

# Results from UNEP 2<sup>nd</sup> Interlaboratory

## Overview on the intercalibration data of **dl-POPs**

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# Objectives UNEP

- To be able to confirm a 50% decline in the levels of POPs within a 10 year period
- Analytical variance of the data
  - < 25%
  - 2 x RSD of 12.5%
  - Z-scores = 2, corresponds to 25%

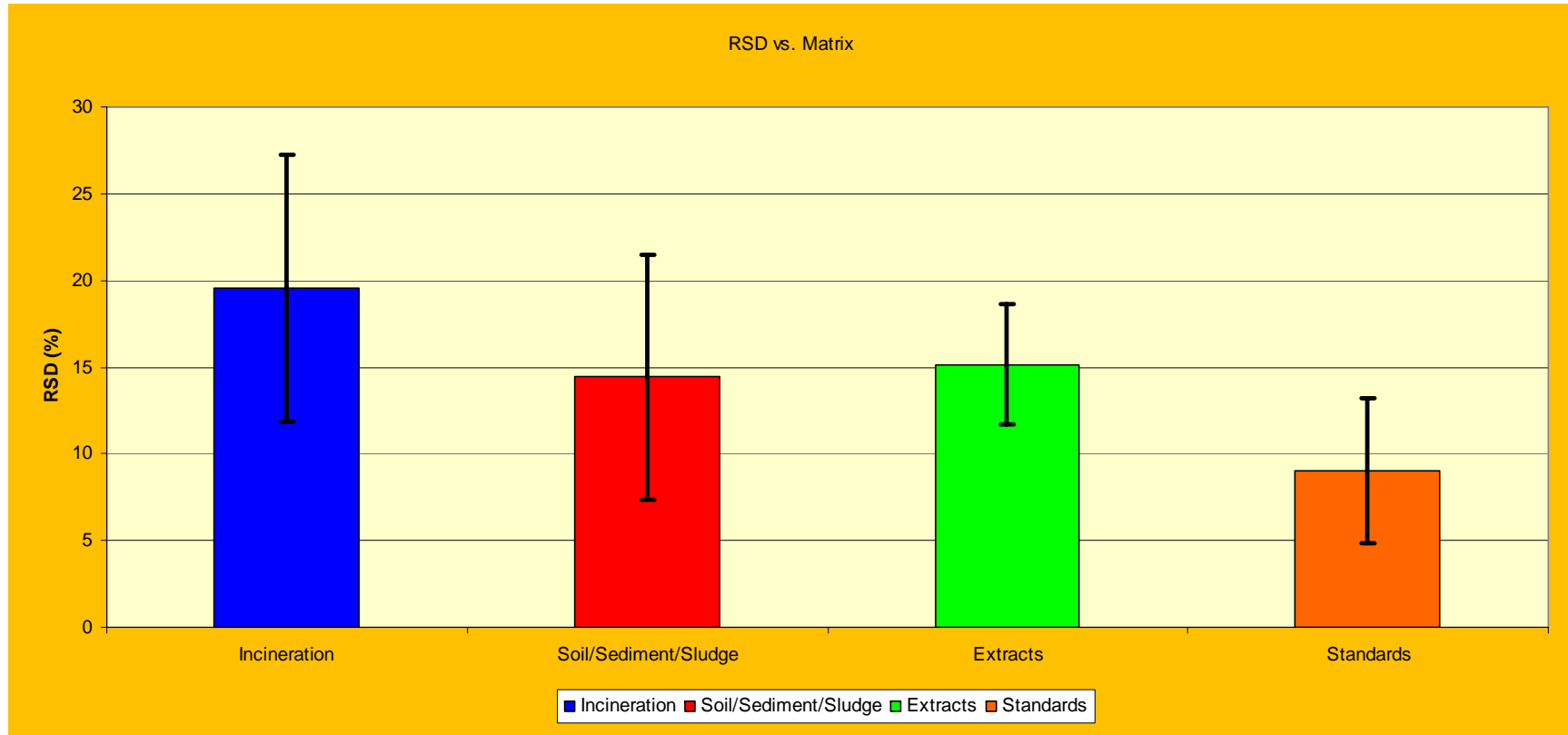


# Present State of the Art dl-POPs 2010

- 15 years of QA/QC studies for dioxins
  - From 1992 to 2011 the 16<sup>th</sup> round
  - More than 200 laboratories registered
  - Participation of around 100 every year
  - More than **100 000** data points
  - Summarized in feature article *Anal. Chem.*<sup>1</sup>

<sup>1</sup> Long-Term Worldwide QA/QC of Dioxins and Dioxin-like PCBs in Environmental Samples .  
*Anal. Chem.* 80 (2008) 3956-3964.

# State of the art dl-POPs 2010



Fly Ash < 20% RSD  
 Soil/Sediment < 15% RSD  
 Standard solution < 10%

# 2<sup>nd</sup> UNEP Interlaboratory Assessment

- Matrices
  - Standard solution
  - Human milk
  - Human blood
  - Air
  - Fish
  - Sediment
  - Water
  - Transformer oil
- All laboratories were asked to re-check data after reporting.



# Traceability Sample Shipment

- Special metal container
- Adsorbent for organic solvents
- Cooling for milk/blood
  
- Samples send by international carrier
  - DHL
- Shipment can be traced on the [www](#)
  
- Problems
  - Clearance problems
  - Clearance problems solved by carrier
- Number of Shipments
  - > 100 shipment in Asia, South America and Africa





# Chemical Analysis of dl-POPs




- Use own method
  - Standard method
  - In house methods
  - UNEP training
- Use own standard solution for calibration
  - Or UNEP standards from training
- Internal QA/QC
  - Check laboratory blanks
  - QA/QC or SRM sample
  - QA/QC charts



Participant code:					
Name:					
Organisation:					
Address:					
<b>UNEP Intercalibration 2013</b>					
	<b>Standard solution</b> (µg/kg)	<b>Sediment</b> (ng/kg)	<b>Fish</b> (µg/kg)*	<b>Mothers' milk</b> (ng/kg)*	<b>Air extract</b> (µg/kg)
Code:					
Sample Code:					
Date Received:					
Date Analyzed:					
(Wet) Weight Received:					
Sample Intake (g):					
Final Volume (µL):					
Injection Volume (µL):					
% Extracted Lipids:					
<b>Dioxins</b>					<b>WHO<sub>1998</sub>-TEF</b>
2,3,7,8-TeCDD					1
1,2,3,7,8-PnCDD					1
1,2,3,4,7,8-HxCDD					0.1
1,2,3,6,7,8-HxCDD					0.1
1,2,3,7,8,9-HxCDD					0.1
1,2,3,4,6,7,8-HpCDD					0.01
OCDD					0.0001
<b>Furans</b>					
2,3,7,8-TeCDF					0.1
1,2,3,7,8-PnCDF					0.05
2,3,4,7,8-PnCDF					0.5
1,2,3,4,7,8-HxCDF					0.1
1,2,3,6,7,8-HxCDF					0.1
1,2,3,7,8,9-HxCDF					0.1
2,3,4,6,7,8-HxCDF					0.1
1,2,3,4,6,7,8-HpCDF					0.01
1,2,3,4,7,8,9-HpCDF					0.01
OCDF					0.0001
<b>WHO<sub>1998</sub>-TEQ (PCDD/PCDF) Lower Bound (ND = 0)</b>					
<b>WHO<sub>1998</sub>-TEQ (PCDD/PCDF) Upper Bound (ND = LOD)</b>					
<b>dl-PCB</b>					
PCB 77					0.0001
PCB 81					0.0001
PCB 126					0.1
PCB 169					0.01
PCB 105					0.0001
PCB 114					0.0005
PCB 118					0.0001
PCB 123					0.0001
PCB 156					0.0005
PCB 157					0.0005
PCB 167					0.0001
PCB 189					0.0001
<b>WHO<sub>1998</sub>-TEQ (dl-PCB) Lower Bound (ND = 0)</b>					
<b>WHO<sub>1998</sub>-TEQ (dl-PCB) Upper Bound (ND = LOD)</b>					
<b>WHO<sub>1998</sub>-TEQ (total) Lower Bound (ND = 0)</b>	0	0	0	0	0
<b>WHO<sub>1998</sub>-TEQ (total) Upper Bound (ND = LOD)</b>	0	0	0	0	0
<b>Notes</b>					
* wet weight					
All values should be reported in µg/kg or ng/kg					
ND: not detected < than value expected					
NA: not analyzed					

# Report form dl-POPs

# Additional Information

Additional Information						
						
	Ash	Sediment	Fish	Mothers' Milk	Standard 1 B	
Sample pretreatment					*	(Acid treatment, HCl, ...)
Extraction technique:						(Soxhlet, SFE, ASE, ...)
Extraction solvent:					*	(Toluene, ...)
Clean Up:						
Silica column					*	
AlOx column					*	
Carbon column					*	
GC column:						(DB-5, SP2330, Dioxin-2...)
GC/MS system:						(High Res/Low Res) (MS/MS, IT, TOF, ...)
Resolution						(Estimation)
<sup>13</sup> C Internal Standards						(Number used 1-17)
<sup>13</sup> C Recovery Standards						(Number used 1-17)
Method:						(EPA 1613, ...)
Calculation LOD						(S/N = 3, 10, ...)
Calculation LOQ						(S/N = 3, 10, ...)
Comments:						

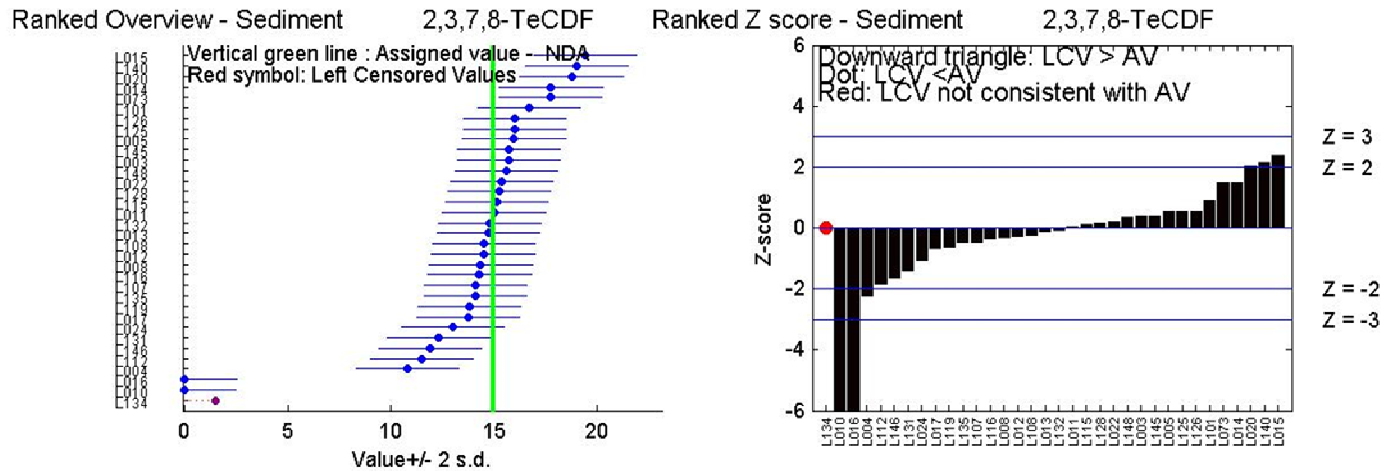
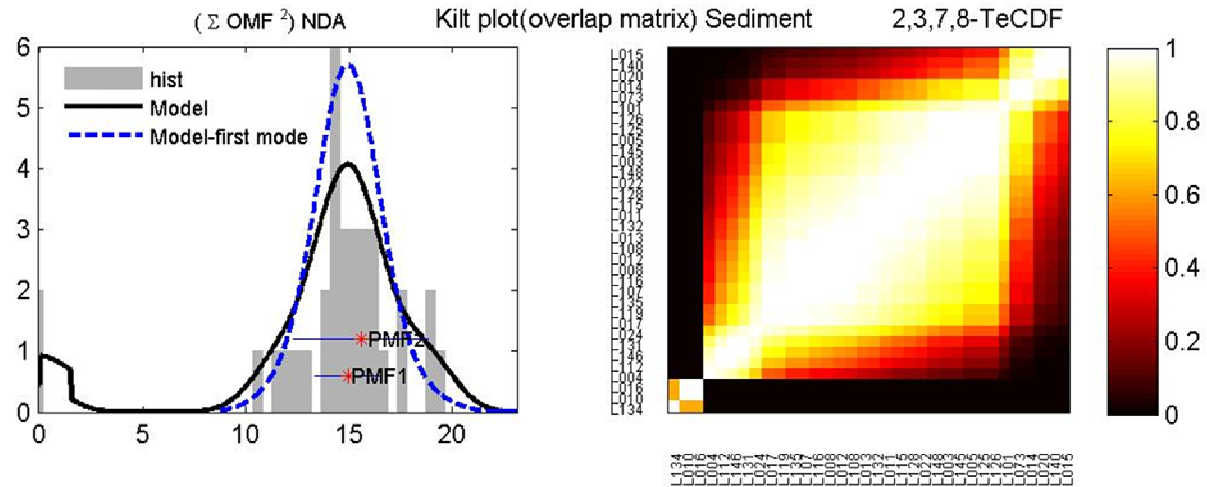
# UNEP Recommendations

- Implementation
  - Recovery 50-130%
    - (Report recovery)
  
  - S/N
    - (Report LOD, LOQ, MDL)
    - Less than value for UB or LB
  
  - Difference upper bound – lower bound
    - Report both UB and LB
  
  - Individual congeners and TEQ
    - PCB TEQ
    - All congeners

# Consensus value

- Outliers/Extreme removal traditional
  - Data does not follow a normal ‘Gaussian’ distribution’
  - Z-scores depending ‘real’ RSD of the data
- Cofino statistic
  - Tolerates also non Gaussian distribution
  - Successfully used in Quasimeme and other studies
  - Often similar to average or median

# Cofino statistics<sup>1</sup>



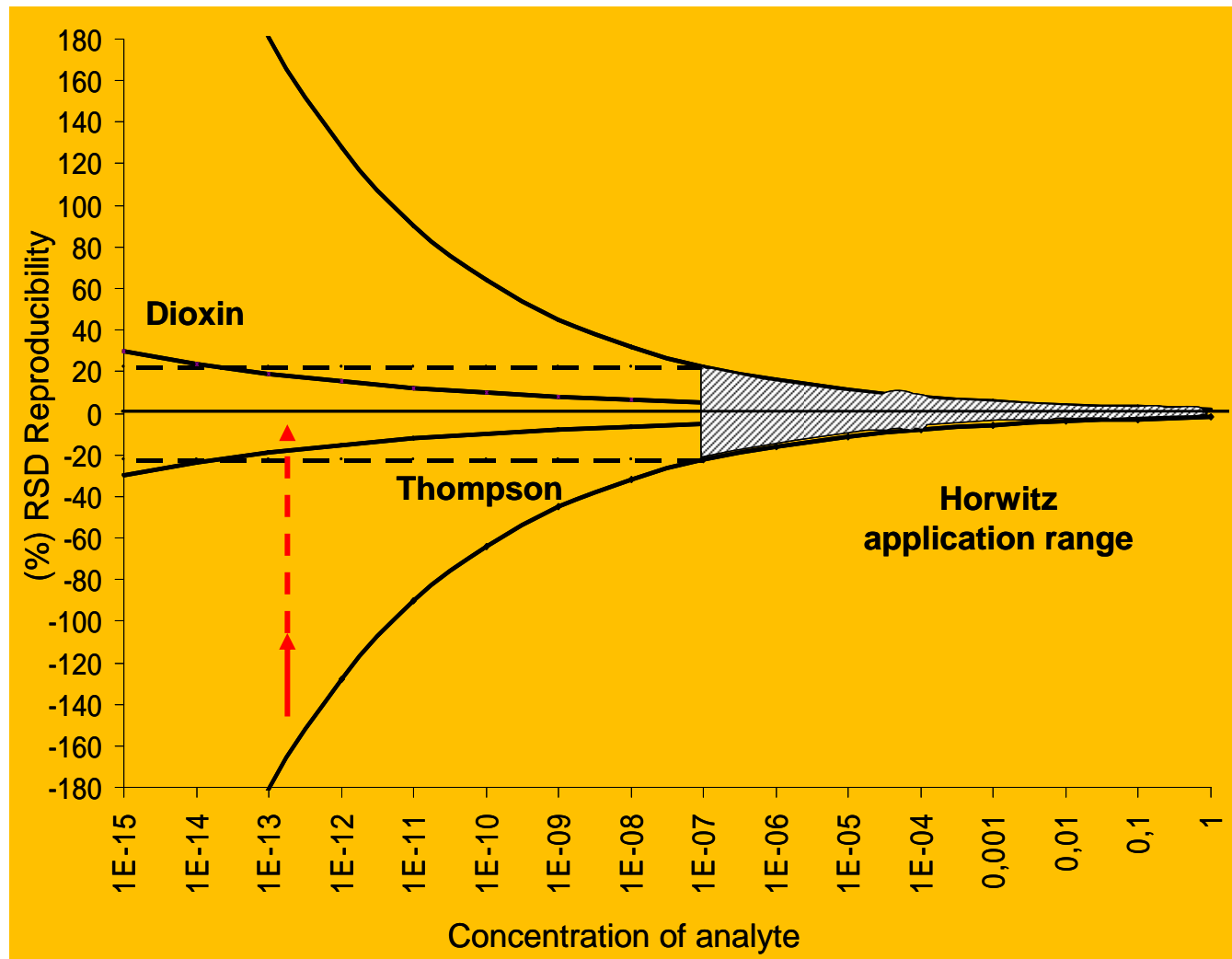
1. W.P. Cofino, I.H.M. van Stokkum, J. van Steenwijk, D.E. Wells, Anal. Chim. Acta 533 (2005) 31.

