OC&EC inter-laboratory comparisons:

results of the third ILCE among ACTRIS and EMEP laboratories (D3.21) and plans for the first ILCE within ACTRIS-2

JP Putaud, EC-JRC-IES, Ispra, Italy

Test samples:

- o-Phthalic acid solution made at the JRC

- ambient PM samples collected on quartz fiber filter

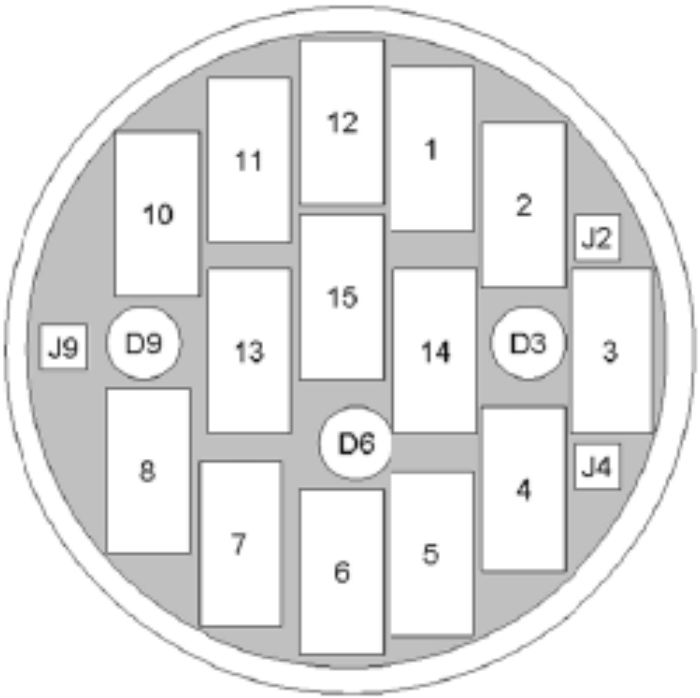
Table 1: filter test samples used for the inter-laboratory comparison

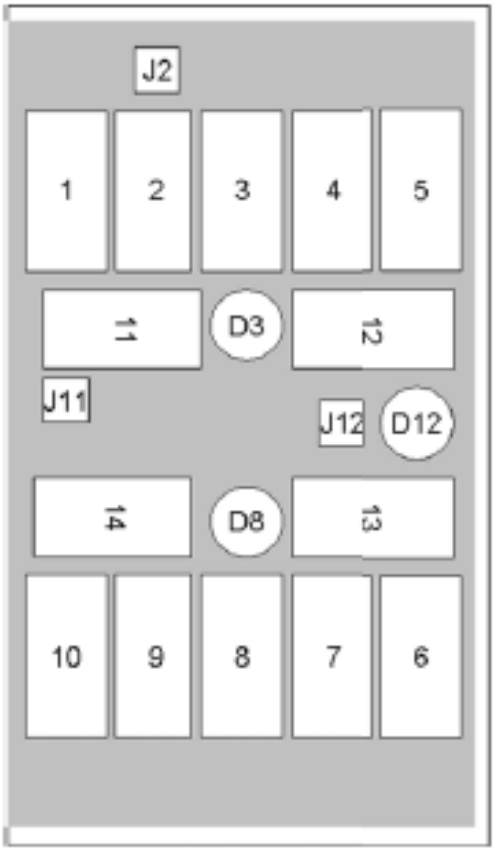
Sampling location				Sample collection		
Station	Country	Symbol	Site type	Period	Size fraction	Filter type
Birkenes	Norway	N	rural	Apr. 2000	PM10	Whatman QMA
Melpitz	Germany	D	rural	Nov. 2014	PM2.5	Munktell MK360
Montseny	Spain	E	rural	Dec. 2014	PM2.5	Whatman QMH
Demokritos	Greece	G	urban	Dec. 2014	PM2.5	MCV-QF1

Test samples:

- o-Phthalic acid solution made at the JRC

- ambient PM samples collected on quartz fiber filter





Test samples:

- o-Phthalic acid solution made at the JRC

- ambient PM samples collected on quartz fiber filter

Table 2: homogeneity of the deposits on filters collected with the samplers used to produce the 8 test filters. Analyses were performed with the protocol EUSAAR_2 and charring correction by transmittance monitoring.

