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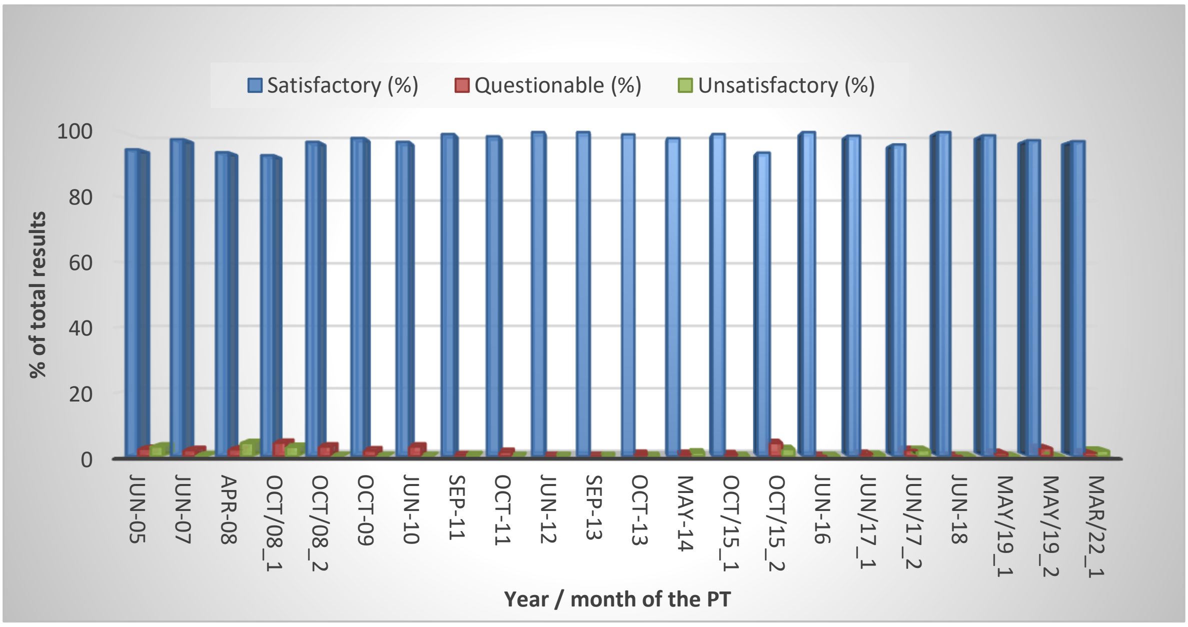
PROFICIENCY TESTING SCHEME Measurement of inorganic gaseous pollutants (SO_2, CO, O_3, NO and NO_2) in filtered ambient air (21-24 March 2022, Ispra-Italy)

European Commission harmonisation programme for air quality measurements

Barbiere M., Tarricone C., Lagler F., Borowiak A.

2022



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Abstract

Within the harmonisation programme of Air Quality monitoring in Europe the European Reference Laboratory of Air Pollution (ERLAP) organises Proficiency Tests (PT). From the **21st to the 24th of March 2022**, including ERLAP, seven Laboratories of AQUILA (Network of European Air Quality Reference Laboratories) met for a laboratory comparison exercise in Ispra (IT) to evaluate their proficiency in the analysis of inorganic gaseous air pollutants (NO, NO2, SO2, CO and O3) covered by the European Air Quality Directive 2008/50 EC [1] and its last amendments 2015/1480/EC [42].

Two laboratories (A and L) didn't report values for NO and NO2. Laboratory F didn't' report uncertainty values for all zero level of concentrations of each pollutant.

The proficiency evaluation, where each participant's bias was compared to two criteria, provides information on the current situation and capabilities to the European Commission and can be used by participants in their quality control system.

Based only on the z/z'-score evaluation, between all the results reported, two values were found to be **questionable (1.1%)** and three were **unsatisfactory (1.7%)** and the rest of the values **(97.2%)** were **satisfactory**.

Considering the repeatability and reproducibility evaluation, the results among AQUILA participants at the highest generated concentration levels is satisfactory for measurements of all pollutants beside the SO2 that is affected by the presence of some unsatisfactory values.

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1 Introduction

The Directive 2008/50/EC [1] and its last amendments 2015/1480/EC [42] on ambient air quality and cleaner air for Europe sets a framework for a harmonised air quality assessment in Europe.