# Advanced Statistics

- Cofino Statistics
  - Best fit to model
  - Assigned value based on consensus values for all data
  - Treatment non normal distributed data
- Z-scores
  - Z-score= \_\_\_\_\_
  - Based on set RSD of 12.5% ( $z = 2$ , 25%)



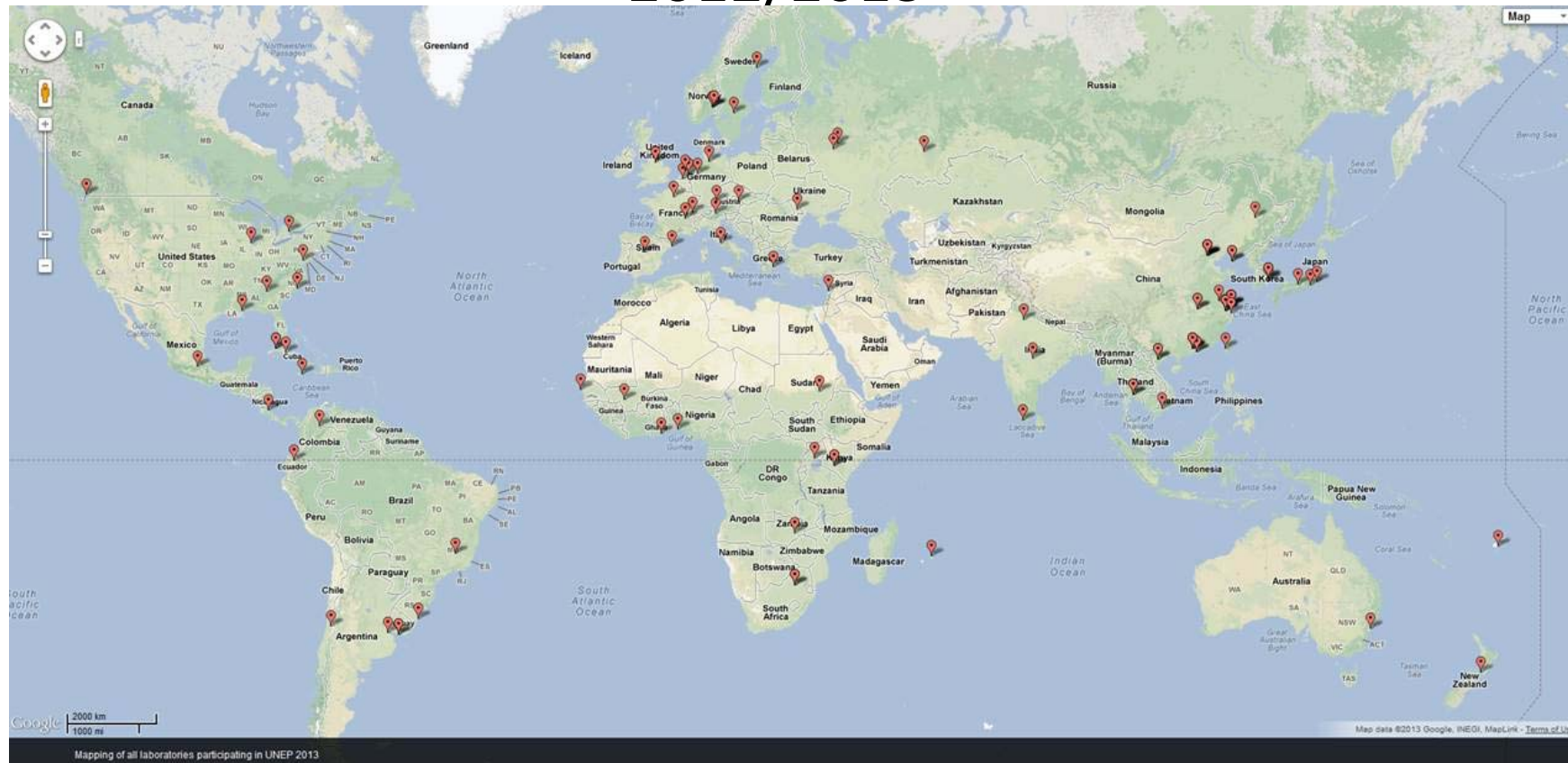
# The Horowitz equation 1980



\* Eppe et al. Chemsphere 2009



# Global distribution of the laboratories participating in the 2<sup>nd</sup> UNEP Interlaboratory Assessment 2012/2013



N=105 laboratories, 90 reported data

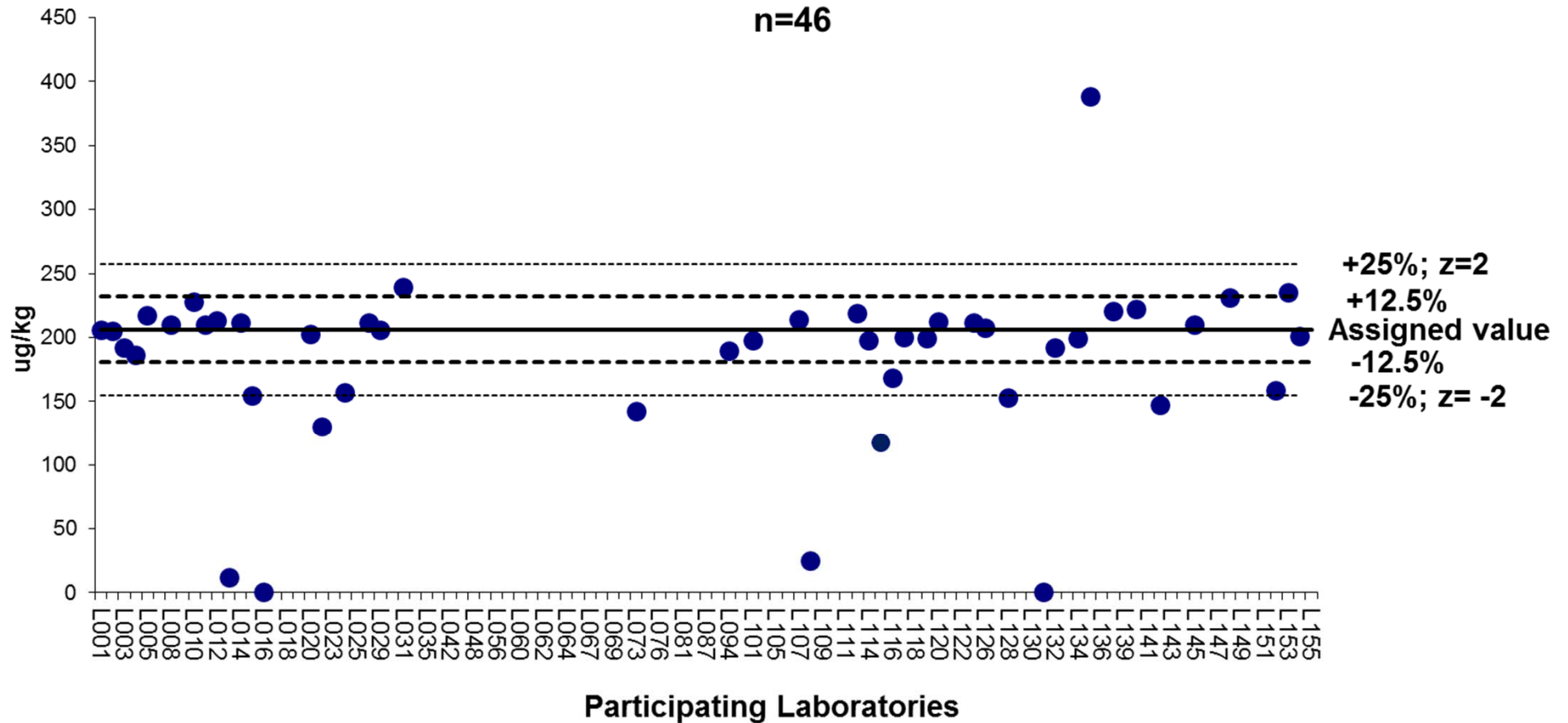


# Participation per compound class

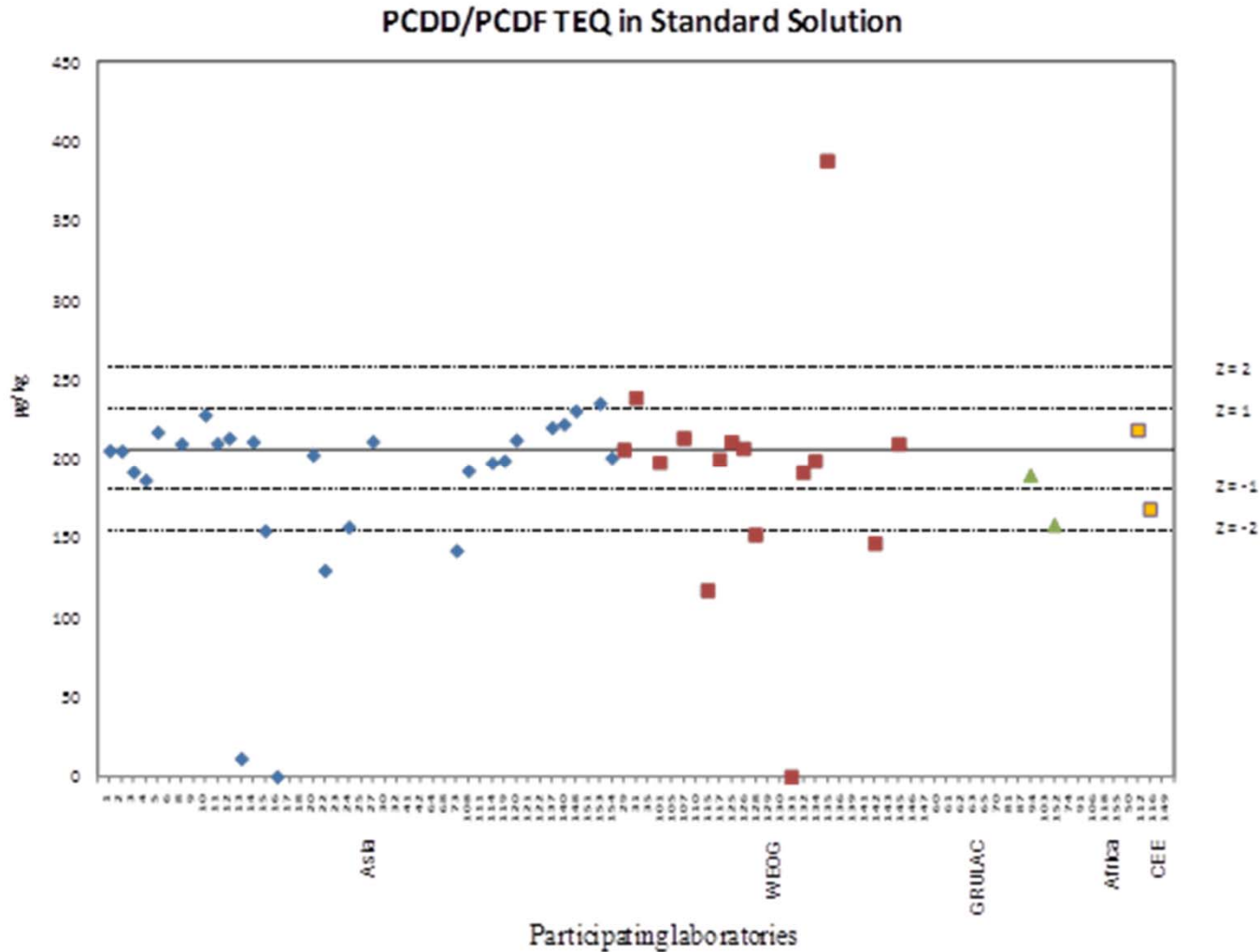
Group	Standard solutions	Sediment	Fish	Mothers' milk	Air	Water	Human serum	Transformer oil
OCP	50	27	36	21	23	-	-	-
PCB	47	38	43	28	25	-	-	19
dl-POPs	48	34	41	29	37	-	-	-
PBDE	42	30	34	19	21	-	-	-
PFAS	22	18	19	8	8	30	8	-

