Deliverable D3.10:
An Inter-laboratory comparison (ILC) studies for the targeted set of OA tracers

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Comments	*Delayed due to:* *The ACTRIS-2 partner to first volunteer to arrange the ILC unexpectedly withdrew their offer for internal reasons. Finding another organizer of the ILC caused a considerable time delay. For this to happen, the work needed to be shared by two partners, splitting the work into that related to the ILC itself (IGE) and the subsequent statistical analysis (JRC).*

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1 Background – Task 3.1 subtask on organic aerosol tracers

This deliverable deals with Task 3.1 of ACTRIS-2 WP3 ("Improvement of instrumentation, standardization and quality assessment of essential climate and air quality variables"). The task includes, among other variables, also selected Organic Aerosol (OA) tracer compounds. The OA tracer subtask aims to establish a set of common European Standard Operating Procedures (SOP) for sampling and analysis of a selection of organic tracers, in order to facilitate their subsequent implementation at several ACTRIS sites for the purpose of organic aerosol (OA) source apportionment across Europe. The work on OA tracers in ACTRIS-2 Task 3.1 is a continuation of that performed within the EU FP7 Infrastructure Project ACTRIS (Task 3.3b). See also the previous ACTRIS-2 WP3 Task 3.1 deliverable related to the work on Organic tracers (D3.1, "Expert workshop to determine the targeted set of OA tracers", public report, M6).

According to the ACTRIS-2 Grant Agreement, Task 3.1 including the OA tracer part aims:

- to increase the amount and quality of delivered data,
- to control implementation of existing Standard Operation Procedures (SOP), and
- to eventually propose revisions.

This will be achieved (here only that relevant for OA tracers) via:

- inter-laboratory comparison exercises (round-robin),
- use of ACTRIS TNA (WP8).

This means that within ACTRIS-2, inter-laboratory comparison (ILC) studies are performed for anhydrous sugars (levoglucosan, mannosan, galactosan) since these were identified in EU FP7 ACTRIS as suitable tracers for biomass burning, and Draft SOPs were presented.

ILC studies for anhydrous sugars were performed also in the EU FP6 I3 project EUSAAR (ILC organized by: NILU, NO; Karl Espen Yttri) and in the EU FP7 ACTRIS project (ILC organized by INERIS, FR; Stephane Verlhac and Alexandre Albinet). These two previous ILCs, with largely the same partners participating as in the ACTRIS-2 ILC, were overall very successful. The EU FP7 ACTRIS project concluded that there was already then a solid basis to suggest Draft SOPs for these compounds for various analytical techniques (GC, LC, HPAEC)[1]. It was noted that none of the techniques was shown to be superior to the others and therefore no single analytical technique was recommended. For more information, see EU FP7 ACTRIS Deliverable D3.19 ("Implementation of organic tracer measurements at European sites"). In 2015, the California Environmental Protection Agency also published an SOP for the same compounds using GC[2].

The chain of events towards establishing an OA tracer for ACTRIS is:

i. Selection of a candidate OA tracers;
ii. Performing ILC for the selected candidate OA tracers to estimate their applicability within ACTRIS;
iii. Establishing new SOPs for the suitable OA tracers for subsequent implementation in ACTRIS;
iv. Establishing control procedures for the suitable OA tracers (merging SOPs and ILC procedures);

[1] http://actris.nilu.no/Content/SOP

[2] Standard Operating Procedure for the analysis of levoglucosan, mannosan, galactosan in ambient air using gas chromatography / mass spectrometry, SOP MLD073, California Environmental Protection Agency, Air Resources Board, 2015-08-04, V. Brock, K. Gill, M. Werst and M. Miguel.

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v. Implementing the control procedures for the OA tracers at regular time intervals to ensure data quality and operability at ACTRIS sites.

For the anhydrous sugars, the steps in the chain of events that have already been completed are (i) Selection, (ii) ILC performed, and (iii) Draft SOPs established. ACTRIS-2 performed work on the remaining steps (iv) Establishing control procedures, and (v) Implementing the control procedures.

An **ACTRIS control procedure** for a specific OA tracer is the combination of the SOP and a predefined schedule for ILC studies to be performed at regular time intervals. It also describes how the ILC should be carried out (ambient air test samples, synthetic standards, reference standards, blanks, instructions for handling, evaluation and reporting etc).

2 Recommendations for an ACTRIS control procedure for anhydrous sugars

On the basis of the work performed within ACTRIS-2, also relying on previous work carried out within the EU FP7 ACTRIS project and the EU FP6 I3 project EUSAAR, the following recommendations for an **ACTRIS control procedure for anhydrous sugars** (levoglucosan, mannosan, galactosan) are given, in support of the implementation of the anhydrous sugars as suitable organic tracers for biomass burning at ACTRIS Aerosol-In-Situ National Facilities:

i. It is the responsibility of the assigned ACTRIS Aerosol In-Situ Central Facility to implement these control procedures in the ACTRIS ERIC.
ii. The ACTRIS Aerosol In-Situ Central Facility that is responsible for the anhydrous sugars shall determine the detailed ILC procedure, including quality assurance and quality control procedures, the use of ambient air test samples, synthetic standards, reference standards, blanks, instructions for handling, evaluation and reporting etcetera.
iii. ILC for the anhydrous sugars shall be performed at regular intervals, every 2-4 years as decided by the responsible ACTRIS Aerosol In-Situ Central Facility.
iv. All ACTRIS partners reporting data to the ACTRIS database shall participate in the ILC. The outcome of the ILC shall be included in the submitted metadata in a predetermined and standardized way to ensure proper interoperability.
v. ACTRIS partners should use the applicable ACTRIS SOP (GCMS, HPLC, HPAEC-PAD etcetera) with minor and well-motivated modifications only. Deviations from the recommended SOPs shall be agreed in advance by the responsible ACTRIS Aerosol In-Situ Central Facility.
vi. ACTRIS partners that do not perform satisfactorily in the ILC shall take corrective actions as recommended by the responsible ACTRIS Aerosol In-Situ Central Facility and the ILC organizer. Potentially erroneous data shall be properly flagged when reporting data to the ACTRIS database. All pertinent information relating to the unsatisfactory ILC outcome shall be included in the metadata in a standardized way. This includes also successful corrective actions taken that are able to explain the unsatisfactory ILC performance and demonstrate the validity of the submitted data.
vii. Failure by the ACTRIS partner to comply with these recommendations will lead to rejection from the ACTRIS database of the potentially erroneous data on anhydrous sugars.

It is important that adequate funding for the organization and implementation of the regular ILC is made clear in the ACTRIS ERIC cost model. This funding should be allocated to the appropriate ACTRIS Aerosol In-Situ Central Facility.

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Results of the ACTRIS-2 inter-laboratory comparison for the measurement of levoglucosan, mannosan and galactosan (Deliverable D3.10)

Summary

This interlaboratory comparison (ILC) for the measurement of levoglucosan, mannosan, and galactosan conducted between December 2017 and June 2018 was open to ACTRIS-2 and EUROCHAMP-2020 partners, and to the laboratories involved in the EMEP/ACTRIS/COLOSSAL winter campaign 2017-2018. Nineteen laboratories participated and eighteen submitted their results in time to be included in the statistical analyses.

This interlaboratory comparison was based on three ambient PM_{10} aerosol samples collected on quartz fiber filters at a site in France, and two aqueous solutions, one of them containing other substances in addition to levoglucosan, mannosan, and galactosan.

The aim of this exercise was to evaluate the performances of the measurement method (i.e. reproducibility and repeatability) and of individual laboratories (z-scores, bias and variability) applying their usual analytical protocols.

Although the sample preparation and analytical methods used by the various participant was very diverse, it was not possible to distinguish different populations among the data reported by the participants. The statistical analyses were therefore carried out considering all the values together, except for the data reported by 2 participants which were mostly discordant with the data reported by the other participants.

Method performance: The measurement method *repeatability* (1 standard deviation) ranged from 1.7 to 3.4% for levoglucosan, from 3.0 to 5.2% for mannosan and from 4.6 to 7.4% for galactosan. The measurement method *reproducibility* (1 standard deviation) ranged from 16 to 19% for levoglucosan, from 19 to 53% for mannosan, and from 23 to 47% for galactosan.

