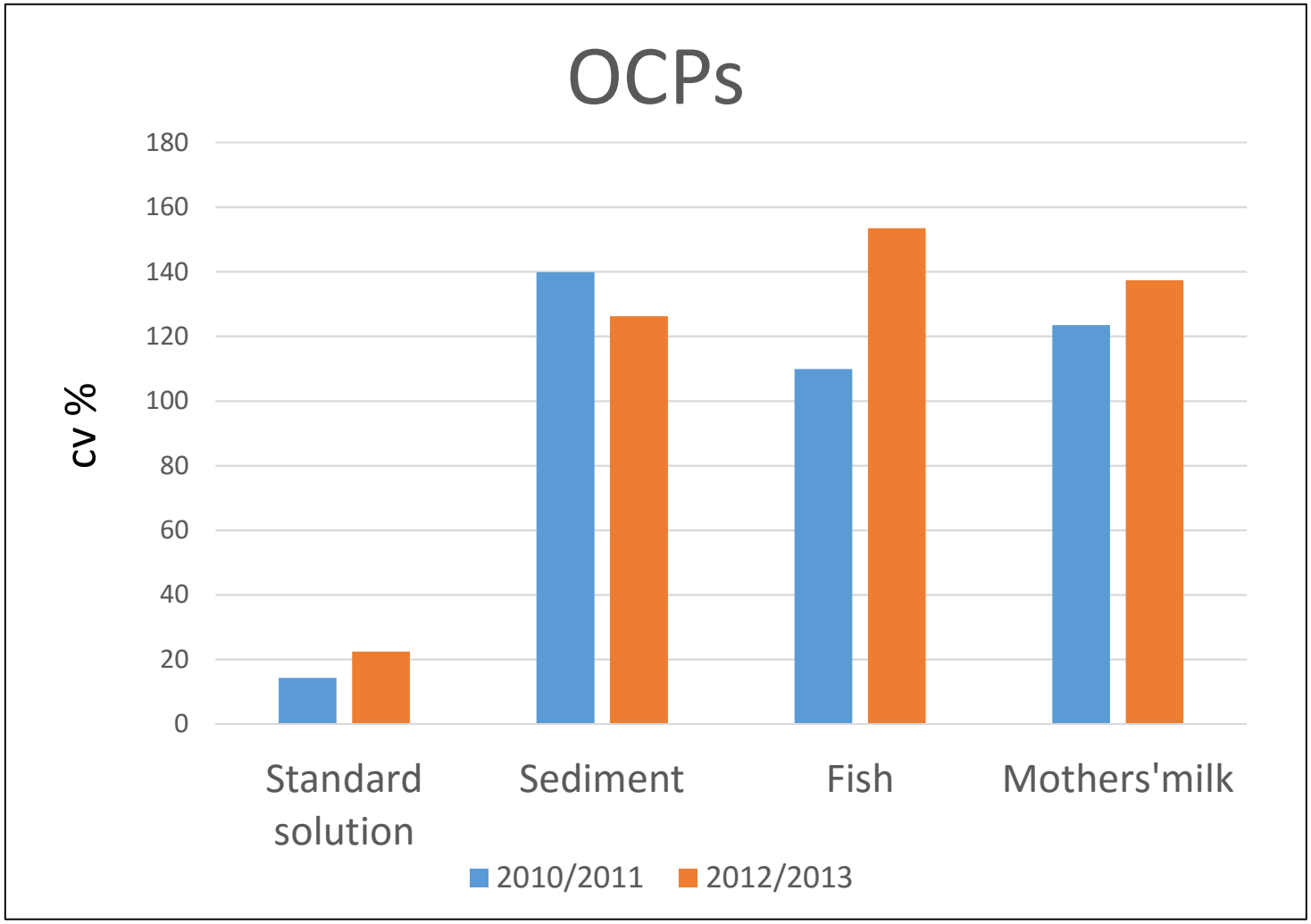
Matrix	% of the	% of z-scores	% of z-scores	% of z-scores	% of z-scores
	data received	|z|<2	3>|z|>2	6>|z|>3	|z|>6
		Satisfactory	Questionable	Unsatisfactory	Extreme
Standard solution	14	73	0	0	27
Human serum	7	86	14	0	0
Air extract	7	0	0	0	0