# Standard solution

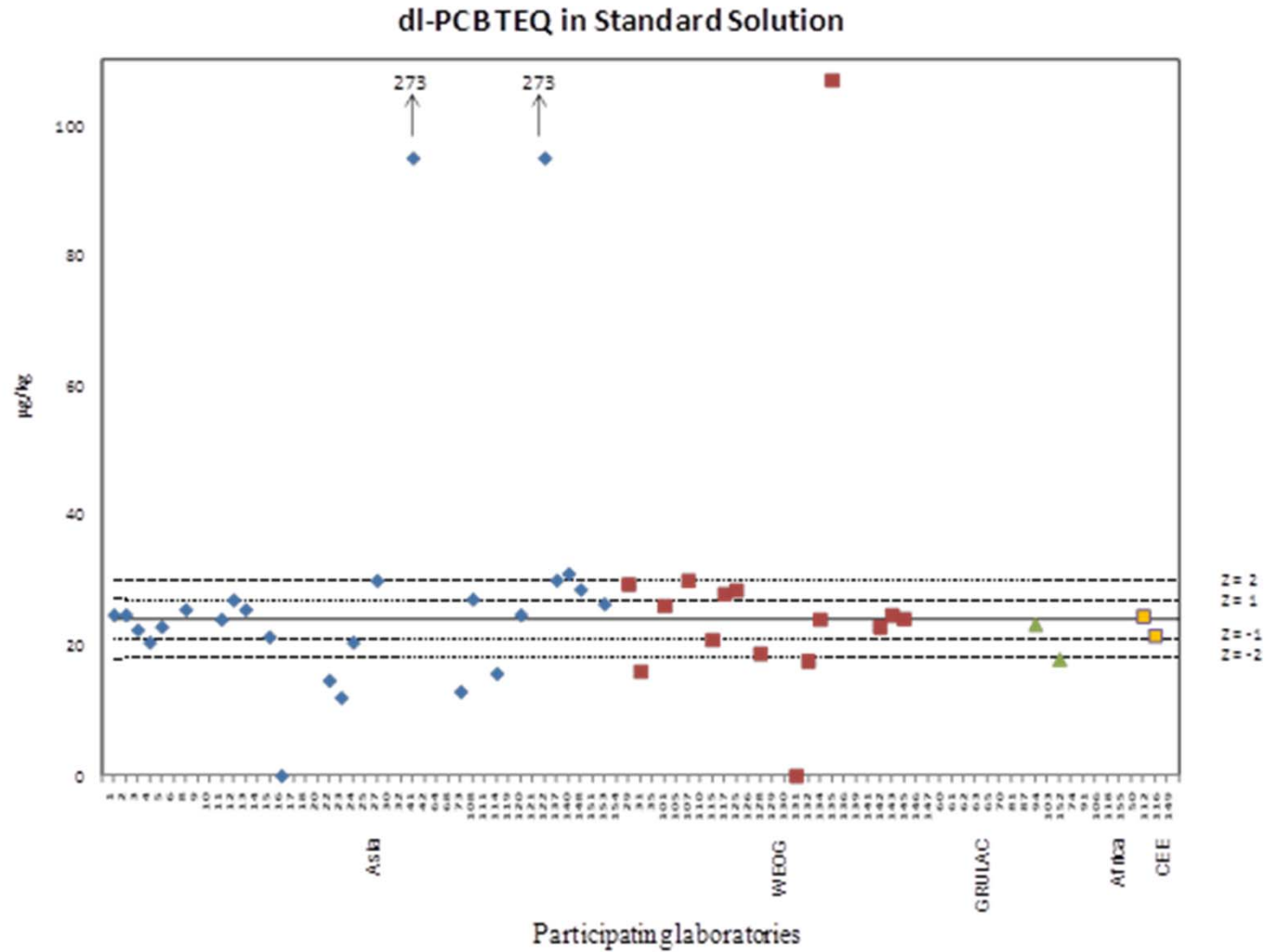
WHO1998-TEQ PCDD/PCDF  
Standard  
n=46



# PCDD/DF TEQ Standard solution



# dl-PCBs TEQ standard solution

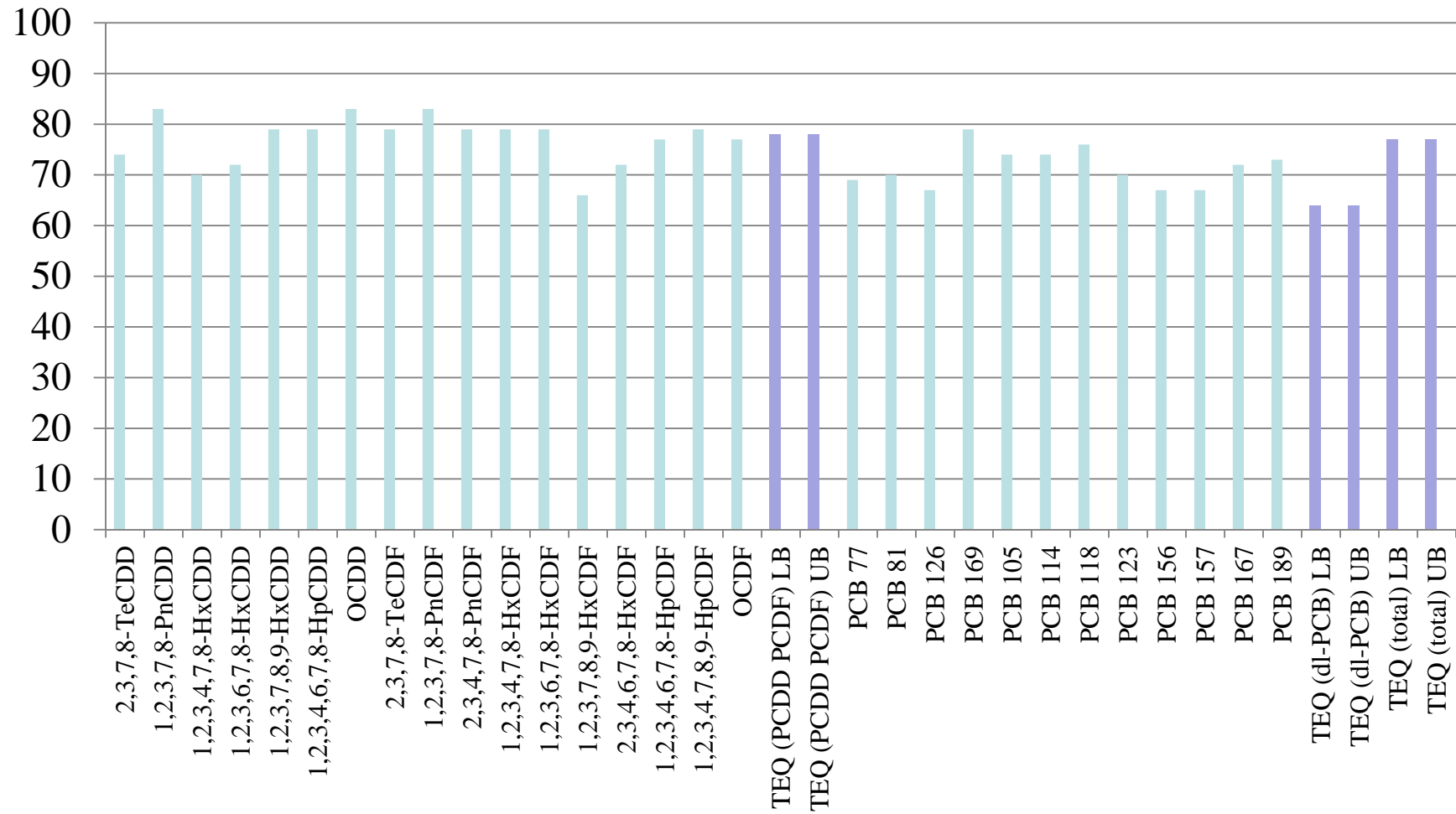


# Summary Standard Solution dl-POPs

Standard solution	n	AV	Median	Mean	Min	Max	Between lab CV (%)	Inclusion rate (%)
Analyte								
2,3,7,8-TeCDD	47	33.9	34.1	33.9	0.020	65.1	13	65
1,2,3,7,8-PnCDD	47	67.3	65.6	67.3	0.041	128	11	66
1,2,3,4,7,8-HxCDD	47	68.5	68.2	68.5	0.040	133	14	66
1,2,3,6,7,8-HxCDD	47	112	112	112	0.051	205	17	72
1,2,3,7,8,9-HxCDD	47	67.8	66.7	67.8	0.041	126	21	77
1,2,3,4,6,7,8-HpCDD	47	135	134	135	0.092	258	10	63
OCDD	47	141	140	141	0.101	254	15	72
2,3,7,8-TeCDF	47	34.2	34.9	34.2	0.021	61.7	13	68
1,2,3,7,8-PnCDF	47	67.9	66.6	67.9	0.040	128	15	74
2,3,4,7,8-PnCDF	47	68.8	68.7	68.8	0.040	132	11	68
1,2,3,4,7,8-HxCDF	47	69.7	68.1	69.7	0.042	131	14	70
1,2,3,6,7,8-HxCDF	47	68.5	68.0	68.5	0.041	133	13	70
1,2,3,7,8,9-HxCDF	47	67.6	70.0	67.6	0.040	132	19	64
2,3,4,6,7,8-HxCDF	47	106	107	106	0.070	214	20	71
1,2,3,4,6,7,8-HpCDF	47	139	138	139	0.097	259	15	71
1,2,3,4,7,8,9-HpCDF	47	181	179	181	0.101	347	11	66
OCDF	47	140	140	140	0.097	266	20	74
WHO1998-TEQ (PCDD PCDF) LB (ND = 0)	46	206	202	206	0.123	388	8	62
WHO1998-TEQ (PCDD PCDF) UB (ND = LOD)	46	206	202	206	0.123	388	8	62
PCB 77	48	151	155	151	0.114	6573	21	71
PCB 81	46	160	165	160	0.108	9278	21	71
PCB 126	48	222	223	222	0.178	2630	22	72
PCB 169	48	155	160	155	0.106	664	22	73
PCB 105	46	286	283	286	0.206	18110	20	71
PCB 114	46	164	168	164	0.111	874	16	65
PCB 118	46	160	162	160	0.109	32501	18	70
PCB 123	46	284	287	284	0.206	7632	19	70
PCB 156	46	159	164	159	0.110	3708	21	70
PCB 157	43	161	165	161	0.114	682	17	66
PCB 167	46	155	160	155	0.101	672	20	70
PCB 189	44	160	164	160	0.106	632	21	73
WHO1998-TEQ (dl-PCB) LB (ND = 0)	44	24.0	24.3	24.0	0.019	273	22	71
WHO1998-TEQ (dl-PCB) UB (ND = LOD)	44	24.0	24.3	24.0	0.019	274	22	71
WHO1998-TEQ (total) LB (ND = 0)	43	229	228	229	0.142	495	14	66
WHO1998-TEQ (total) UB (ND = LOD)	43	229	228	229	0.142	495	14	66

# Percentage satisfactory data n = 48

## Standard Solution dl-POPs



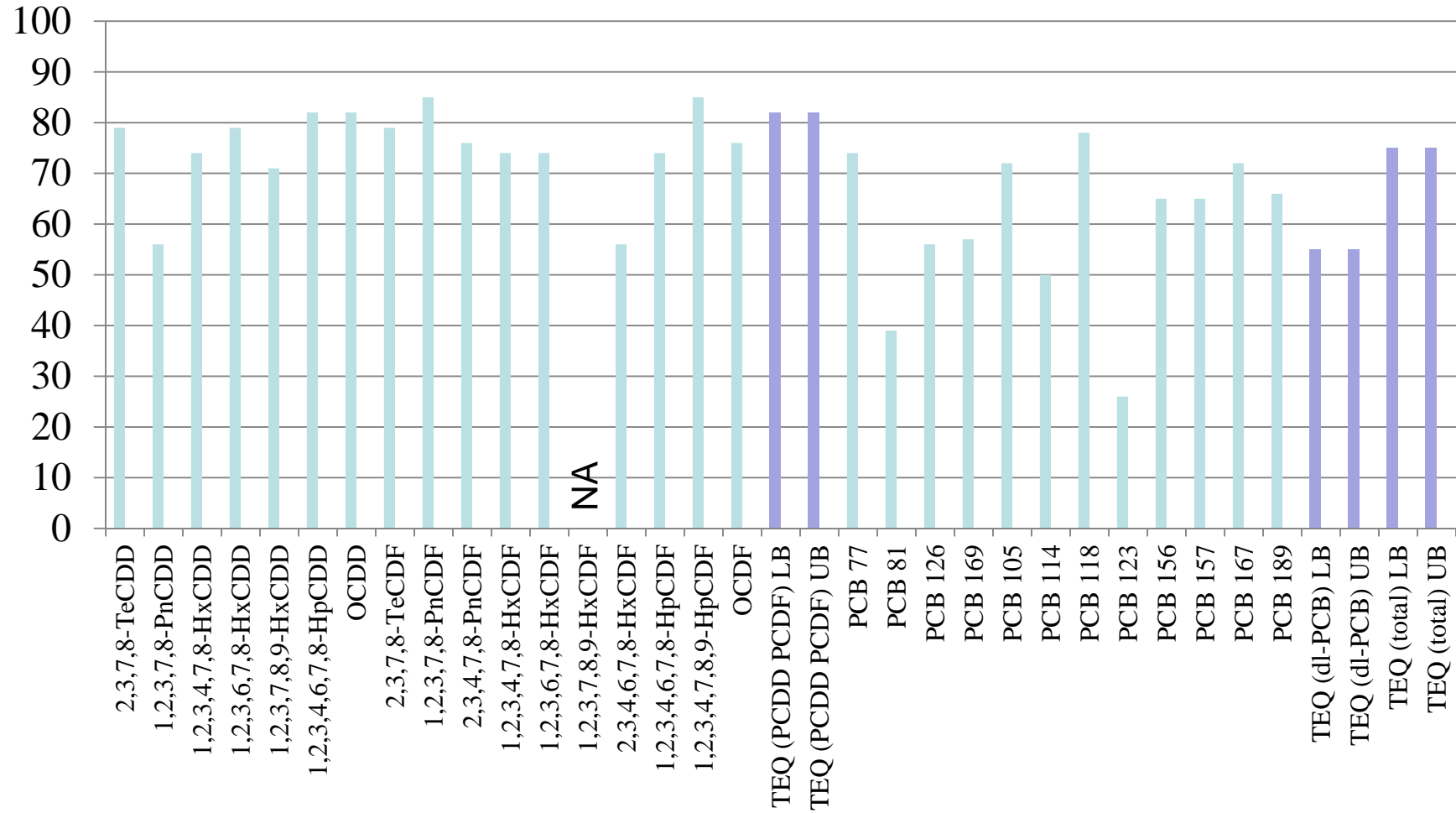
# Summary Sediment dl-POPs n = 34

Sediment	n	AV	Median	Mean	Min	Max	Between lab CV (%)	Inclusion rate (%)
2,3,7,8-TeCDD	34	9.18	9.12	9.18	0.019	22.1	16	71
1,2,3,7,8-PnCDD	34	2.54	2.54	2.54	0.003	10.5	28	67
1,2,3,4,7,8-HxCDD	33	3.23	3.27	3.23	0.003	11.2	20	72
1,2,3,6,7,8-HxCDD	34	6.92	7.03	6.92	0.006	19.3	16	72
1,2,3,7,8,9-HxCDD	33	4.75	4.85	4.75	0.005	13.3	16	69
1,2,3,4,6,7,8-HpCDD	34	83.9	85.0	83.9	0.076	220	16	72
OCDD	34	848	851	848	0.770	2480	18	73
2,3,7,8-TeCDF	33	15.0	15.0	15.0	0.015	26.1	10	62
1,2,3,7,8-PnCDF	34	15.0	14.9	15.0	0.007	33.3	12	70
2,3,4,7,8-PnCDF	34	17.2	17.5	17.2	0.015	73.1	20	72
1,2,3,4,7,8-HxCDF	34	52.4	53.1	52.4	0.048	102	21	74
1,2,3,6,7,8-HxCDF	34	26.2	26.7	26.2	0.025	73.7	12	60
1,2,3,7,8,9-HxCDF	32	NA	6.68	6.35	0.002	40.9	101	69
2,3,4,6,7,8-HxCDF	34	16.5	15.5	16.5	0.014	72.7	36	76
1,2,3,4,6,7,8-HpCDF	34	171	171	171	0.155	326	23	76
1,2,3,4,7,8,9-HpCDF	34	28.5	28.4	28.5	0.030	60.1	17	75
OCDF	34	741	723	741	0.456	2086	21	75
WHO1998-TEQ (PCDD PCDF) LB (ND = 0)	<b>34</b>	<b>37.3</b>	<b>38.0</b>	<b>37.3</b>	<b>0.044</b>	<b>98.5</b>	<b>12</b>	<b>69</b>
WHO1998-TEQ (PCDD PCDF) UB (ND = LOD)	<b>34</b>	<b>37.4</b>	<b>38.0</b>	<b>37.4</b>	<b>0.044</b>	<b>98.5</b>	<b>11</b>	<b>68</b>
PCB 77	30	746	747	746	0.677	2654	15	64
PCB 81	30	9.14	9.55	9.14	0.005	79.4	41	62
PCB 126	32	28.2	27.9	28.2	0.024	88.1	18	58
PCB 169	27	6.02	5.80	6.02	0.005	17.9	23	62
PCB 105	32	1284	1287	1284	1.209	2498	18	68
PCB 114	29	60.3	62.6	60.3	0.050	338	31	63
PCB 118	32	6102	6137	6102	5.714	10786	17	69
PCB 123	28	64.3	90.0	64.3	0.053	1605	91	56
PCB 156	34	923	876	923	0.803	1687	22	67
PCB 157	31	162	171	162	0.150	826	24	65
PCB 167	32	484	489	484	0.412	1571	19	67
PCB 189	32	183	186	183	0.156	514	20	64
WHO1998-TEQ (dl-PCB) LB (ND = 0)	<b>33</b>	<b>4.22</b>	<b>4.28</b>	<b>4.22</b>	<b>0.004</b>	<b>10.3</b>	<b>22</b>	<b>62</b>
WHO1998-TEQ (dl-PCB) UB (ND = LOD)	<b>33</b>	<b>4.20</b>	<b>4.28</b>	<b>4.20</b>	<b>0.004</b>	<b>10.3</b>	<b>23</b>	<b>63</b>
WHO1998-TEQ (total) LB (ND = 0)	<b>32</b>	<b>41.2</b>	<b>41.4</b>	<b>41.2</b>	<b>0.048</b>	<b>67.8</b>	<b>11</b>	<b>60</b>
WHO1998-TEQ (total) UB (ND = LOD)	<b>32</b>	<b>41.3</b>	<b>41.4</b>	<b>41.3</b>	<b>0.048</b>	<b>67.8</b>	<b>10</b>	<b>60</b>