Origin of the test filter	Homogeneity for TC (%)	Homogeneity for EC (%)
BIR (N)	2.4	3.2
MEL (D)	1.9	9.3
MSY (E)	5.3	27.0
DEM (G)	2.0	2.9

Participants

Table 3: List of participants in the inter-laboratory comparison 2015, and contact persons

	Code	Participant	Acronym	Contact Person
	1	Stockholm University - Department of Applied Environmaental Science	ITM	Hans Areskoug
	2	Norsk institutt for luftforskning	NILU	Karl Espen Yttri
*	3	Instituto de Salud Carlos III	ISCIII	Rosalia Fernandez Patier
*	4	Institute of Environmental Engineering of the Polish Academy of Sciences	IPIS	Barbara Mathews
	5	University of Crete - Environmental Chemical Processes Laboratory	UOC-ECPL	Nikos Mihalopoulos
*	6	Agencija Republike Slovenije za Okolie	ARSO	Irena Kranjc
	7	Czech Hydrometeorological Institute	CHMI	Jiri Novak
	8	Leibniz-Institut für Troposphärenforschung	TROPOS	Gerald Spindler
	9	Institute de Diagnóstico Ambiental y Estudios del Agua	IDAEA	Andres Alastuey
	10	Laboratoire de Glaciologie et Geophysique de l'Environnement	LGGE	Jean-Luc Jaffrezo
	11	Lund University - Centre for Environmental and Climate Research	ULUND	Johan Martinsson
*	12	Umweltbundesamt - Deutschland	UBA-DE	Elke Bieber
*	13	Gemeentelijke Geneeskundige Dienst Amsterdam	GGD	Pavlos Panteliadis
	14	Swiss Federal Laboratories for Materials Science and Technology	EMPA	Andrea Fischer
	15	Joint Research Centre - Institute for Environment and Sustainability	JRC-IES	Fabrizia Cavalli
	16	National Center for Scientific Research "Demokritos"	NCSR	Lila Diapouli

Participants

Table 4: List of the analytical protocol and punch size used by each participant

Code	Participant	Instrument	Protocol	Punch size (cm^2)
1	ITM	Sunset	EUSAAR_2	1.00
2	NILU	Sunset	EUSAAR_2	1.50
3	ISCIII	Sunset	QUARTZ	1.50
4	IPIS	Sunset	EUSAAR_2	1.50
5	UOC-ECPL	Sunset	EUSAAR_2	1.50
6	ARSO	Sunset	EUSAAR_2	1.50
7	CHMI	Sunset	EUSAAR_2	1.50
8	TROPOS	Sunset	EUSAAR_2	1.50
9	IDAEA	Sunset	EUSAAR_2	1.50
10	LGGE	Sunset	EUSAAR_2	1.50
11	ULUND	DRI	EUSAAR_2	0.50
12	UBA-DE	Sunset	EUSAAR_2	1.50
13	GGD	Sunset	NIOSH870	1.50
14	EMPA	Sunset	EUSAAR_2	1.50
15	JRC-IES	Sunset	EUSAAR_2	1.00
16	NCSR	Sunset (on-line)	EUSAAR_2	2.14

Results: method performance for TC [ISO5725-2]

