Annual INTERCIND meeting:
Lasceremo un mondo migliore di come l'abbiamo trovato?
Effetti dell'uomo sull'uomo
1 June 2017, Bologna

Results of the 5th InterCinD and thoughts: being different is difficult but needed

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ACCREDIA
L'ENTE ITALIANO DI ACCREDITAMENTO

PTP N° 0007

Membro di MLA EA per gli schemi di accreditamento
SGQ, SGA, PRD, PRS, ISP, GHG, LAB e LAT,
di MLA IAF per gli schemi di accreditamento
SGQ, SGA, SSI, FSM e PRD
e di MRA ILAC per gli schemi di accreditamento LAB, MED, LAT e ISP

Signatory of EA MLA for the accreditation schemes
QMS, EMS, PRD, PRS, INSP, GHG, TL and CL,
of IAF MLA for the accreditation schemes
QMS, EMS, ISMS, FSMS and PRD
and of ILAC MRA for the accreditation schemes TL, ML, CL and INSP

The interlaboratory circuit is organized in agreement with international guidelines relative to the organization and management of interlaboratory circuits UNI CEI EN ISO/IEC 17043: 2010

Statistical data treatment in Intercind is INSPIRED by ISO 13528/2015 and IUPAC Guidelines

Peculiarities of INTERCIND

1) **Natural matrixes** (unknown concentration)

2) **Replicates** (accuracy&precision)

3) **Statistical treatment** (Determination of extremes and outliers with non-parametric method)

3 different samples of "natural" matrixes:
1) Environmental: Natural Sediment   (SEDIMENT)
2) Industrial: ash   (ASH)
3) Food: eggs   (FOOD)

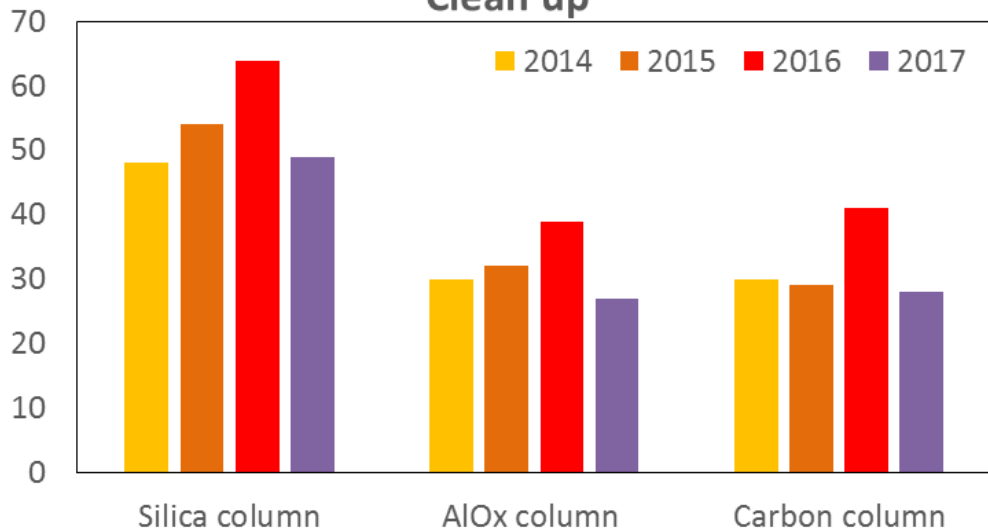Every sample was send in 3 different jars 3 different analysis (replicates) were requested to check laboratory reproducibility. Analysis of:
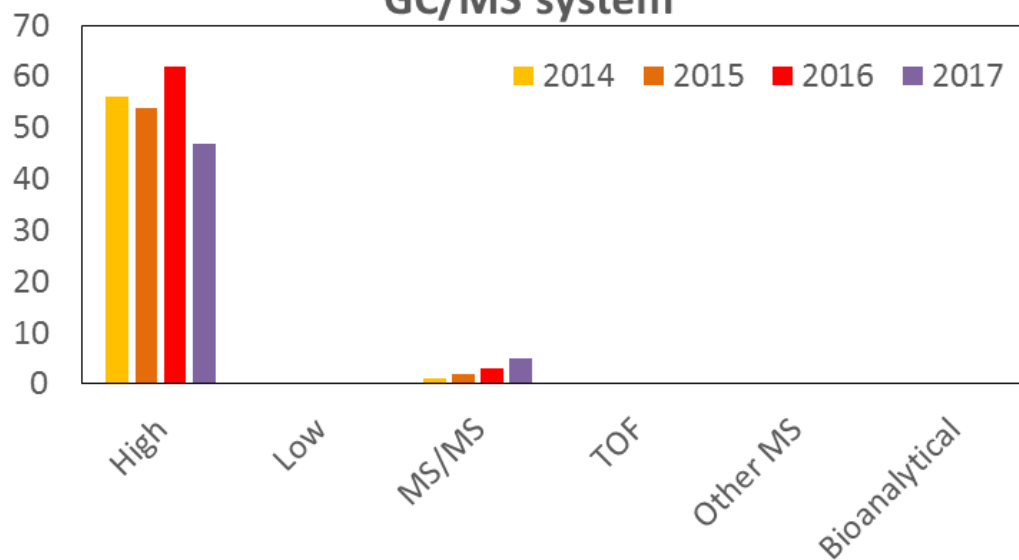-   dioxins and furans (PCDD/F)   [17]   - PCBs dioxin-like   [12]
-    PCBs ICES-6   [6]   - PAHs   [7]
-    PBDE   [28]   - Heavy metals   [14]

the participants

Matrix SEDIMENT

Test 1) Minimum number of valid data 15 (from min 15 different labs)

Test 1b) RSD%<55% and Outliers <20% valid data

Test 2) & 2b) simmetry & presence of more modes

Test 3) Uncertainty of assigned value <= 0.3 uncertainty used for assessing performances (from consensus)

