



Overview on the intercalibration data of dl-POPs and PFOS

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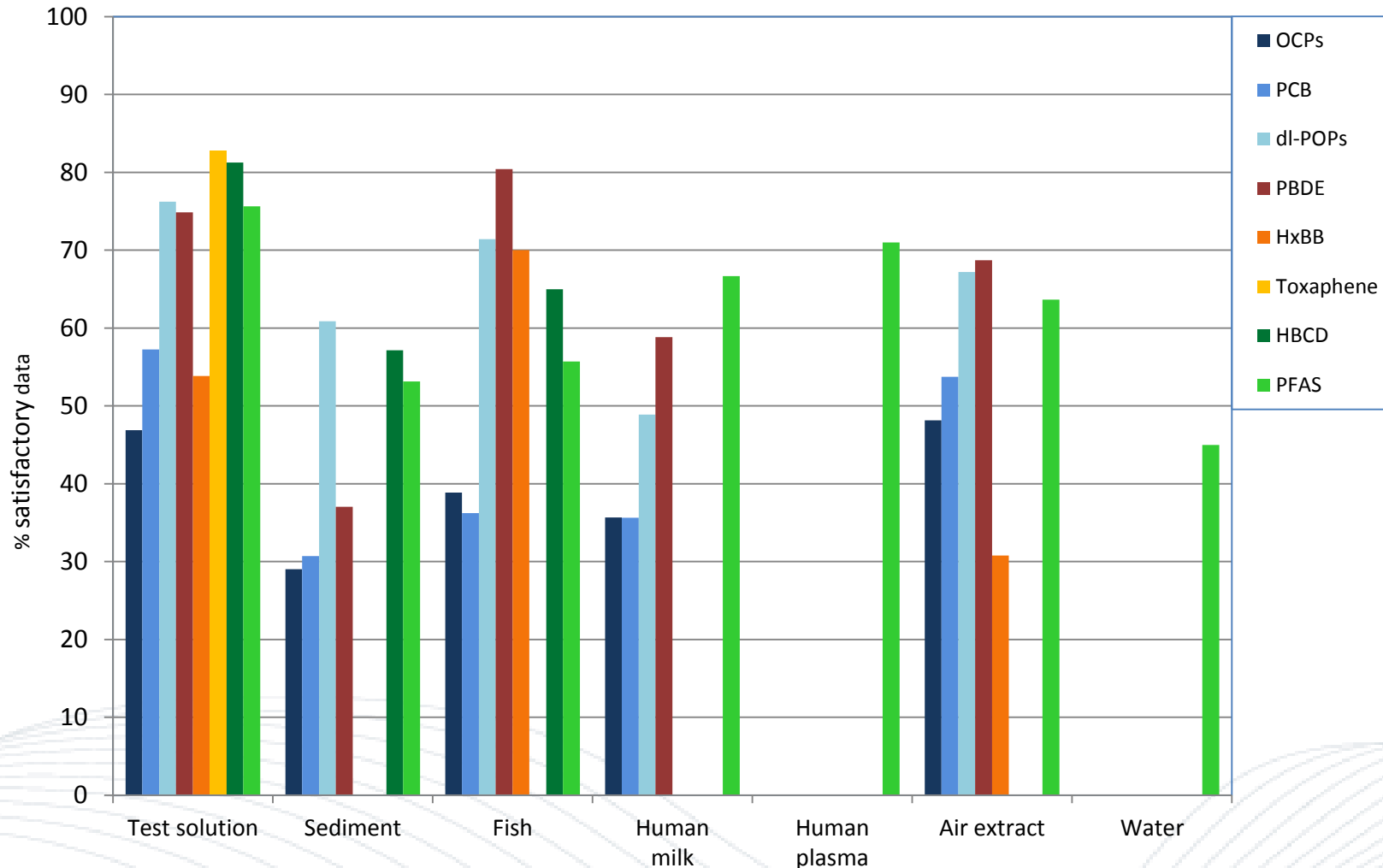
Number of labs reporting for dl-POPs and PFAS

Region PCDD/PCDF	total	test solution	sediment	fish	human milk	air extract
Asia	30	28	23	15	13	21
WEOG	16	13	9	9	6	12
GRULAC	6	3	3	4	0	2
Africa	2	2	2	1	1	1
CEE	5	3	3	2	2	2
total	59	49	40	31	22	38

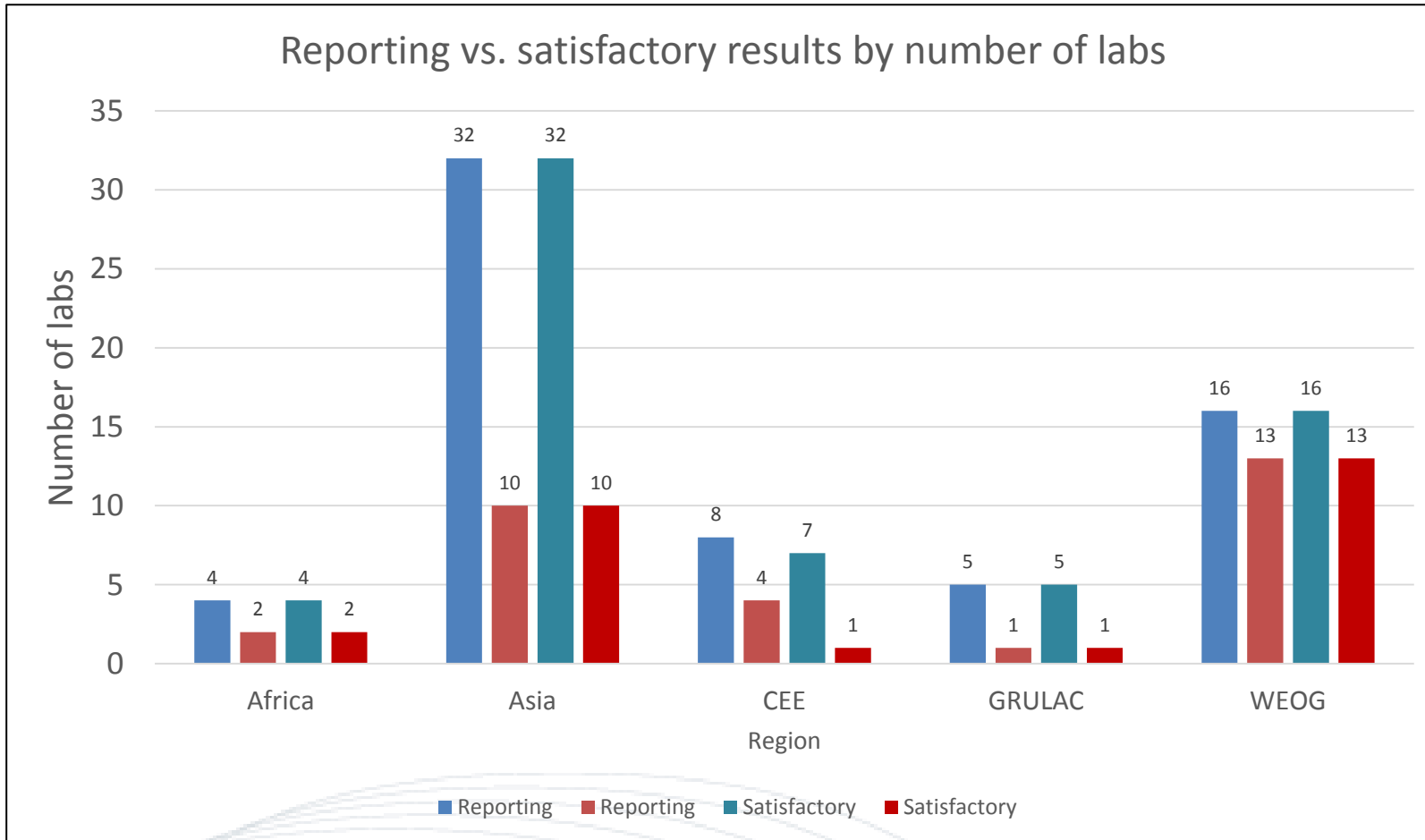
Region / dl-PCB	total	test solution	sediment	fish	human milk	air extract
Asia	26	24	18	15	13	17
WEOG	15	12	8	9	7	12
GRULAC	4	2	2	3	0	2
Africa	3	3	3	3	3	3
CEE	8	5	6	4	3	4
total	56	46	37	34	26	38

Region / PFAS	total	test solution	Sediment	Fish	Human milk	Human plasma	Air extract	Water
Asia	10	9	5	5	3	6	3	6
WEOG	14	14	9	8	3	6	6	9
GRULAC	1	1	0	0	0	0	1	1
Africa	2	2	2	1	0	0	1	2
CEE	2	1	1	1	0	0	0	2
total	29	27	17	15	6	12	11	20

Percentage of laboratories with satisfactory results (and with a z-score)



Labs reporting vs. labs with satisfactory results



Only in the CEE region, some laboratories did not generate any satisfactory results for either dl-POPs or PFAS

dl-POPs and PFAS: Capacity and performance



Region	# Labs Reporting		# Labs with Satisfactory	
	PCDD/PCDF	PFAS	PCDD/PCDF	PFAS
Africa	4	2	4	2
Asia	32	10	32	10
CEE	7	2	6	1
GRULAC	5	1	5	1
WEOG	16	13	16	13
Total	64	28	63	27

PFAS:

- The capacity is located in the Asia (10 labs) and the WEOG (13) regions;
- In all regions there is at least one laboratory capable to generate satisfactory results; however, the sample number is very low, esp. in Africa, CEE and GRULAC

From 133 laboratories that submitted results

- 64 labs were assigned z-scores for dl-POPs analysis
- 28 labs were assigned z-scores for PFAS analysis

PCDD/PCDF:

- The capacity is located in the Asia (32 labs) and the WEOG (16) regions;
- All of the Asia and WEOG labs generated S(atisfactory) results;
- All labs in GRULAC had S(atisfactory) results;
- Africa, CEE: not all laboratories did receive S(atisfactory) results:
 - AFR: 2 out of 4
 - CEE: 2 out of 7