# Percentage satisfactory data n = 34

## Sediment dl-POPs

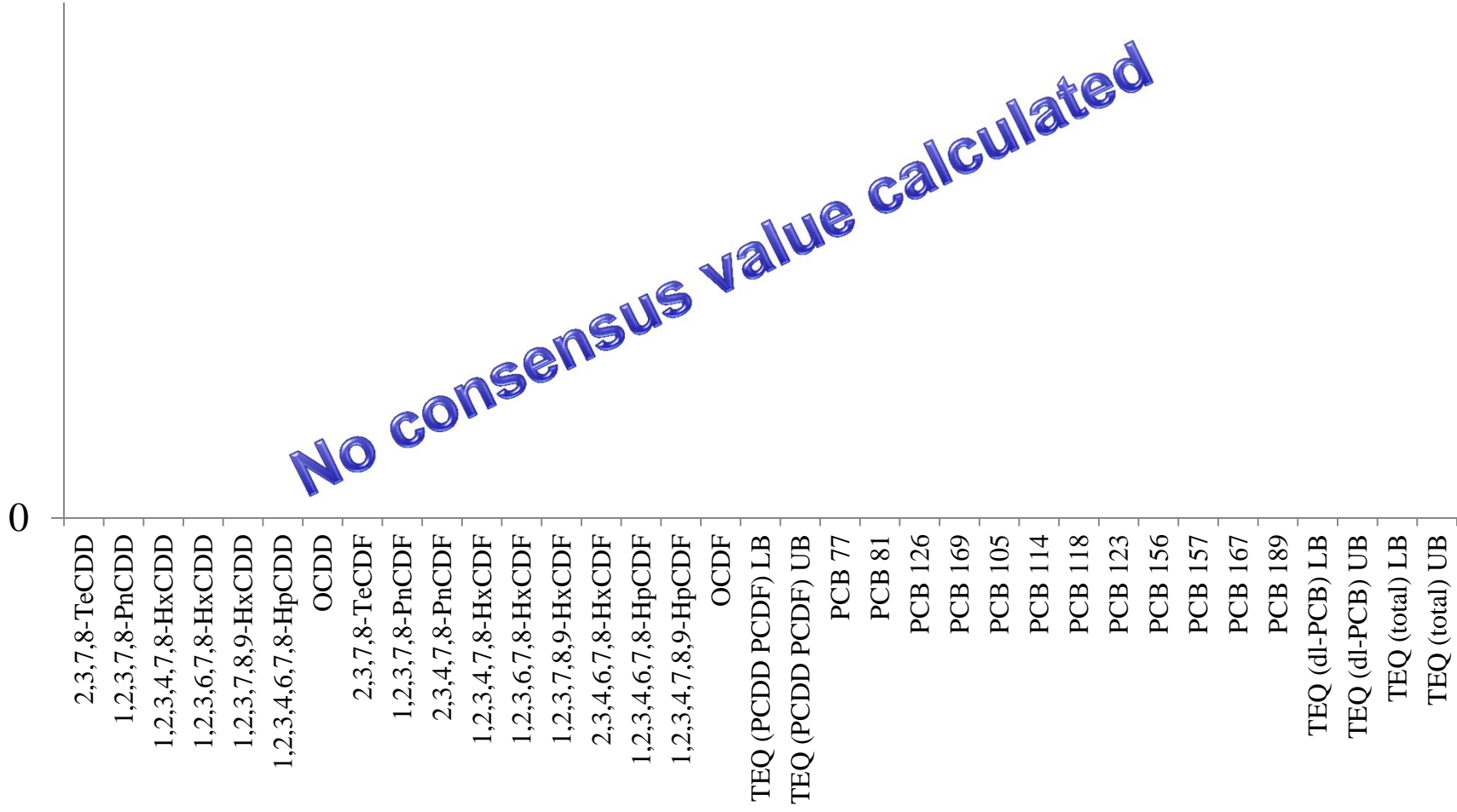


# Summary Fish dl-POPs n = 41

Fish	n	AV	Median	Mean	Min	Max	Between lab CV (%)	Inclusion rate (%)
2,3,7,8-TeCDD	32	NA	0.00062	0.00064	0.000006	0.0010	26	63
1,2,3,7,8-PnCDD	26	NA	0.00005	0.00004	0.000004	0.0010	70	68
1,2,3,4,7,8-HxCDD	16	NA	0.00001	0.00001	0.0000001	0.0014	159	52
1,2,3,6,7,8-HxCDD	22	NA	0.00004	0.00003	0.000002	0.0005	73	58
1,2,3,7,8,9-HxCDD	18	NA	0.00002	0.00001	0.0000006	0.0068	150	55
1,2,3,4,6,7,8-HpCDD	26	NA	0.00007	0.00006	0.000016	0.0009	112	63
OCDD	31	NA	0.00030	0.00026	0.000035	131.673	90	66
2,3,7,8-TeCDF	36	NA	0.00084	0.00085	0.000006	2.727	30	60
1,2,3,7,8-PnCDF	34	NA	0.00022	0.00020	0.000008	3.407	31	58
2,3,4,7,8-PnCDF	33	NA	0.00026	0.00027	0.000016	0.0013	31	59
1,2,3,4,7,8-HxCDF	31	NA	0.00007	0.00007	0.000007	8.343	51	67
1,2,3,6,7,8-HxCDF	27	NA	0.00003	0.00003	0.000007	0.0023	91	65
1,2,3,7,8,9-HxCDF	15	NA	0.00006	0.00004	0.000001	0.0009	167	51
2,3,4,6,7,8-HxCDF	18	NA	0.00002	0.00002	0.000003	0.0007	92	52
1,2,3,4,6,7,8-HpCDF	23	NA	0.00006	0.00004	0.000005	0.0083	140	57
1,2,3,4,7,8,9-HpCDF	18	NA	0.00002	0.00002	0.0000001	0.0008	147	52
OCDF	22	NA	0.00005	0.00004	0.000006	0.0023	125	57
WHO1998-TEQ (PCDD PCDF) LB (ND = 0)	<b>38</b>	<b>NA</b>	<b>0.00089</b>	<b>0.00079</b>	<b>0.0000000</b>	<b>1.291</b>	<b>62</b>	<b>70</b>
WHO1998-TEQ (PCDD PCDF) UB (ND = LOD)	<b>37</b>	<b>NA</b>	<b>0.00098</b>	<b>0.00093</b>	<b>0.000046</b>	<b>6.249</b>	<b>45</b>	<b>64</b>
PCB 77	37	0.1	0.05400	0.05480	0.001189	3.970	39	65
PCB 81	31	NA	0.00141	0.00128	0.000013	1.600	107	65
PCB 126	36	NA	0.01185	0.01062	0.000024	0.1706	39	63
PCB 169	28	NA	0.00123	0.00115	0.000134	0.0056	57	66
PCB 105	41	0.9	0.96000	0.94535	0.016930	3.8000	45	69
PCB 114	37	0.1	0.07300	0.07201	0.0000000	0.648	29	57
PCB 118	38	5.9	6.06750	5.89420	0.253729	9.043	45	74
PCB 123	38	0.1	0.07900	0.06112	0.003326	11.20	97	62
PCB 156	39	0.9	0.85000	0.88008	0.042064	1.500	46	76
PCB 157	37	0.1	0.15000	0.14534	0.004013	1.254	44	65
PCB 167	39	0.5	0.54000	0.53131	0.037745	1.725	40	71
PCB 189	38	0.1	0.12030	0.12314	0.008696	0.190	44	77
WHO1998-TEQ (dl-PCB) LB (ND = 0)	<b>41</b>	<b>NA</b>	<b>0.00240</b>	<b>0.00230</b>	<b>0.0000000</b>	<b>4.240</b>	<b>44</b>	<b>69</b>
WHO1998-TEQ (dl-PCB) UB (ND = LOD)	<b>40</b>	<b>NA</b>	<b>0.00250</b>	<b>0.00241</b>	<b>0.0000000</b>	<b>8.455</b>	<b>37</b>	<b>66</b>
WHO1998-TEQ (total) LB (ND = 0)	<b>39</b>	<b>NA</b>	<b>0.00369</b>	<b>0.00324</b>	<b>0.000119</b>	<b>4.241</b>	<b>53</b>	<b>68</b>
WHO1998-TEQ (total) UB (ND = LOD)	<b>39</b>	<b>NA</b>	<b>0.00371</b>	<b>0.00335</b>	<b>0.000143</b>	<b>8.460</b>	<b>51</b>	<b>67</b>

# Percentage satisfactory data n = 41

## Fish dl-POPs

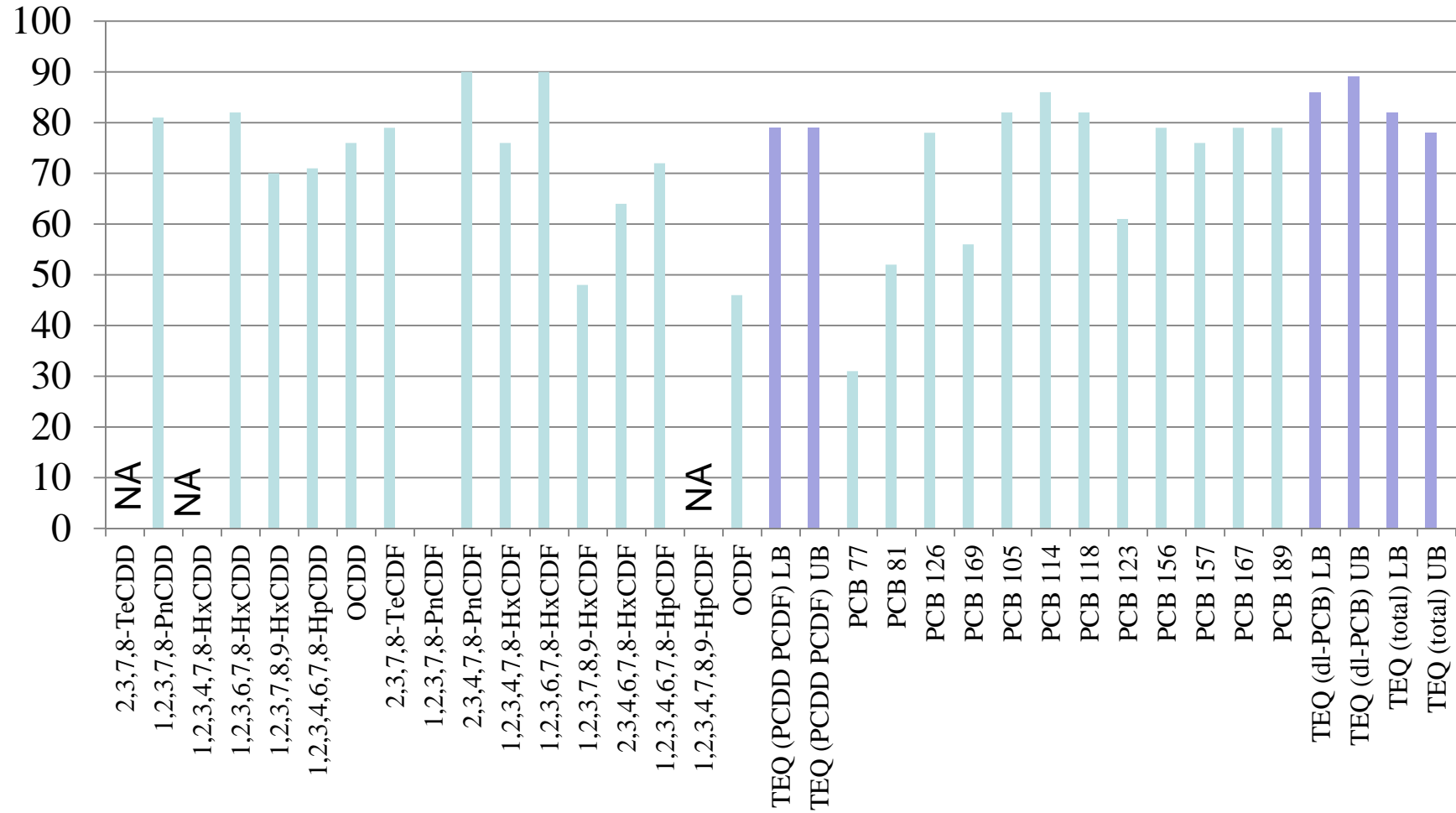


# Summary Mothers Milk dl-POPs n = 29

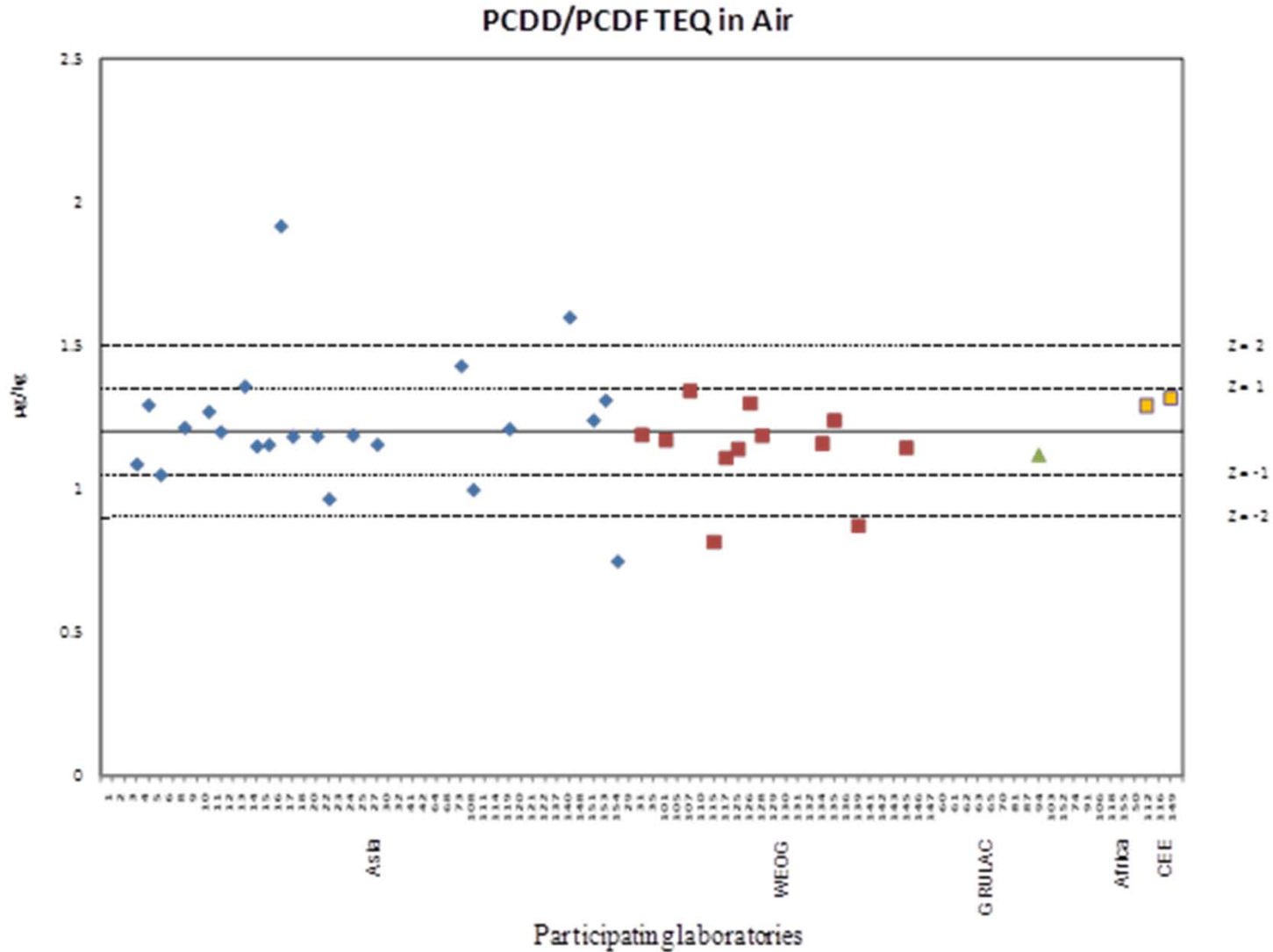
Mothers' milk	n	AV	Median	Mean	Min	Max	Between lab CV (%)	Inclusion rate (%)
2,3,7,8-TeCDD	18	NA	0.010	0.008	0.0003	0.47	46	65
1,2,3,7,8-PnCDD	25	0.0	0.027	0.026	0.0112	0.15	34	71
1,2,3,4,7,8-HxCDD	19	NA	0.011	0.011	0.0003	0.06	89	69
1,2,3,6,7,8-HxCDD	27	0.1	0.079	0.078	0.0066	0.17	23	67
1,2,3,7,8,9-HxCDD	21	0.0	0.020	0.019	0.0038	0.09	42	68
1,2,3,4,6,7,8-HpCDD	27	0.1	0.131	0.130	0.0560	0.48	38	73
OCDD	28	0.9	0.869	0.860	0.2895	1.44	13	61
2,3,7,8-TeCDF	23	0.0	0.015	0.015	0.0006	0.08	69	64
1,2,3,7,8-PnCDF	19	NA	0.010	0.008	0.0055	0.06	42	57
2,3,4,7,8-PnCDF	28	0.1	0.081	0.080	0.0504	0.14	20	69
1,2,3,4,7,8-HxCDF	28	0.0	0.033	0.032	0.0150	0.16	33	64
1,2,3,6,7,8-HxCDF	29	0.0	0.033	0.031	0.0160	0.09	20	63
1,2,3,7,8,9-HxCDF	13	0.0	0.019	0.015	0.0002	0.05	134	60
2,3,4,6,7,8-HxCDF	24	0.0	0.021	0.018	0.0020	0.09	68	64
1,2,3,4,6,7,8-HpCDF	28	0.1	0.078	0.075	0.0225	0.62	38	68
1,2,3,4,7,8,9-HpCDF	16	NA	0.007	0.005	0.0024	0.09	125	56
OCDF	17	0.0	0.046	0.037	0.0070	0.39	123	67
WHO1998-TEQ (PCDD PCDF) LB (ND = 0)	29	0.1	0.107	0.100	0.0215	0.67	23	65
WHO1998-TEQ (PCDD PCDF) UB (ND = LOD)	28	0.1	0.110	0.103	0.0320	0.67	21	66
PCB 77	21	0.2	0.280	0.244	0.0370	0.81	85	73
PCB 81	17	0.0	0.027	0.027	0.0049	0.09	91	76
PCB 126	27	0.5	0.439	0.453	0.1837	0.82	25	73
PCB 169	25	0.3	0.297	0.285	0.0725	5.02	37	69
PCB 105	28	16.7	17.34	16.73	8.1751	45.1	23	79
PCB 114	28	4.0	3.918	3.978	1.8950	5.17	18	78
PCB 118	28	88.8	90.10	88.75	39.95	221	20	76
PCB 123	28	0.9	0.971	0.941	0.2897	38.5	25	63
PCB 156	29	54.6	53.80	54.62	9.7341	105	14	68
PCB 157	29	9.4	9.360	9.425	4.9828	63.7	21	73
PCB 167	29	14.0	14.39	14.02	3.5143	31.1	20	76
PCB 189	28	6.1	6.042	6.065	2.3018	9.59	14	66
WHO1998-TEQ (dl-PCB) LB (ND = 0)	28	0.1	0.089	0.094	0.0329	0.16	29	75
WHO1998-TEQ (dl-PCB) UB (ND = LOD)	27	0.1	0.093	0.095	0.0416	0.73	26	74
WHO1998-TEQ (total) LB (ND = 0)	28	0.2	0.195	0.192	0.0695	0.37	24	72
WHO1998-TEQ (total) UB (ND = LOD)	27	0.2	0.209	0.203	0.0703	1.30	25	70