Repeatability

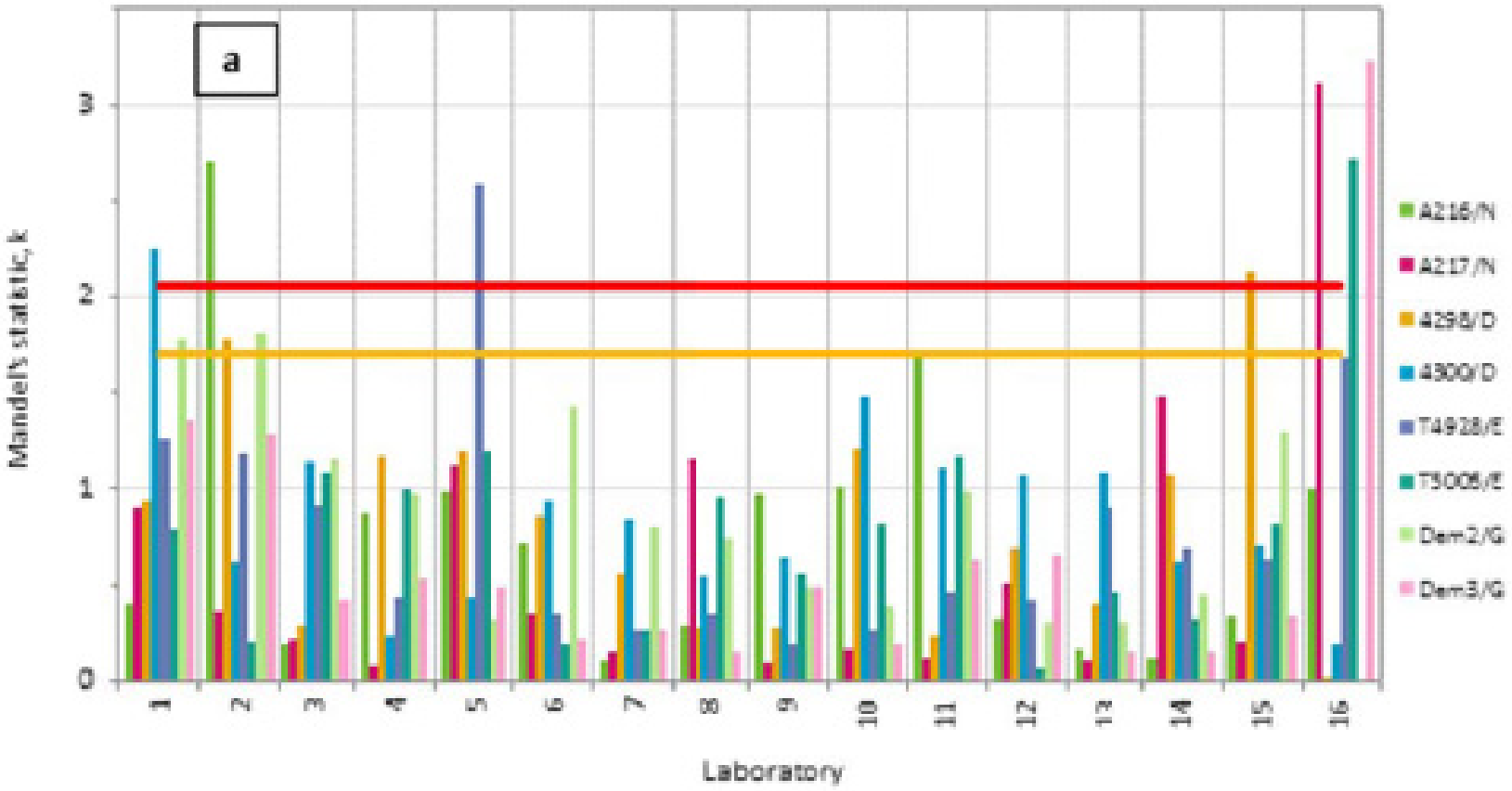


Fig. 1: Mandel's k statistic values for within laboratory consistency of TC data. For 16 participants and 3 replicates, k values should be < 2.05 at the 1% s.l. , and < 1.70 at the 5% significance level.

Results: method performance for TC [ISO5725-2]