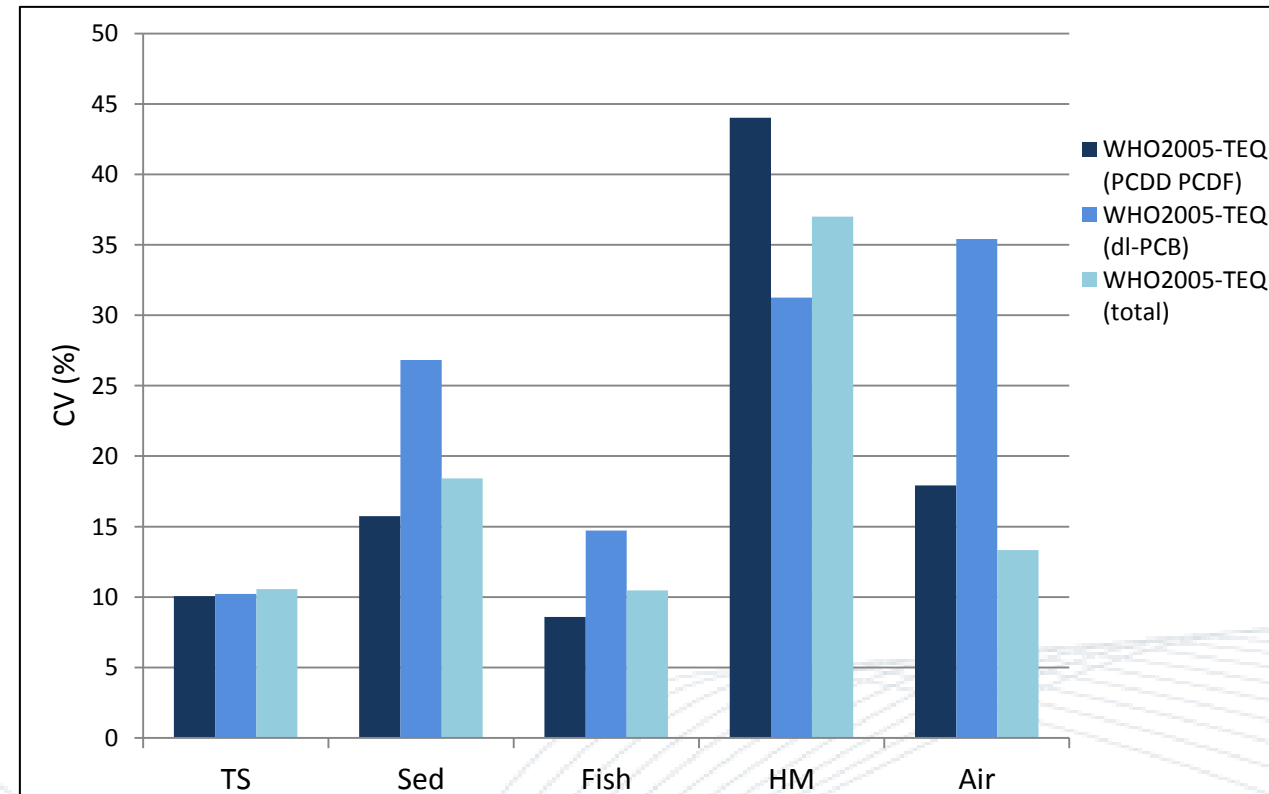
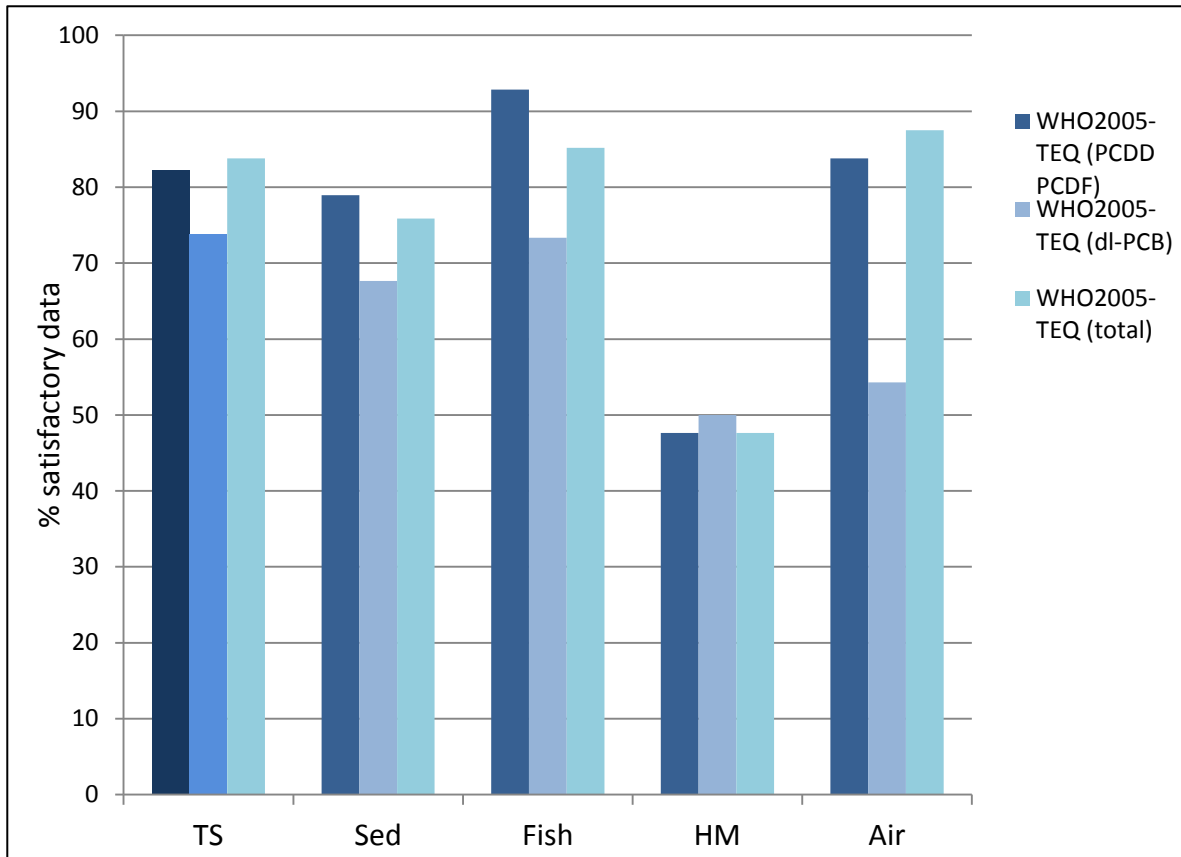
Dioxin-like POPs

PCDD/PCDF (17 congeners + TEQ)

dl-PCB (12 congeners + TEQ)

TEQ (WHO₂₀₀₅-TEF; LB and UB)

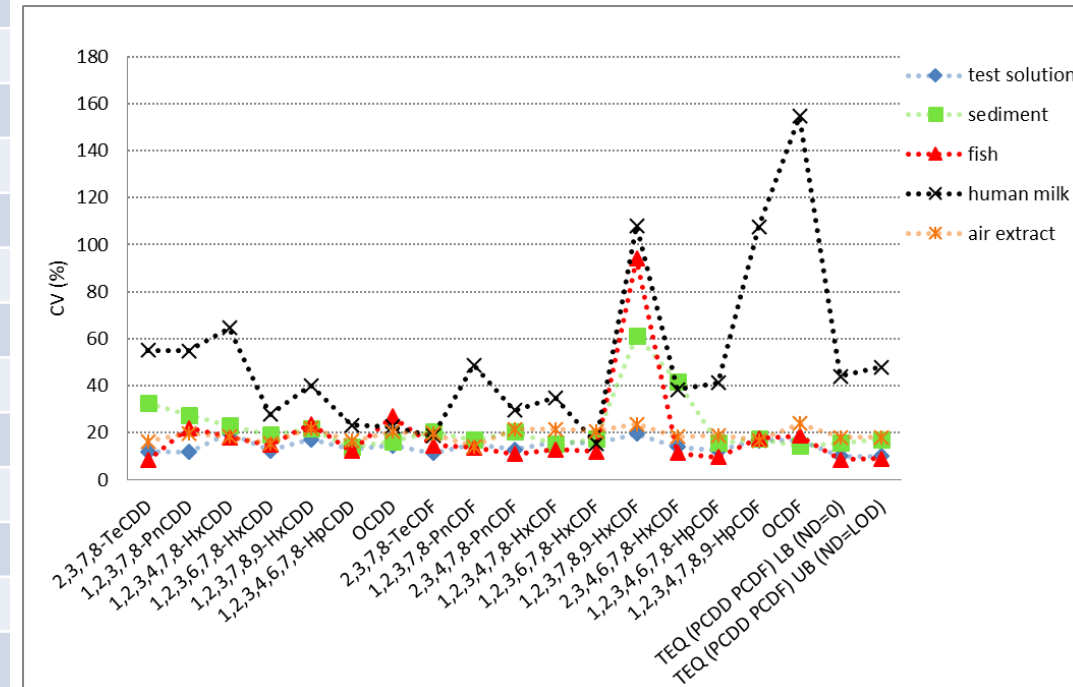
Summary performance for dl-POPs (TEQ, LB)



Except for the human milk sample, the performance of laboratories for PCDD/PCDF was better than for dl-PCB

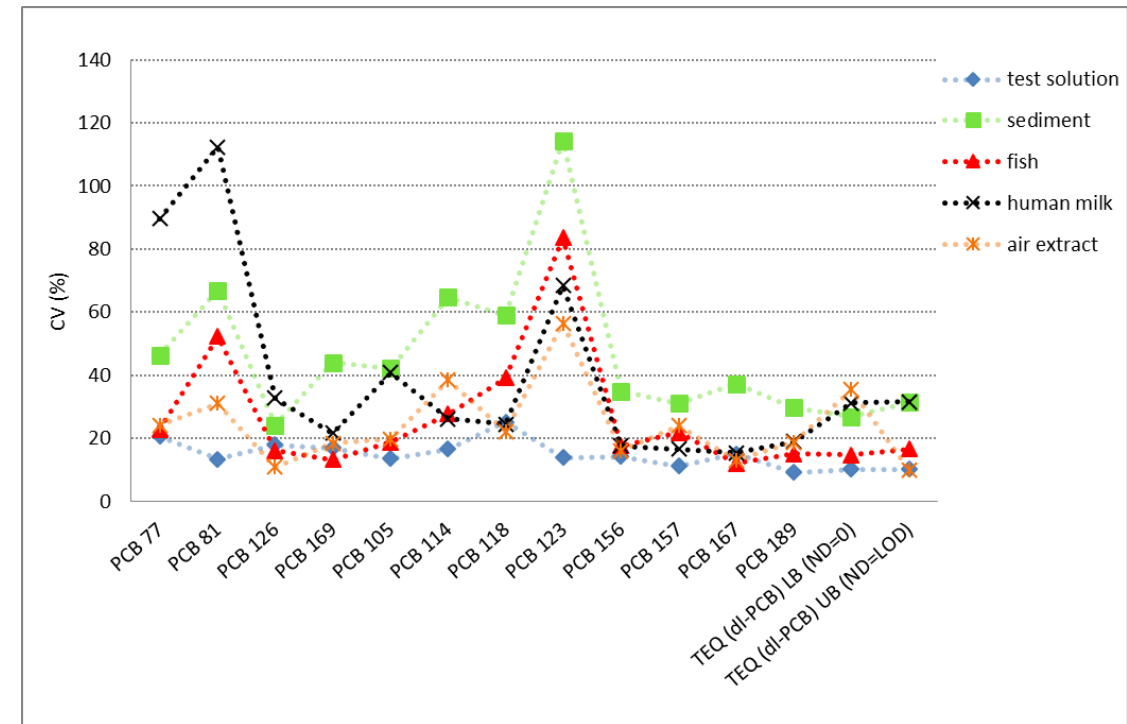
CV values for PCDD/PCDF according to matrix