One important objective of the Directive [1] is that the ambient air quality shall be assessed on the basis of common methods and criteria. It deals with the air pollutants sulphur dioxide (SO2), nitrogen dioxide (NO2) and nitrogen monoxide (NO), particulate matter, lead, benzene, carbon monoxide (CO) and ozone (O3). Among others it specifies the reference methods for measurements and Data Quality Objectives (DQOs) for the accuracy of measurements.

The European Commission (EC) has supported the development and publication of reference measurement methods for CO [2], SO2 [3], NO-NO2 [4] and O3 [5] as European standards. Appropriate calibration methods [6], [7] and [8] have been standardised by the International Organization for Standardization (ISO).

As foreseen in the Air Quality Directive [1, 42], the European Reference Laboratory of Air Pollution (ERLAP) of the Directorate for Energy, Transport and Climate at the Joint Research Centre (JRC) organises Proficiency Tests (PT) to assess and improve the status of comparability of measurements of National Reference Laboratories (NRL) of the Member States of the European Union.

The World Health Organization Collaborating Centre for Air Quality Management and Air Pollution Control, Berlin (WHO CC) is carrying out similar activities since 1994 [9] [10], [24], [31], [35], [38], [45] and [50] but with a view to obtaining harmonised air quality data for health related studies. Their programme integrates within the WHO EURO region, which includes public health institutes and other national institutes - especially from the Central Eastern Europe, Caucasus and countries from Central Asia.

Starting in 2004, it has been decided to bring together the efforts of both the JRC-ERLAP and WHO CC and to coordinate activities as far as possible, with a view to optimise resources and improve international harmonisation.

This report deals with the PT that took place from the **21st to the 24th of March 2022** in Ispra (IT).

Since 1990 ERLAP has organised PT in order to evaluate the comparability of measurements carried out by NRLs and promote information exchange among the expert laboratories. Recently, a more systematic approach has been adopted, in agreement with the Network of National Reference Laboratories for Air Quality (AQUILA) [11], aiming to both provide an alert mechanism for the purposes of the EC legislation and support the implementation of quality schemes by NRLs.

ERLAP is accredited to the latest version of the standard ISO 17025 and ISO 17043 for the pollutants and EN standard methods used during this proficiency test (EN 14211:2012-NO/NO2, EN 14212:2012-SO2, EN 14625:2012-O3, EN 14626:2012-CO) as proved by the certificate in Annex F.

The methodology for the organisation of PT was developed by ERLAP in collaboration with AQUILA and is described in a paper on the organisation of laboratory comparison exercises for gaseous air pollutants [12].

This evaluation scheme was adopted by AQUILA in December 2008 and is applied to all PT since then. It contains common criteria to alert the EC on possible performance failures, which do not rely solely on the uncertainty claimed by participants. The evaluation scheme implements the z-score and z'-score method [13] with the uncertainty requirements for calibration gases stated in the European standards [2], [3], [4] and [5], which are consistent with the DQOs of European Directives.

According to the above-mentioned Directive [1, 42], NRLs with an overall unsatisfactory performance in the z/z'-score evaluation **(one unsatisfactory or two questionable results per parameter)** is asked to repeat their participation in the following PT in order to demonstrate remediation measures [12]. In addition, considering that the evaluation scheme should be useful to participants for accreditation according to ISO 17025, they are requested to include their measurement uncertainty. Hence, participants' results (measurement values and uncertainties) are also compared to the assigned values applying the En–score method [13].

Beside the proficiency of participating laboratories, the repeatability and reproducibility of standardised measurement methods [14], [15] and [16] are evaluated as well. These group evaluations are useful indicators of trends in measurement quality over different proficiency tests.

2 Proficiency test organisation

In September 2021**,** ERLAP announced to the members of the AQUILA network and the WHO CC representative the PT programme for the following year. Due to the large number of requests an extra PT was organised in March 2022. Registration was opened in **February 2021** and closed the second week of **March 2021**.

Every participant, together with the registration confirmation, received a detailed protocol with all the necessary information about the PT. Each laboratory was required to bring their own measurement instruments, data acquisition equipment and travelling standards (to be used for calibrations or checks during the PT).