Reproducibility

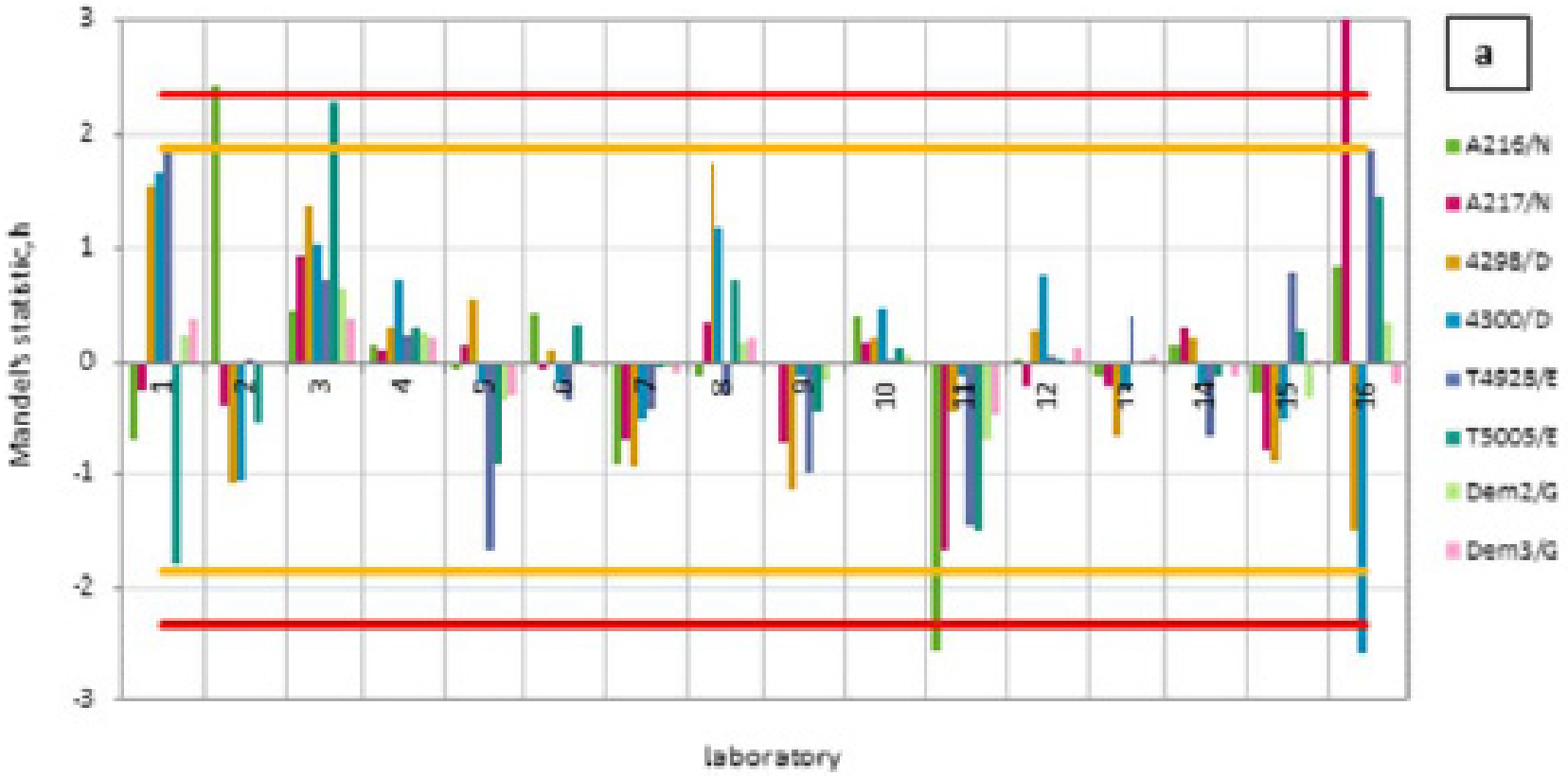


Fig. 2: Mandel's h statistic values for between- laboratory consistency of TC data. For 16 participants, h values should be < 2.33 at the 1% significance level, and < 1.86 at the 5% significance level.

Results: method performance [ISO5725-2]

Table 6: General mean, repeatability (s_r) and reproducibility (s_R) standard and relative standard deviations for TC.

test sample	general mean	sr		sR	
	µgC / cm²	µgC / cm²	%	µgC / cm²	%
A216/N	7.8	0.4	5.0	0.8	10.5
A217/N	5.7	0.4	6.8	0.5	8.9
4298/D	42.8	0.6	1.5	2.1	5.0
4300/D	47.2	0.7	1.6	3.2	6.8
T4928/E	5.9	0.4	6.2	0.7	11.6
T5005/E	7.5	0.4	5.1	0.9	11.8
Dem2/G	9.7	0.4	4.4	0.8	8.2
Dem3/G	10.1	0.4	4.1	0.7	6.8

Results: method performance for EC/TC [ISO5725-2]