global	test solution	sediment	fish	human milk	air extract
2,3,7,8-TeCDD	12	33	8	55	16
1,2,3,7,8-PnCDD	12	28	22	55	20
1,2,3,4,7,8-HxCDD	20	23	18	65	18
1,2,3,6,7,8-HxCDD	12	19	15	28	15
1,2,3,7,8,9-HxCDD	17	22	24	40	22
1,2,3,4,6,7,8-HpCDD	13	14	12	23	17
OCDD	15	16	27	23	20
2,3,7,8-TeCDF	11	20	15	19	19
1,2,3,7,8-PnCDF	15	17	14	49	14
2,3,4,7,8-PnCDF	13	20	11	30	22
1,2,3,4,7,8-HxCDF	16	15	13	35	22
1,2,3,6,7,8-HxCDF	15	17	12	15	21
1,2,3,7,8,9-HxCDF	20	61	94	108	24
2,3,4,6,7,8-HxCDF	14	42	11	38	18
1,2,3,4,6,7,8-HpCDF	12	16	9	41	19
1,2,3,4,7,8,9-HpCDF	17	17	18	108	17
OCDF	17	14	19	155	24
TEQ _{PCDD PCDF} LB (ND=0)	10	16	9	44	18
TEQ _{PCDD PCDF} UB (ND=LOD)	10	17	9	48	18

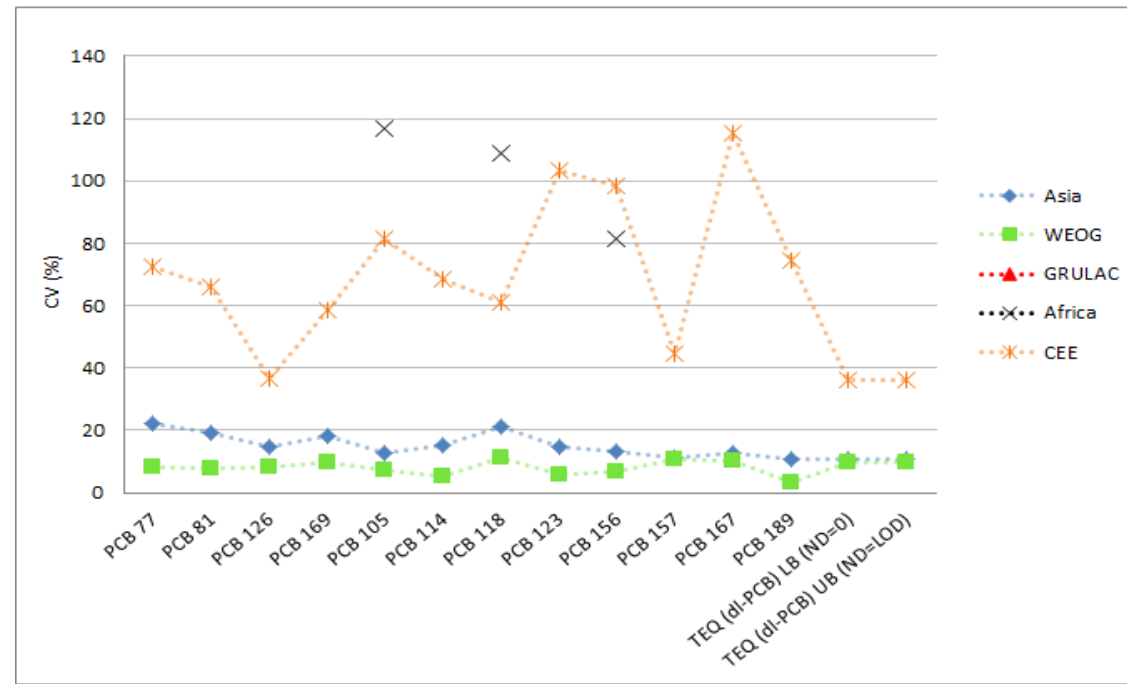
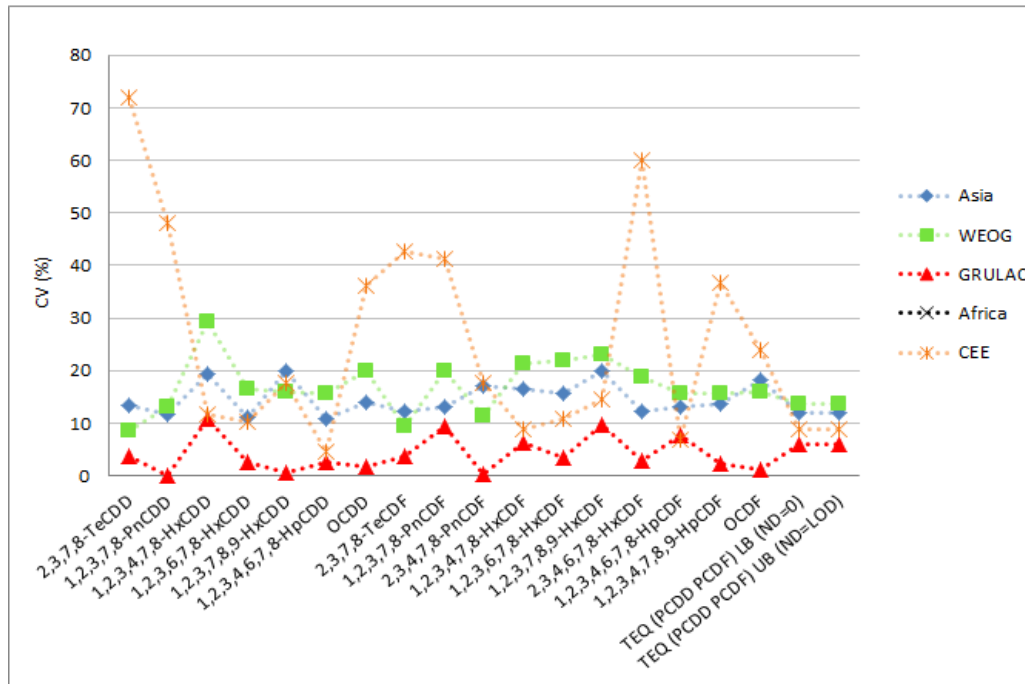


CV values for dl-PCB according to matrix

global	test solution	sediment	fish	human milk	air extract
PCB 77	21	46	23	90	24
PCB 81	13	67	52	112	31
PCB 126	18	24	16	33	11
PCB 169	17	44	13	22	18
PCB 105	14	42	19	41	20
PCB 114	17	65	28	26	38
PCB 118	25	59	39	24	22
PCB 123	14	114	84	68	56
PCB 156	14	35	18	18	16
PCB 157	11	31	22	17	24
PCB 167	15	37	12	15	13
PCB 189	9	30	15	19	19
TEQ _{PCB} LB (ND=0)	10	27	15	31	35
TEQ _{PCB} UB (ND=LOD)	10	31	17	31	10



Test solutions (dl-POPs) – regional performance



PCDD/PCDF test solution:

No lab from Africa present

All regions but the CEE region performed well (CV <25%);

TEQ <15% for all regions

dl-PCB test solution:

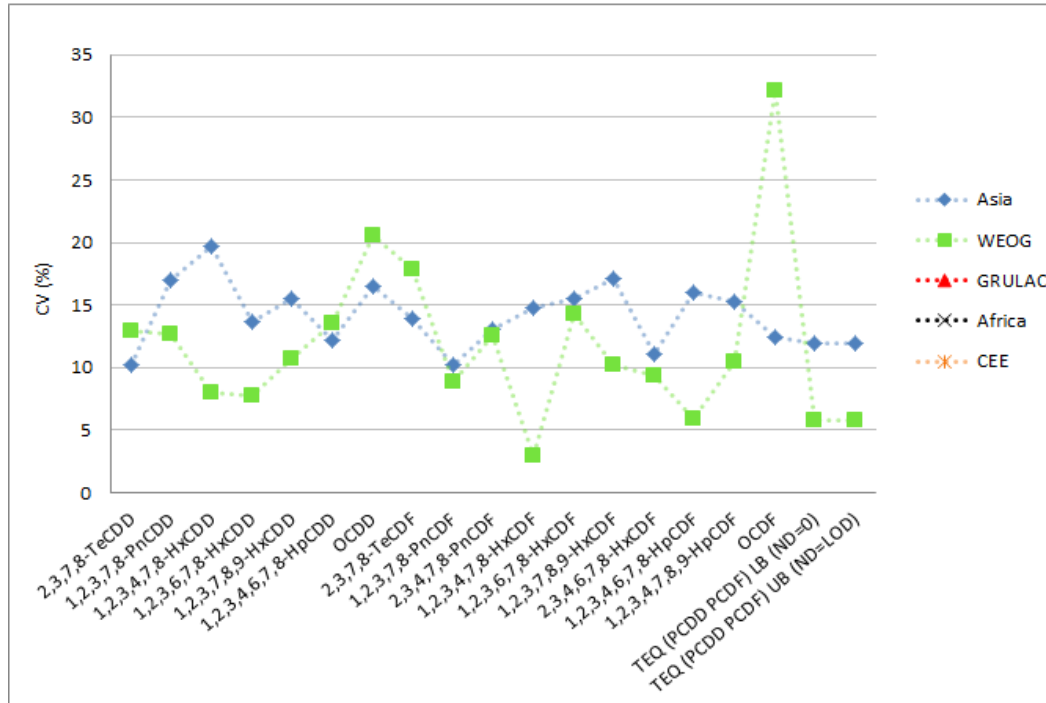
CV values for dl-PCB were higher than for PCDD/PCDF;