Treated data - SEDIMENT							Assigned value	
	Test1	Test2	Test2b	Test 1b	Test3	Final	X	σ_p
PCDD/F (values in pg/g)								
2,3,7,8-TeCDD	Y	Y		Y	Y	Y	1.074	0.166
1,2,3,7,8-PeCDD	Y	N	median	Y	Y	Y	2.370	0.311
1,2,3,4,7,8-HxCDD	Y	Y		Y	Y	Y	3.516	0.533
1,2,3,6,7,8-HxCDD	Y	Y		Y	Y	Y	4.286	0.690
1,2,3,7,8,9-HxCDD	Y	Y		Y	Y	Y	3.257	0.798
1,2,3,4,6,7,8-HpCDD	Y	Y		Y	Y	Y	58.254	7.231
OCDD	Y	Y		Y	Y	Y	274.744	44.613
2,3,7,8-TeCDF	Y	Y		Y	Y	Y	28.993	3.817
1,2,3,7,8-PeCDF	Y	Y		Y	Y	Y	34.002	3.345
2,3,4,7,8-PeCDF	Y	N	median	Y	Y	Y	26.626	8.624
1,2,3,4,7,8-HxCDF	Y	Y		Y	Y	Y	129.889	16.188
1,2,3,6,7,8-HxCDF	Y	Y		Y	Y	Y	57.564	6.417
1,2,3,7,8,9-HxCDF	Y	N	median	N	Y	Y	10.948	17.829
2,3,4,6,7,8-HxCDF	Y	Y		Y	Y	Y	34.666	8.049
1,2,3,4,6,7,8-HpCDF	Y	Y		Y	Y	Y	442.443	69.335
1,2,3,4,7,8,9-HpCDF	Y	Y		Y	Y	Y	84.333	11.544
OCDF	Y	Y		Y	Y	Y	1106.945	213.709
TEQ (PCDD/F)	Y	Y		Y	Y	Y	47.191	5.350
TEQ (PCDD/F) UpB	Y	Y		Y	Y	Y	47.373	5.103
PCB-DL (values in pg/g)								
PCB #77	Y	Y		Y	Y	Y	267.03	35.12
PCB #81	Y	Y		Y	Y	Y	9.79	2.18
PCB #105	Y	Y		Y	Y	Y	1901.80	316.49
PCB #114	Y	Y		Y	Y	Y	99.87	19.56
PCB #118	Y	Y		Y	Y	Y	6352.92	890.29
PCB #123	Y	N	median	Y	Y	Y	95.80	35.33
PCB #126	Y	Y		Y	Y	Y	32.07	4.24
PCB #156	Y	Y		Y	Y	Y	1099.57	201.57
PCB #157	Y	N	median	Y	Y	Y	184.76	32.95
PCB #167	Y	Y		Y	Y	Y	539.18	101.42
PCB #169	Y	N	median	Y	Y	Y	10.49	1.69
PCB #189	Y	Y		Y	Y	Y	184.61	31.77
TEQ (PCB)	Y	Y		Y	Y	Y	3.87	0.46
TEQ (PCB) Upperbound	Y	Y		Y	Y	Y	3.88	0.46
TEQ (PCDD/F+PCB)	Y	Y		Y	Y	Y	52.21	5.73
TEQ(PCDD/F+PCB) UpB	Y	Y		Y	Y	Y	52.43	5.56
PCB ICES-6 (values in ng/g)								
PCB #28	Y	Y		Y	Y	Y	3.21	0.58
PCB #52	Y	Y		Y	Y	Y	5.06	0.92
PCB #101	Y	Y		Y	Y	Y	9.00	1.61
PCB #138	Y	Y		Y	Y	Y	10.97	2.57
PCB #153	Y	Y		Y	Y	Y	13.58	2.11
PCB #180	Y	Y		Y	Y	Y	8.65	1.63
Total PCB ICES-6	Y	Y		Y	Y	Y	51.11	7.40