Repeatability

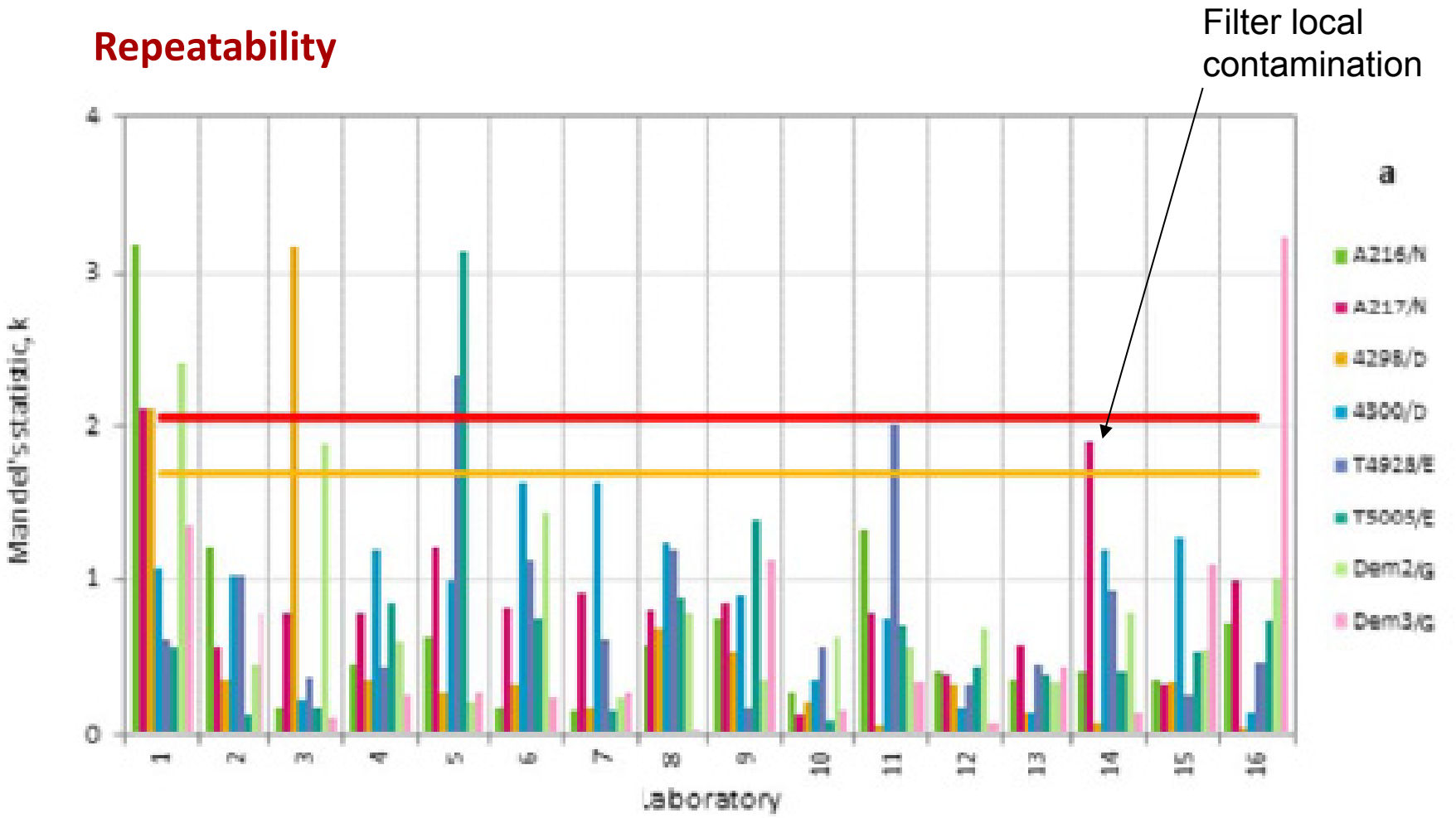


Fig. 3: Mandel's k statistic values for within laboratory consistency of EC/TC data. For 16 participants and 3 replicates, k values should be < 2.05 at the 1% s.l. , and < 1.70 at the 5% significance level.

Results: method performance for EC/TC [ISO5725-2]