# Percentage satisfactory data n = 29

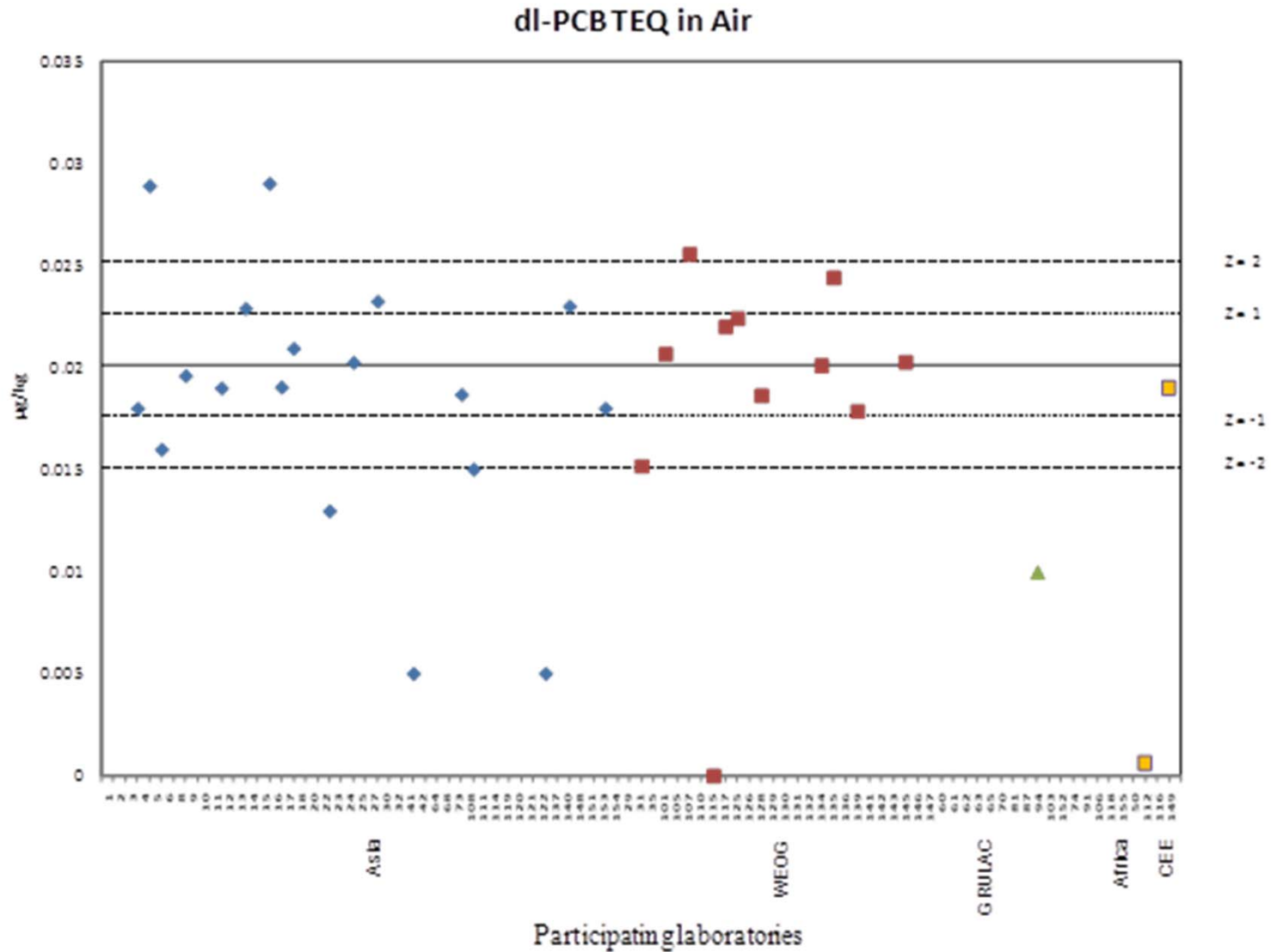
## Mothers Milk dl-POPs



# PCDD/DF in Air Extract



# DI-PCB TEQ Air Extract



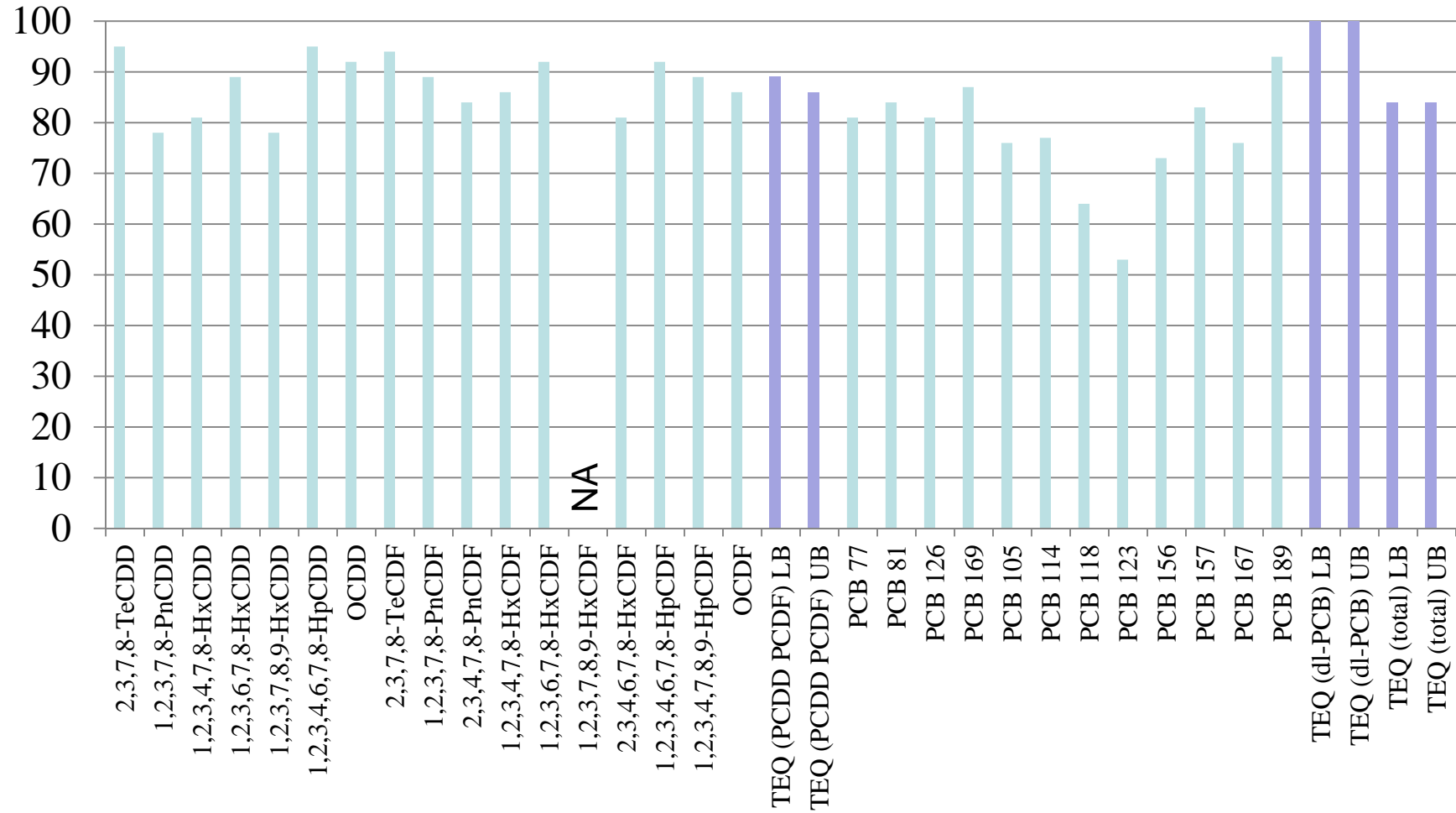
# Summary Air Extract dl-POPs n = 37

Air extract	n	AV	Median	Mean	Min	Max	Between lab CV (%)	Inclusion rate (%)
2,3,7,8-TeCDD	37	0.0	0.038	0.037	0.019	0.613	14	63
1,2,3,7,8-PnCDD	37	0.2	0.231	0.233	0.065	0.751	14	64
1,2,3,4,7,8-HxCDD	37	0.4	0.400	0.397	0.027	1.239	9	63
1,2,3,6,7,8-HxCDD	37	0.7	0.650	0.650	0.051	0.904	10	66
1,2,3,7,8,9-HxCDD	37	0.6	0.665	0.643	0.029	1.551	12	65
1,2,3,4,6,7,8-HpCDD	37	7.1	7.100	7.147	0.292	8.489	6	69
OCDD	37	13.5	13.470	13.55	0.58	16.08	7	67
2,3,7,8-TeCDF	36	0.1	0.108	0.107	0.087	0.641	11	72
1,2,3,7,8-PnCDF	37	0.2	0.227	0.223	0.130	1.793	13	66
2,3,4,7,8-PnCDF	37	0.5	0.532	0.516	0.203	0.869	23	77
1,2,3,4,7,8-HxCDF	36	0.6	0.642	0.649	0.132	1.448	14	72
1,2,3,6,7,8-HxCDF	37	0.8	0.791	0.796	0.148	1.019	7	65
1,2,3,7,8,9-HxCDF	37		0.204	0.202	0.031	1.845	102	71
2,3,4,6,7,8-HxCDF	37	1.5	1.499	1.538	0.042	1.986	13	70
1,2,3,4,6,7,8-HpCDF	37	4.7	4.653	4.723	0.251	5.502	8	70
1,2,3,4,7,8,9-HpCDF	37	0.9	0.840	0.854	0.101	0.997	8	66
OCDF	37	4.3	4.300	4.302	1.988	6.637	12	70
WHO1998-TEQ (PCDD PCDF) LB (ND = 0)	37	1.2	1.187	1.197	0.749	1.917	9	70
WHO1998-TEQ (PCDD PCDF) UB (ND = LOD)	37	1.2	1.187	1.199	0.749	1.917	9	70
PCB 77	32	0.2	0.170	0.166	0.110	13.30	23	73
PCB 81	29	0.1	0.069	0.068	0.040	3.350	14	63
PCB 126	32	0.2	0.188	0.185	0.070	4.800	18	67
PCB 169	28	0.1	0.098	0.097	0.016	0.126	13	68
PCB 105	32	0.2	0.192	0.186	0.082	11.40	23	67
PCB 114	26	0.0	0.044	0.042	0.022	0.132	25	65
PCB 118	33	0.3	0.310	0.290	0.160	5.900	34	67
PCB 123	27	0.0	0.029	0.024	0.016	3.100	56	58
PCB 156	31	0.2	0.160	0.159	0.016	10.90	22	67
PCB 157	28	0.1	0.089	0.086	0.053	5.900	18	70
PCB 167	27	0.1	0.055	0.054	0.012	0.170	22	66
PCB 189	29	0.1	0.139	0.136	0.099	4.750	15	73
WHO1998-TEQ (dl-PCB) LB (ND = 0)	32	0.0	0.019	0.020	0.000	0.029	22	70
WHO1998-TEQ (dl-PCB) UB (ND = LOD)	32	0.0	0.020	0.020	0.000	0.029	18	69
WHO1998-TEQ (total) LB (ND = 0)	32	1.2	1.198	1.206	0.005	1.936	11	68
WHO1998-TEQ (total) UB (ND = LOD)	32	1.2	1.202	1.210	0.005	1.936	12	71