After statistical analysis   Before statistical analysis

Intercind represents performances also when consensus values are not statistically robust (in grey)
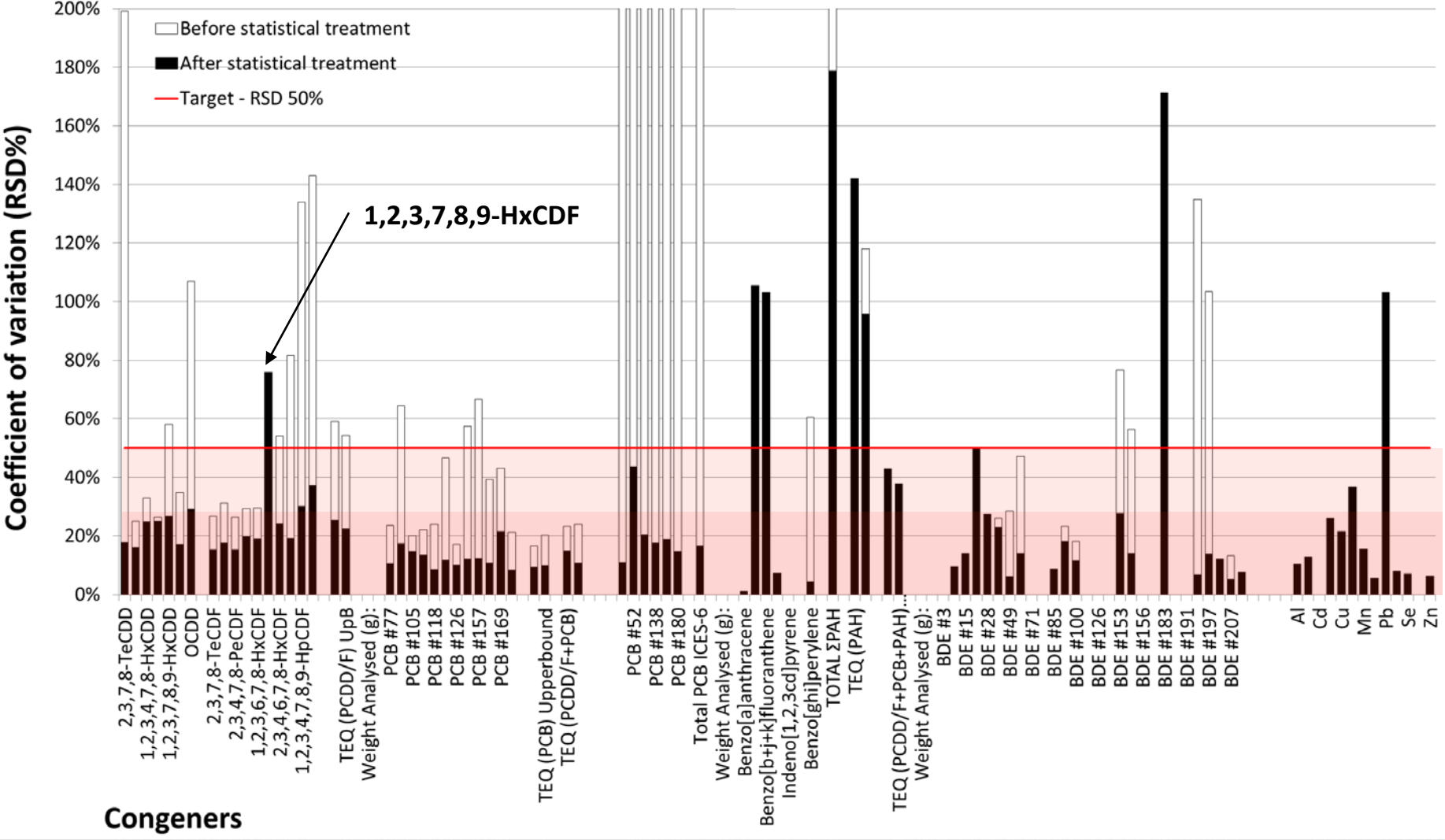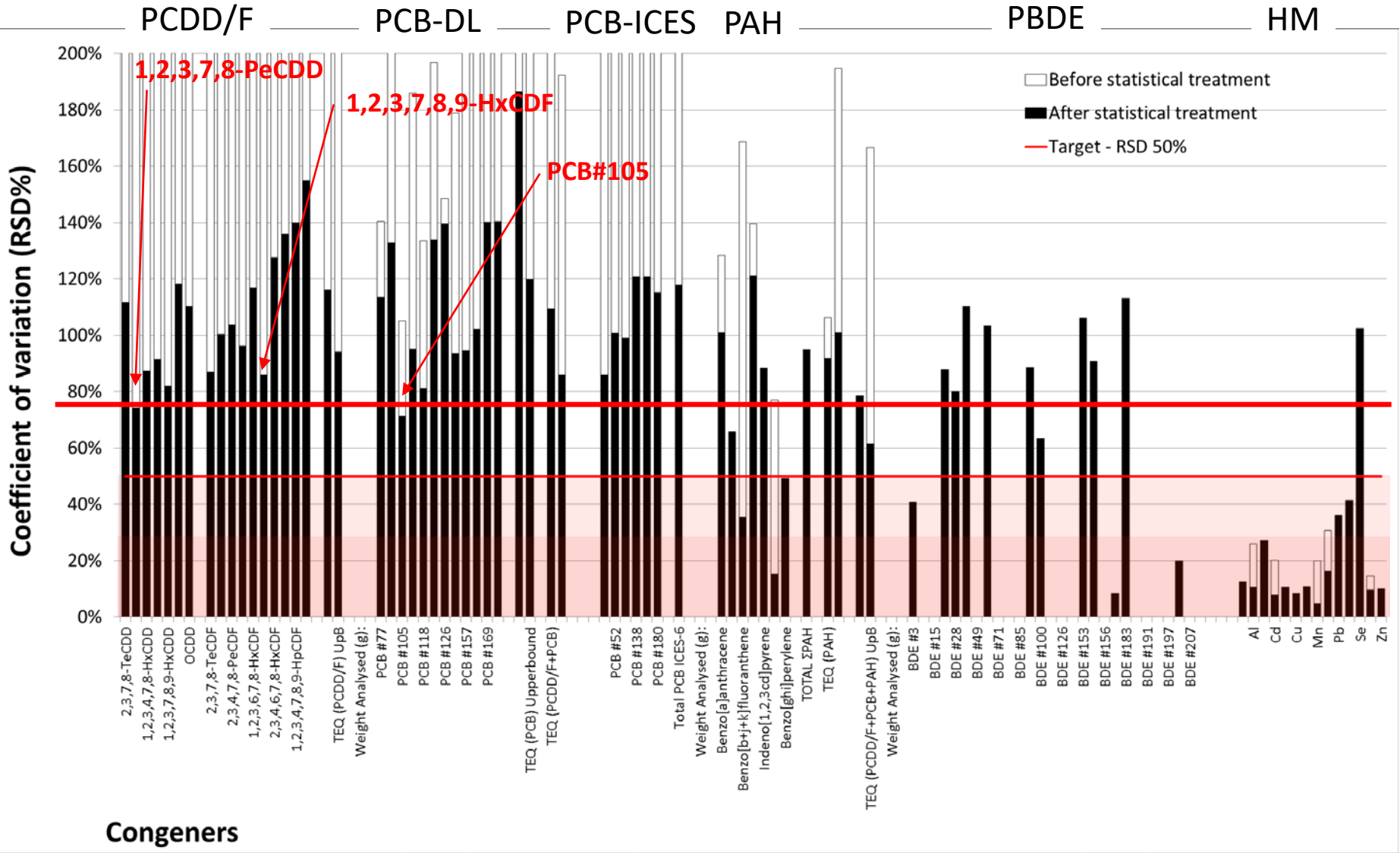
Z-scores - SEDIMENT