GRULAC is no longer present but few results from Africa

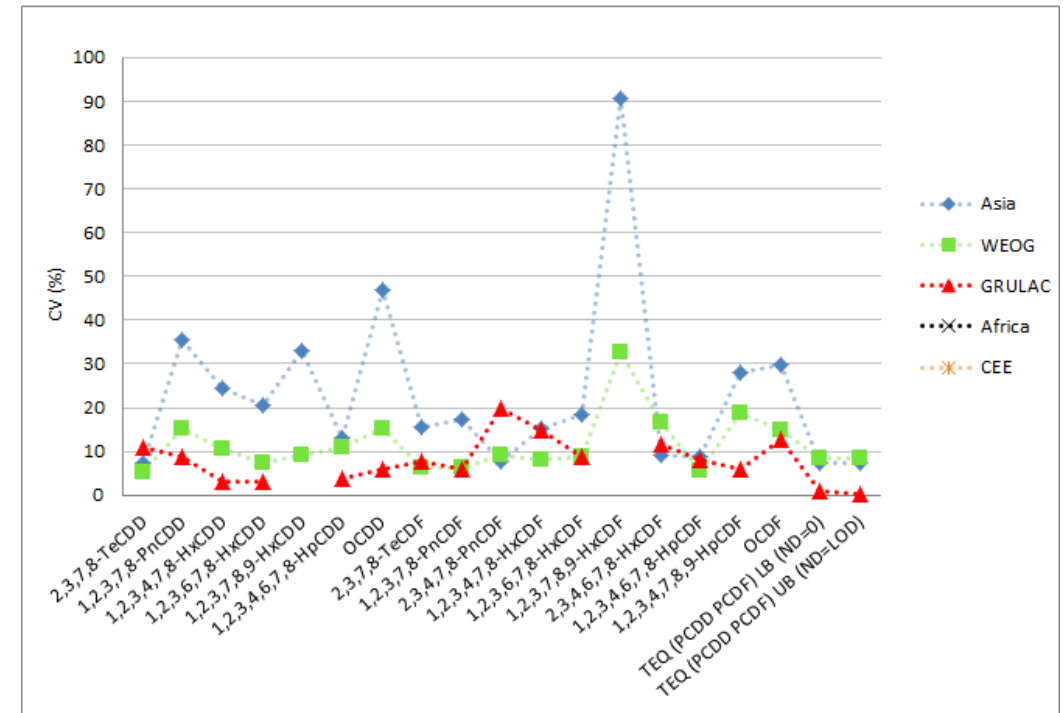
Surprising that the highest CV value in the test solution is for 2,3,7,8-TeCDD.

Air extract and fish – regional performance

Air extract (TOL)



Fish



For the real samples, the values were in the same range as for the test solutions;

For real samples, the Asian region performed less well as for the test solutions;

CVs for TEQs below 15% ⇒ ⇒ ⇒ **Proposal to lower the performance criterion for TEQ values from 25% to 15%**

Summary of z-scores for dl-POPs

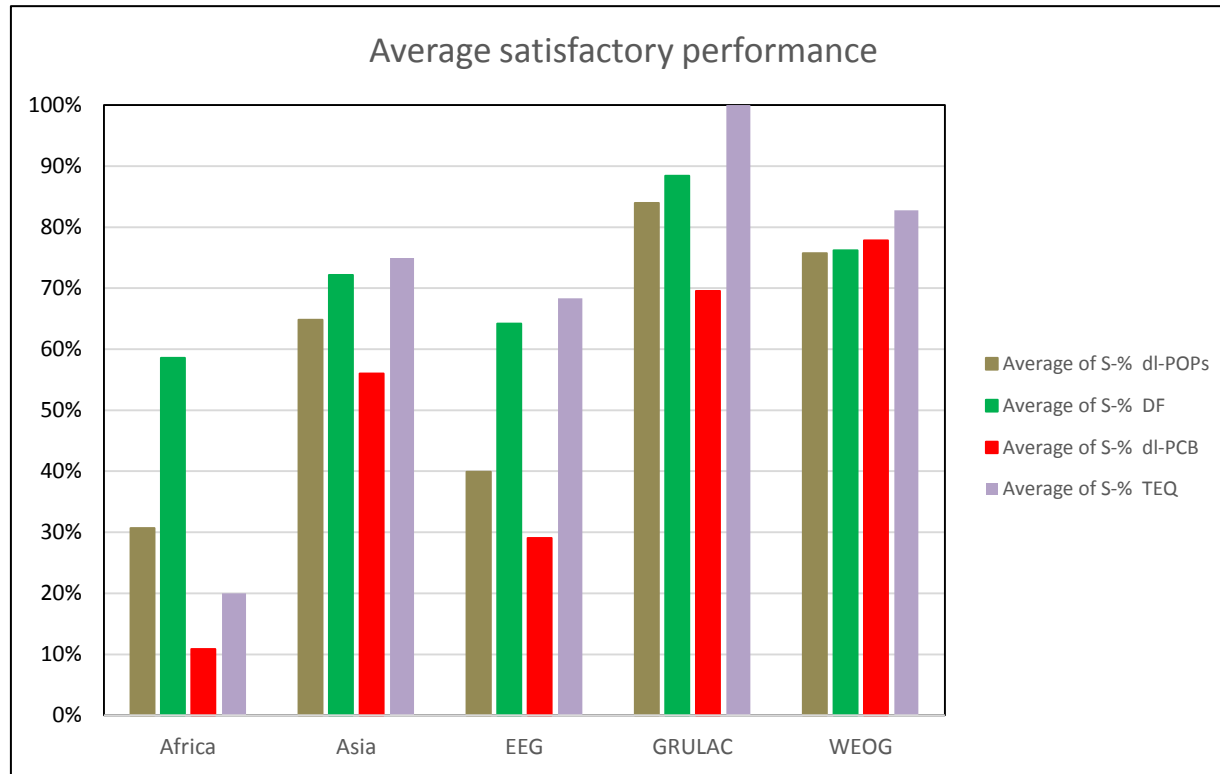
Rating	# z-scores	%	#labs dl-POPs
S	4,040	69%	65
Q	536	9%	58
U	1,129	19%	60
C	25	0%	14
I	167	3%	25
B			
All	5,897	100%	66

Rating	# z-scores	%	#labs dl-PCB
S	1,387	24%	53
Q	209	4%	46
U	659	11%	49
C	5	0%	3
I	86	1%	15
B			
All	2,346	40%	56

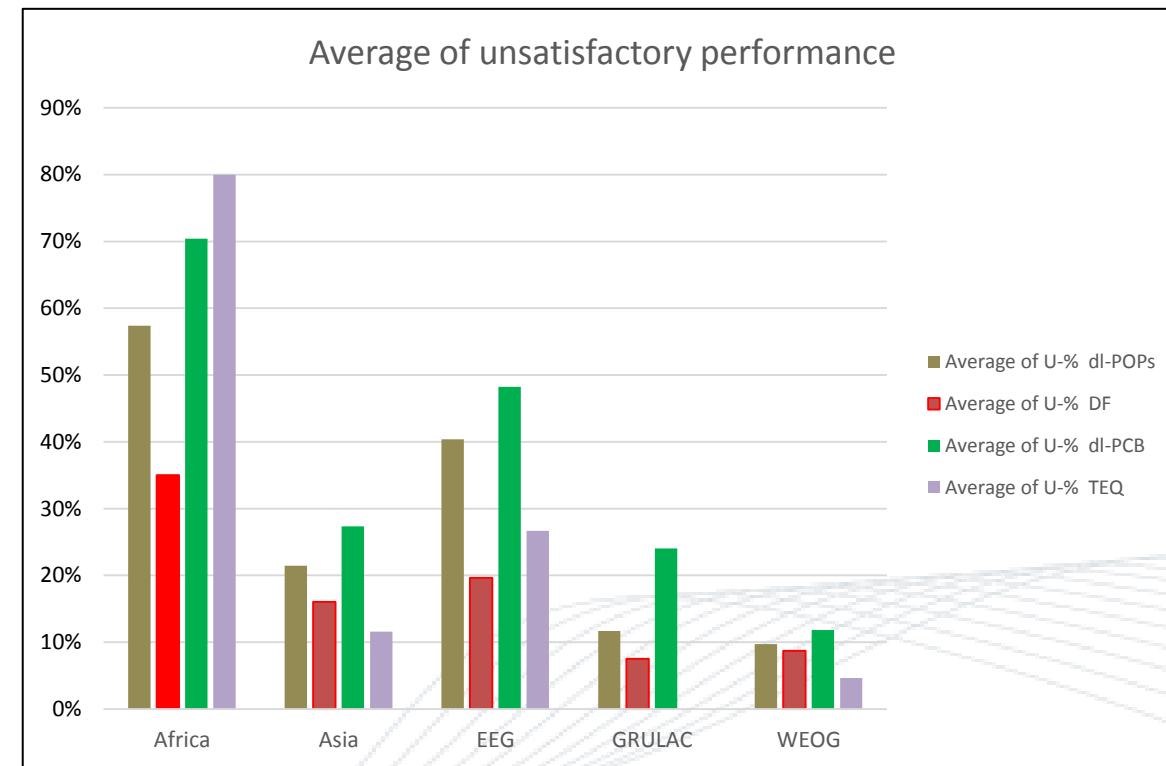
Rating	# z-scores	%	#labs PCDD/PCDF
S	2,423	41%	58
Q	296	5%	44
U	439	7%	48
C	20	0%	12
I	81	1%	13
B			
All	3,259	55%	59

Rating	# z-scores	%	#labs TEQ
S	230	4%	46
Q	31	1%	16
U	31	1%	13
C	-	0%	0
I	-	0%	0
B			
All	292	5%	49