Laboratory performance: Participants' performances were assessed in terms of *z-scores*, calculated from the *assigned values* and the *standard deviations for proficiency assessment*. For the test filter samples, the *assigned values* and the *standard deviation for proficiency assessment* were calculated from the data obtained in the current interlaboratory comparison. For the test solutions, the *assigned values* were derived from the mass of analytes and solvent used, and the *standard deviations for proficiency assessment* were determined from the level of performance the organizer wished participants to achieve.

Most values reported by the two participants of which data had been discarded *a priori* were outliers. More than one outlier + straggler were reported by 4 more participants regarding the analysis of the filter samples, and also 4 more participants (all different but one) regarding the aqueous solutions.

For the filter samples, the percentage of submitted values within ±15% of the assigned values was 70%, 71% and 51% for levoglucosan, mannosan, and galactosan, respectively. For the test solution containing levoglucosan, mannosan, and galactosan only, the fraction of submitted values within ±15% of the assigned values was 50% for levoglucosan, 69% for mannosan and 65% for galactosan. The determination of mannosan in the solution containing also other substances led to many more outliers.

Participants' *bias and variability* relative to the determination of levoglucosan, mannosan and galactosan in ambient PM deposited on filters were also estimated. However, since the number of test filter samples was low (3), the statistical significance of these measures is questionable.

Introduction

Levoglucosan and its stereoisomers are important organic tracers of bio-fuel combustion. An inter-laboratory comparison (ILC) for the analysis of levoglucosan, mannosan, and galactosan was organized by IGE (Grenoble, France) under the EU H2020 ACTRIS-2 project to evaluate the analytical repeatability and reproducibility of the data obtained by the participants when using their own analytical methods, and possibly determine factors influencing the data quality. The measurement data reported by the participants were processed by the JRC (Air and Climate Unit, Ispra, Italy) to assess the *method performance* (section 2.2) and the *laboratory performances* (section 2.3). This effort was also supported by the EU H2020 EUROCHAMP-2020 project.

Since several participants in the current ILC also determined the concentrations of levoglucosan and other sugars in ambient particulate matter (PM) samples collected during the EMEP/ACTRIS/COLOSSAL Intensive Observation Period held in winter 2017 – 2018, the data quality measures "bias" and "variability" were also calculated (section 2.4).

1 Organization

1.1 Samples and sub-samples

This ILC was based on:

- Three (3) ambient (outdoor) PM_{10} aerosol samples (A, B, and C) collected with a high-volume sampler Tisch environmental TE-5000 total suspended particulate on quartz fiber filters during the winter period in Grenoble, France. Filters (Pallflex Tissuquartz 2500 QAT-UP 150mm in diameter and 432 µm in thickness) were stored in a refrigerator after sampling. Loadings of levoglucosan in the filters were declared by the organizer to be in the range 0.03 – 10 µg cm^{-2} prior to the beginning of the ILC.
- Two (2) aqueous standard solutions (E and F) prepared at IGE by dissolving a precisely known mass of pure (≥ 99.5%) levoglucosan, mannosan, and galactosan in a precisely known volume of ultra-pure water (resistivity ≥18.2 MΩ cm). Concentrations of levoglucosan in the solutions were declared by the organizer to be in the range 50 – 100 µg ml^{-1} prior to the beginning of the ILC. The difference between solution E and F (not disclosed to participants before the completion of the ILC) was that E contained other common species (like glucose, arabitol and sorbitol) on top of levoglucosan, mannosan, and galactosan.

The amounts of mannosan and galactosan were declared by the organizer to be in the range 5 – 20% of those of levoglucosan prior to the beginning of the ILC.

Aliquots of 2 ml for the solutions and 38 mm diameter punches randomly punched out from the test filters were distributed to participants in December 2017 and January 2018 for the participants that needed methanol matrix to allow them to perform triplicate measurements of each test sample.
The homogeneity of the test filter samples was determined from a filter sampled during the same period as filters A, B and C. The standard deviation of the average of the 13 punch analyses

was 5.6% for levoglucosan and 6.4% for both mannosan and galactosan. This values are upper limits for the filter homogeneity since they include the repeatability of the analyses.

1.2 Participants

Participation was open to ACTRIS-2 and EUROCHAMP partners, and to the laboratories involved in the EMEP/ACTRIS/COLOSSAL winter campaign 2017-2018. Nineteen laboratories volunteered to participate and were sent the test samples. Results were reported by 18 of the participants (Table 1). For brevity, the number assigned to each participant will be used in the remainder of the document.

Table 1: List of participants in the levoglucosan ILC 2018.

Code	Participant	Acronym	Analytical Technique
1	CONFIDENTIAL IN PUBLIC REPORT VERSION		HPLC-PAD
2	CONFIDENTIAL IN PUBLIC REPORT VERSION		HPAEC-PAD
3	CONFIDENTIAL IN PUBLIC REPORT VERSION		ICMS (quadrupole)
4	CONFIDENTIAL IN PUBLIC REPORT VERSION		GCMS
5	CONFIDENTIAL IN PUBLIC REPORT VERSION		HPAEC-PAD
6	CONFIDENTIAL IN PUBLIC REPORT VERSION		LCMS(TOF)
7	CONFIDENTIAL IN PUBLIC REPORT VERSION		HPAEC-PAD
8	CONFIDENTIAL IN PUBLIC REPORT VERSION		HPAEC-PAD
9	CONFIDENTIAL IN PUBLIC REPORT VERSION		GCMS
10	CONFIDENTIAL IN PUBLIC REPORT VERSION		GCMS
11	CONFIDENTIAL IN PUBLIC REPORT VERSION		HPAE-PAD
12	CONFIDENTIAL IN PUBLIC REPORT VERSION		GCMS
14	CONFIDENTIAL IN PUBLIC REPORT VERSION		GCMS
15	CONFIDENTIAL IN PUBLIC REPORT VERSION		HPAEC-PAD
16	CONFIDENTIAL IN PUBLIC REPORT VERSION		HPAEC-PAD
17	CONFIDENTIAL IN PUBLIC REPORT VERSION		GCMS
18	CONFIDENTIAL IN PUBLIC REPORT VERSION		GCMS
19	CONFIDENTIAL IN PUBLIC REPORT VERSION		GCMS

1.3 Shipment of samples and reporting of results

Test samples were shipped in closed vials and Petri dishes to all participants (except the "local" participant IGE) at ambient temperature without record. Participants were asked to report by 30 March 2018 the amounts of levoglucosan, galactosan and mannosan in μg cm^{-2} for the filter punches, and ng ml^{-1} for the solutions, as determined from three replicate analyses of each test samples. Due to a lack of information concerning the matrix needed for the analysis, samples were shipped again to participants # 4, 9, 10, 12, 14, 16, 17, 18, and 19 between January 30th and April 30th, 2018. Results were submitted by all participants within the deadline (Annex 1).

1.4 Analytical techniques

A complete description of all the various analytical techniques used by the participants will not be reported here. Instead, the SOPs of the successful participants will be posted on the ACTRIS SOP web page.

2 Data evaluation

2.1 Preliminary data screening and corrections

Prior to any statistical analysis, the data reported by the 18 participants were plotted to detect possible obvious errors.
The values reported by participants #18 for filter sample C seemed to correspond to the results of the analysis of the blank filter (Filter D) and vice-versa. The data reported for filters C and D by participants #18 were therefore swapped by the ILC coordinator.
The values reported by participants #4 and #9 for solutions E and F were all 3 orders of magnitude lower than the expected values. A unit error was suspected. The values reported by participants #4 and #9 for solutions E and F were therefore multiplied by 1000 by the ILC coordinator.

Several values reported by participants #9 and #14 were obviously discordant with the ensemble of values reported by the other participants. As recommended in ISO 13528:2015 (section 6.3), all values reported by participants were excluded for the calculation of the general averages, the method repeatability and reproducibility standard deviations, and the consensus values from participants to the round of the proficiency testing scheme.
It was not possible to clearly distinguish 2 (or more) populations of data in relation to the various extraction or analytical techniques applied. All data were therefore analyzed as a single set, data from Participant #9 and #14 excluded. The term "*method*" used in the remainder of this document therefore refers to the "*determination of levoglucosan, mannosan, and galactosan in filter and liquid samples*" without further details.