Lab&replicate	007-A	007-B	007-C	011-A	011-B	011-C	012-A	012-B	012-C	013-A	013-B	013-C	014-A	014-B	014-C
PCDD/F															
2,3,7,8-TeCDD	-0.68	-0.34	-0.58	2.02	-0.80	NA	-0.94	-1.30	-1.44	-0.53	-0.50	-0.63	ND	ND	ND
1,2,3,7,8-PeCDD	0.65	0.55	0.27	-1.23	-2.55	NA	-0.21	-0.07	-0.27	-0.54	-0.35	-0.38	ND	ND	ND
1,2,3,4,7,8-HxCDD	0.63	0.78	0.47	0.43	-0.59	NA	0.73	0.76	0.94	0.62	0.77	0.70	ND	ND	ND
1,2,3,6,7,8-HxCDD	0.62	0.74	0.28	1.87	0.43	NA	0.20	-0.68	0.06	0.97	1.17	1.22	ND	ND	ND
1,2,3,7,8,9-HxCDD	0.34	0.44	0.09	1.03	-1.42	NA	-0.10	-0.10	-0.10	0.65	0.83	0.75	ND	ND	ND
1,2,3,4,6,7,8-HpCDD	1.95	1.73	1.76	0.61	1.33	NA	0.40	0.86	0.71	0.81	1.08	1.22	-3.01	-1.28	-2.45
OCDD	0.82	0.64	0.42	-0.04	0.31	NA	0.99	1.28	1.37	1.31	1.49	2.05	-1.61	-1.73	-1.85
2,3,7,8-TeCDF	-0.38	0.29	0.02	0.28	0.05	NA	0.28	0.69	0.92	0.89	1.43	1.37	-1.29	-2.42	-3.13
1,2,3,7,8-PeCDF	1.97	2.11	2.00	2.49	0.45	NA	0.59	0.54	0.21	0.45	0.73	0.90	0.53	0.52	0.02
2,3,4,7,8-PeCDF	1.45	1.34	1.15	1.13	0.71	NA	1.13	1.09	1.16	-0.88	-0.74	-0.72	ND	ND	ND
1,2,3,4,7,8-HxCDF	1.00	0.96	1.04	0.51	0.83	NA	0.51	0.22	0.32	1.03	0.93	0.88	-1.94	-2.10	-3.02
1,2,3,6,7,8-HxCDF	1.31	1.34	1.03	1.42	1.37	NA	1.21	0.98	0.74	0.90	1.06	1.14	-1.17	-2.02	-2.35
1,2,3,7,8,9-HxCDF	-0.84	-0.86	-0.85	-0.73	-0.75	NA	-0.82	-0.82	-0.81	-0.82	-0.80	-0.82	ND	ND	ND
2,3,4,6,7,8-HxCDF	1.16	1.63	1.82	-0.95	-0.14	NA	-0.48	-0.63	-0.43	-1.17	-1.11	-1.18	1.11	0.16	ND
1,2,3,4,6,7,8-HpCDF	1.40	0.89	1.02	0.52	1.02	NA	0.93	0.68	0.70	1.47	1.52	1.69	-1.64	-1.54	-1.66
1,2,3,4,7,8,9-HpCDF	2.43	1.75	1.59	0.61	1.66	NA	1.08	0.81	0.94	0.78	0.91	0.89	-1.01	0.87	-0.55
OCDF	0.67	0.56	0.51	0.07	0.54	NA	0.85	0.61	0.67	0.28	0.32	0.13	-1.51	-1.45	-1.25
TEQ (PCDD/F)	1.38	1.36	1.26	0.63	0.46	NA	0.63	0.44	0.51	-0.02	0.11	0.11	-3.67	-3.94	-5.16
TEQ (PCDD/F) UpB	1.20	1.18	1.08	0.47	0.31	NA	0.47	0.29	0.35	-0.16	-0.03	-0.03	-4.98	1.86	1.45
PCB-DL															
PCB #77	1.30	1.18	1.06	1.98	-0.65	NA	0.89	1.05	0.82	-0.20	-0.15	-0.07	0.14	-0.52	-0.38
PCB #81	-0.52	-0.90	-0.64	1.35	-0.97	NA	1.35	1.35	0.77	-0.11	-0.11	-0.14	-0.86	-0.22	-0.44
PCB #105	0.80	0.38	-0.04	-0.96	-1.21	NA	-0.19	-0.55	-0.34	-0.66	-0.66	-0.77	-0.82	-0.76	-1.29
PCB #114	0.47	0.34	0.21	-0.69	-0.54	NA	-0.18	-0.33	-0.44	-0.46	-0.45	-0.54	-0.69	-0.69	-1.05
PCB #118	0.61	0.39	0.18	-0.63	-1.20	NA	0.09	-0.66	-0.50	-0.30	-0.26	-0.42	-0.56	-1.04	-1.46
PCB #123	0.85	1.36	0.63	-0.55	-0.71	NA	0.60	0.51	0.44	-0.87	-0.85	-0.92	-1.02	-1.22	-1.14
PCB #126	1.43	0.63	0.72	-0.22	-1.30	NA	0.59	0.05	-0.49	-0.14	-0.33	-0.22	0.60	-0.43	-0.18
PCB #156	1.54	1.80	1.67	-1.74	-1.40	NA	-0.54	-0.56	-0.66	-0.75	-0.63	-0.72	3.21	0.36	-0.23
PCB #157	0.01	-0.21	-0.43	-1.54	-1.20	NA	-0.29	-0.35	-0.32	-0.46	-0.27	-0.53	1.00	-0.21	-0.69
PCB #167	-0.33	-0.37	-0.42	-1.32	-1.17	NA	-0.26	-0.58	-0.65	-1.38	-1.54	-1.71	2.47	-0.13	-0.49
PCB #169	2.01	1.16	0.79	0.66	-1.48	NA	1.38	1.38	1.38	0.06	-0.02	0.07	0.92	-0.27	0.07
PCB #189	0.27	0.14	0.00	-1.60	-1.51	NA	-0.52	-0.38	-0.75	-0.30	0.04	-0.32	4.73	0.64	-0.29
TEQ (PCB)	1.61	0.76	0.77	-0.22	-1.50	NA	0.68	0.13	-0.36	-0.19	-0.36	-0.27	0.66	-0.52	-0.29
TEQ (PCB) Upperbound	1.60	0.76	0.77	-0.22	-1.48	NA	0.68	0.13	-0.35	-0.19	-0.36	-0.26	0.66	-0.51	-0.29
TEQ (PCDD/F+PCB)	1.37	1.26	1.17	0.48	0.19	NA	0.58	0.34	0.35	-0.13	-0.02	-0.01	-3.43	-3.81	-4.92
TEQ(PCDD/F+PCB) UpB	1.24	1.13	1.04	0.36	0.07	NA	0.45	0.22	0.23	-0.24	-0.14	-0.12	-4.74	1.65	1.29
PCB ICES-6															
PCB #28	0.61	0.67	0.61	NA	NA	NA	-0.53	-0.53	-0.53	0.07	0.09	0.09	-0.41	-0.19	-0.38
PCB #52	0.95	2.20	0.61	NA	NA	NA	-0.97	-0.97	-1.19	0.29	0.30	0.20	-0.31	-0.15	-1.29
PCB #101	0.91	1.57	1.24	NA	NA	NA	-0.78	-0.78	-0.93	-0.16	-0.11	-0.13	0.54	0.08	-0.52
PCB #138	-0.15	0.48	0.17	NA	NA	NA	-1.40	-1.40	-1.36	-0.86	-0.81	-0.80	1.45	-0.11	-0.64
PCB #153	0.86	1.53	1.20	NA	NA	NA	-0.99	-1.05	-1.11	-0.45	-0.53	-0.47	3.28	0.59	-0.33
PCB #180	1.66	1.57	1.61	NA	NA	NA	-1.56	-1.56	-1.56	-0.25	-0.22	-0.20	4.25	1.00	-0.06
Total PCB ICES-6	0.76	1.33	0.98	NA	NA	NA	-1.36	-1.37	-1.42	-0.51	-0.49	-0.48	2.31	0.30	-0.55

NA: not analyzed;
ND: below detection level (< expected);
red bold italic: absolute values >3