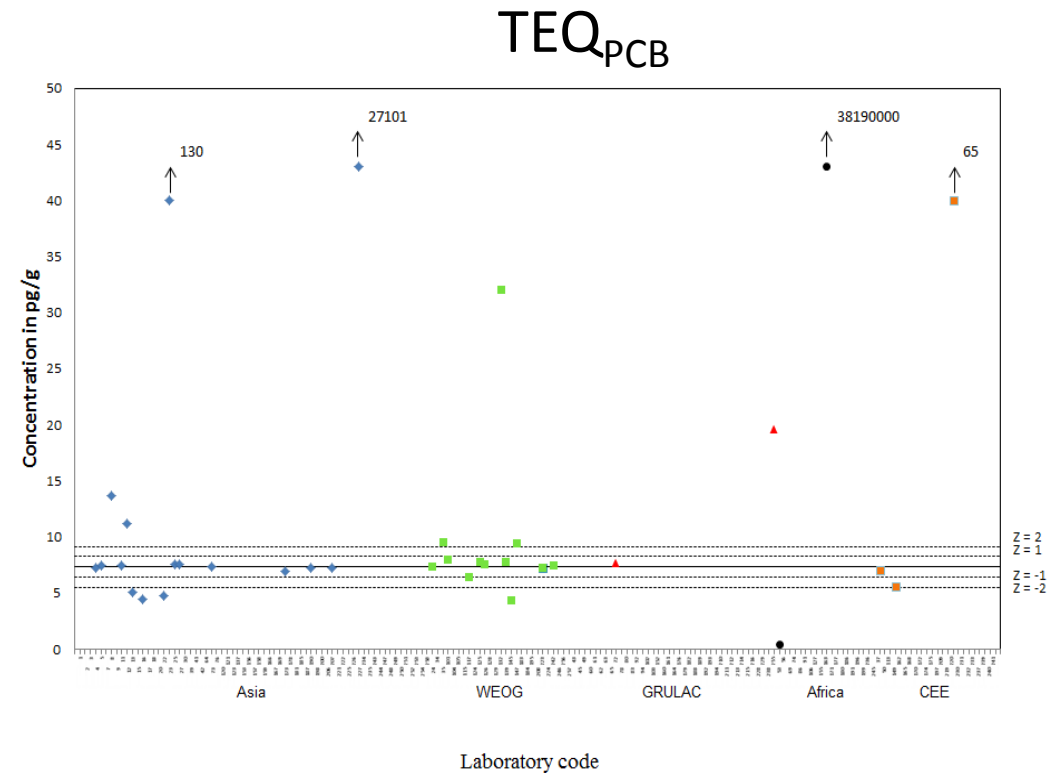
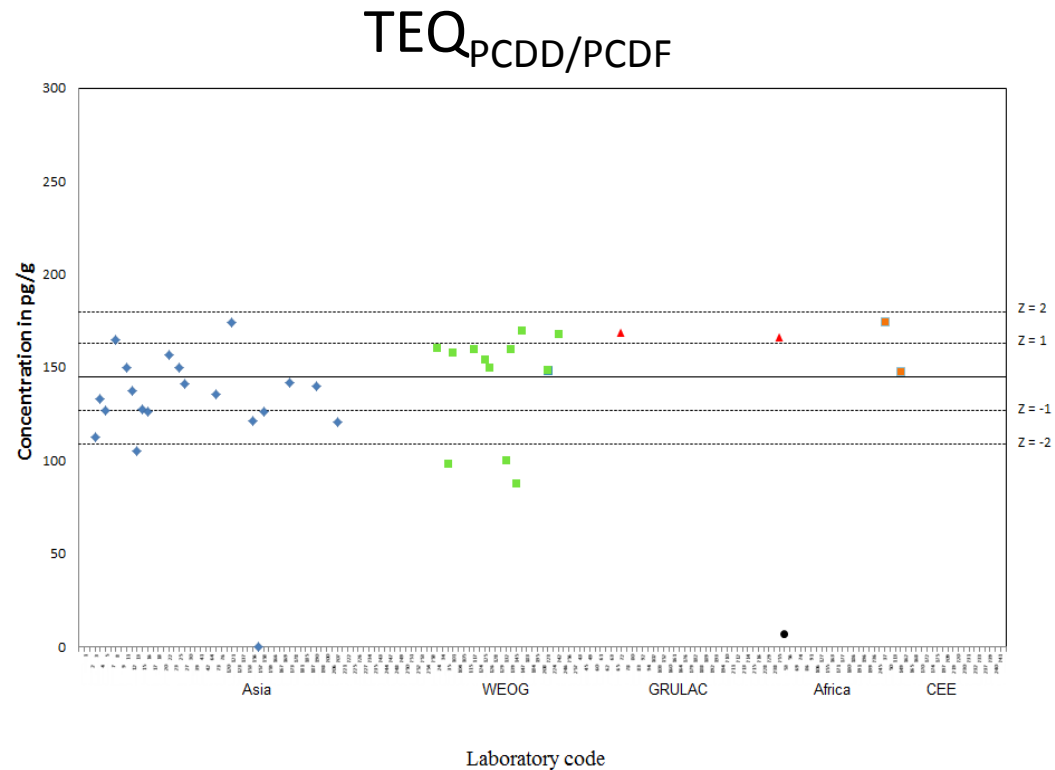
Regional performance for dl-POPs



Region	# of Labs
Africa	4
Asia	32
EEG	8
GRULAC	6
WEOG	16
Grand Total	66



Results of dl-POPs in air extract



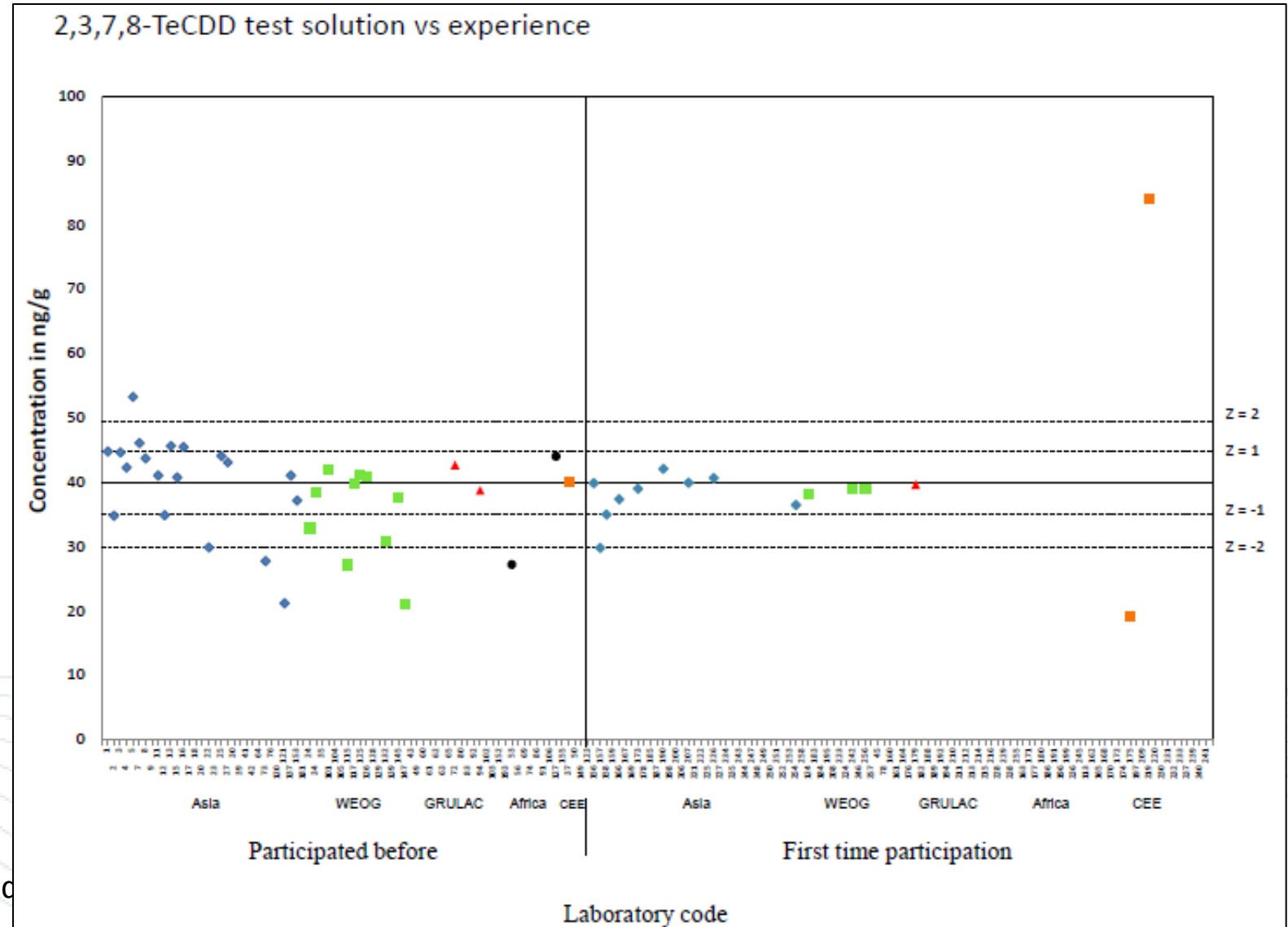
Laboratory code on the x-axis, concentration in pg/g on the y-axis.

The assigned value given by straight line, $z = \pm 1$ (12.5%) and $z = \pm 2$ (25%) are given by the dotted lines.

Blue \blacklozenge symbols represent Asia, green \blacksquare WEOG, red \blacktriangle GRULAC, black \bullet Africa, orange \blacksquare CEE.

Experienced vs. new laboratories

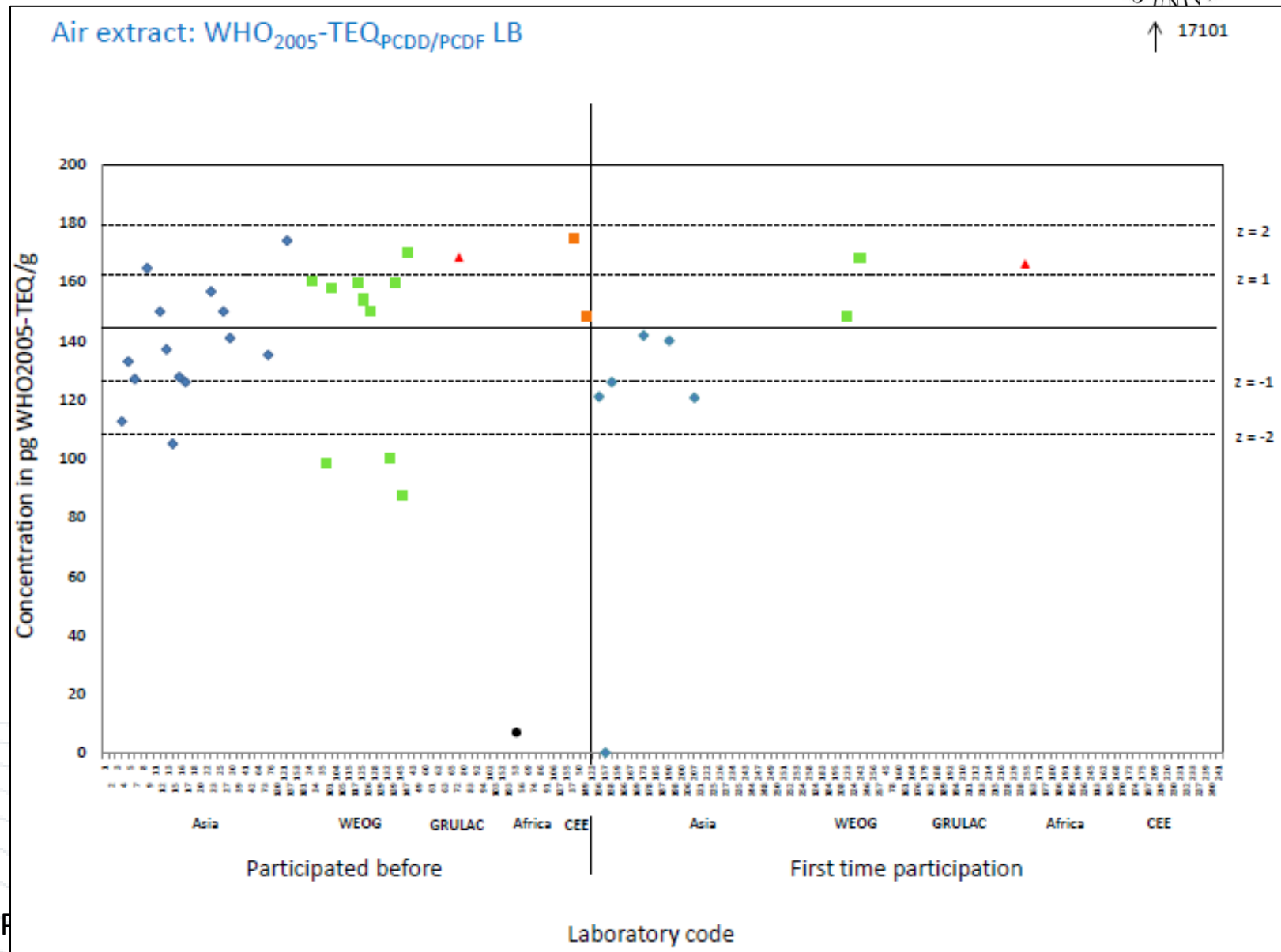
mean experienced	38.3
mean new	39.9
assigned	39.9