Reproducibility

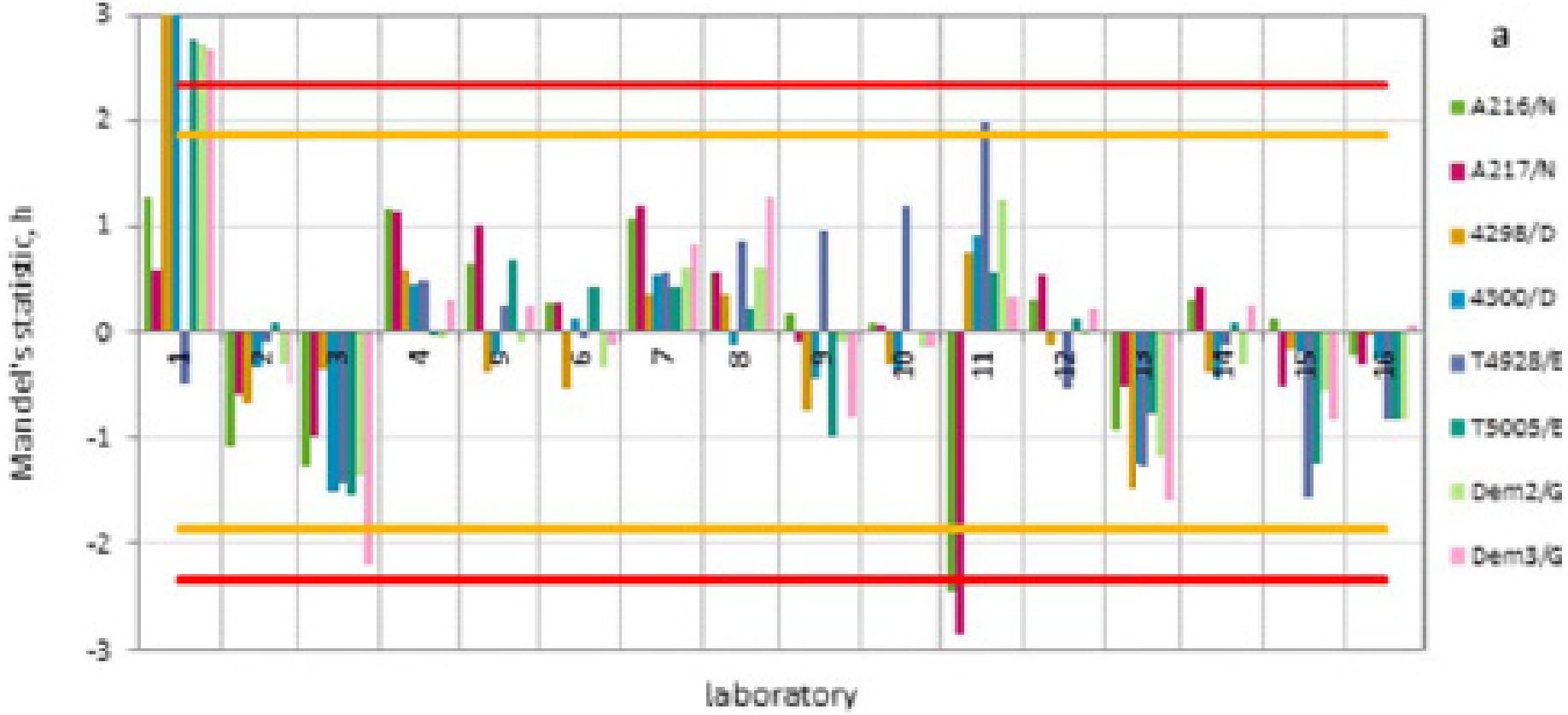


Fig. 4: Mandel's h statistic values for between- laboratory consistency of EC/TC data. For 16 participants, h values should be < 2.33 at the 1% significance level, and < 1.86 at the 5% significance level.

Results: method performance for EC/TC [ISO5725-2]

Table 7: General mean, repeatability (s_r) and reproducibility (s_R) standard and relative standard deviations for EC/TC.

test sample	general mean	sr		sR	
	ratio	ratio	%	ratio	%
A216/N	0.09	0.01	8.8	0.02	26
A217/N	0.09	0.01	8.7	0.02	19
4298/D	0.10	0.01	6.0	0.01	13
4300/D	0.11	0.01	6.2	0.02	17
T4928/E	0.10	0.01	11.1	0.02	24
T5005/E	0.10	0.01	9.2	0.02	24
Dem2/G	0.11	0.01	9.3	0.02	21
Dem3/G	0.17	0.01	7.2	0.03	17

Results: laboratories' performance for TC [ISO13528]

Assigned value = consensus value

Table 8: Assigned values and standard deviations for proficiency assessment σ* *from data obtained in a round of a proficiency testing scheme* for TC.

		A216/N	A217/N	4298/D	4300/D	T4928/E	T5005/E	Dem2/G	Dem3/G
assigned value	µg/cm2	8.0	5.7	42.7	47.2	5.8	7.5	9.7	10.1
standard	µg/cm2	0.5	0.4	2.4	2.5	0.6	0.6	0.6	0.5
deviation	%	6.4	6.5	5.6	5.2	10.2	7.3	6.3	5.2
2σ*	%	13	13	11	10	20	15	13	10
3σ*	%	19	20	17	16	31	22	19	16

Results: laboratories' performance for TC [ISO13528]

Figure 5. z-scores for TC calculated using σ* *from data obtained in a round of a proficiency testing scheme.*

Results: laboratories' performance for EC/TC [ISO13528]

Assigned value = consensus value

Table 9: Assigned values and standard deviations for proficiency assessment σ* *from data obtained in a round of a proficiency testing scheme* for EC/TC.

		A216/N	A217/N	4298/D	4300/D	T4928/E	T5005/E	Dem2/G	Dem3/G
assigned value	ratio	0.09	0.09	0.10	0.11	0.10	0.10	0.11	0.17
standard	ratio	0.02	0.01	0.01	0.01	0.02	0.02	0.01	0.02
deviation	%	18	14	11	10	24	15	12	11
2σ*	%	37	28	23	21	48	30	25	22
3σ*	%	55	42	34	31	72	45	37	33

Results: laboratories' performance for EC/TC [ISO13528]