Lab&replicate	007-A	007-B	007-C	011-A	011-B	011-C	012-A	012-B	012-C	013-A	013-B	013-C	014-A	014-B	014-C
PAH															
Benzo[a]anthracene	NA	NA	NA	NA	NA	NA	0.80	0.11	1.49	NA	NA	NA	NA	NA	NA
Chrysene	NA	NA	NA	NA	NA	NA	1.20	0.68	1.47	NA	NA	NA	NA	NA	NA
Benzo[b+k]fluoranthene	NA	NA	NA	NA	NA	NA	0.94	0.37	1.29	NA	NA	NA	NA	NA	NA
Benzo[a]pyrene	NA	NA	NA	NA	NA	NA	1.14	0.61	1.40	NA	NA	NA	NA	NA	NA
Indeno[1,2,3cd]pyrene	NA	NA	NA	NA	NA	NA	0.21	-0.17	0.97	NA	NA	NA	NA	NA	NA
Dibenzo[a,h]anthracene	NA	NA	NA	NA	NA	NA	0.64	0.64	0.64	NA	NA	NA	NA	NA	NA
Benzo[ghi]perylene	NA	NA	NA	NA	NA	NA	0.29	0.08	0.71	NA	NA	NA	NA	NA	NA
TOTAL ΣPAH	NA	NA	NA	NA	NA	NA	0.89	0.35	1.35	NA	NA	NA	NA	NA	NA
TEQ (PAH)							0.90	0.36	1.24						
TEQ (PAH) Upperbound							0.89	0.36	1.24						
TEQ (PCDD/F+PCB+PAH)							0.70	0.21	0.99						
TEQ (PCDD/F+PCB+PAH) UpB							0.69	0.19	0.97						
PBDE															
BDE #3	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
BDE #7	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
BDE #15	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
BDE #17	NA	NA	NA	NA	NA	NA	NA	NA	NA	ND	ND	ND	NA	NA	NA
BDE #28	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.39	0.39	0.72	NA	NA	NA
BDE #47	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
BDE #49	NA	NA	NA	NA	NA	NA	NA	NA	NA	ND	ND	ND	NA	NA	NA
BDE #66	NA	NA	NA	NA	NA	NA	NA	NA	NA	ND	ND	ND	NA	NA	NA
BDE #71	NA	NA	NA	NA	NA	NA	NA	NA	NA	ND	ND	ND	NA	NA	NA
BDE #77	NA	NA	NA	NA	NA	NA	NA	NA	NA	ND	ND	ND	NA	NA	NA
BDE #85	NA	NA	NA	NA	NA	NA	NA	NA	NA	ND	ND	ND	NA	NA	NA
BDE #99	NA	NA	NA	NA	NA	NA	NA	NA	NA	ND	ND	ND	NA	NA	NA
BDE #100	NA	NA	NA	NA	NA	NA	NA	NA	NA	ND	ND	ND	NA	NA	NA
BDE #119	NA	NA	NA	NA	NA	NA	NA	NA	NA	ND	ND	ND	NA	NA	NA
BDE #126	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
BDE #138	NA	NA	NA	NA	NA	NA	NA	NA	NA	ND	ND	ND	NA	NA	NA
BDE #153	NA	NA	NA	NA	NA	NA	NA	NA	NA	ND	ND	ND	NA	NA	NA
BDE #154	NA	NA	NA	NA	NA	NA	NA	NA	NA	ND	ND	ND	NA	NA	NA
BDE #156	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
BDE #175	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
BDE #183	NA	NA	NA	NA	NA	NA	NA	NA	NA	ND	ND	ND	NA	NA	NA
BDE #184	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
BDE #191	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
BDE #196	NA	NA	NA	NA	NA	NA	NA	NA	NA	ND	ND	ND	NA	NA	NA
BDE #197	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
BDE #206	NA	NA	NA	NA	NA	NA	NA	NA	NA	ND	ND	ND	NA	NA	NA
BDE #207	NA	NA	NA	NA	NA	NA	NA	NA	NA	ND	ND	ND	NA	NA	NA
BDE #209	NA	NA	NA	NA	NA	NA	NA	NA	NA	1.38	1.57	1.34	NA	NA	NA
Heavy metals															
Ag	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	1.79	0.01	-1.12
Al	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	-0.72	-0.75	-0.72
As	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	-0.60	-0.62	-0.78
Cd	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.73	-0.67	-0.68
Cr	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	-1.16	-1.29	-1.27
Cu	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.94	0.62	0.35
Hg	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	-0.40	-0.22	-0.19
Mn	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	2.20	1.41	2.10
Ni	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	-0.22	-0.35	-0.31
Pb	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.36	0.23	0.10
Sb	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	-0.22	-0.22	-0.28
Se	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	ND	ND	ND
Sn	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.03	0.05	-0.04
Zn	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	1.10	0.66	0.41

NA: not analyzed; ND: below detection level (< expected);
red bold italic: absolute values >3

What does it mean to be **PTP 0007** In terms of data treatment?

From **ISO 13528**, to which we refer for statistical analyses – five different ways to

determine assigned value and its uncertainty:

1) Estimated from formulation;   **Potentially used but not considered**

2) Certified reference values;

3) Non-Certified reference values;

4) Consensus value from expert laboratories;   **Future?**

5) Consensus value from all laboratories.   **Intercind!**

InterCinD statistical method

SED_123789HxCDF
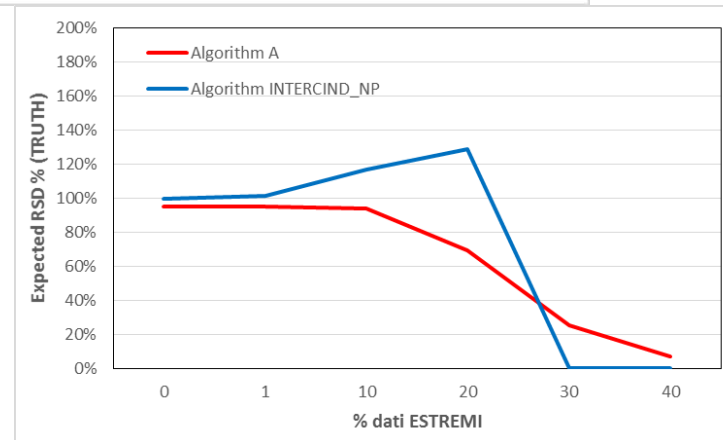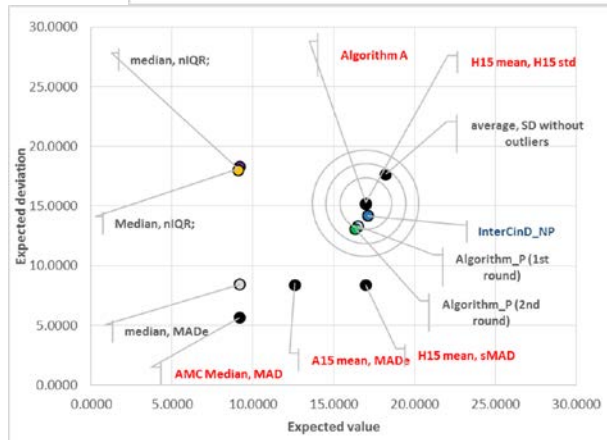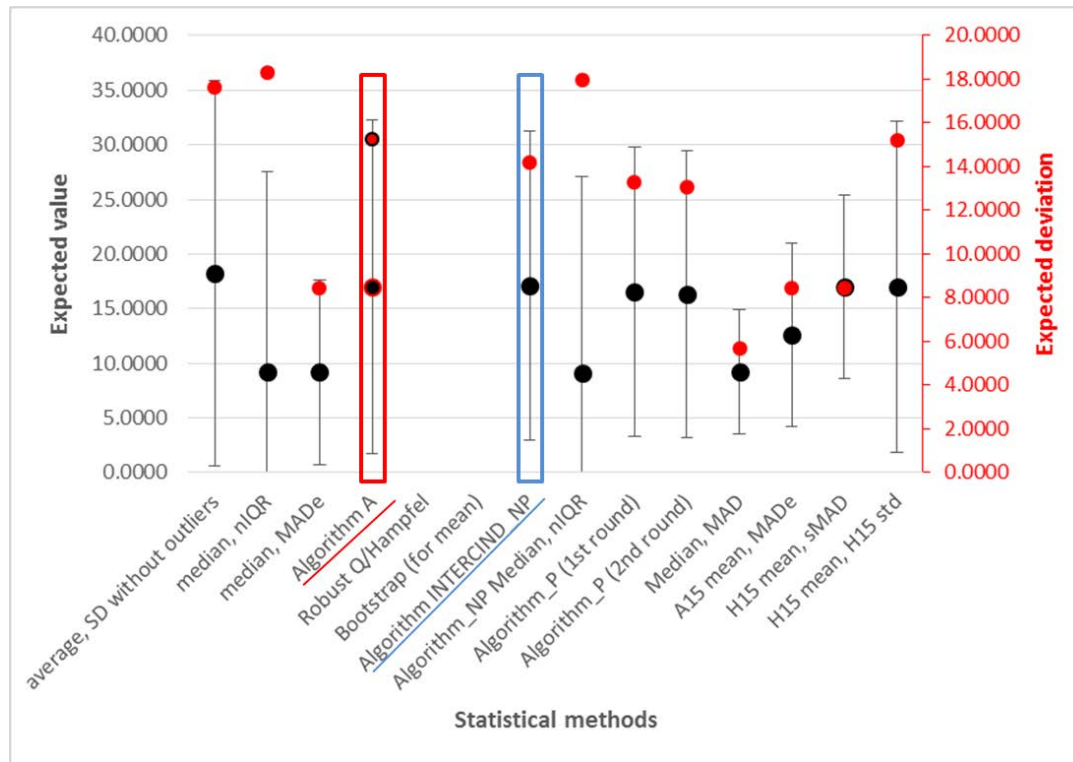
Test 3) Uncertainty of assigned value and uncertainty used for assessing performances (from consensus)