2.2 Method performance

2.2.1 Data evaluation description

The assessment of the *method performance* aims at deriving from the results of the ILC, the precision of the measurement method in terms of repeatability and reproducibility standard deviations. For this, the consistency of the dataset is evaluated by means of Cochran's test and Grubbs' test [ISO5725-2] for possible outliers (i.e. observations greater than the critical value at the 99% confidence level) or stragglers (i.e. observations greater than the critical value at the 95% confidence level but less or equal to the critical value at the 99% confidence level).

Cochran's test checks if the repeatability (within-laboratory consistency) of each participant is consistent with the repeatability reported by the ensemble of participants: for each test sample separately, Cochran's test assesses the consistency of the highest standard deviation value with those obtained by the other participants. After the removal of the outlier, if any, the test is repeated on the remaining standard deviations values. The critical values for Cochran's test vary upon the number of participants and the number of replicate measurements. In this ILC, 14 to 16 participants reported retained values for 3 replicates of every sample. Cochran's critical values ranged therefore from 0.388 to 0.407(outliers), and from 0.319 to 0.335 (stragglers).

Grubb's test regards the reproducibility (between-laboratory consistency) and checks the validity of the largest observation (or two largest as for G_2), and the validity of the smallest observation (or two smallest as for G_2). The critical values for Grubb's test vary upon the number

of participants. In this ILC, 14 (mannosan) to 16 (levoglucosan) participants reported retained values for every sample. The critical values for Grubb's test were for G_1 2.75-2.85 and 2.51-2.59, and for G_2 0.23-0.28 and 0.31-0.36, for outliers and stragglers, respectively.

Based on the outcomes of Grubbs' and Cochran's tests, outliers are discarded for the calculation of the general mean values, and the method repeatability and reproducibility standard deviations. Subsequently, the dependence of the method precision (i.e. repeatability and reproducibility) upon the mean values can be investigated [ISO 5725-2, section 7.4.5].

2.2.2 Results: method repeatability and reproducibility

2.2.2.1 *Within-laboratory consistency (repeatability).*

Figure 1 shows the normalized highest reproducibility variances calculated from the three analyses of each test sample. Data from participants #9 and #14 were excluded. Cochran's test identified the highest reproducibility standard deviations to be outliers for test samples A, E and F for levoglucosan, A for mannosan, and A, B, C and D for galactosan. The second highest reproducibility standard deviations of galactosan analyses were also detected as outliers for test samples B and D. Outliers were reported by 8 different participants, and no participant produced more than 2. Therefore, no data were further discarded based on the reproducibility standard deviation of the 3 replicates.

2.2.2.2 *Between-laboratory consistency*

Figure 2 shows the highest repeatability relative deviations to the general average normalized to the standard deviation of all data for each test sample, data from participants #9 and #14 excluded. For each couple (participant, test sample), the average of the 3 replicates is used as entry value. Grubb's test G_1 for 1 outlier (i.e. 1 positive and 1 negative value) did not detect any outlier (Figure 2). Grubb's test G_2 for 2 outliers neither. Therefore no data were further discarded based on their deviation from the general mean of the average value reported by the participants for each test sample.

2.2.2.3 *Repeatability and reproducibility standard deviations*

From the retained values (i.e. all data except those reported by participants #9 and #14) and for each sample separately, the general mean value, and the method repeatability (s_r) and reproducibility (s_R) standard deviations were calculated. The general means and the values of s_r and s_R for the 5 test samples are listed in Table 2 to Table 4.

The repeatability standard deviation s_r was quite similar in all test samples for all 3 compounds and ranged from 1.7 to 3.4% for levoglucosan, from 3.0 to 5.2% for mannosan and from 4.6 to 7.4% for galactosan. The reproducibility standard deviation s_R was quite similar in all test samples for levoglucosan (range = 16 to 19%). For mannosan, s_R ranged from 19 to 31%, except for the test solution E (53%). For galactosan, s_R ranged from 23 to 29%, except for the test filter C (47%). The relative standard deviations s_r and s_R (%) did not clearly depend on the general mean loadings m of filters A, B and C (µg/cm²), except perhaps for s_r of galactosan.

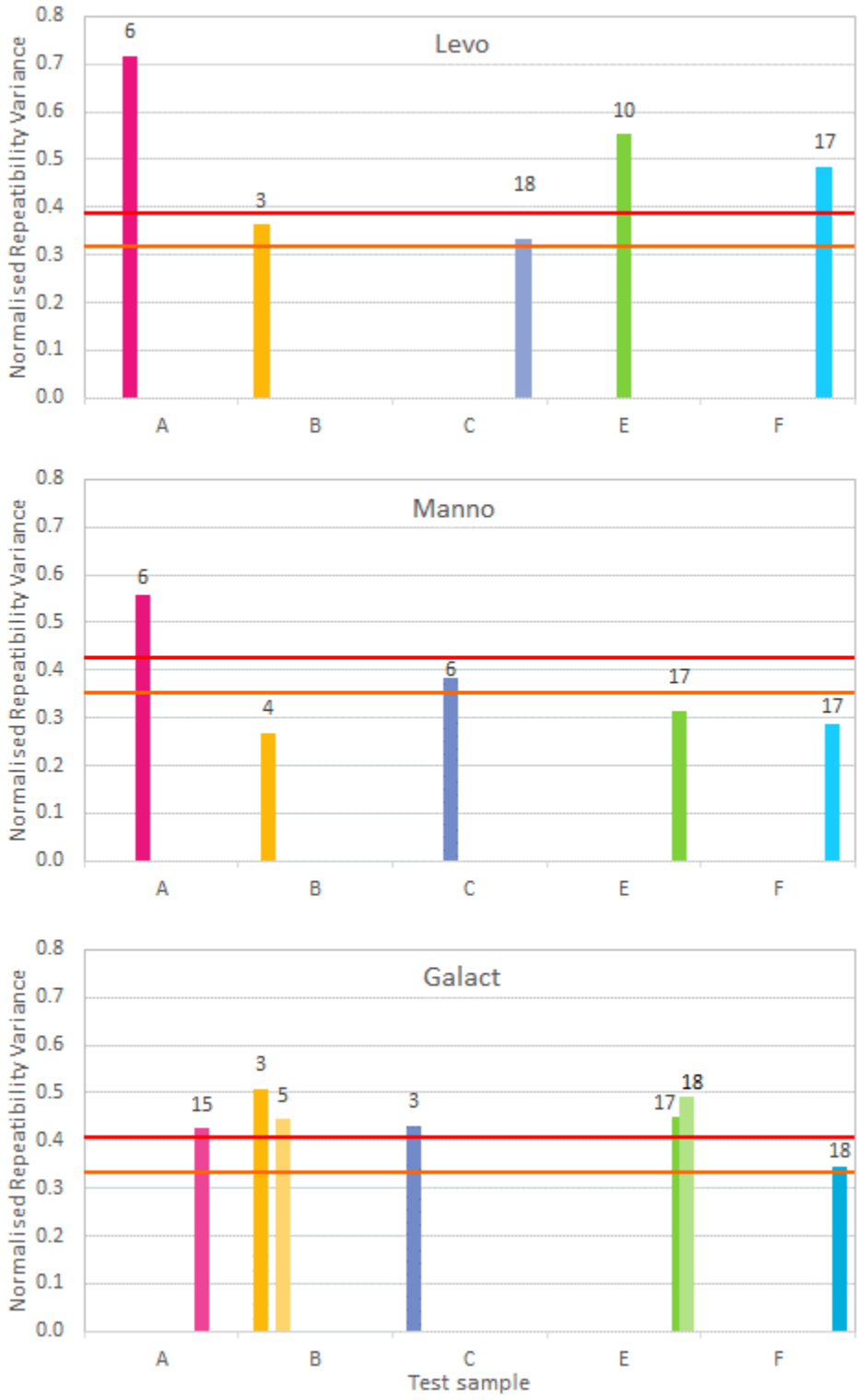

Figure 1. Highest normalized variance for each test sample, labelled as participant number (Cochran's test). Data from Participant #9 and #14 were excluded.

Table 2: General mean**,** repeatability (s_r) and reproducibility (s_R) standard and relative standard deviations for levoglucosan.