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

Comparison 1st round *vs.* 2nd round



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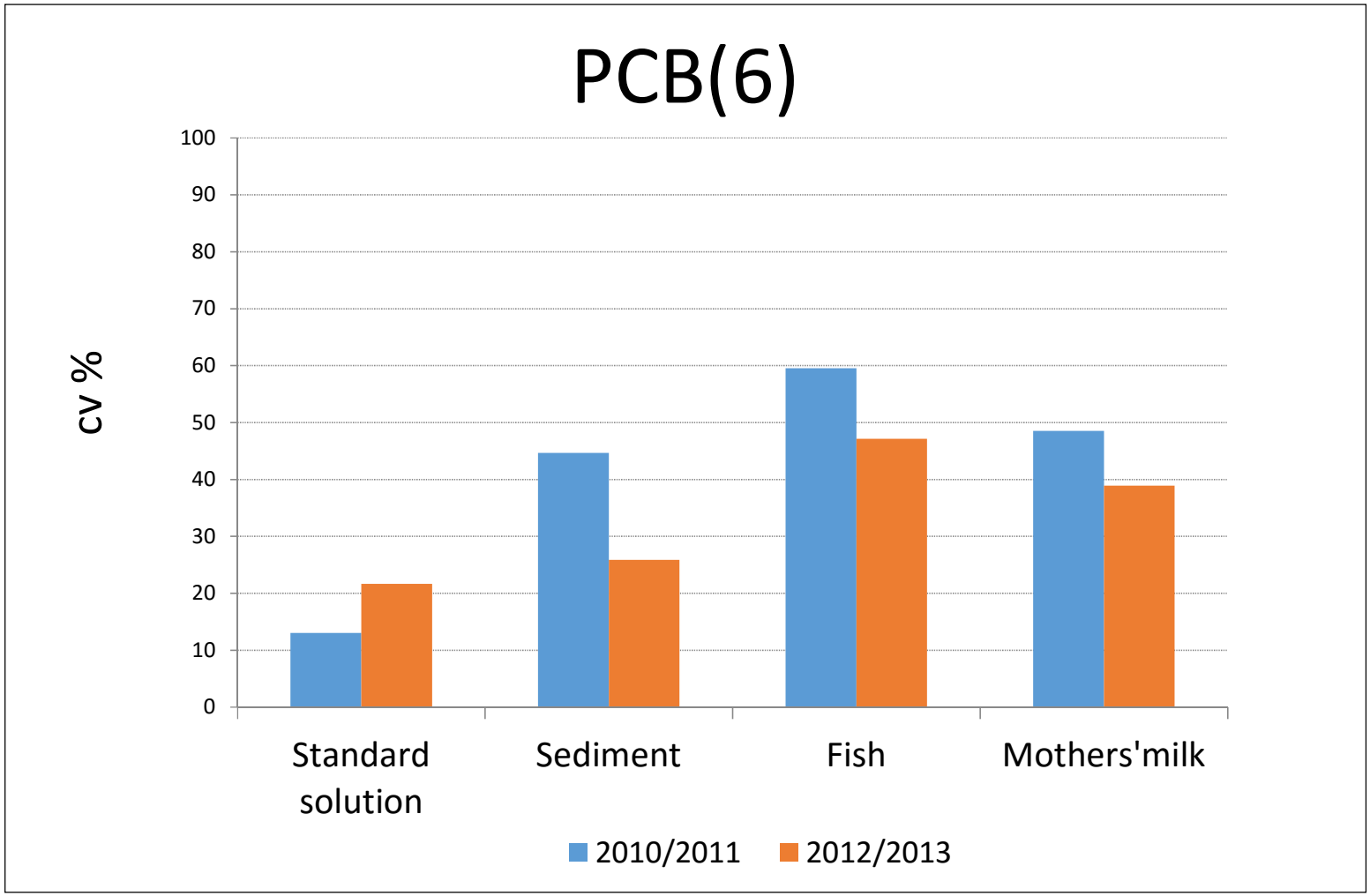
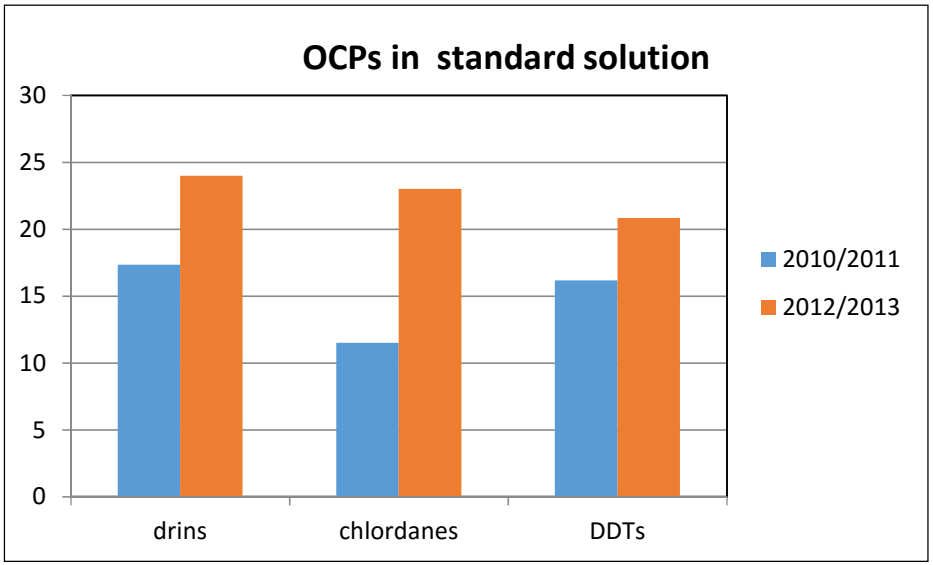
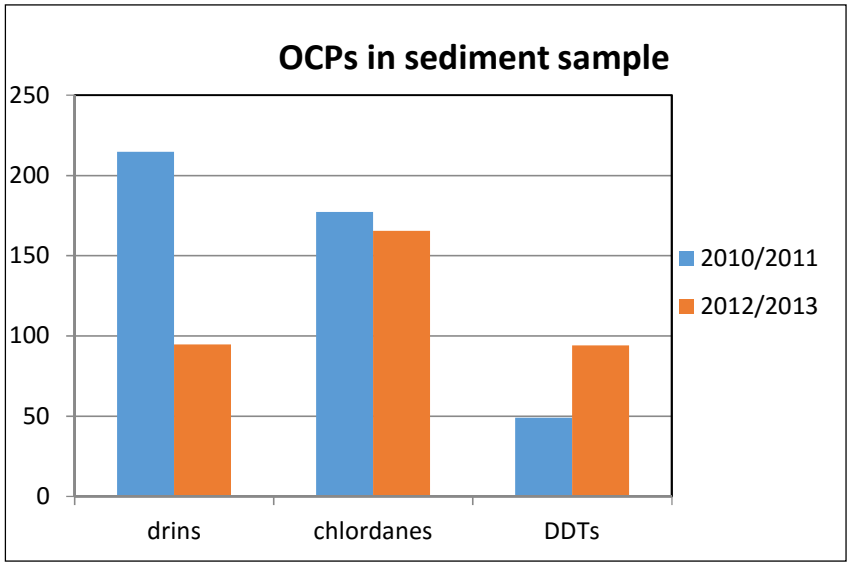
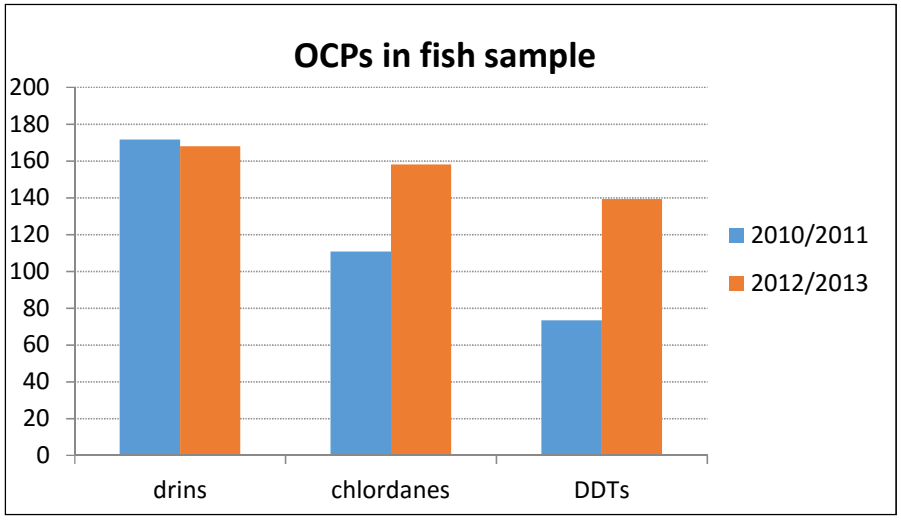
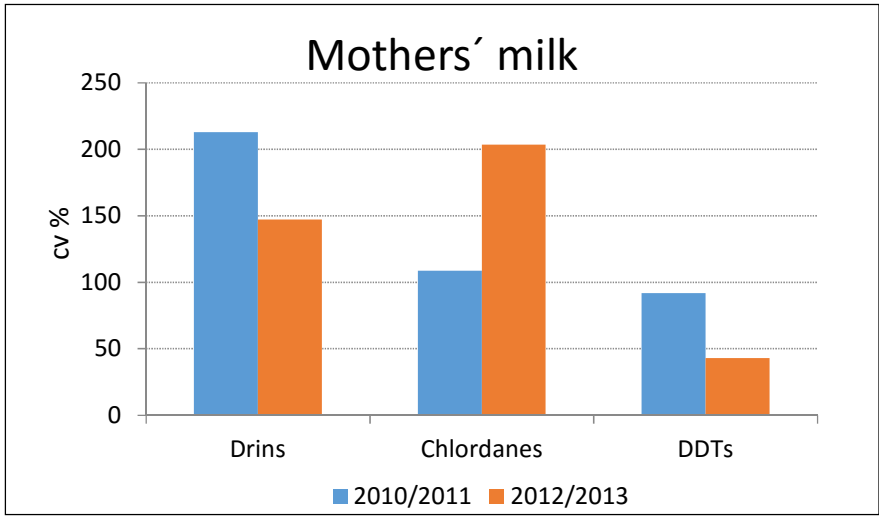