Uncertainty of assigned value is defined as the standard deviation divided by the squared root of the number of laboratories (n) with valid data

$$u_{Xj} = \frac{S_j}{\sqrt{n}}$$

uncertainty used for assessing performances

$$\sigma_{pj} = \sqrt{\frac{\sum_{i=1}^{n}\sum_{k=1}^{r}\left(x_{i,k,j} - \bar{x}_j\right)^2}{\left(\sum_{i=1}^{n}\sum_{k=1}^{r}1\right) - 1}}$$

Problem with the use of replicates?

Test: comparing Intercind method as it is (use of three replicates) and when applying it to the average of three replicates, using a real case, SEDIMENT Intercind 2016

(treatment &) Consensus value obtained from the mean of the three replicates

valore assegnato
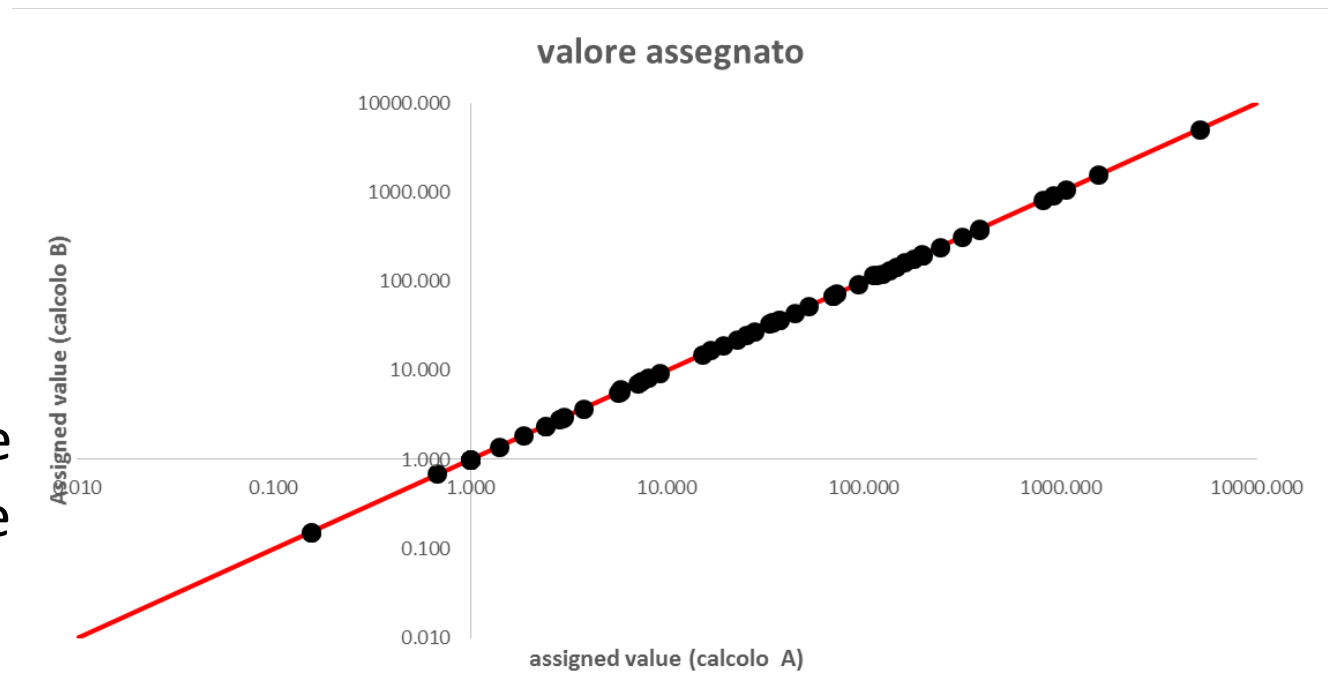
(treatment &) Consensus value using directly the three replicates