# Percentage satisfactory data n = 37

## Air Extract

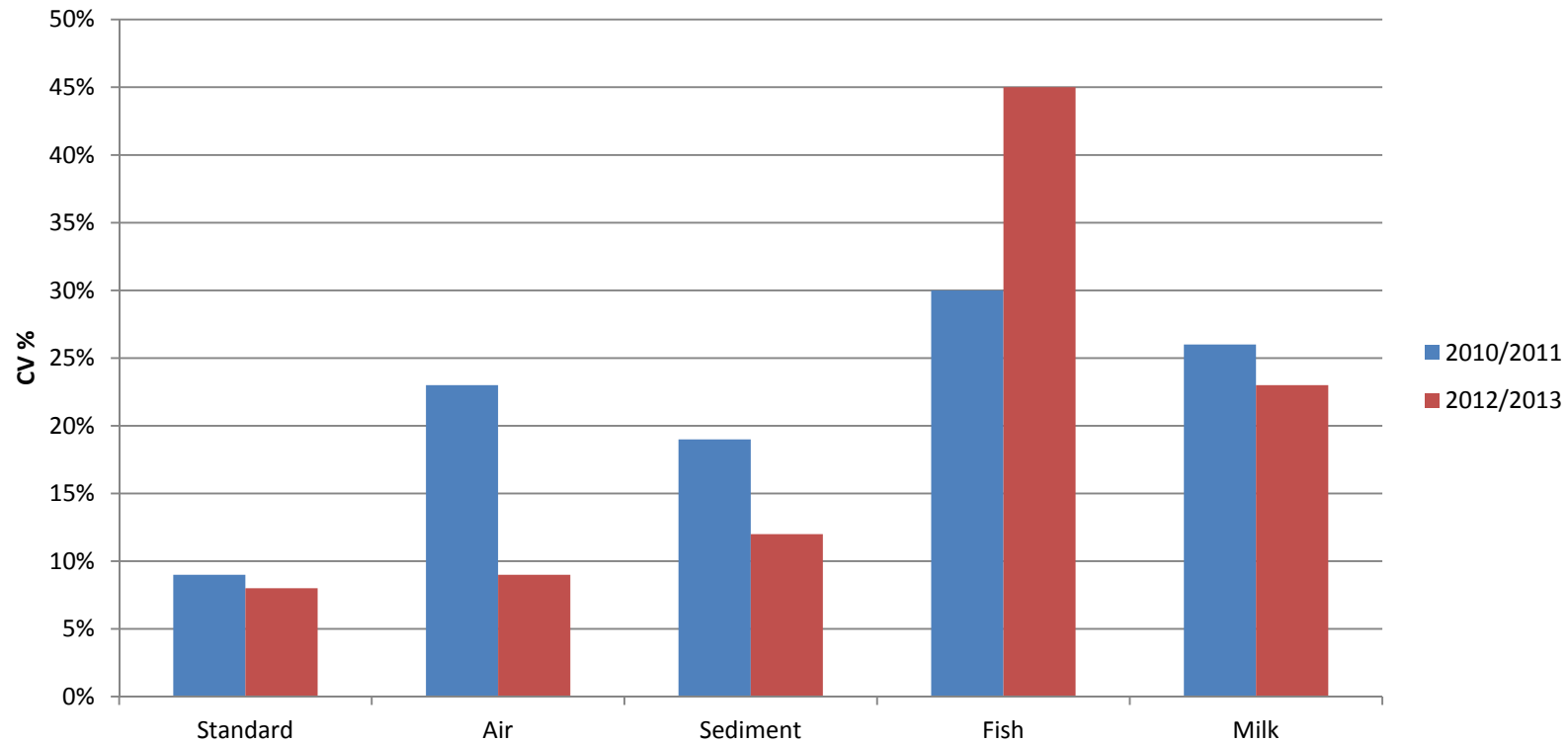


## Number of reporting laboratories for PCDD/PCDF per region

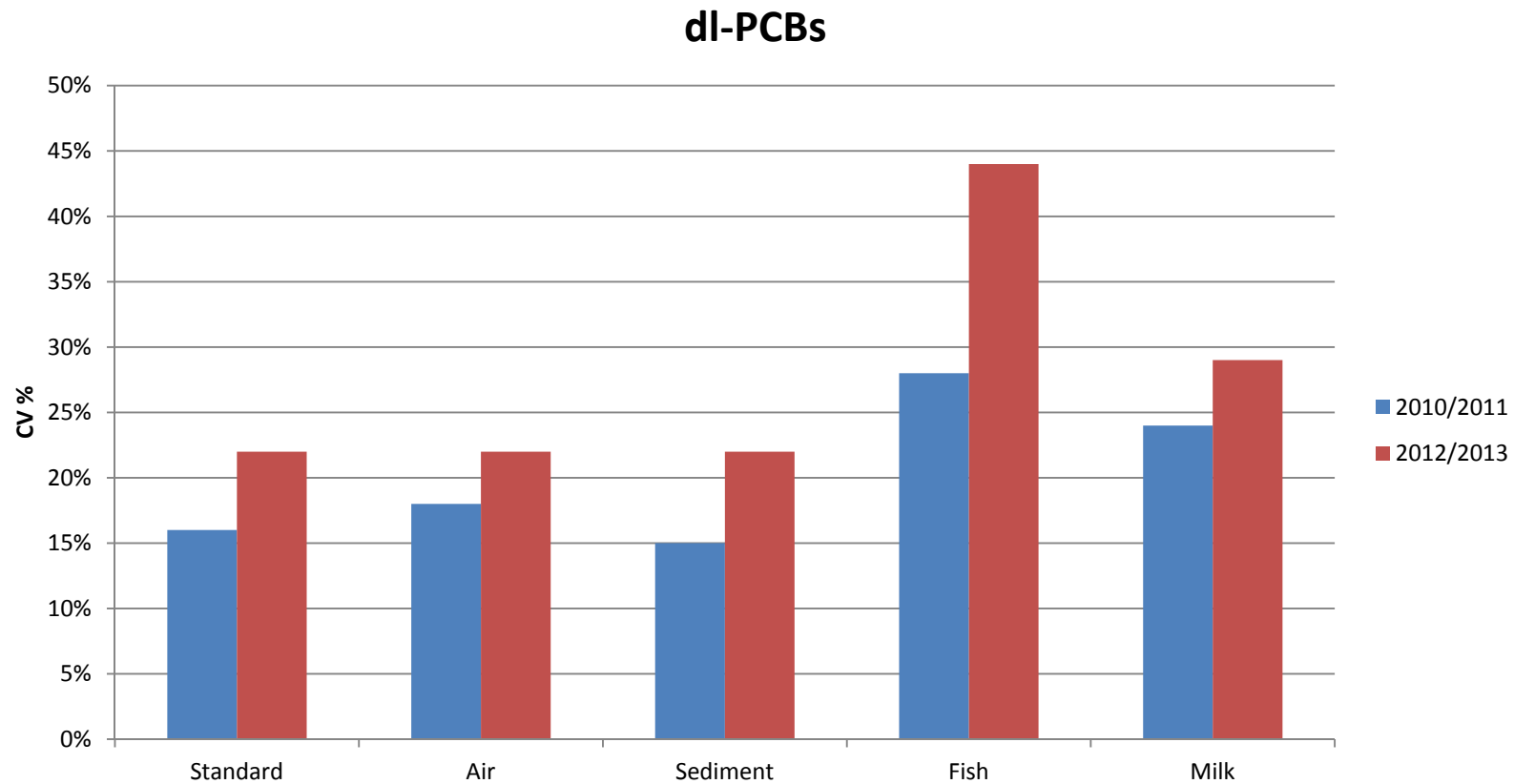
PCDD/PCDF Region	Total	Standard solution	Sediment	Fish	Mothers' milk	Air extract
ASIA	31	27	21	22	18	22
WEOG	18	16	12	13	10	13
GRULAC	2	2	0	2	0	1
AFRICA	0	0	0	0	0	0
CEE	3	3	3	3	1	3
<b>Total</b>	<b>54</b>	<b>48</b>	<b>36</b>	<b>40</b>	<b>29</b>	<b>39</b>

# Comparison 1<sup>st</sup> and 2<sup>nd</sup> UNEP Interlaboratory Assessment

## PCDD/DF TEQ



# Comparison 1<sup>st</sup> and 2<sup>nd</sup> UNEP Interlaboratory Assessment



# Conclusions dl-POPs

- Results 2<sup>nd</sup> UNEP Interlaboratory Assessment
  - Overall results good
  - In agreement with other assessment
  - Air test sample generated very good results for PCDD/PCDF and dl-PCBs (RSD < 20%)
- Regional capacity
  - Unevenly distributed
  - WEOG
  - Asia (Japan, Korea, China)
- Areas for improvement
  - More experience needed, especially for fish matrices
  - Need for frequent participation in interlaboratory assessments

# Results from UNEP 2<sup>nd</sup> Interlaboratory

## Overview on the intercalibration data of **PFOS**

Van Bavel B<sup>1</sup>, Van der Veen I<sup>2</sup>, Nilsson H<sup>1</sup>, De Boer J<sup>2</sup>, Fiedler H<sup>3</sup>

<sup>1</sup> Örebro University, School of Science and Technology, MTM Research Center, SE 70182 Örebro, Sweden

<sup>2</sup> VU University, Institute for Environmental Studies (IVM), De Boelelaan 1087, NL-1081 HV Amsterdam, The Netherlands

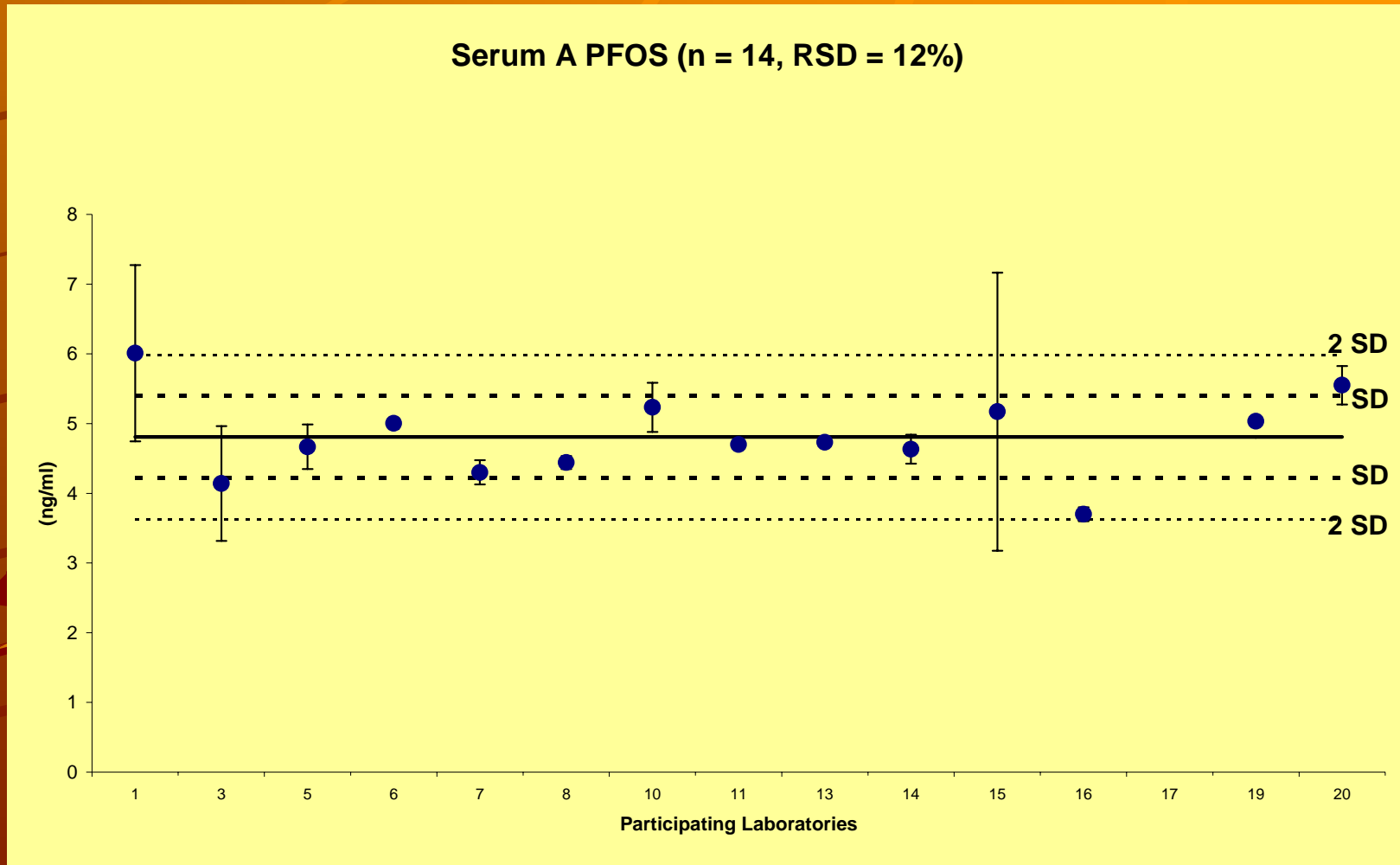
<sup>3</sup> UNEP Chemicals Branch, chemin des Anémones, CH-1219 Châtelaine (GE), Switzerland



# Results Milk 2010

4 <sup>rd</sup> Fluoros Intercalibration 2010							
Standard MX4	(ng/ml)						After removal of obvious outliers
PFCA	Average	Median	Min	Max	SD	%RSD	n
PFBA	24.7	23.3	18.4	34.9	5.1	21%	11
PFPeA	23.7	22.8	15.3	36.0	5.3	22%	11
<b>PFHxA</b>	<b>24.1</b>	<b>23.0</b>	<b>16.2</b>	<b>38.0</b>	<b>5.0</b>	<b>21%</b>	<b>15</b>
<b>PFHpA</b>	<b>22.6</b>	<b>22.3</b>	<b>16.4</b>	<b>27.0</b>	<b>2.8</b>	<b>12%</b>	<b>15</b>
<b>PFOA</b>	<b>23.8</b>	<b>23.9</b>	<b>18.8</b>	<b>32.0</b>	<b>3.9</b>	<b>16%</b>	<b>20</b>
<b>PFNA</b>	<b>23.5</b>	<b>23.2</b>	<b>8.5</b>	<b>35.8</b>	<b>6.2</b>	<b>26%</b>	<b>19</b>
<b>PFDA</b>	<b>10.1</b>	<b>9.8</b>	<b>5.3</b>	<b>22.2</b>	<b>3.5</b>	<b>35%</b>	<b>19</b>
PFUdA	10.0	9.6	6.6	15.8	2.2	22%	13
PFDoA	9.2	10.0	5.7	11.5	2.0	21%	14
PFTTrDA	11.0	10.1	6.0	24.6	5.3	48%	9
PFTeDA	10.5	9.5	7.0	20.7	3.8	36%	10
PFHxDA	10.2	10.2	10.2	10.2	NA	NA	1
PFODA	16.5	16.5	10.9	22.1	7.9	48%	2
PFAS	Average	Median	Min	Max	SD	%RSD	n
Linear-PFBS**	21.8	21.8	18.1	27.0	2.5	11%	16
<b>Linear-PFHxS**</b>	<b>23.0</b>	<b>22.6</b>	<b>17.1</b>	<b>37.3</b>	<b>4.3</b>	<b>18%</b>	<b>19</b>
Linear-PFHpS**	21.8	22.2	18.0	25.1	2.4	11%	8
<b>Linear-PFOS**</b>	<b>22.9</b>	<b>22.9</b>	<b>18.0</b>	<b>28.0</b>	<b>2.8</b>	<b>12%</b>	<b>20</b>
Linear-PFDS**	9.8	9.1	6.6	19.0	3.1	31%	12
Other PFCs optional							
PFOSA	30.3	30.0	11.0	50.0	19.5	64%	3

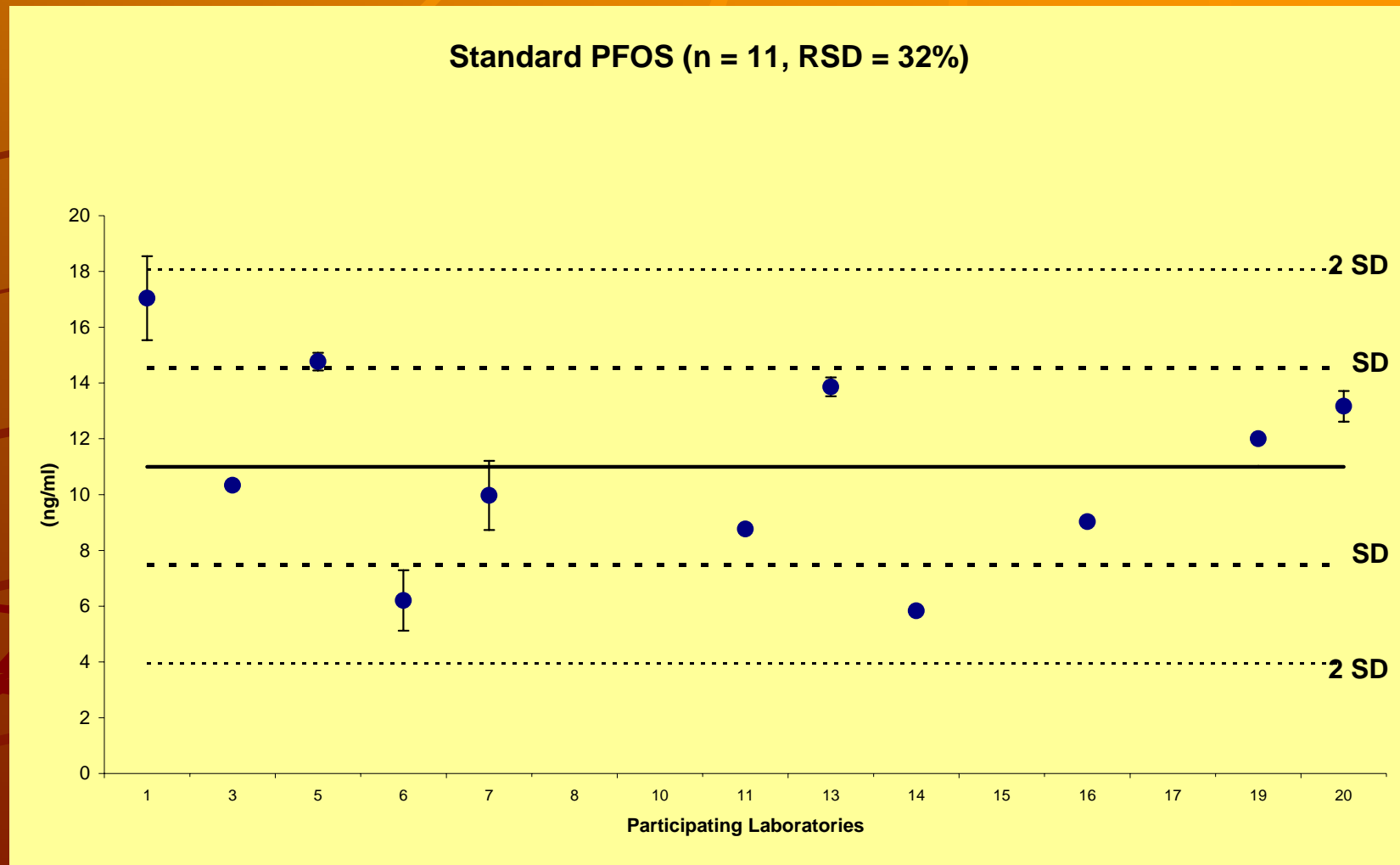
# Results PFOS Serum A (RSD 12%)