Levoglucosan		A	B	C	E	F
		µg/cm²	µg/cm²	µg/cm²	µg/ml	µg/ml
General mean	m	3.93	2.02	1.04	43.6	44.1
Repeatability	sr	0.11	0.03	0.03	0.9	1.5
	sr/m	2.9%	1.7%	3.2%	2.2%	3.4%
Reproducibility	sR	0.63	0.34	0.17	8.1	7.8
	sR/m	16%	17%	16%	19%	18%

Table 3: General mean, repeatability (s_r) and reproducibility (s_R) standard and relative standard deviations for mannosan**.**

Mannosan		A	B	C	E	F
		µg/cm²	µg/cm²	µg/cm²	µg/ml	µg/ml
General mean	m	0.434	0.235	0.101	7.05	5.32
Repeatability	sr	0.014	0.007	0.005	0.25	0.19
	sr/m	3.1%	3.0%	5.2%	3.6%	3.6%
Reproducibility	sR	0.084	0.050	0.022	3.73	1.63
	sR/m	19%	21%	22%	53%	31%

Table 4: General mean, repeatability (s_r) and reproducibility (s_R) standard and relative standard deviations for galactosan.

Galactosan		A	B	C	E	F
		µg/cm²	µg/cm²	µg/cm²	µg/ml	µg/ml
General mean	m	0.171	0.088	0.041	1.76	1.74
Repeatability	sr	0.008	0.005	0.003	0.09	0.08
	sr/m	4.7%	6.2%	7.4%	5.4%	4.6%
Reproducibility	sR	0.050	0.020	0.019	0.43	0.48
	sR/m	29%	23%	47%	25%	27%

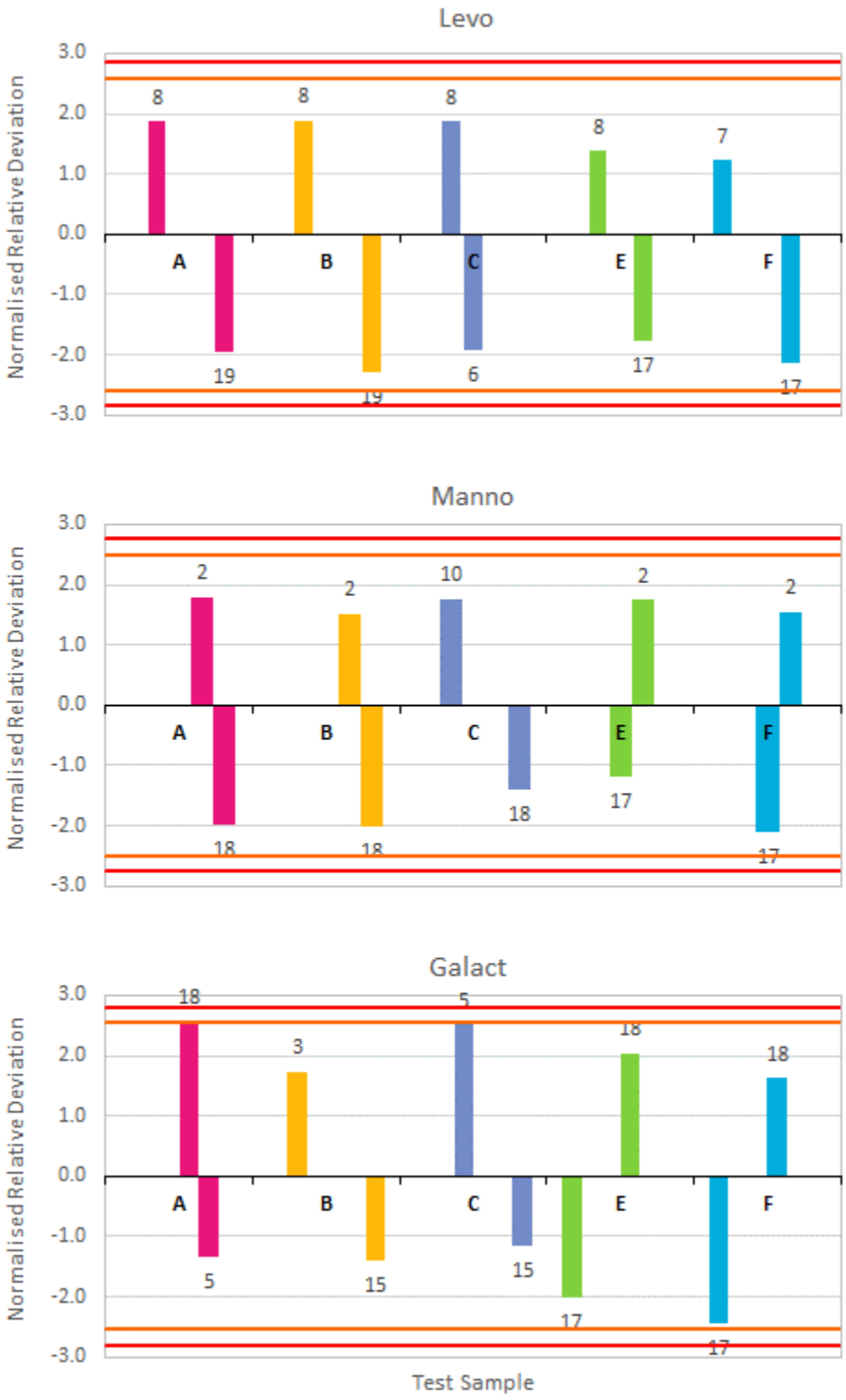

Figure 2. Highest relative deviations to the general mean normalized by the general standard deviation for each test sample (Grubb's test G_1). Labels indicate the number of the participant.

2.3 Participants' performance assessment

The assessment of the *laboratory performance* aims at describing the laboratory bias compared to the assigned value associated with its standard deviation. Each participant's performance is determined in terms of *z-scores,* a measure of the deviation from the assigned value. To calculate *z-scores*, an assigned value and its standard deviation have to be determined for each test sample.

2.3.1 Data evaluation

For each laboratory and test sample, the *z-score* was calculated as:

$$z = \frac{x_i - X}{\sigma^*} \quad (1)$$

where x_i is the result from the participant I (average from the 3 replicates), X is the assigned value for the sample; and σ^* is the standard deviation for proficiency assessment.

When a participant reports an entry that produces a bias greater than +3 z or less than -3 z (i.e. deviating from the assigned value for more than 3 standard deviations), this entry is considered to give an "action signal". Likewise, a laboratory bias above +2 z or below -2 z (i.e. deviating from the assigned value for more than 2 but less than 3 standard deviations) is considered to give a "warning signal". A laboratory bias between -2 z and +2 z indicates a satisfactory laboratory performance with respect to the standard deviation for proficiency assessment.

2.3.1.1 Filter samples

- *Determining the assigned value*: Among the available methods for determining the assigned value, the approach of the *consensus value from participants to a round of a proficiency testing scheme* was chosen, since the true values for levoglucosan, mannosan and galactosan in the ambient PM test filter samples cannot be known. With this approach, the assigned value *X* for each species in each test sample is determined as the robust average calculated, with a recursive algorithm, from the results reported by all participants, except those of which data were discarded a priori [ISO 13528:2015, section 7.7]. This approach might become statistically ineffective, for example if the number of participants is lower than twenty [ISO 13528:2015]. To verify their reliability, the robust mean (and its standard deviation) were also calculated applying the Q/Hampel method (ISO 13528:2015, Annex C). The robust mean did not significantly differ by more than ±2% from those obtained by the *consensus value from participant results* in Table 5, which are then used in the remainder of the statistical analysis.

- *Determining the standard deviation for proficiency assessment*: Among the available methods for determining the standard deviation for proficiency assessment (σ*), the approach of calculating σ* *from data obtained in a round of a proficiency testing scheme* was chosen. With this approach, σ* is the robust standard deviation calculated, with a recursive algorithm, from the results reported by all participants, except those of which data were discarded a priori [ISO 13528:2015, section 8.6].

- *Assigned values and standard uncertainties:* The assigned values *X* and the related standard deviations for proficiency assessment σ* calculated for each filter sample from the entire database (data from participant #9 and #14 excluded) are reported in Table 5.

Table 5: Loading values ± deviations for proficiency assessment assigned to Filters A, B and C (µg cm^{-2}).