scarto tipo

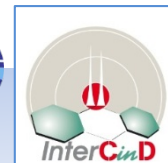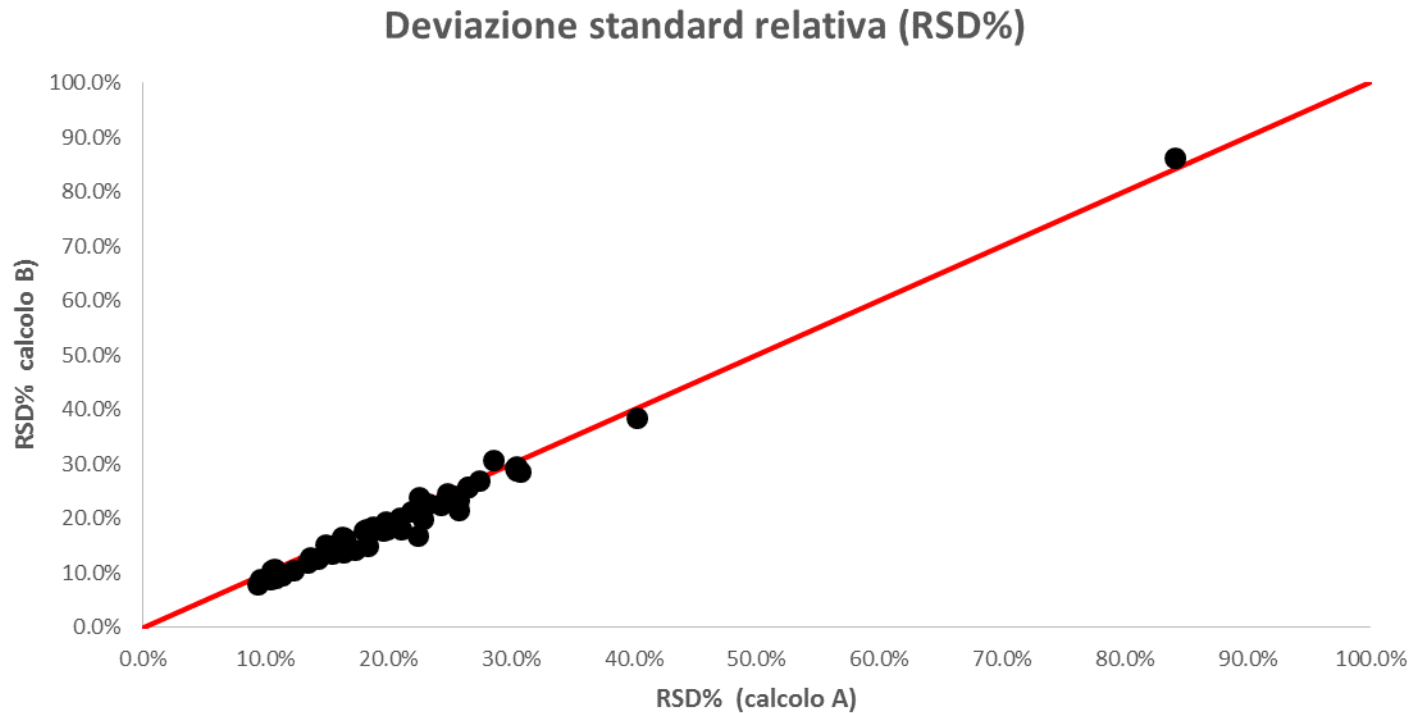obtained from the mean of the three replicates

incertezza del valore assegnato
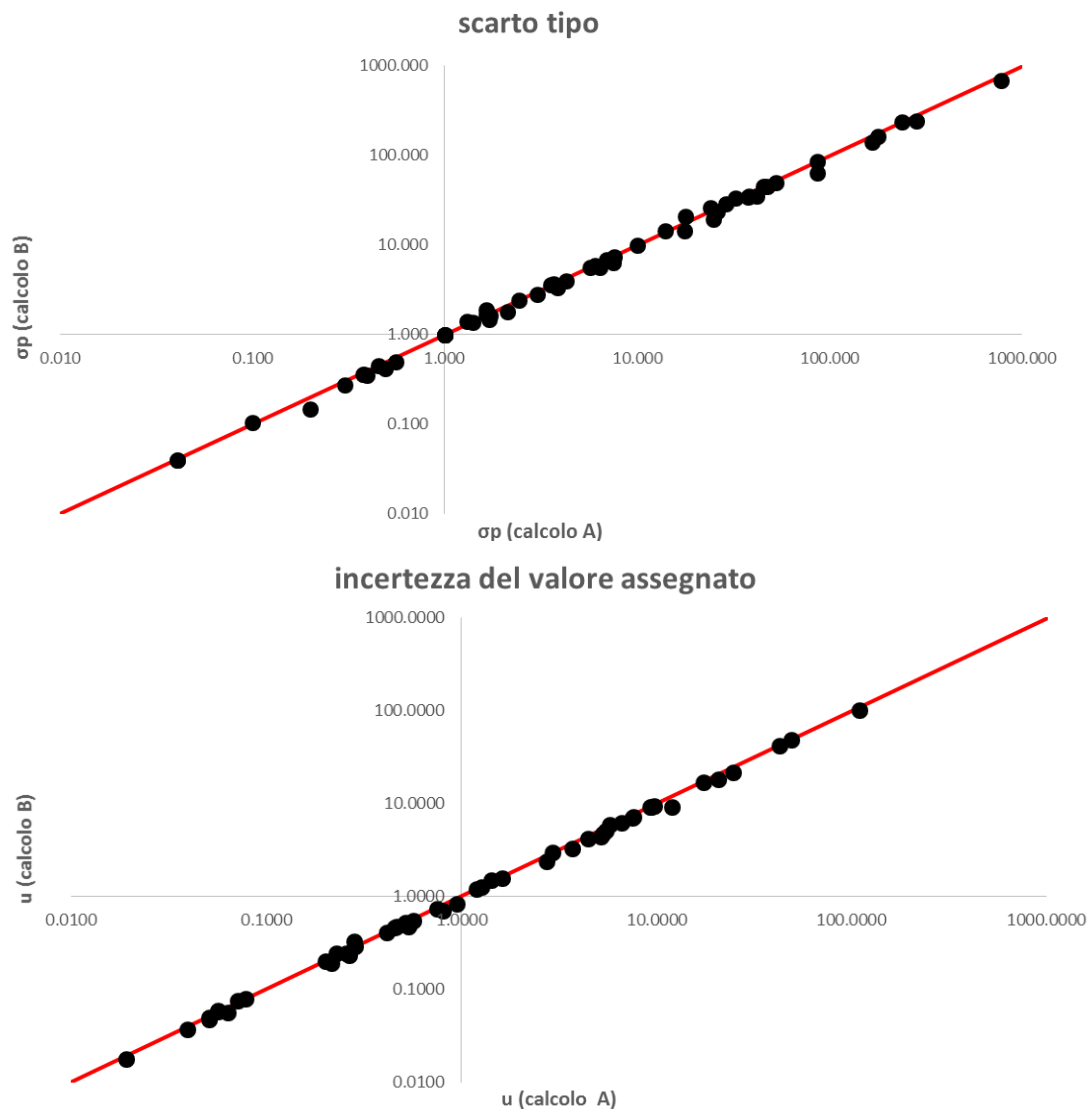
using directly the three replicates
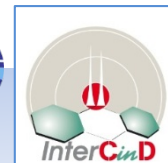
Using a very sensitive indicator: RSD%

Deviazione standard relativa (RSD%)

Effects on z-scores?