Comparison 1st round *vs.* 2nd round

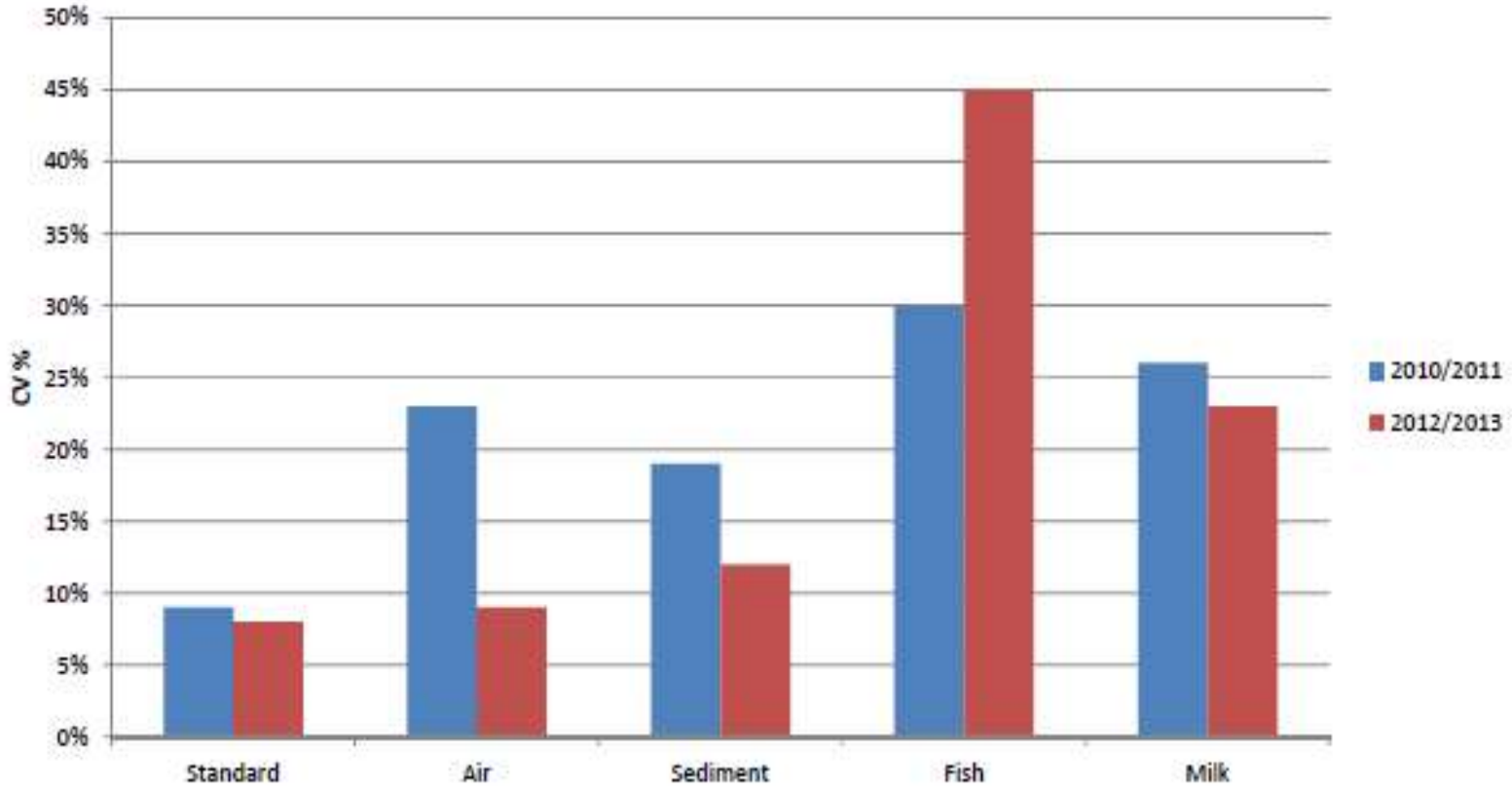






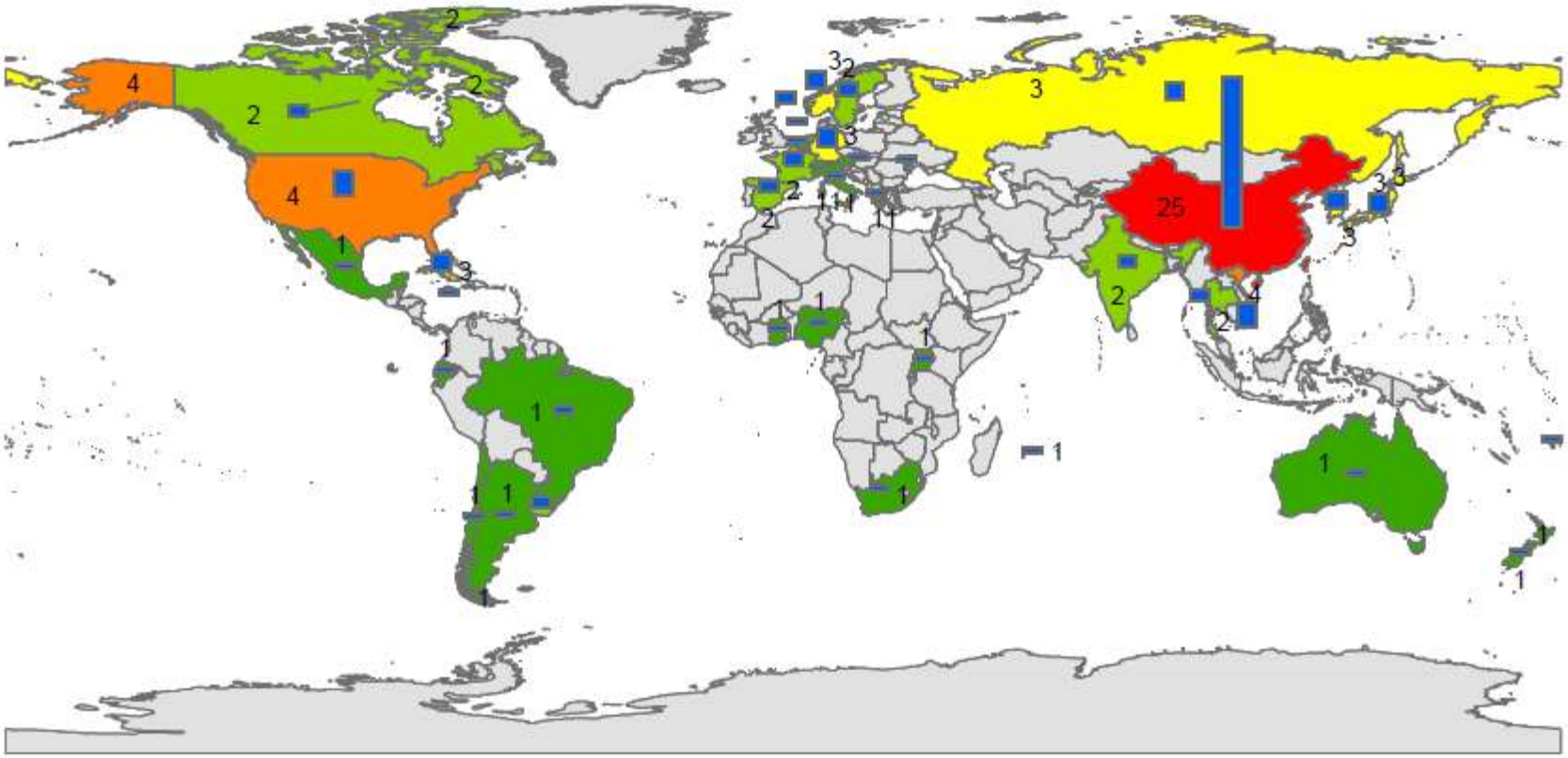


Comparison PCDD/PCDF analysis: 1st round *vs.* 2nd round



Regional performance *per* group of POPs and test sample