Filter	Levoglucosan	Mannosan	Galactosan
A	3.98 ± 0.51	0.433 ± 0.079	0.161 ± 0.031
B	2.08 ± 0.21	0.234 ± 0.048	0.087 ± 0.021
C	1.05 ± 0.14	0.100 ± 0.022	0.039 ± 0.017

2.3.1.2 Solution samples

- *Determining the assigned values*: The concentrations *X* of levoglucosan, mannosan and galactosan in the test solutions E and F were assigned by formulation: each X was derived by calculation from the water volume used to make the solution, and the mass of each compound dissolved in this water volume [ISO 13528:2015, Section 7.3]. These concentrations are traceable to primary measurements.

- *Determining the standard uncertainty of the assigned values* u_X: the standard uncertainty is estimated by combination of uncertainties according to the law of propagation of errors as described in the *Guide to the expression of Uncertainty in Measurements*.

- *Determining the standard deviation for proficiency assessment*: For the test solutions E and F the standard deviation for proficiency assessment (σ*) was set by perception, i.e. reflecting the level of performance the ILC coordinator would wish participants to be able to achieve.

- *Assigned values and standard uncertainties:* The assigned values *X*, the expanded uncertainties (k = 2), and the related standard deviations for proficiency assessment σ* for the test solutions are reported in Table 6. The concentrations of levoglucosan, mannosan, and galactosan were the same in both solutions. The related standard deviations for proficiency assessment σ* were set to 15% of the assigned concentrations of levoglucosan, mannosan and galactosan, in line with the reproducibility that participants could practically achieve taking into account the reproducibility and repeatability of the method [ISO 13528:2015, section 8.2].

Table 6: Concentrations (*X*), expanded uncertainty (u_X) and standard deviations for proficiency assessment (σ^*) assigned to Solutions E and F (µg ml^{-1}).

	Levoglucosan	Mannosan	Galactosan
X	50.0	6.22	1.94
u_X	5.0	0.62	0.19
σ^*	7.5	0.93	0.29

2.3.2 Laboratory performance results

2.3.2.1 Test filter samples

Figure 3 shows the z-scores of all participants for the test filters A, B, and C. All numerical values are listed in Annex 2. The values reported by Participants #9 and #14 (which were so far excluded from the data analysis because they were obviously discordant) are generally outliers or stragglers. On top of those, one outlier was reported by each of Participants #18 (galactosan in C) and #19 (mannosan in B). Stragglers were reported by Participants #3 (galactosan in A), #4 (levoglucosan in B), #5 (galactosan in C), #6 (levoglucosan in B and C), #8 (levoglucosan in A, B and C), #10 (levoglucosan in A), #18 (mannosan in A, B), #19 (levoglucosan in B). In this ILC, all outliers and stragglers arise from a systematic over- or underestimation of the compound in question.

For each filter sample, 8 to 12 out of 16 to 18 participants show deviations from the assigned values within ±1 σ* (i.e. within 1 z-score) as listed in Table 5. The fraction of submitted values within ±15% of the assigned values was 70% for levoglucosan, 71% for and mannosan, and 57% for galactosan.

Although a contribution of filter heterogeneities to poor laboratory performances cannot be completely excluded, the recurrence of stragglers and/or outliers for single participants most probably suggests analytical biases compared to the other laboratories. Participants #9 and #14, and to a certain extent Participants #6, #8, #18 and #19 shall examine their procedures and identify appropriate corrective actions to improve the accuracy of their determination of levoglucosan and/or mannosan and/or galactosan.

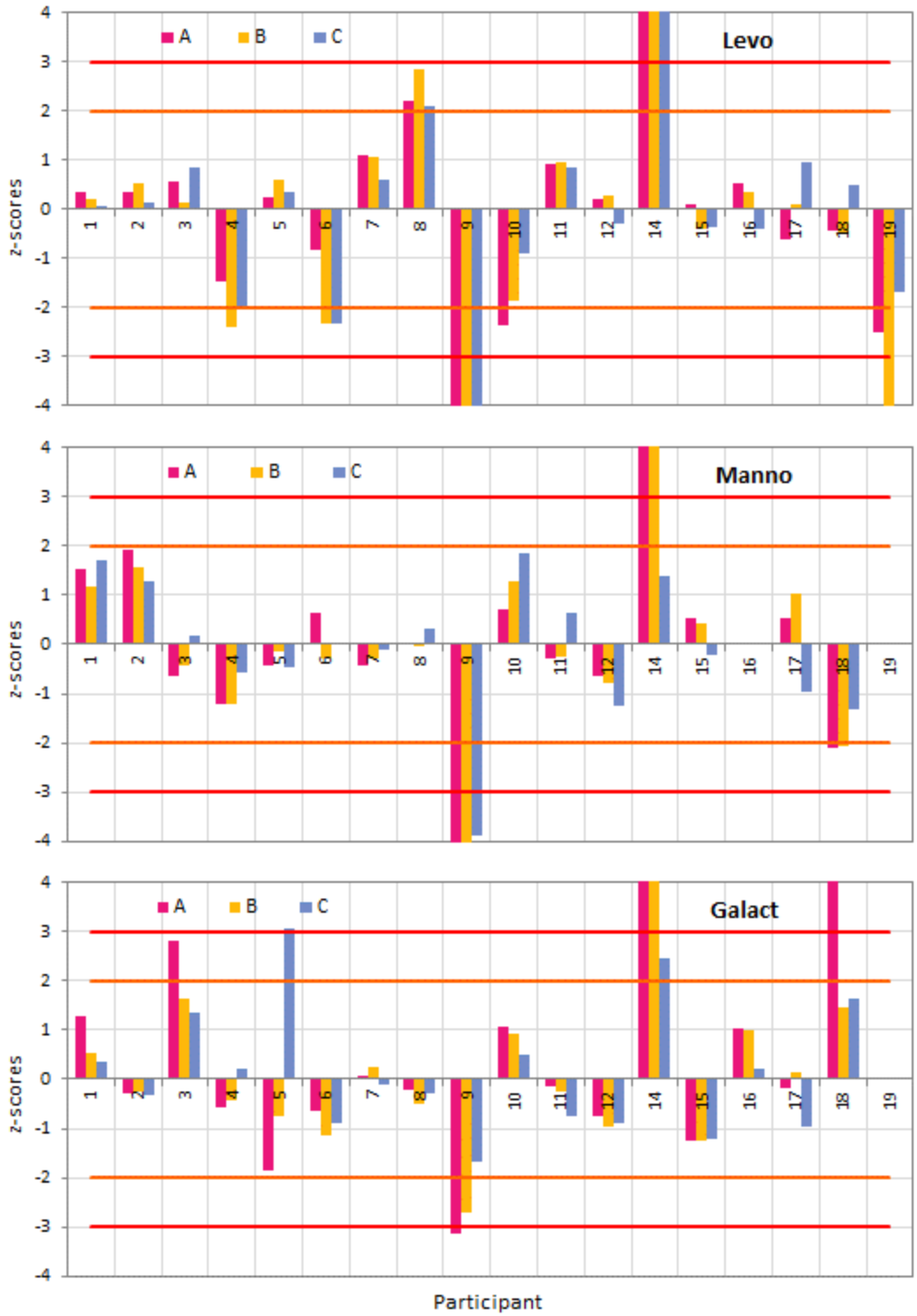

Figure 3. z-scores for levoglucosan, mannosan, and galactosan loadings in test filter samples A, B, and C calculated using σ* *from data obtained in the round of the proficiency testing scheme*. The scale for z-scores is arbitrary set to [-4, 4]. Participant #16 did not report mannosan concentrations, and Participant #19 did not report neither mannosan nor galactosan concentrations.

2.3.2.2 Standard solutions

Figure 4 shows the z-scores of all participants for the analysis of the test solutions E and F. All numerical values are listed in Annex 2. Most values reported by Participants #9 and #14 (which where a priori excluded from the data analysis because they were obviously discordant) were outliers. On top of those, a total of 10 outliers and 13 stragglers (Table 7) was reported by 10 different participants. Participants that reported more than 1 outlier or straggler are #9, #10, #12, #14, #17 and #18. In this ILC, most outliers and stragglers arise from a systematic over- or underestimation of the compound in question. However, 5 outliers were specific to solution E (i.e. not corresponding to a similar bias in Solution F), which suggests a probable interference of other compounds in the analysis of mannosan.

Table 7: number of outliers + stragglers in the determination of levoglucosan, mannosan, and galactosan in test solutions E and F, values reported by Participants #9 and #14 excluded.