replicates

concentration
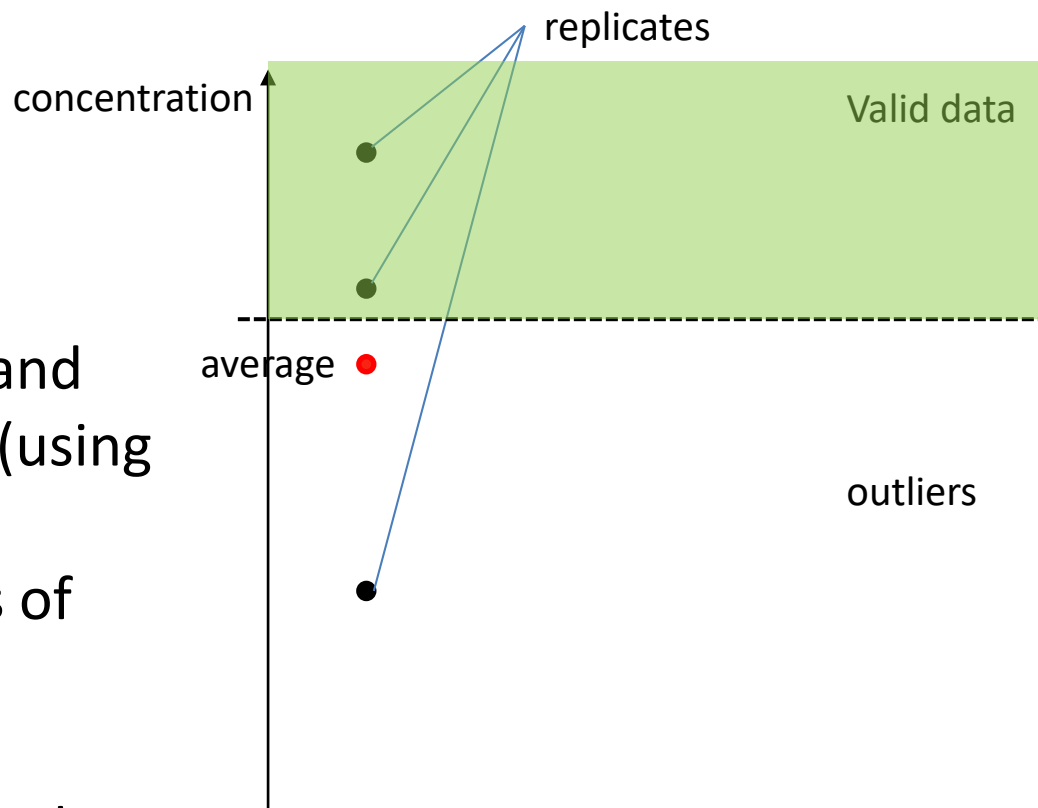
Valid data

average ●

outliers
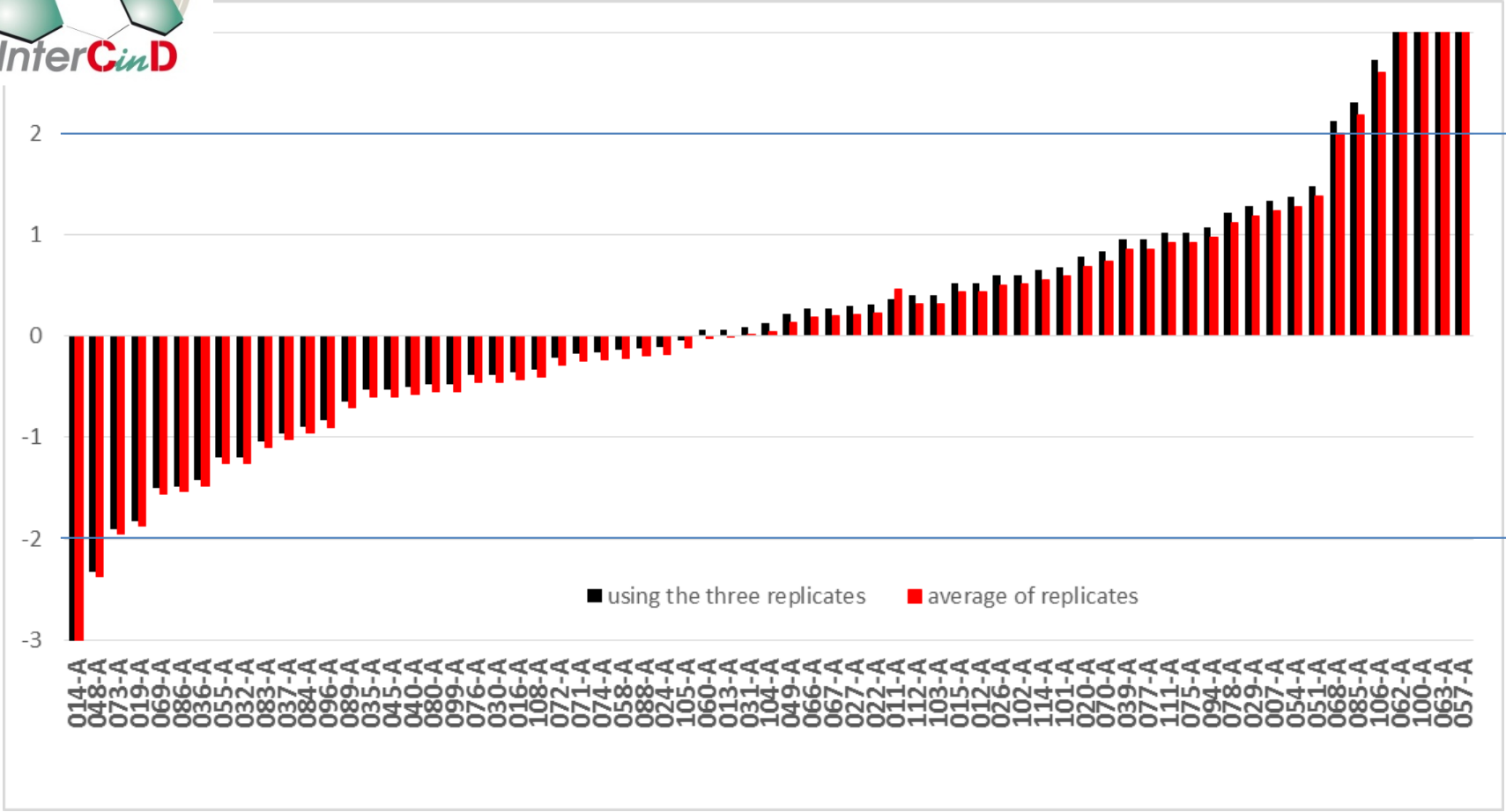
The pragmatic and standardized way (using the average) results in a loss of information

But also we loose the possibility for a detailed evaluation of the laboratory
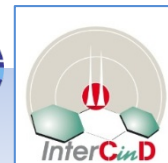
Annual INTERCIND meeting:
Lasceremo un mondo migliore di come l'abbiamo trovato?
Effetti dell'uomo sull'uomo
1 June 2017, Bologna

Thank you!

Simone Libralato

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