Laboratories in the 2nd Interlaboratory Assessment 2012/2013



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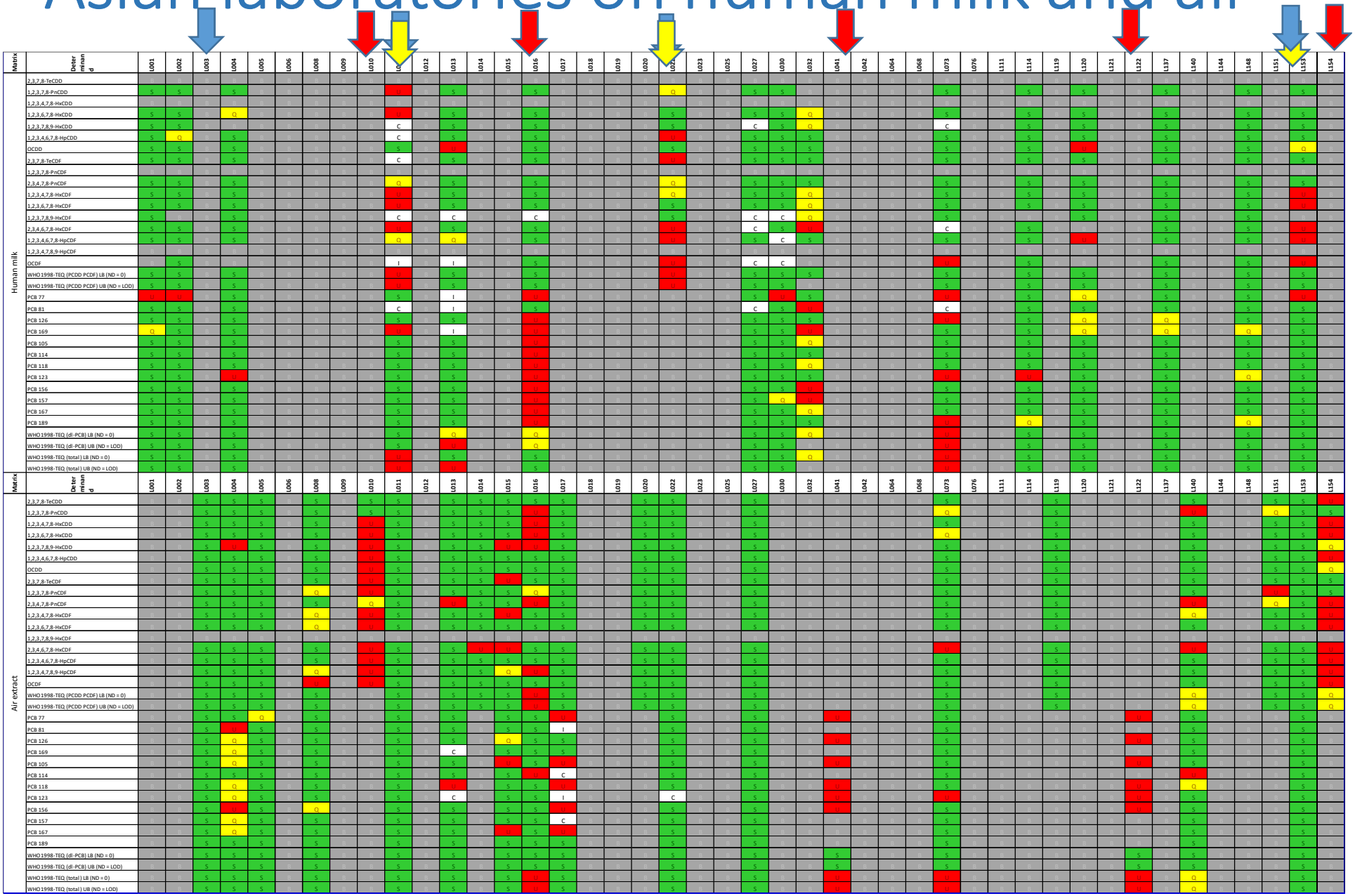
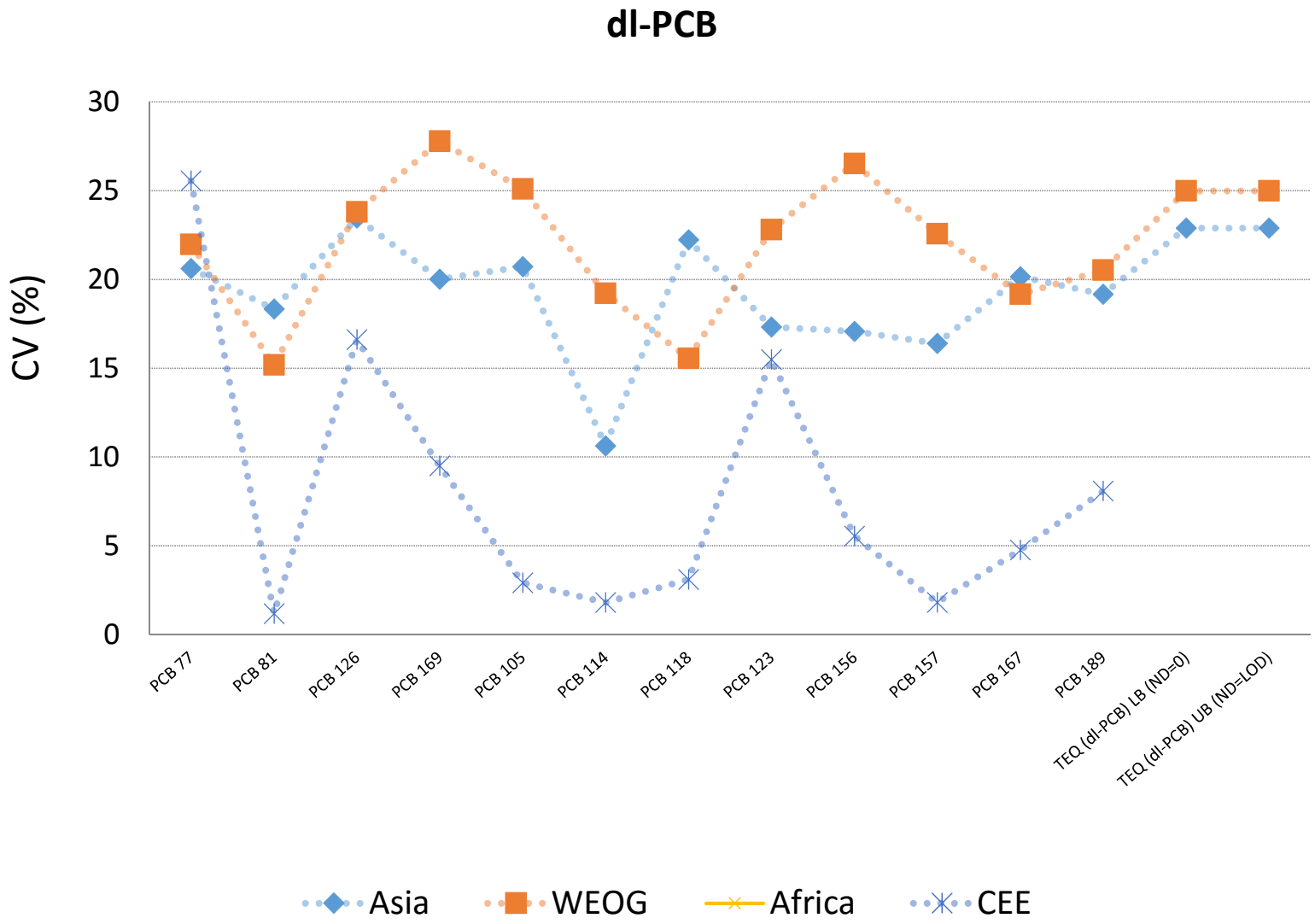
Of the Asian labs: 25 from China