Low level sample, triplicate






# Results PFOS Standard (RSD 32%)






Standard, triplicate

# Report form PFAS

								
Participant code:								
Name:								
Organisation:								
Address:								
UNEP Intercalibration 2013								
Code:	Standard solution I (µg/kg)	Standard solution J (µg/kg)	Sediment (µg/kg)	Fish (µg/kg)*	Mothers' milk (ng/kg)*	Human serum (ng/mL)	Air extract (µg/kg)	Water (ng/kg)
Sample Code:								
Date Received:								
Date Analyzed:								
(Wet) Weight Received:								
Sample Intake (g):								
Final Volume (µL)								
Injection Volume (µL)								
% Extracted Lipids:								
<b>PFAS</b>								
L-PFOS anion								
FOSA								
MeFOSA								
EtFOSA								
MeFOSE								
EtFOSE								
<b>Optional PFAS</b>								
PFBA								
PFPeA								
PFHxA								
PFHpA								
PFOA								
PFNA								
PFDA								
PFUdA								
PFDoA								
PFTrDA								
PFTeDA								
L-PFBS								
L-PFHxS								
L-PFHpS								
L-PFDS								
<b>Notes</b>								
* wet weight								
All values should be reported in µg/kg, ng/kg or ng/mL								
ND: not detected < than value expected								
NA: not analyzed								

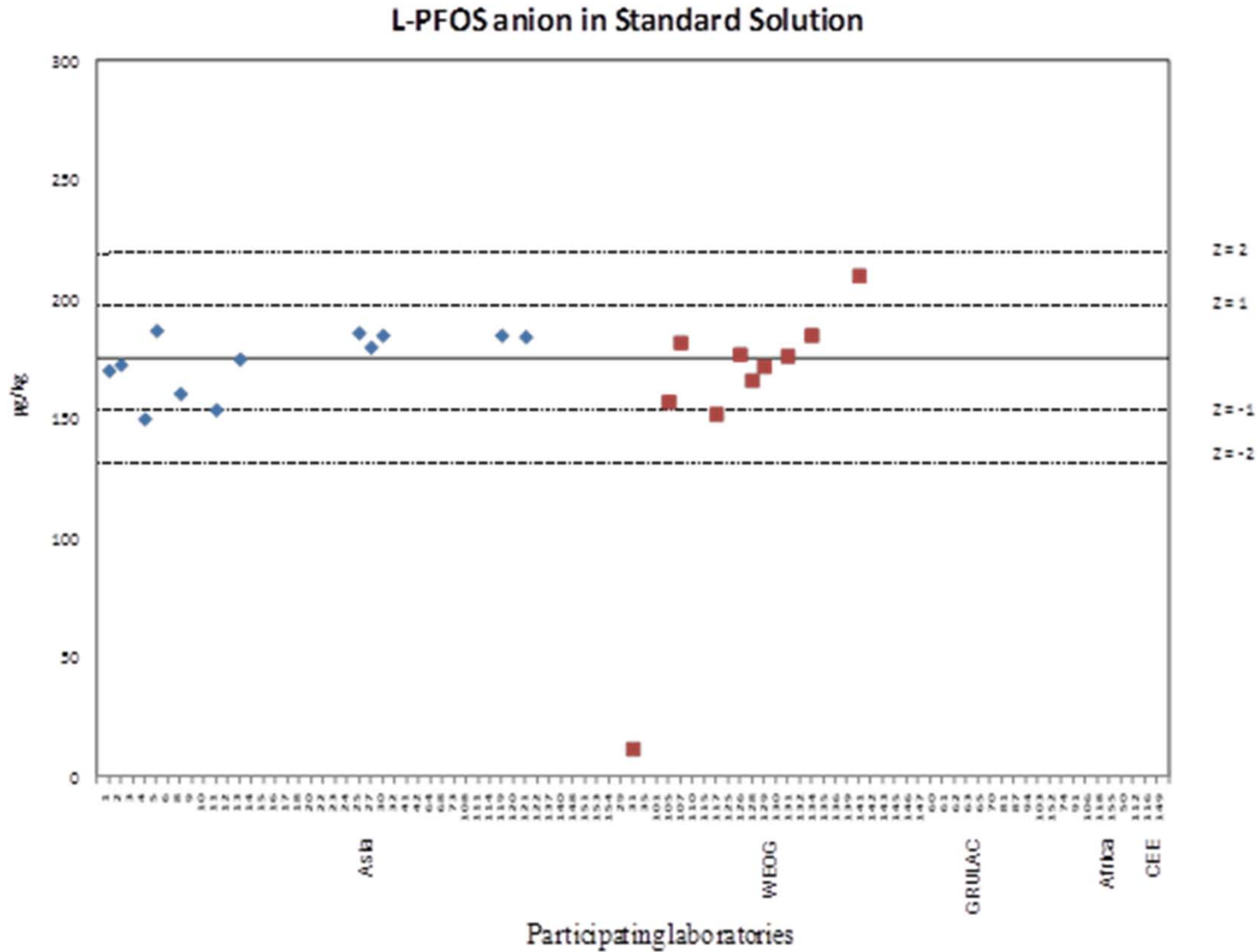
# Assitional information PFAs

Additional Information PFOS							
							
	<b>Standard solution</b>	<b>Sediment</b>	<b>Fish</b>	<b>Mothers' milk</b>	<b>Human serum</b>	<b>Air extract</b>	<b>Water</b>
<b>Sample pretreatment:</b>							
<b>Extraction</b>							
Extraction technique:							(LLE/ SPE/ ion pair,...)
Extraction solvent(s):							(Methanol,acetonitrile,...)
<b>Clean Up:</b>							(SPE, active carbon,...)
<b>Instrument:</b>							
LC/ GC							
<b>System:</b>							
High Res/Low Res:							
Type :							(MS/MS, Ion Trap, TOF,...)
<b>Column:</b>							
Type:							(C <sub>18</sub> , fluoro,...)
Specifications:							(15 cm x 2.1 mm x 3.5 µm,...)
Extra column for blank separation (yes/no)							
<b>Internal Standard</b>							
Number:							(Number used)
Which:							(Which compounds)
<b>Recovery Standards</b>							
Number:							(Number used)
Which:							(Which compounds)
<b>Recovery correction</b>							
yes/no							
If yes, which method?							<sup>13</sup> C Int. std., external recovery,...
<b>Standard Method used</b>							
yes/no							
If yes, which method?							(EPA, CEN, ISO, ...)
Blank corrected (yes/no)							
<b>Comments:</b>							

# Participation per compound class

Group	Standard solutions	Sediment	Fish	Mothers' milk	Air	Water	Human serum	Transformer 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	-

# L-PFOS Standard Solution



# L-PFOS Standard Solution

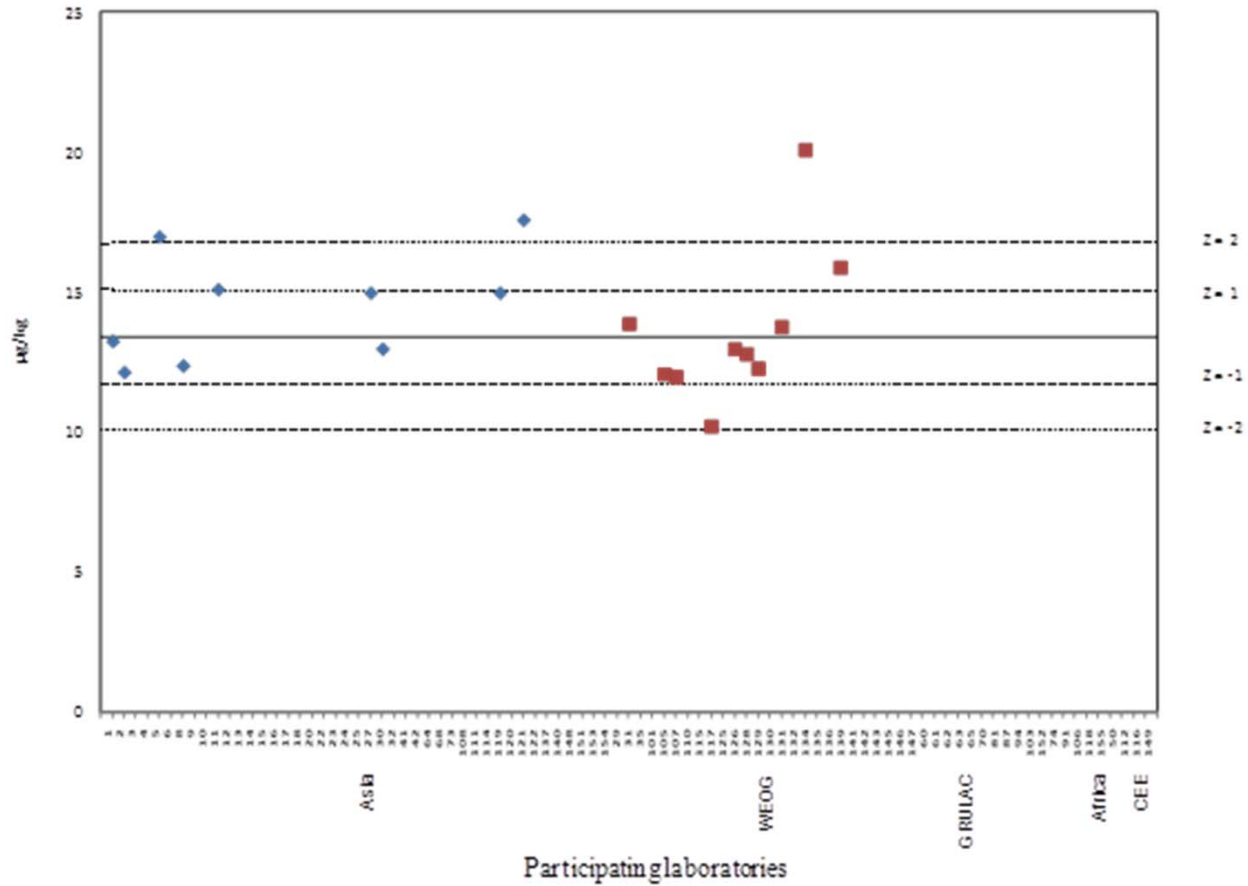
Standard solution	n	AV	Median	Mean	Min	Max	Between lab CV (%)	Inclusion rate (%)
Analyte								
L-PFOS anion	22	175	176	175	12	210	8	73
FOSA	13	320	320	320	255	446	3	65
PFBA	13	122	120	122	108	158	11	75
PFPeA	10	130	131	130	107	167	16	81
PFHxA	16	249	249	249	215	295	3	64
PFHpA	16	130	129	130	107	264	10	69
PFOA	18	128	128	128	106	142	9	80
PFNA	17	129	126	129	93	146	11	80
PFDA	17	247	250	247	220	288	5	64
PFUnDA	15	124	125	124	111	145	7	70
PFDoDA	12	128	125	128	112	190	13	73
PFTTrDA	10	131	131	131	78	148	9	71
PFTeDA	10	136	139	136	105	159	14	78
L-PFBS	13	265	259	265	110	311	12	71
L-PFHxS	17	174	177	174	142	240	8	68
L-PFHpS	4	181	180	181	168	199	9	80
L-PFDS	11	172	173	172	160	203	8	78
MeFOSA	7	807	838	807	489	1300	41	78
EtFOSA	4	NA	1164	1035	596	2500	44	67
MeFOSE	5	NA	1207	1202	584	2500	3	56
EtFOSE	5	NA	658	632	599	1130	11	58

# PFOS in Sediment

Sediment	n	AV	Median	Mean	Min	Max	Between lab CV (%)	Inclusion rate (%)
Analyte								
L-PFOS anion	18	7.99	8.00	7.99	6.00	11.8	15	71
FOSA	10	0.28	0.31	0.28	0.16	0.85	46	68

Sediment	% of the data received	% of z-scores $ z  < 2$	% of z-scores $3 >  z  > 2$	% of z-scores $6 >  z  > 3$	% of z-scores $ z  > 6$
Analyte		Satisfactory	Questionable	Unsatisfactory	Extreme
L-PFOS anion	17	89	0	11	0
FOSA	11	42	17	8	17

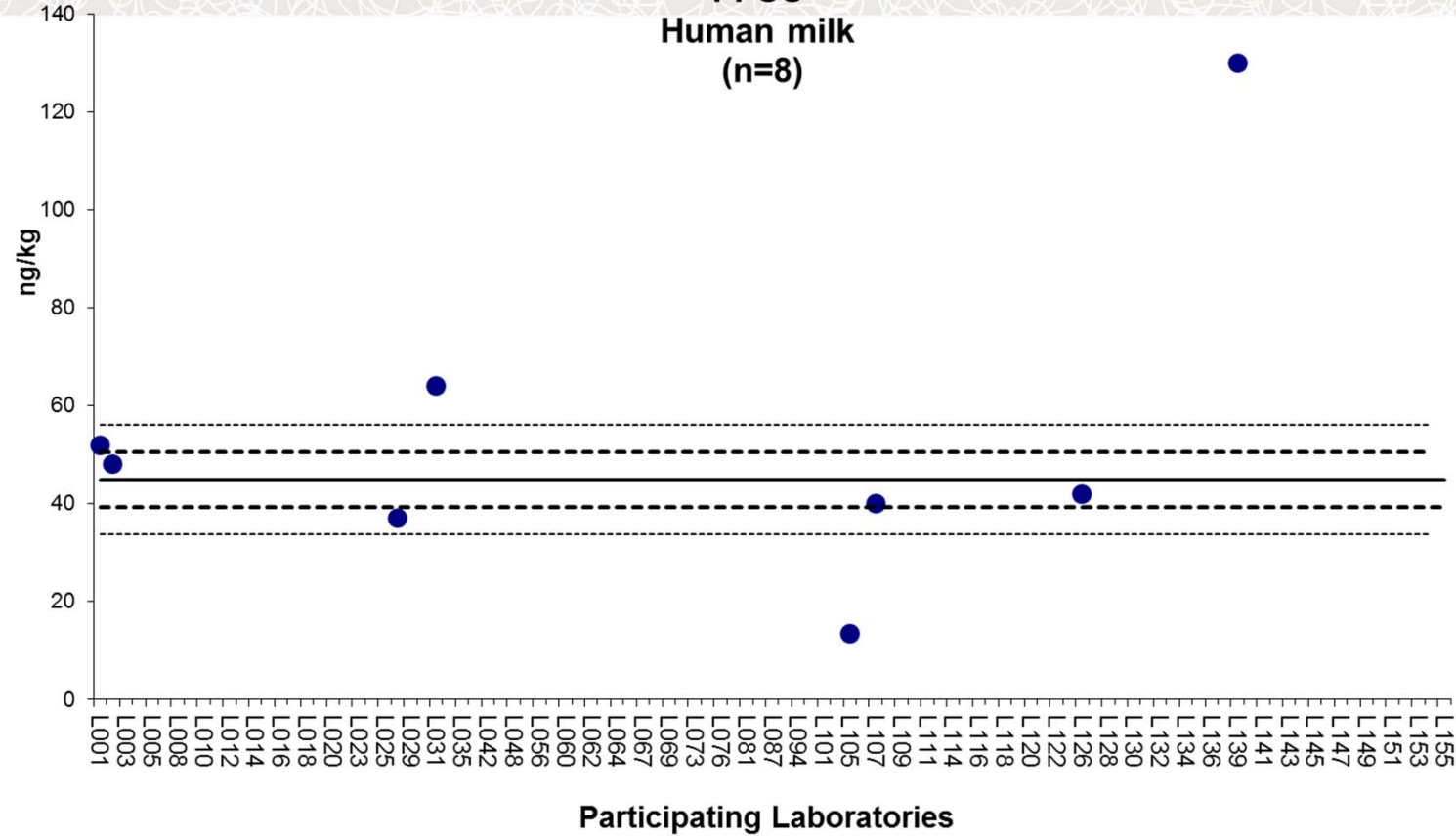
L-PFOS anion in Fish



Fish	n	AV	Median	Mean	Min	Max	Between lab CV (%)	Satisfactory (%)
L-PFOS anion	19	13.4	13.3	13.4	10.2	20.1	13	84
FOSA	13	2.25	2.28	2.25	1.67	3.00	18	86