Solution	Levoglucosan	Mannosan	Galactosan
E	0^a + 2	6 + 4	1^d + 2
F	1^b + 1	1^c + 3	1^e + 1

Note: taking into account the values reported by Participants #9 and #14, numbers become: a = 2, b = 3, c = 2, d = 3, and e = 3.

For Solution F, the number of participants reporting deviations from the assigned values within ± 1 σ* (i.e. within ± 15%) were 9/18 for levoglucosan, 11/16 for mannosan and 11/17 for galactosan. For solution E, these numbers are still 9/18 for levoglucosan, and decrease to 5/16 for mannosan and 10/17 for galactosan.

A significant contribution of the solutions' heterogeneity to poor laboratory performances can be excluded. The recurrence of stragglers and/or outliers for single participants most probably suggests analytical biases compared to the other laboratories. Participants #9, #10, #12, #14, #17 and #18 (all using gas chromatography techniques) shall examine their procedures and identify appropriate corrective actions to improve the accuracy of their determination of levoglucosan and/or mannosan and/or galactosan. Participants #2, #7, #8, #11, and #15 (all using liquid chromatography techniques) should investigate the possible interference of other species in their determination of mannosan concentrations.

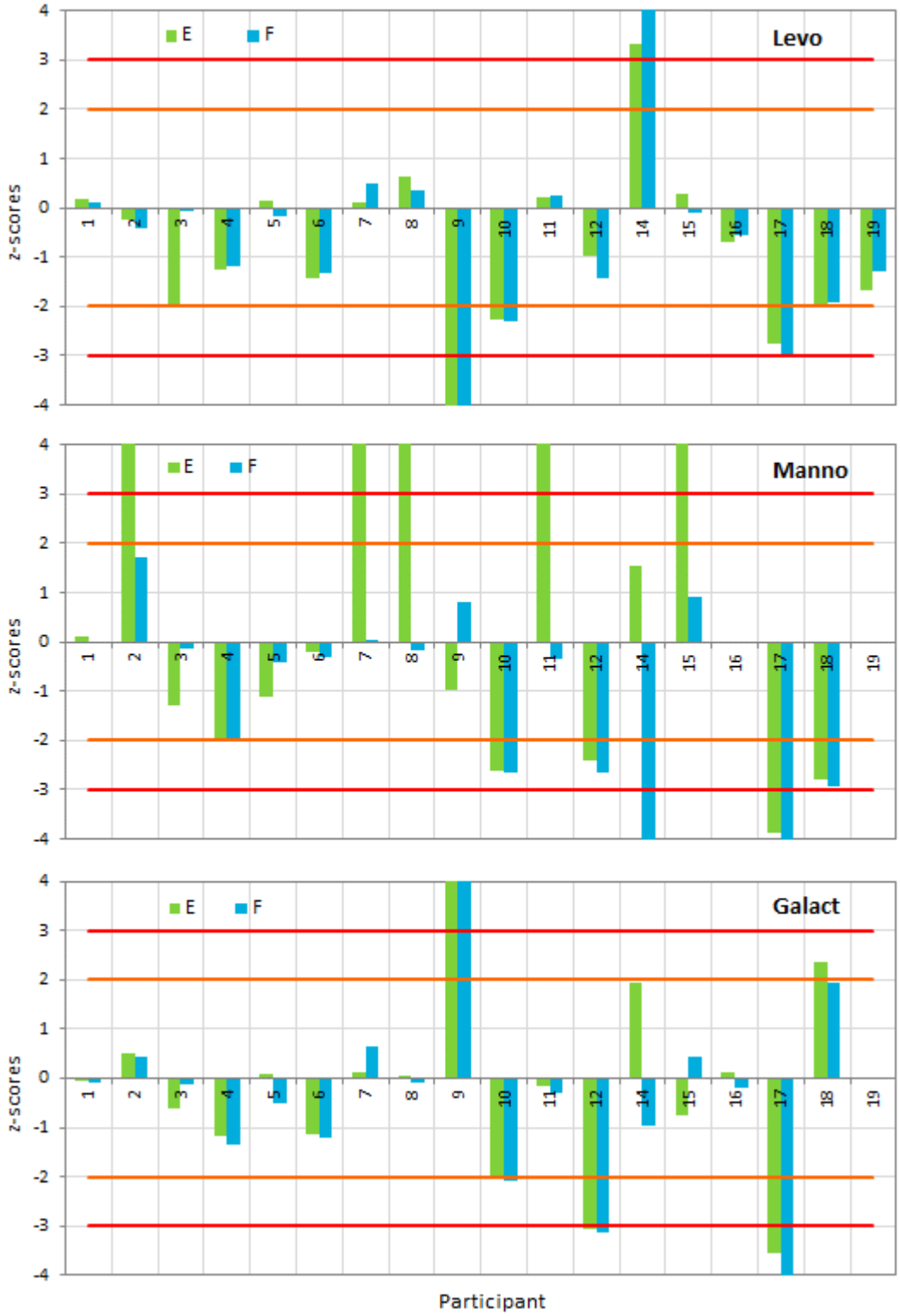

Figure 4. z-scores for levoglucosan, mannosan, and galactosan concentrations in test solutions E and F calculated using σ* *set by perception* (= 15% of the assigned values). The scale for z-scores is arbitrary set to [-4, 4]. Participant #16 did not report mannosan concentrations, and Participant #19 did not report neither mannosan nor galactosan concentrations.

2.4 Bias and variability

When reporting data to EBAS (ebas.nilu.no) for instance under the ACTRIS-2 project (www.actris.eu), it may be useful (and asked) to also report quality control measures (QCM) such as the bias and variability of the measurement data. These QCM were calculated based on the values reported for the loadings of levoglucosan, mannosan and galactosan in the test sample filters A, B, and C. Since the number of samples (3) was quite low, the statistical significance of these QCM can be questioned. However, systematic under- or overestimations of levoglucosan, mannosan and galactosan can probably provide useful hints for the interpretation of data obtained by different laboratories.

2.4.1 Data evaluation

2.4.1.1 Calculation of the systematic error or *"bias"*

For each laboratory and analyte, the QCM "*bias*" is calculated as the median of the relative differences δ_i between the values x_i reported by the participant and the assigned value X.

$$bias = median(\delta_i) = median(\frac{x_i - X}{X}) \quad (2)$$

where *i* is the test sample number.

2.4.1.2 Calculation of the random error or *"variability"*

For each laboratory and analyte, the QCM "*variability*" is estimated from the relative standard deviation (RSD) of the relative differences δ_i between the values x_i reported by the participant and the assigned value X. Assuming a triangular distribution of the relative differences, the RSD is estimated by:

$$u(\delta) = \frac{\delta_{max} - \delta_{min}}{2\sqrt{6}} \quad (3)$$

To cover the 95% confidence interval (k=2), the QCM "*variability*" is calculated as:

$$variability = 2\,.\,u(\delta) = \frac{\delta_{max} - \delta_{min}}{\sqrt{6}} \quad (4)$$

2.4.2 Bias and variability values

The QCM "*bias*" and "*variability*" for the determination of levoglucosan, mannosan and galactosan filter loadings are listed in Table 8. This Table translates the z-score results shown in Figure 3 into numerical values. When the QCM *bias* was not systematic for all 3 test filter samples, the *bias* value is reported in grey. It should be kept in mind that considering the low number of test samples, the statistical significance of the values listed in Table 8 is questionable.

The Table also indicates the type of chromatography used by the participants from the row fill color: no fill for liquid chromatography and light grey for gas chromatography. The blue and red fonts of the *bias* values indicate that some of the values reported by the participant for the compound in question were not retained by the iteration process which computed the assigned values and standard deviations used for the determination of z-scores (section 2.3.2.1) because they were too low or too high.

Table 8: Quality control measures "*bias*" and "*variability*" derived from the loading values reported by the participants for filter samples A, B, and C.