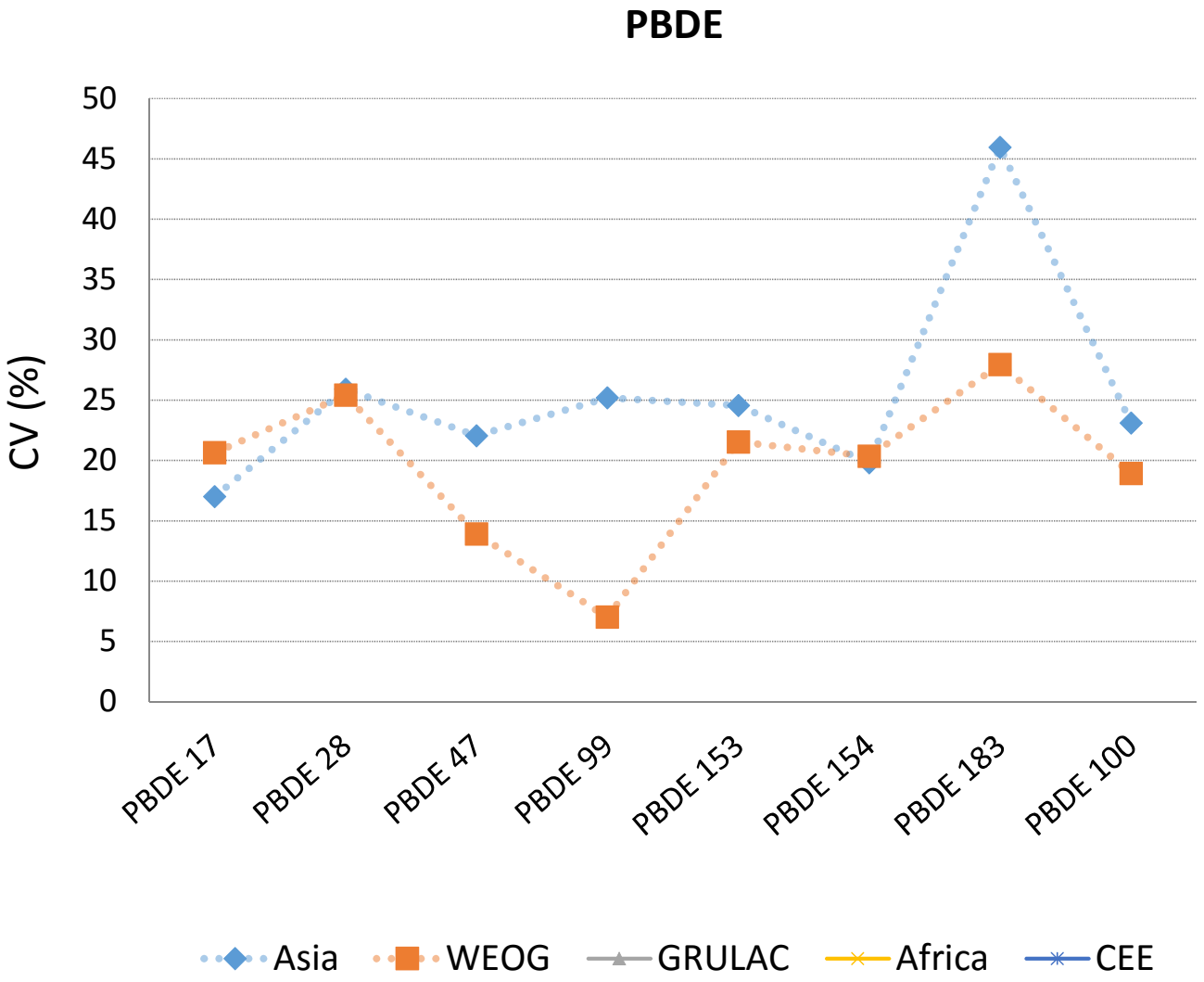
Asian laboratories on human milk and air