Experienced vs. new laboratories

mean experienced	137
mean new	126
assigned	144

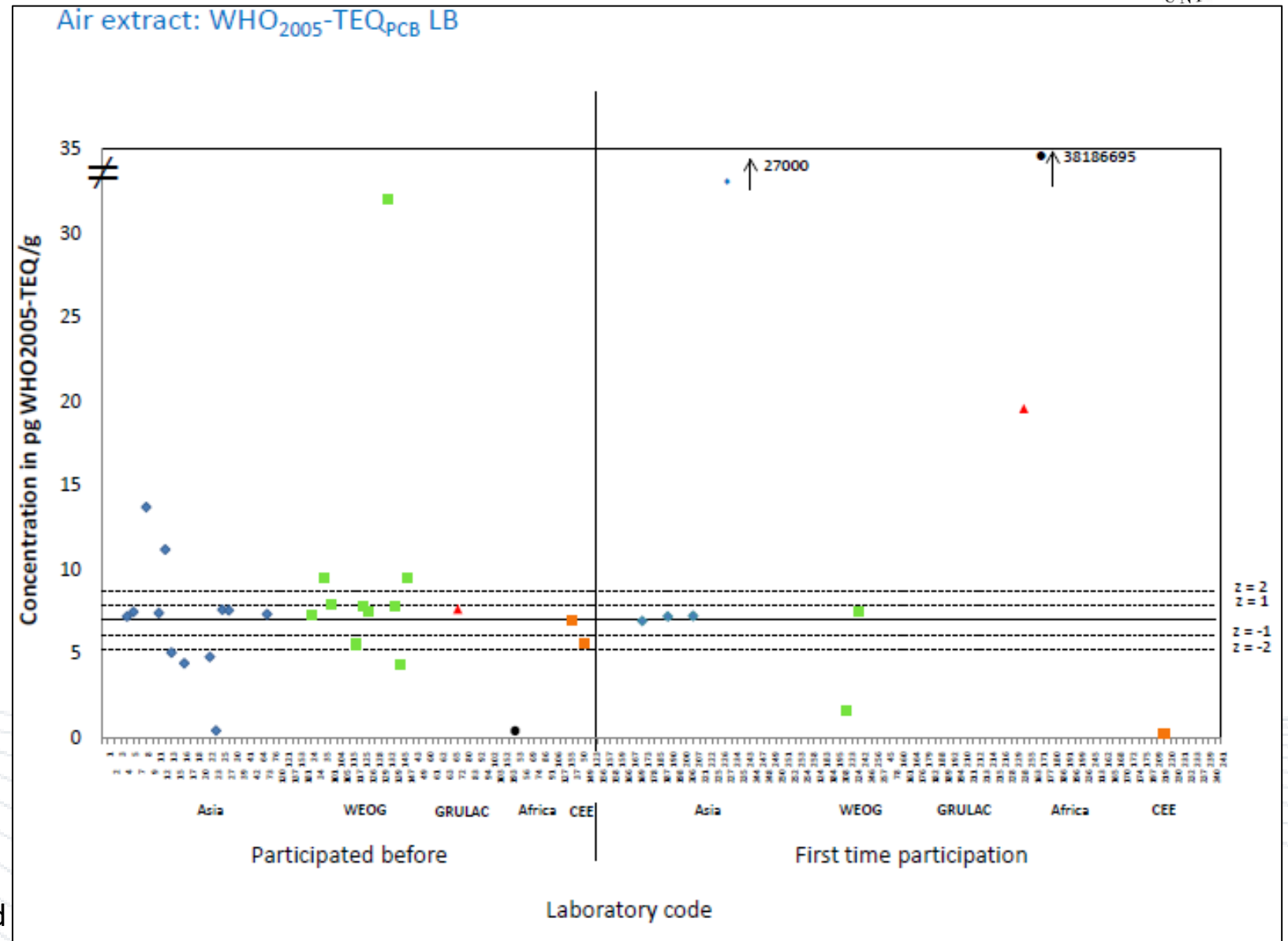
max Labs	175
outside 2 z scores	6
outside 2 z scores	0
counta old	28
counta new	9



Experienced vs. new laboratories

mean experienced	7.8
mean new	4245972
assigned	7.0

max Labs	38,186,695	
outside -2 z scores	7	
outside 2 z scores	8	
counta old	26	16 inside, 10 outside
counta new	9	4 inside, 5 outside



dl-POPs instrumentation and results



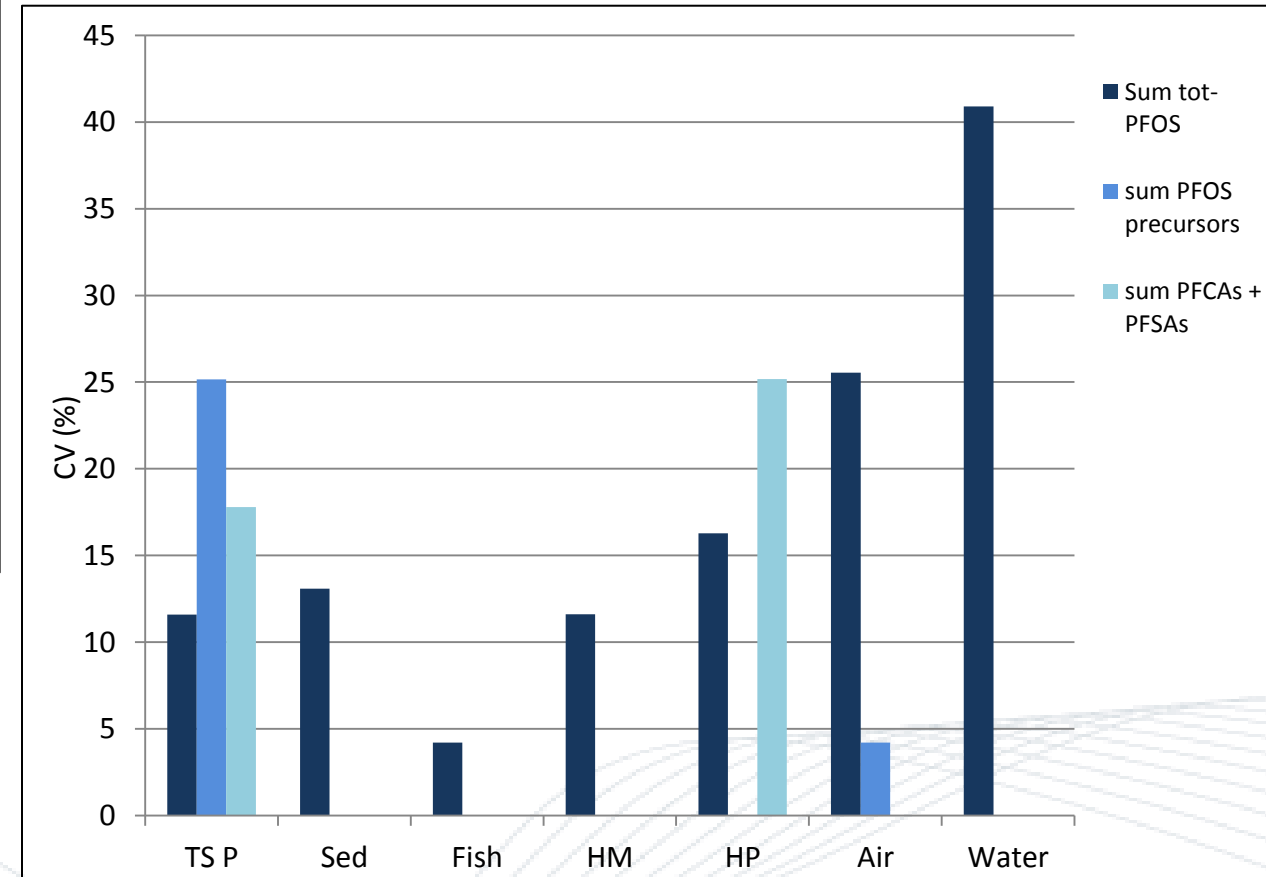
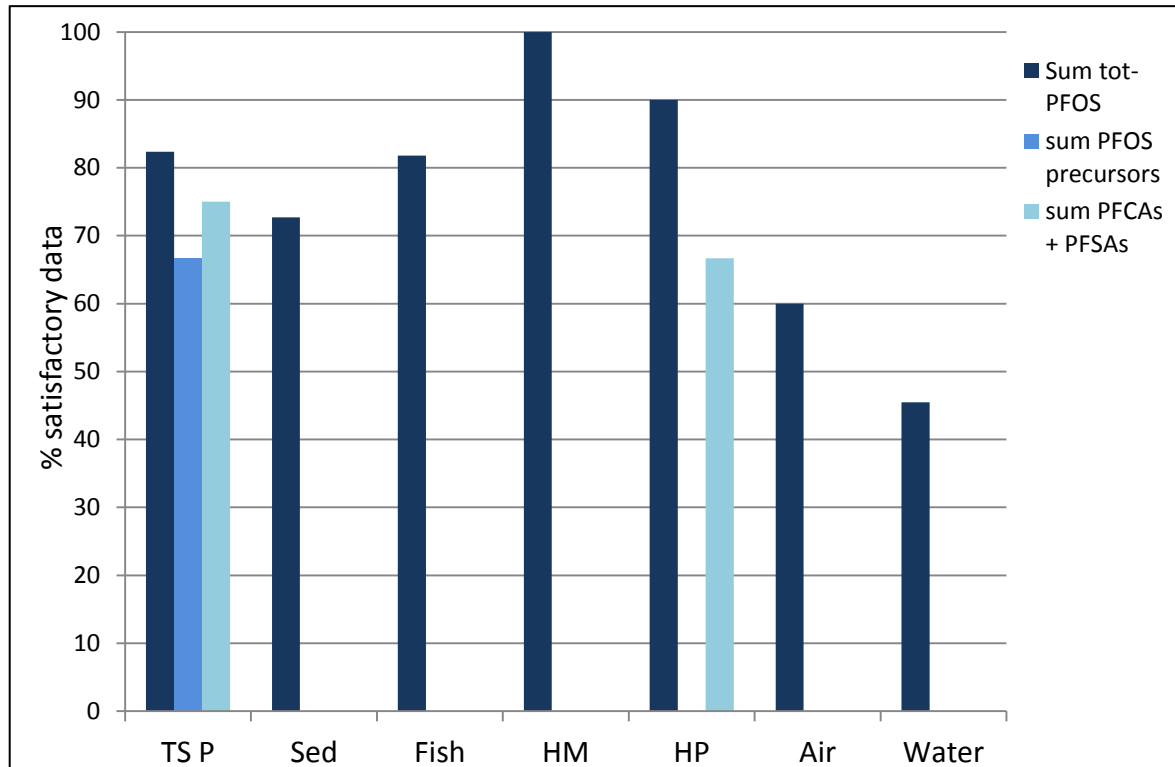
Instrument	# S-dl-POPs	# Q-dl-POPs	# U-dl-POPs	Subtotal	% S of all S	% Q of all Q	% U of all U	% of all	% S of all instrument
HRMS	3,406	451	612	4,469	84%	84%	55%	79%	76%
LRMS	322	58	285	665	8%	11%	26%	12%	48%
ECD	12	3	90	105	0.3%	0.6%	8%	2%	11%
NR	300	24	142	466	7%	4%	13%	8%	64%
GrandTotal	4,040	536	1,129	5,705	100%	100%	100%	100%	71%