**PFOS**  
Human milk  
(n=8)

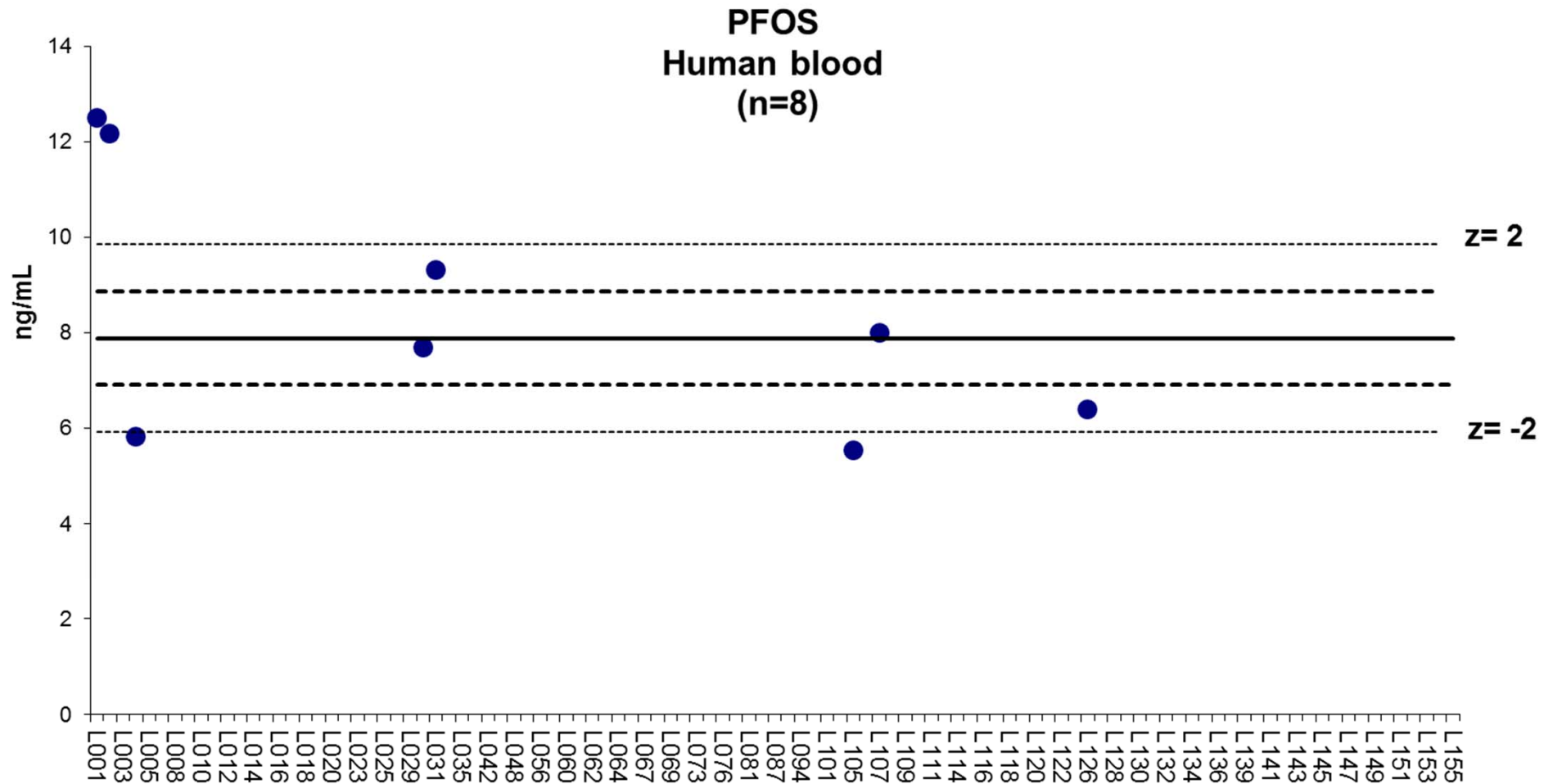


**z= 2**

**z= -2**

Mothers' milk	n	AV	Median	Mean	Min	Max	Between lab CV (%)	Satisfactory (%)
Analyte								
L-PFOS anion	8	44.9	45.0	44.9	13.5	130	25	63
FOSA	0	NA	NA	NA	NA	NA	NA	NA

# Human blood



Participating Laboratories

Satisfactory 50%

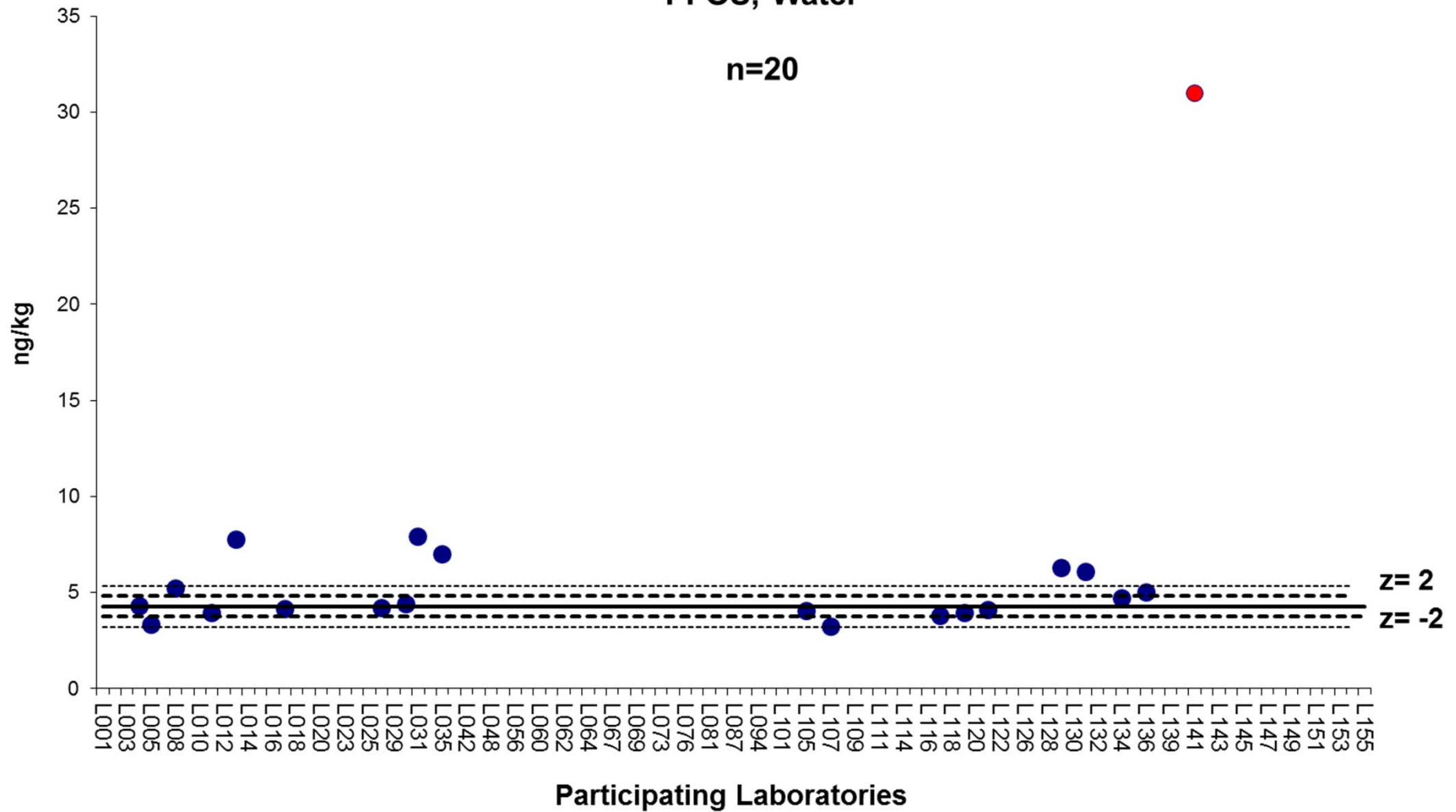
# PFAS Human blood

Human serum	n	AV	Median	Mean	Min	Max	Between lab CV (%)	Inclusion rate (%)
Analyte								
L-PFOS anion	8	7.89	7.85	7.89	5.53	12.51	34	76
FOSA	0	NA	NA	NA	NA	0.00	NA	NA
PFBA	3	NA	2.60	2.63	2.23	3.10	19	86
PFPeA	0	NA	NA	NA	NA	NA	NA	NA
PFHxA	6	0.28	0.28	0.28	0.22	0.36	26	82
PFHpA	7	1.15	1.20	1.15	0.84	1.36	22	78
PFOA	9	72.7	71.0	72.7	50.5	80.0	10	75
PFNA	7	5.31	5.40	5.31	5.25	7.00	4	57
PFDA	7	3.44	3.40	3.44	3.16	4.60	10	72
PFUnDA	7	0.50	0.51	0.50	0.39	0.69	21	78
PFDoDA	7	0.67	0.71	0.67	0.56	1.07	26	83
PFTTrDA	4	0.18	0.19	0.18	0.13	0.23	32	67
PFTeDA	5	NA	0.35	0.44	0.20	0.76	55	75
L-PFBS	2	NA	NA	NA	0.02	0.10	NA	NA
L-PFHxS	7	0.90	0.87	0.90	0.78	1.20	16	72
L-PFHpS	1	NA	NA	NA	0.29	0.29	NA	NA
L-PFDS	0	NA	NA	NA	0.00	0.00	NA	NA

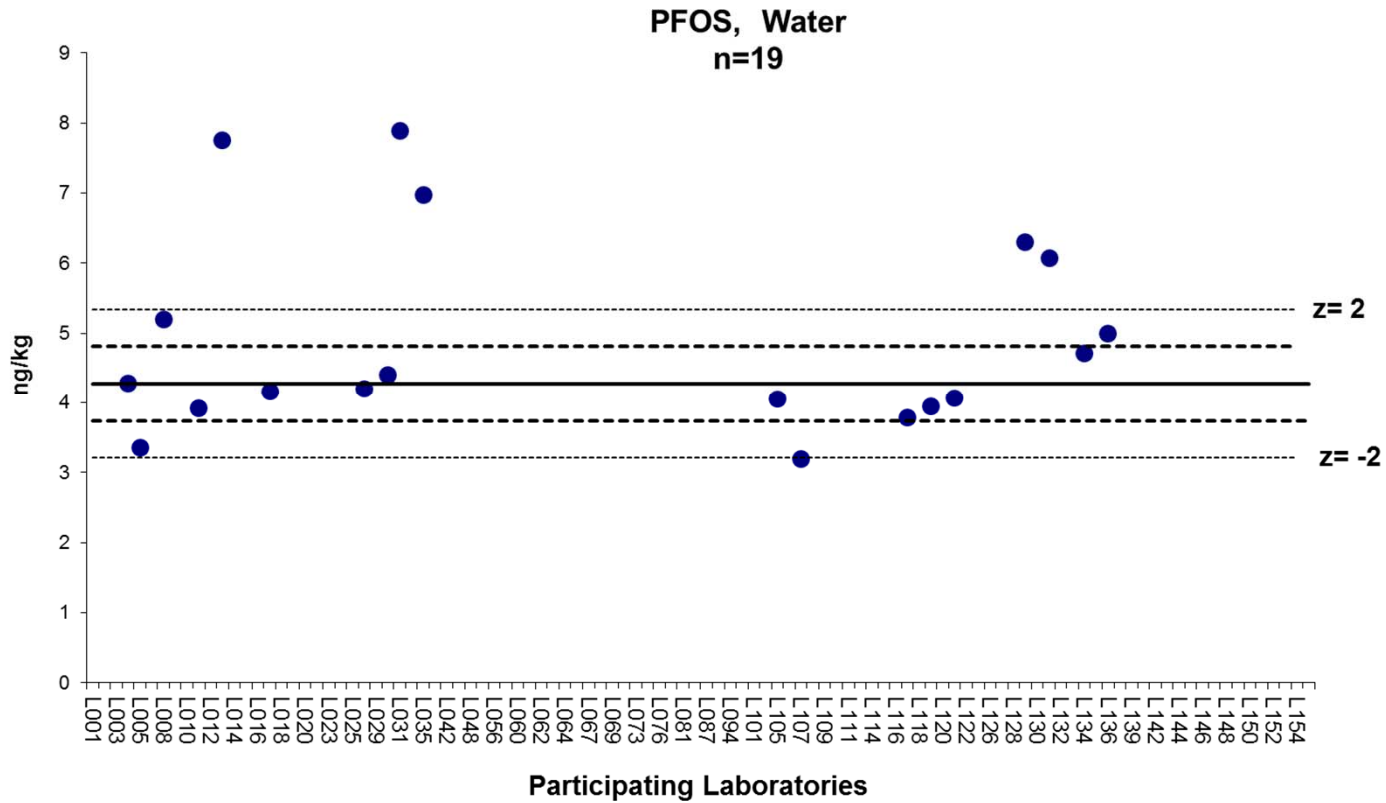
# Water

PFOS, Water

n=20



# Water (extreme value removed)



Water								
Analyte	n	AV	Median	Mean	Min	Max	Between lab CV (%)	Satisfactory
L-PFOS anion	20	4.28	4.34	4.28	3.20	31.0	21	19
FOSA	5	NA	0.31	0.26	0.10	1.08	115	10

# PFAS in Air

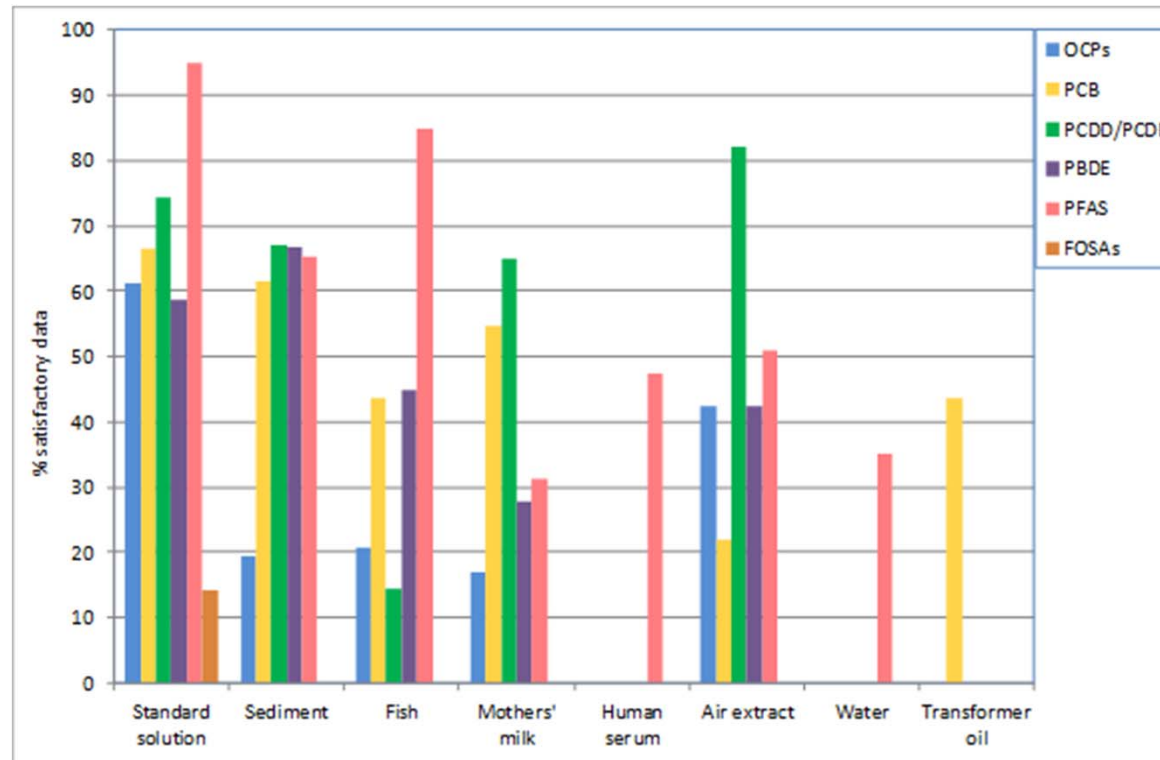
Air extract								
Analyte	n	AV	Median	Mean	Min	Max	Between lab CV (%)	Inclusion rate (%)
L-PFOS anion	8	10.7	11.9	10.7	4.74	99.2	39	59
FOSA	7	6.40	6.00	6.40	0.15	9.32	27	60
MeFOSA	3	NA	23.5	23.0	18.0	26.6	19	82
EtFOSA	3	NA	27.3	27.5	19.0	27.8	2	64
MeFOSE	3	NA	63.4	62.6	53.9	68.0	11	79
EtFOSE	3	NA	61.7	62.3	51.5	63.0	3	64

Air extract	% of the data received	% of z-scores $ z  < 2$	% of z-scores $3 >  z  > 2$	% of z-scores $6 >  z  > 3$	% of z-scores $ z  > 6$
Analyte		Satisfactory	Questionable	Unsatisfactory	Extreme
L-PFOS anion	9	44	11	11	22
FOSA	7	57	0	29	14
MeFOSA	3	0	0	0	0
EtFOSA	3	0	0	0	0
MeFOSE	3	0	0	0	0
EtFOSE	3	0	0	0	0

## Number of reporting laboratories for PFAS per region

PFAS 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
<b>Total</b>	<b>31</b>	<b>26</b>	<b>22</b>	<b>22</b>	<b>12</b>	<b>13</b>	<b>13</b>	<b>25</b>

# Summary





Thank you  
for your attention!

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