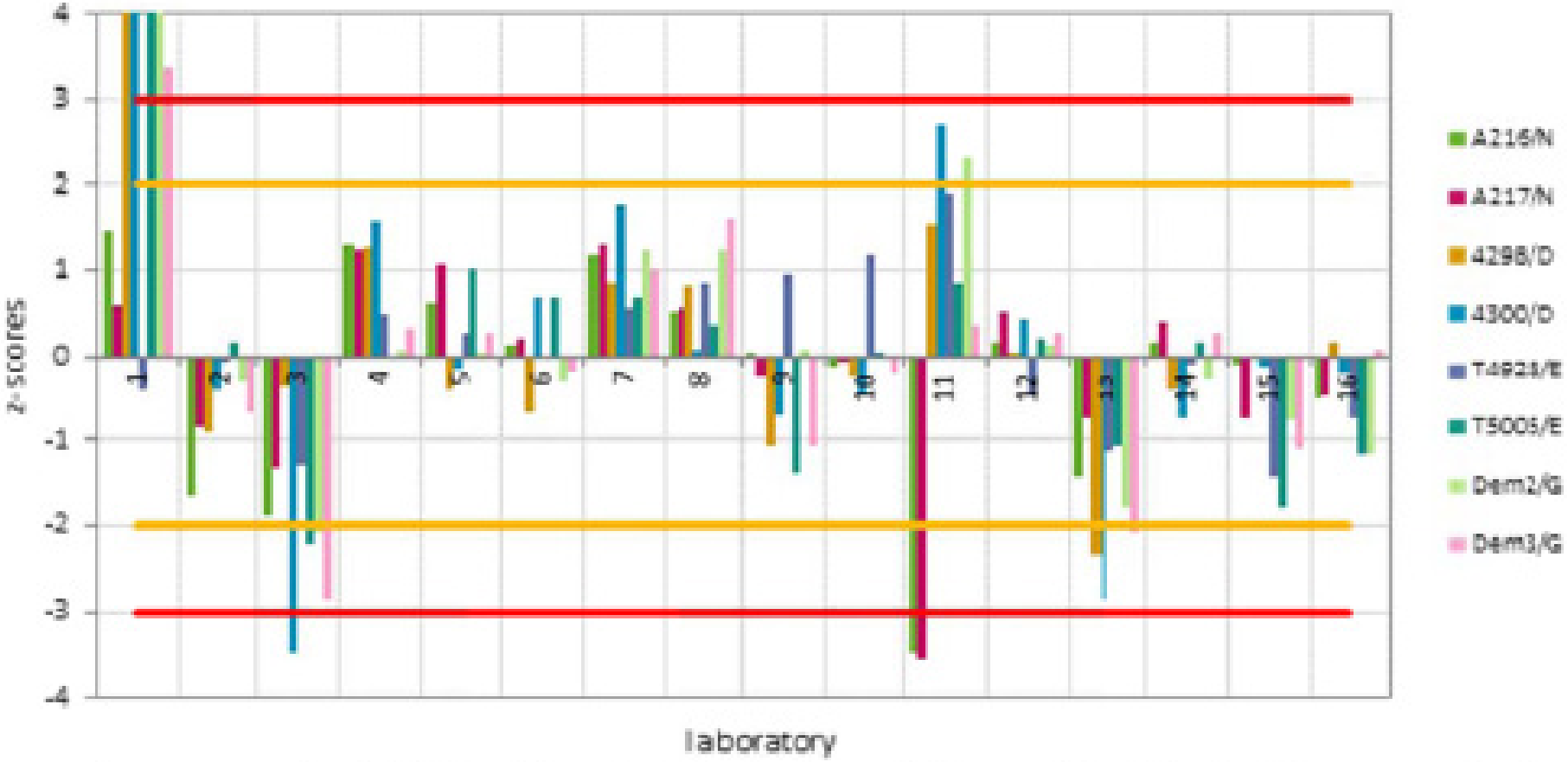


Figure 6. z-scores for EC/TC ratio calculated using σ* *from data obtained in a round of a proficiency testing scheme.*

Results: o-phthalic acid

Assigned value = calculated from weighing, dilution volume, etc..