- The majority of the labs used HRGC/HRMS (magnetic sector-field instruments) for dl-POPs;
- This combination seems to generate the best results;
- ECD detection is not capable to analyze dl-POPs; Should not be used for dl-PCB;
- Most laboratories used 60 m long GC columns; some used 30 m long columns;
- Two columns of different polarity hardly used (← EPA methods);
- No laboratory used GCxGC for separation.

PFAS

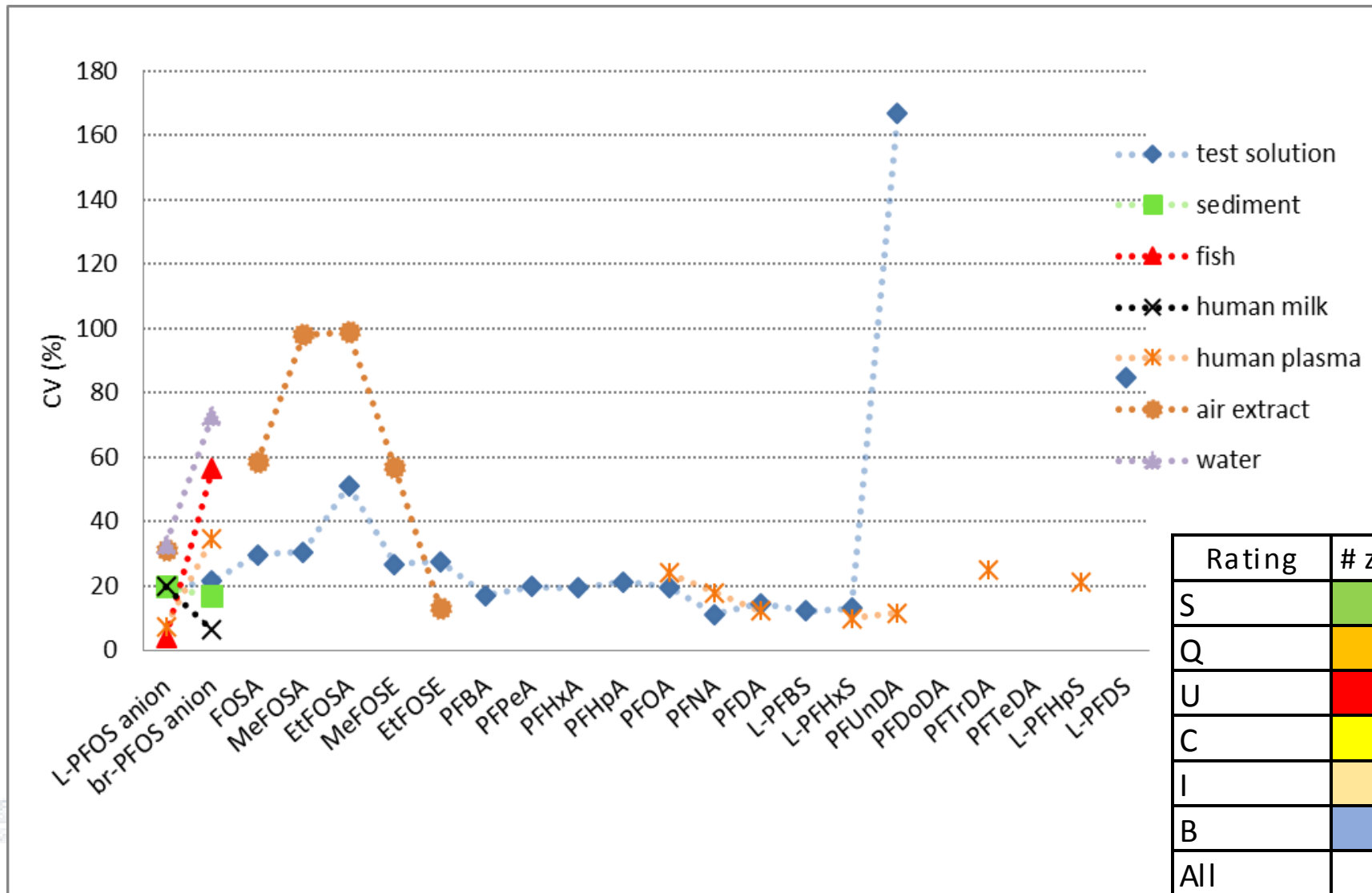
PFOS [anion] (L- and br-PFOS, PFOS_{total})
PFOS precursors (FOSA, Me-/EtFOSA and Me-/EtFOSE)
per-/polyfluorinated acids, -sulfonamides)

Summary performance for PFAS



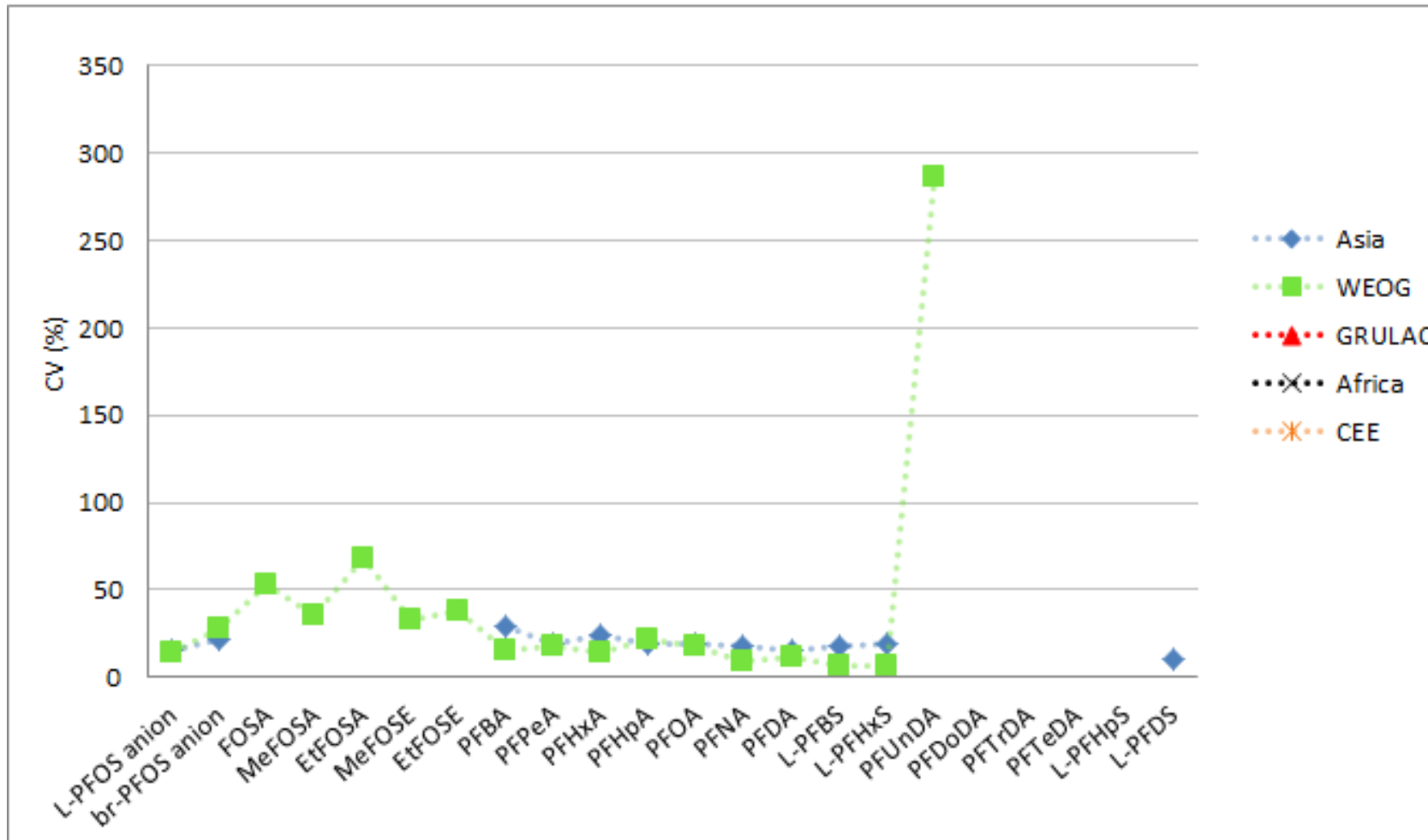
Whereas 60% of the z-scores for PFOS were satisfactory for the air extract;
No z-scores could be assigned for the precursors