Regional performance per group of POP



Regional performance per group of POP



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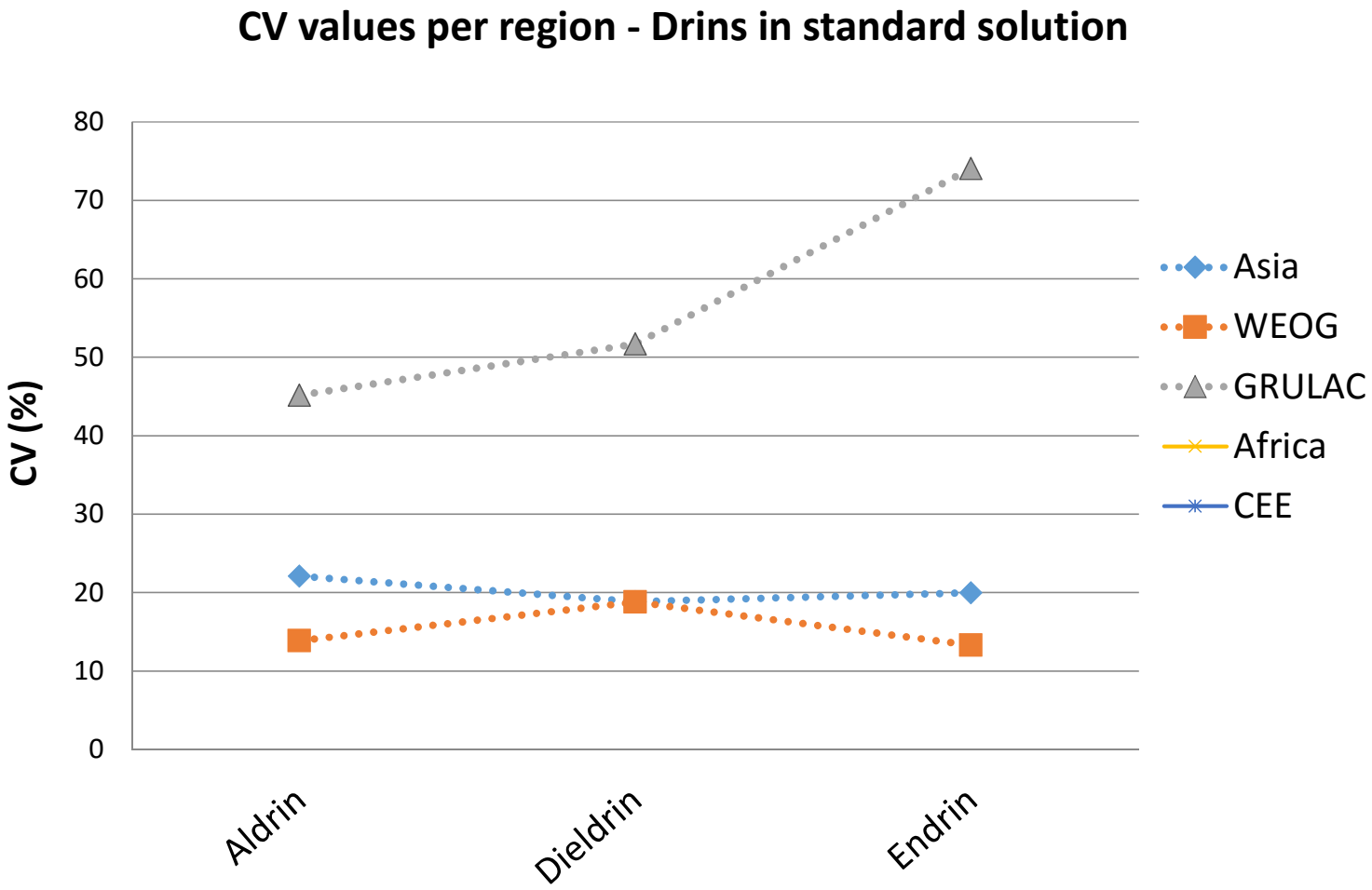

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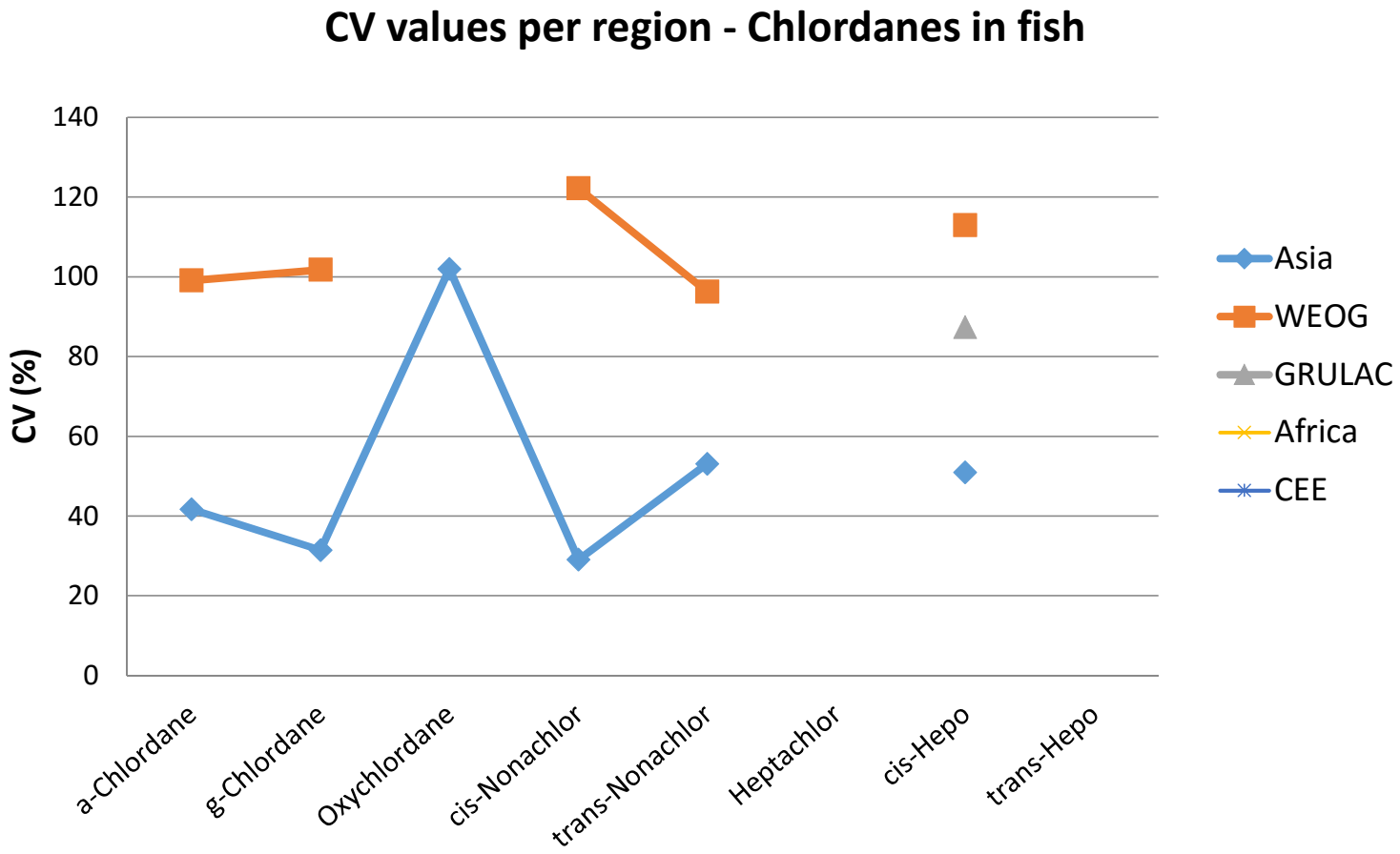