Participant	Levoglucosan		Mannosan		Galactosan	
	bias	variability	bias	variability	bias	variability
1	2%	1%	28%	5%	15%	5%
2	4%	1%	32%	3%	-6%	3%
3	7%	4%	-9%	6%	54%	7%
4	-24%	3%	-22%	5%	-11%	8%
5	5%	1%	-8%	3%	-18%	67%
6	-23%	9%	0.2%	7%	-28%	10%
7	11%	2%	-6%	2%	1%	4%
8	28%	0.2%	1%	3%	-13%	3%
9	-71%	9%	-84%	1%	-66%	5%
10	-18%	7%	27%	11%	20%	1%
11	12%	1%	-5%	8%	-6%	12%
12	2%	3%	-16%	6%	-24%	9%
14	207%	110%	193%	136%	267%	92%
15	-4%	3%	9%	6%	-31%	11%
16	4%	5%			19%	6%
17	1%	8%	10%	17%	-3%	18%
18	-5%	5%	-38%	6%	69%	20%
19	-32%	7%				

Note: Participant #5 reported mannosan values which were not all retained by the iteration process to compute the assigned values because one was too low (in A) and one was too high (in C).

Conclusions

This interlaboratory comparison for the measurement of levoglucosan, mannosan and galactosan in ambient PM samples deposited on filters and standard aqueous solutions led to the following main observations and results:

- The extraction solvent and techniques, as well as the analytical methods applied by the 18 participants were very diverse. Namely, 10 participants (1, 2, 3, 5, 6, 7, 8, 11, 15, 16) used liquid chromatography, 7 participants (4, 9, 10, 12, 14, 18, 19) used gas chromatography, and 1 participant (17) used gas chromatography for the filter samples, and liquid chromatography to analyze the liquid samples.
- Some of the results reported by Participants #4, #9, and #18 were obviously erroneous (wrong units, swapped samples) and were corrected by the ILC organizer. Most values reported by Participants #9 and #14 were discordant with the data reported by the other participants and were not considered for the calculation of statistics regarding the ensemble of the participants. All other data were analyzed as a single set, since it was not possible to distinguish data sub-sets in relation to the techniques applied.
- The method ***repeatability*** (1 standard deviation) ranged from 1.7 to 3.4% for levoglucosan, from 3.0 to 5.2% for mannosan and from 4.6 to 7.4% for galactosan. The method ***reproducibility*** (1 standard deviation) ranged from 16 to 19% for levoglucosan, from 19 to 53% for mannosan, and from 23 to 47% for galactosan. The repeatability and reproducibility relative standard deviations did not clearly depend on the loadings of samples A, B and C.
- ***Participants' performance*** in determining levoglucosan, mannosan and galactosan in ambient PM samples deposited on filters was assessed by calculating z-scores from the assigned values and the standard deviations for proficiency assessment σ*calculated from the data obtained by the participants in this ILC. Almost all values reported by Participant #9 and #14 were outliers or stragglers. In addition, Participants #6, #8, #18, and #19 reported 2 to 3 outliers + stragglers, of which 9/14 regarded levoglucosan. However, the percentages of values that were within ±15% of the assigned values were 70%, 71% and 57% for levoglucosan, mannosan, and galactosan, respectively.
- ***Participants' performance*** in determining levoglucosan, mannosan and galactosan in aqueous solutions was assessed by calculating z-scores from the assigned values derived from the solutions' formulation and the standard deviations for proficiency assessment σ* corresponding to the level of performance the ILC coordinator wished participants to achieve. σ* was set to 15% of the assigned concentration for levoglucosan, mannosan and galactosan. Most values reported by Participants #9 and #14 were outliers. However, Participants #10, #12, #17 and #18 also reported more than 1 outlier or straggler. While 8 participants (1, 3, 5, 7, 8, 11, 15, 16; all applying liquid chromatography) reported values all within ± 1σ* of the assigned values for solution F, only 2 (Participants #1 and #16) reported values all within ± 1σ* of the assigned values for solution E, where also other substances were present.
- ***Participants' bias and variability*** relative to the determination of levoglucosan, mannosan and galactosan in ambient PM deposited on filters were estimated since these data quality measures may be useful to the participants that submit data to EBAS. Most biases (>70%) were systematic and the variability of the bias was generally (>75%) less than the bias itself. However, considering the low number of test samples, the statistical significance of these "*bias*" and "*variability*" measures is questionable.

Glossary

- ACTRIS-2: EU funded H2020 project 654109 "Aerosol, Clouds and TRace gases Research Infrastructure" (www.actris.eu)
- COLOSSAL: EU funded COST Action CA16109 Chemical On-Line cOmpoSition and Source Apportionment of fine aerosoL (www.costcolossal.eu)
- EBAS: EMEP data base (emep.nilu.no)
- EMEP: co-operative programme for monitoring and evaluation of the long range transmission of air pollutants in Europe under the UN-ECE Convention on Long-Range Transboundary Air pollution (www.emep.int)
- EUROCHAMP: EU funded H2020 project 730997 "Integration of European Simulation Chambers for Investigating Atmospheric Processes" (www.eurochamp.org)
- Galactosan: 1,6-anhydro-D-galactose
- Levoglucosan: 1,6-anhydro-D-glucopyranose
- Mannosan: 1,6-anhydro-D-mannopyranose

References

ISO 5725-2. Accuracy (trueness and precision) of measurement methods and results -- Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method. ISO, Geneva, 1994.

ISO 13528. Statistical methods for use in proficiency testing by inter-laboratory comparisons. ISO, Geneva, 2015.

Annex 1. Numerical results reported by participants

Levoglucosan

Sample >	A	B	C	D	E	F
Participant #	µg/cm²	µg/cm²	µg/cm²	µg/cm²	ng/ml	ng/ml
1	4.141	2.106	1.074		51222	50672
	4.201	2.160	1.069		51881	50892
	4.141	2.100	1.031		51222	50782
2	4.116	2.182	1.091		48259	46967
	4.084	2.188	1.108		47800	46795
	4.262	2.189	1.010		48261	46941
3	4.274	2.047	1.194		35081	48710
	4.236	2.202	1.130		35733	50790
	4.282	2.082	1.188		35100	49294
4	3.260	1.570	0.765		40.676	41.234
	3.240	1.620	0.767		41.272	41.485
	3.210	1.580	0.779		40.100	40.995
5	4.100	2.200	1.100		50127	48426
	4.100	2.200	1.100		51365	49107
	4.100	2.200	1.100		51699	48801
6	3.440	1.590	0.680	0.000	38600	39200
	4.000	1.620	0.700	0.011	39700	41400
	3.260	1.600	0.770	0.013	40000	39900
7	4.527	2.298	1.113		50868	53408
	4.542	2.311	1.143		50906	53658
	4.536	2.292	1.143		50687	53761
8	5.055	2.658	1.344		54702	52738
	5.106	2.659	1.347		54693	52668
	5.155	2.661	1.349		54691	52693
9	1.580	0.624	0.192	0.001	16.25	4.59
	1.630	0.624	0.199	0.001	14.85	3.33
	1.490	0.581	0.181	0.001	11.23	3.01
10	2.950	1.780	0.970		31340	35380
	2.710	1.670	0.920		31290	32130
	2.710	1.650	0.880		36180	30910
11	4.370	2.250	1.150		51260	51910
	4.450	2.290	1.170		52120	52080
	4.550	2.290	1.190		51600	51940
12	4.134	2.121	1.045	0.003	42316	38430
	4.021	2.153	1.001	0.003	42449	40060
	4.088	2.123	0.981	0.003	43597	39223
14	12.160	9.670	1.860	0.090	74354	107986
	12.090	9.780	2.190	0.090	74786	107035
	12.400	9.880	2.280	0.090	75786	109591
15	4.000	1.980	0.996		52100	49400
	4.050	2.010	0.997		52100	49090
	4.060	2.000	0.999		52400	49200
16	4.240	2.150	0.998		45700	45900
	4.260	2.160	0.978		44900	45900
	4.240	2.150	0.994		43700	45600
17	3.674	2.142	1.196		29850	31956
	3.693	2.116	1.159		30192	26828
	3.643	2.048	1.196		27929	23630
18	3.738	2.011	0.004	1.206	34218	34761
	3.885	1.964	0.004	1.080	35896	33360
	3.672	1.956	0.003	1.070	35599	38564
19	2.710	1.240	0.780		36074	40264
	2.680	1.250	0.780		37373	36929
	2.700	1.220	0.810		36723	38596