Performance for PFAS according to matrix

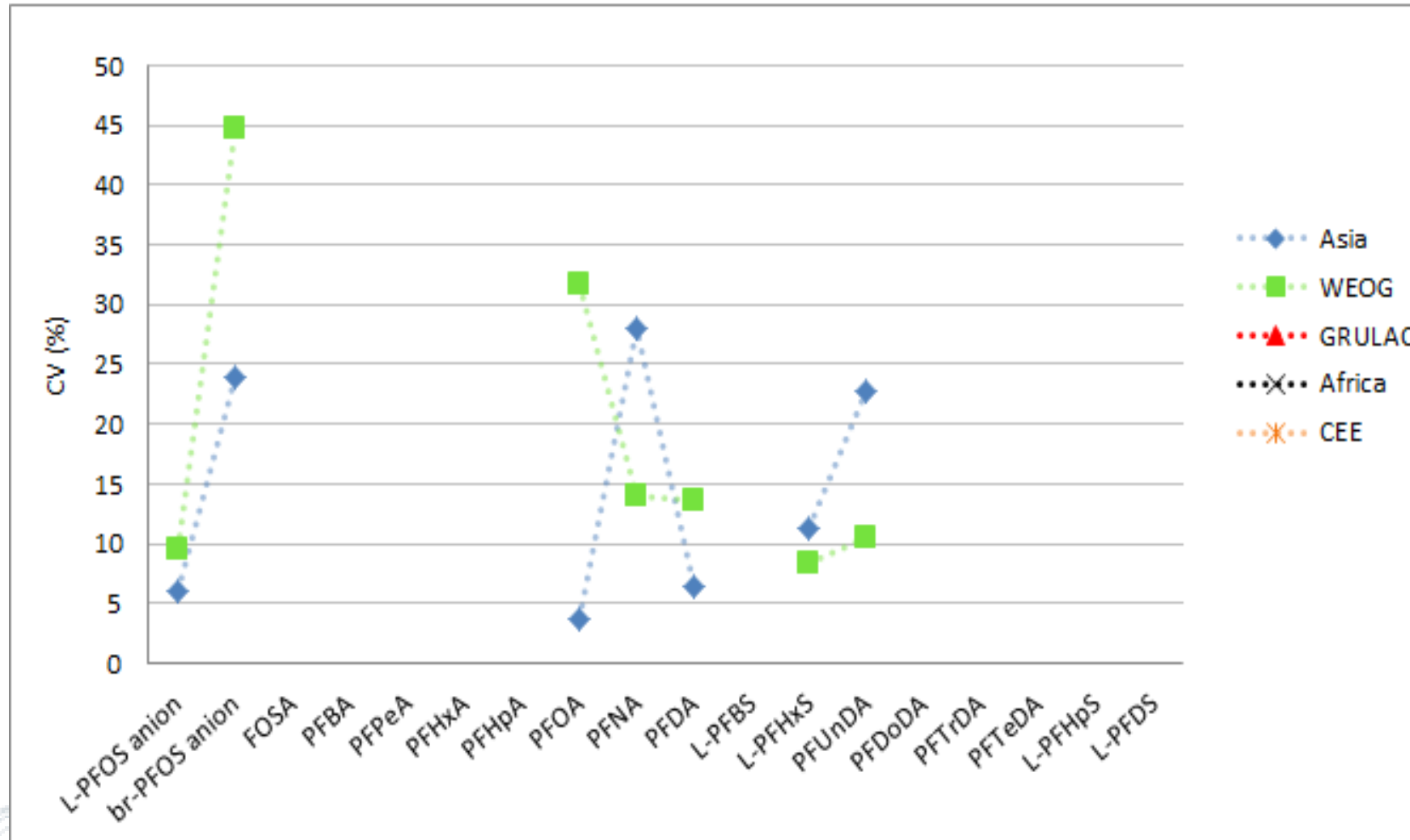


Rating	# z-scores	%	#labs PFAS
S	459	74%	27
Q	62	10%	21
U	86	14%	20
C	6	1%	5
I	7	1%	5
B			
All	620	100%	28

PFAS test solution



Regional PFAS in human plasma



PFAS (z-scores)

Test solution N	% z-scores $ Z < 2$	% z-scores $3 > Z > 2$	% z-scores $6 > Z > 3$	% z-scores $ Z > 6$
L-PFOS anion	80	16	0	4
br-PFOS anion	53.3	33.3	0	13.3
tot-PFOS LB (ND=0)	82.4	17.7	0	0
tot-PFOS UB (ND=LOD)	88.2	11.8	0	0
FOSA	57.1	14.3	14.3	14.3
MeFOSA	50	37.5	12.5	0
EtFOSA	0	0	0	0
MeFOSE	71.4	14.3	14.3	0
EtFOSE	83.3	0	16.7	0
PFOS precursors (5) LB (ND=0)	66.7	33.3	0	0
PFOS precursors (5) UB (ND=LOD)	66.7	33.3	0	0

Sediment	% z-scores $ Z < 2$	% z-scores $3 > Z > 2$	% z-scores $6 > Z > 3$	% z-scores $ Z > 6$
L-PFOS anion	56.3	6.25	12.5	12.5
br-PFOS anion	50	0	0	20
tot-PFOS LB (ND=0)	72.7	0	9.09	9.09
tot-PFOS UB (ND=LOD)	63.6	0	9.09	27.3

Fish	% z-scores $ Z < 2$	% z-scores $3 > Z > 2$	% z-scores $6 > Z > 3$	% z-scores $ Z > 6$
L-PFOS anion	71.4	0	0	21.4
br-PFOS anion	40	0	30	10
tot-PFOS LB (ND=0)	81.8	0	9.09	9.09
tot-PFOS UB (ND=LOD)	81.8	0	9.09	9.09

PFAS (z-scores)

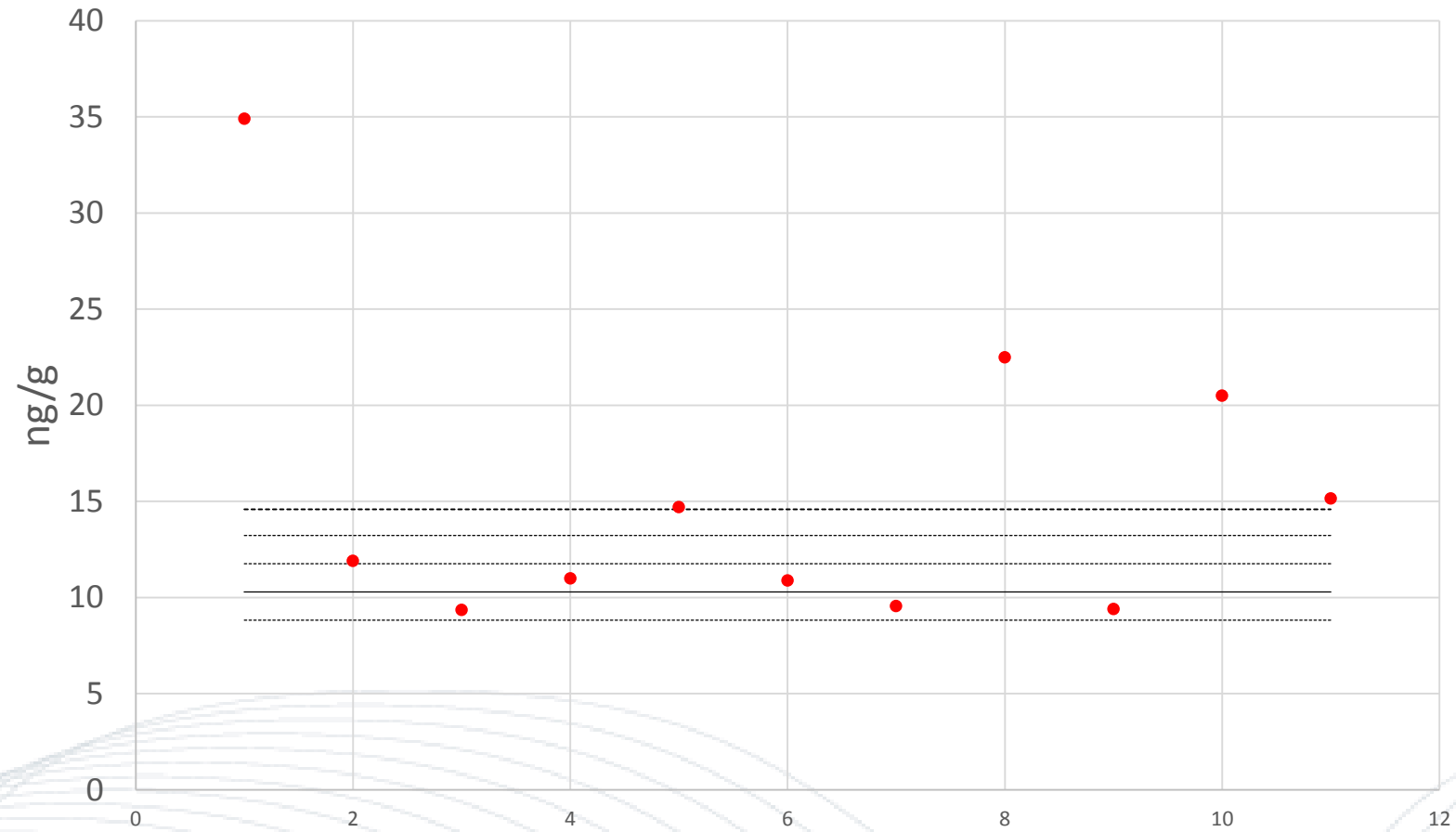
Human milk	% z-scores $ Z < 2$	% z-scores $3 > Z > 2$	% z-scores $6 > Z > 3$	% z-scores $ Z > 6$
L-PFOS anion	66.7	16.7	0	0
br-PFOS anion	0	0	0	0
tot-PFOS LB (ND=0)	100	0	0	0
tot-PFOS UB (ND=LOD)	80	0	20	0

Water	% z-scores $ Z < 2$	% z-scores $3 > Z > 2$	% z-scores $6 > Z > 3$	% z-scores $ Z > 6$
L-PFOS anion	45	5	15	25
br-PFOS anion	0	0	0	0
tot-PFOS LB (ND=0)	45.5	9.09	9.09	36.4
tot-PFOS UB (ND=LOD)	45.5	18.2	0	36.4

Air extract (MeOH)	% z-scores $ Z < 2$	% z-scores $3 > Z > 2$	% z-scores $6 > Z > 3$	% z-scores $ Z > 6$
L-PFOS anion	63.6	9.09	9.09	18.2
br-PFOS anion	0	0	0	0
tot-PFOS LB (ND=0)	60	20	0	20
tot-PFOS UB (ND=LOD)	0	0	0	0
FOSA	0	0	0	0
MeFOSA	0	0	0	0
EtFOSA	0	0	0	0
MeFOSE	0	0	0	0
EtFOSE	0	0	0	0
PFOS precursors (5) LB (ND=0)	0	0	0	0
PFOS precursors (5) UB (ND=LOD)	0	0	0	0

L-PFOS in air (n=11)

L-PFOS anion air



PFAS



- All but one laboratory used LC/MS/MS instrumentation;
- One laboratory in WEOG used a TOF instrument (S-Q-U: 11-2-5);
- Overall, more laboratories used HPLC columns for separation than UPLC columns;
- One laboratory used HRGC/LRMS (30 m long GC column) for determination of Me-/EtFOSE and Me-/EtFOSA

Thank you