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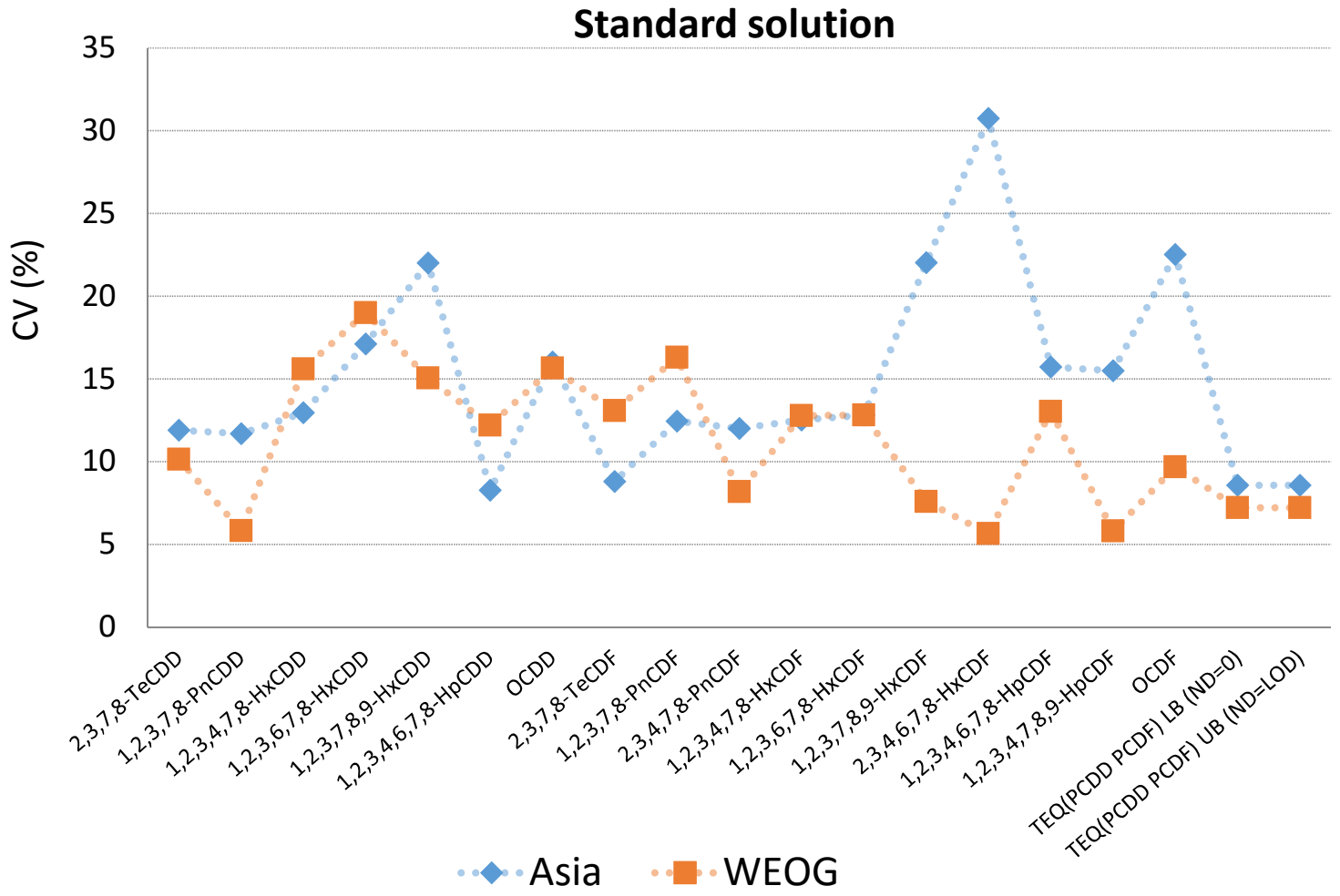
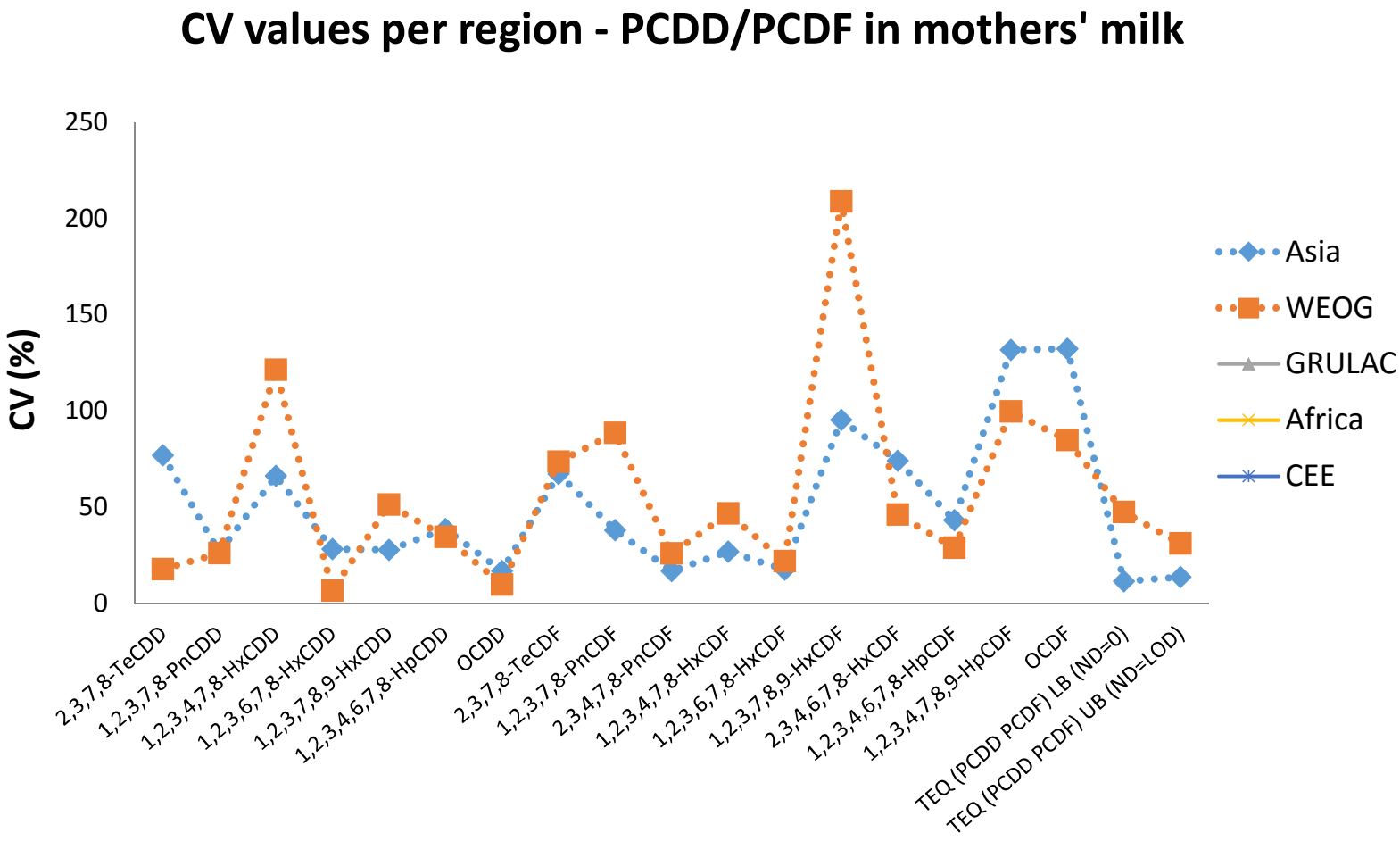
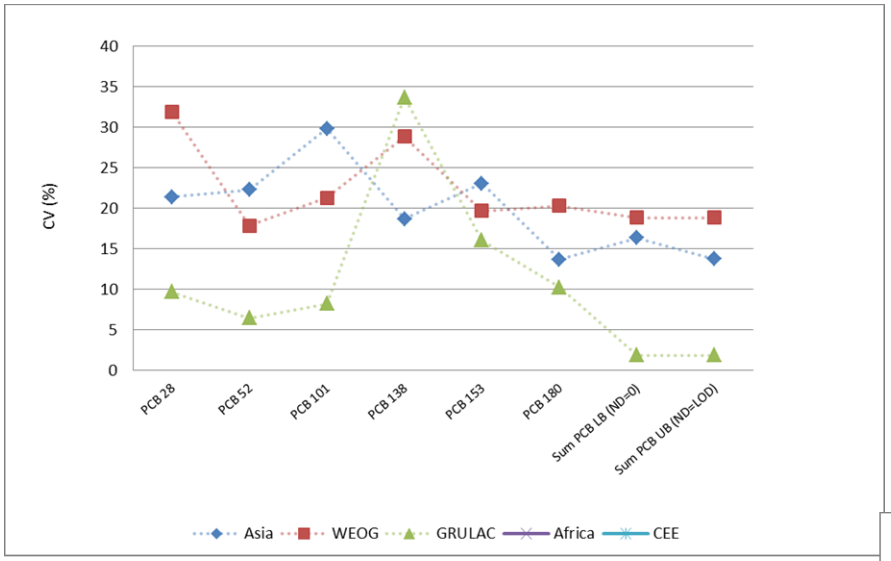