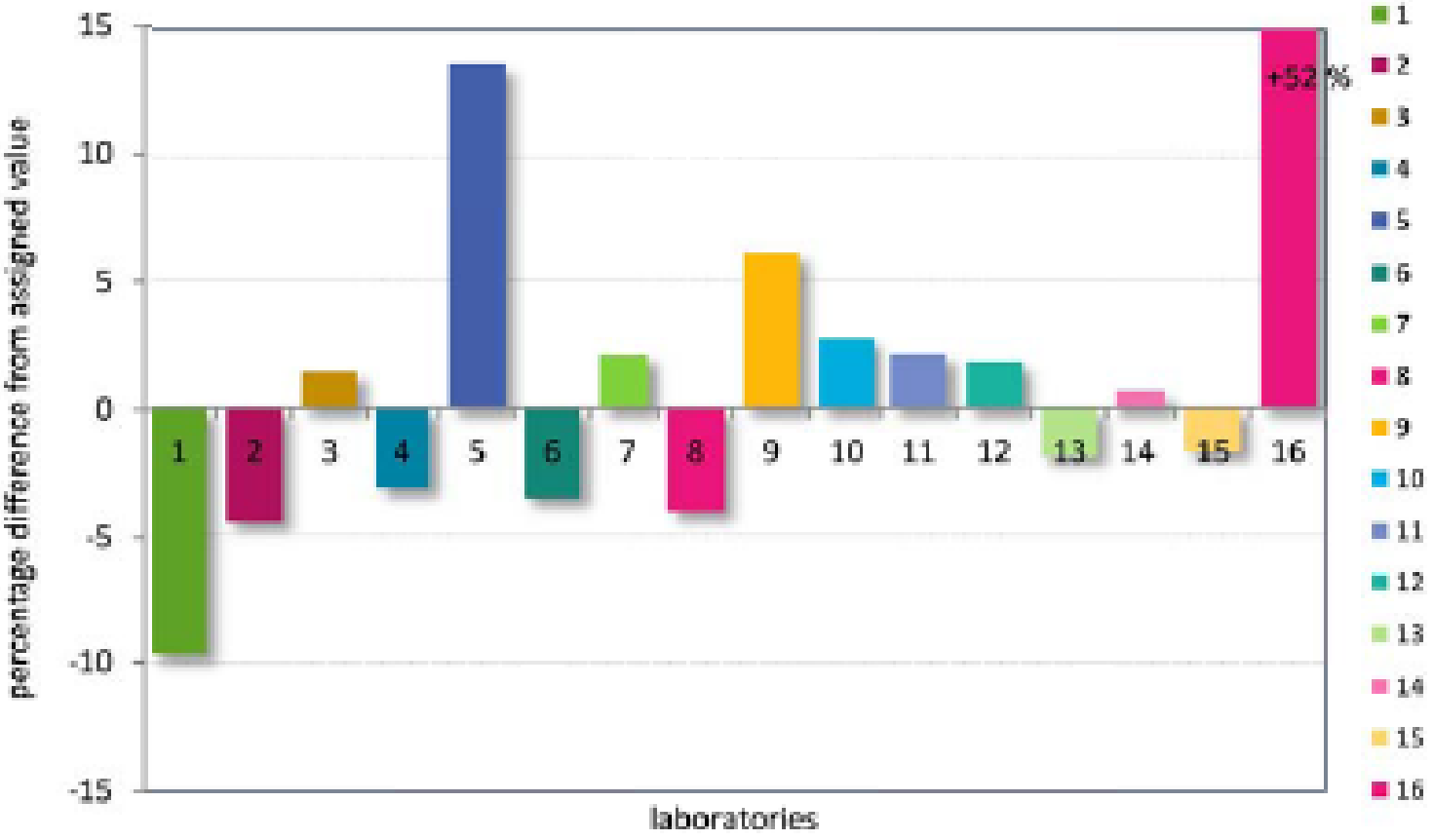


Figure 7. Phthalic acid solution –percentage differences from the assigned value, i.e. the C concentration of the test solution calculated from the mass of phthalic acid and the volume of ultra-pure water used to make the solution.

ILC Conclusions

• **TC repeatability = 1.5% to 6.8%** and **reproducibility = 5.0% to 12%**

These figures are very similar to the ones obtained during previous exercises.

• **EC/TC ratio repeatability = 6% to 11% and reproducibility = 13% to 26%.**

Compared with the previous inter-laboratory comparison, the reproducibility improved (- 5 percentage points).

• **Laboratories' performance for TC**: participants 1, 3, 11, and 16 accounted for 90% of the total number of stragglers + outliers. TC values reported by participants 3 and 11 were systematically high and low, respectively.

• **Laboratories' performance in EC/TC ratios**: all 18 outliers and stragglers were produced by participants 1, 3, 11, and 13.

- The EC/TC ratios obtained by participants 3 and 13, using a NIOSH-like protocol, are lower than average as expected.
- The performance of participants 1 and 11 in determining EC/TC ratios was not sufficient, as for determining TC loadings.

Next steps

- **Responses and feedbacks from your side are essential**

- **Implement the CEN 16909 standard**

- **Next OC&EC inter-laboratory comparison**
  - **Jan. - Apr. 2016**
  - **Compulsory for laboratories that submit OC&EC data to EBAS**
    - ➢ **application to ECAC**
  - **Our proposal:**
    - Ambient PM filters (volunteers?)
    - o-Phthalic solution ?
    - JRC-made synthetic reference material for OC and EC