Mannosan

Sample >	A	B	C	D	E	F
Participant #	µg/cm²	µg/cm²	µg/cm²	µg/cm²	ng/ml	ng/ml
1	0.549	0.289	0.140		6323	6200
	0.554	0.299	0.140		6353	6200
	0.553	0.288	0.130		6315	6193
2	0.582	0.308	0.128		13400	7870
	0.582	0.310	0.128		13500	7840
	0.587	0.312	0.128		13800	7810
3	0.388	0.202	0.106		4820	5780
	0.385	0.223	0.102		5040	6320
	0.378	0.217	0.102		5190	6210
4	0.344	0.187	0.088		4.324	4.404
	0.324	0.179	0.085		4.120	4.180
	0.342	0.160	0.089		4.540	4.606
5	0.390	0.240	0.087		5165	5778
	0.400	0.220	0.092		5222	5879
	0.410	0.220	0.090		5188	5847
6	0.510	0.230	0.086	0.000	6200	6300
	0.440	0.220	0.108	0.003	6300	5800
	0.500	0.213	0.106	0.003	5600	5700
7	0.405	0.221	0.099		10616	6245
	0.398	0.221	0.097		10564	6210
	0.397	0.222	0.096		10635	6267
8	0.439	0.233	0.107		10162	6065
	0.436	0.233	0.107		10065	6071
	0.433	0.233	0.106		10099	6091
9	0.079	0.039	0.016	0.0004	5.36	7.06
	0.079	0.038	0.016	0.0003	5.05	6.87
	0.072	0.034	0.015	0.0004	5.48	6.99
10	0.510	0.300	0.150		3574	3978
	0.480	0.300	0.140		3537	3696
	0.480	0.290	0.130		4183	3525
11	0.401	0.220	0.110		10636	5955
	0.408	0.224	0.114		10675	5946
	0.422	0.222	0.116		10526	5843
12	0.375	0.195	0.076	0.0004	3899	3944
	0.386	0.197	0.071	0.0003	4038	3676
	0.382	0.196	0.071	0.0003	4001	3606
14	1.150	1.030	0.120		7710	2348
	1.280	1.080	0.130		7750	2274
	1.370	1.150	0.140		7500	2406
15	0.487	0.251	0.102		13314	6961
	0.477	0.259	0.097		12722	7302
	0.458	0.255	0.086		12895	6944
16						
17	0.485	0.280	0.078		2936	2187
	0.471	0.294	0.079		2901	1988
	0.469	0.282	0.080		1997	1447
18	0.256	0.137	0.0004	0.072	3643	3481
	0.273	0.126	0.0004	0.069	3260	3429
	0.276	0.139	0.0004	0.071	3920	3547
19						

Galactosan

Sample >	A	B	C	D	E	F
Participant #	µg/cm²	µg/cm²	µg/cm²	µg/cm²	ng/ml	ng/ml
1	0.200	0.100	0.049		1913	1886
	0.201	0.099	0.046		1953	1920
	0.200	0.098	0.041		1913	1926
2	0.149	0.080	0.034		2070	2040
	0.151	0.083	0.034		2060	2080
	0.157	0.082	0.034		2120	2070
3	0.235	0.107	0.060		1700	1990
	0.244	0.137	0.055		1690	1880
	0.261	0.122	0.070		1900	1840
4	0.141	0.078	0.044		1.597	1.578
	0.144	0.080	0.042		1.602	1.438
	0.145	0.075	0.044		1.594	1.628
5	0.098	0.083	0.087		1932	1790
	0.112	0.066	0.092		1969	1770
	0.102	0.066	0.090		1988	1810
6	0.136	0.061	0.022		1640	1620
	0.156	0.062	0.027		1610	1620
	0.132	0.066	0.025		1590	1540
7	0.164	0.093	0.035		1965	2119
	0.161	0.092	0.042		1989	2167
	0.162	0.093	0.036		1982	2107
8	0.154	0.071	0.034		1957	1920
	0.153	0.080	0.033		1953	1925
	0.153	0.079	0.035		1963	1913
9	0.067	0.031	0.011	0.001	4.12	5.06
	0.066	0.030	0.012	0.001	4.07	4.86
	0.061	0.028	0.011	0.001	4.19	4.91
10	0.200	0.107	0.049		1280	1402
	0.190	0.107	0.047		1293	1327
	0.190	0.107	0.046		1471	1288
11	0.154	0.081	0.026		1848	1885
	0.153	0.083	0.027		1929	1840
	0.162	0.082	0.027		1903	1844
12	0.134	0.068	0.026	0.0001	1025	1087
	0.139	0.067	0.024	0.0001	1069	1025
	0.139	0.065	0.024	0.0001	1042	981
14	0.560	0.360	0.080		2210	1657
	0.570	0.370	0.080		2761	1623
	0.640	0.390	0.080		2532	1696
15	0.140	0.060	0.020		1758	2030
	0.129	0.061	0.019		1633	2031
	0.100	0.061	0.019		1759	2145
16	0.193	0.105	0.047		1940	1890
	0.192	0.110	0.038		1990	1980
	0.191	0.111	0.043		2000	1780
17	0.155	0.089	0.024		1106	739
	0.155	0.092	0.023		973	583
	0.156	0.091	0.023		631	443
18	0.307	0.111	0.0003	0.069	2428	2640
	0.290	0.117	0.0004	0.067	2632	2587
	0.294	0.127	0.0003	0.063	2807	2299
19						

Annex 2: z-scores

Levoglucosan

Participant #	A	B	C	E	F
1	0.3	0.2	0.1	0.19	0.10
2	0.3	0.5	0.1	-0.25	-0.41
3	0.6	0.2	0.9	-1.96	-0.05
4	-1.5	-2.4	-2.0	-1.24	-1.17
5	0.2	0.6	0.4	0.14	-0.16
6	-0.8	-2.3	-2.3	-1.41	-1.31
7	1.1	1.1	0.6	0.11	0.48
8	2.2	2.8	2.1	0.62	0.36
9	-4.8	-7.2	-6.0	-4.79	-6.18
10	-2.4	-1.8	-0.9	-2.28	-2.29
11	0.9	1.0	0.9	0.22	0.26
12	0.2	0.3	-0.3	-0.96	-1.44
14	16.3	37.5	7.5	3.33	7.76
15	0.1	-0.4	-0.4	0.29	-0.10
16	0.5	0.4	-0.4	-0.70	-0.56
17	-0.6	0.1	1.0	-2.76	-3.00
18	-0.4	-0.5	0.5	-1.97	-1.93
19	-2.5	-4.0	-1.7	-1.68	-1.30

Mannosan

Participant #	A	B	C	E	F
1	1.5	1.2	1.7	0.12	-0.02
2	1.9	1.6	1.3	7.87	1.74
3	-0.6	-0.4	0.2	-1.29	-0.13
4	-1.2	-1.2	-0.6	-2.03	-1.95
5	-0.4	-0.2	-0.5	-1.10	-0.41
6	0.6	-0.3	0.0	-0.20	-0.31
7	-0.4	-0.3	-0.1	4.70	0.02
8	0.0	0.0	0.3	4.17	-0.15
9	-4.5	-4.1	-3.9	-0.99	0.81
10	0.7	1.3	1.9	-2.63	-2.67
11	-0.3	-0.3	0.6	4.71	-0.33
12	-0.7	-0.8	-1.2	-2.40	-2.66
14	10.6	17.6	1.4	1.54	-4.16
15	0.5	0.4	-0.2	7.24	0.91
16					
17	0.5	1.0	-1.0	-3.87	-4.66
18	-2.1	-2.1	-1.3	-2.80	-2.93
19					

Annex 2: z-scores (cont'd)

Mannosan

Participant #	A	B	C	E	F
1	1.5	1.2	1.7	0.12	-0.02
2	1.9	1.6	1.3	7.87	1.74
3	-0.6	-0.4	0.2	-1.29	-0.13
4	-1.2	-1.2	-0.6	-2.03	-1.95
5	-0.4	-0.2	-0.5	-1.10	-0.41
6	0.6	-0.3	0.0	-0.20	-0.31
7	-0.4	-0.3	-0.1	4.70	0.02
8	0.0	0.0	0.3	4.17	-0.15
9	-4.5	-4.1	-3.9	-0.99	0.81
10	0.7	1.3	1.9	-2.63	-2.67
11	-0.3	-0.3	0.6	4.71	-0.33
12	-0.7	-0.8	-1.2	-2.40	-2.66
14	10.6	17.6	1.4	1.54	-4.16
15	0.5	0.4	-0.2	7.24	0.91
16					
17	0.5	1.0	-1.0	-3.87	-4.66
18	-2.1	-2.1	-1.3	-2.80	-2.93
19					