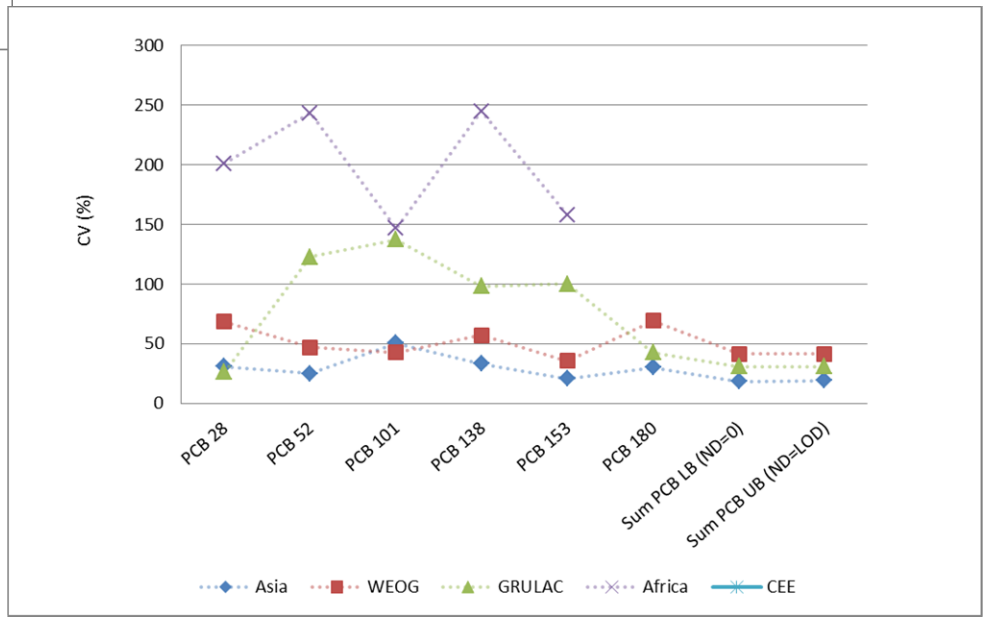
Regional performance per group of POP



Regional performance for PCB_6



PCB_6 in standard solution



PCB_6 in air extract

Conclusions (1)

- The degree of participation (105 laboratories from 48 countries) showed high interest of laboratories to participate in this assessment;
- All test materials were successfully prepared and distributed; new POPs were added to the scheme of the initial twelve groups of POPs;
- High interest for capacity-building resulted in a wealth of information on POP analysis and an enormous data set for this report from which the laboratories can evaluate their methods.
- Ongoing development in many laboratories shown since more laboratories analysed the environmental test samples – sediment, fish – whereas in first round many laboratories only analysed the standard solutions.

Conclusions (2)

- Repeat performance tests on initial POPs, include new POPs and new matrices;
- Problems were seen with fatty fish sample;
- Improvement in performance of initial POPs not satisfactory for UNEP criteria;
- Results for new POPs – PBDE, PFAS - were promising;
- 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.

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