The participants were invited to arrive on **Monday, 21st of March 2022**, for the installation of their equipment. The calibration of NOx and O3 analysers was carried out the morning of the following day and the generation of NOx and O3 gas mixtures started at 11:00 on Tuesday.

The calibration of SO2 and CO analysers was carried out on Wednesday afternoon and the generation of CO and SO2 gas mixtures started at 20:00 of the same day.

The test gases generation and measurements finished on Thursday at 9:00.

3 Participants

All participants (Table 1) were organisations dealing with the routine ambient air monitoring or institutions involved in environmental or public health protection. The national representatives came from France, Estonia, Croatia, Germany, Spain and Greece.

Table 1: List of participating organizations.

Acronym	Institute	Country	Code
INERIS	Institut National de l'Environnement Industriel et des Risques	France	A
EERC	Estonian Environmental Research Centre	Estonia	B
DHZ-TEST	Meteorological and Hydrological Service - TEST	Croatia	C
UBA	Federal Environment Agency	Germany	E
ISCIII	Instituto De Salud Carlos III	Spain	F
ERLAP	European Reference Laboratory for Air Pollution	European Commission	G
NRLAQ	Ministry of Environment & Energy	Greece	L

Source: JRC 2022

The following Table 2 reports the manufacturer and model of the instrumentations used by every participant during the Proficiency Test, including those used in the calculation of the assigned values. This information has been reported by the participants through a web interfaced questionnaire as described in the protocol.
The list contains technical information and cannot be considered as an implicit or explicit endorsement by the organisers of any specific instrumentation.
Some laboratories didn't fill in the questionnaire about this PT so some information are missing in Table 2.

Table 2: List of instruments used by participants.

Code	Parameter	Analyser
A	SO_2	*Not reported*
B		Horiba APSA 360
C		Teledyne API T100
E		Horiba APSA 370
F		Teledyne T100
G		Thermo 43i TLE, 2015
L		Teledyne-API T100
A	NO/NO_2	*Not reported*
B		Horiba APNA 360
C		Teledyne API T200
E		Horiba APNA 370
F		Thermo, TE42i
G		Thermo, TE42iTL, 2015
L		Teledyne-API T200
A	CO	*Not reported*
B		Horiba APMA 360
C		Horiba APMA 370
E		Horiba, APMA-370
F		Thermo 48i
G		Horiba, APMA-370, 2021
L		Teledyne-API T300
A	O_3	*Not reported*
B		Horiba OZGU 360
C		Teledyne API T400
E		Thermo 49I B2NAB
F		Thermo 49i
G		Thermo, 49-iPS , 2015
L		Teledyne-API T400

Source: JRC 2022

4 Preparation of test mixtures

The ERLAP PT facility has been described in several reports [17], [18]. During this PT, gas mixtures were prepared for SO2, CO, O3, NO and NO2 at concentration levels around limit values, critical levels and assessment thresholds set by the European Air Quality Directive [1].

Table 3: Sequence program of generated test gases with indicative pollutant concentrations

day	start time	duration	parameter	installation	calibration	Zero Air	NO	NO2	O3	CO	SO2
		h				nmol/mol	nmol/mol	nmol/mol	nmol/mol	µmol/mol	nmol/mol
1st	09:00		/	X							
2nd	08:00	3	/		X						
2nd	11:00	1	NO-NO2-O3			X					
2nd	12:00	2	NO-NO2				120				
2nd	14:00	2	NO-NO2				70	50			
2nd	16:00	2	O3						60		
2nd	18:00	2	NO-NO2				25				
2nd	20:00	2	NO-NO2				15	10			
2nd	22:00	2	O3						15		
3rd	00:00	2	NO-NO2				60				
3rd	02:00	2	NO-NO2				35	25			
3rd	04:00	2	O3						35		
3rd	06:00	2	NO-NO2				480				
3rd	08:00	2	NO-NO2				380	100			
3rd	10:00	2	O3						110		
3rd	12:00	2	NO-NO2				300				
3rd	14:00	2	NO-NO2				170	130			
3rd	16:00	2	O3						130		
3rd	18:00	2	/		X						
3rd	20:00	1	CO-SO2			X					
3rd	21:00	2	CO-SO2							3	125
3rd	23:00	2	CO-SO2							8	50
4th	01:00	1	CO-SO2				X	Not to be reported			
4th	02:00	2	CO-SO2							5	35
4th	04:00	2	CO-SO2							1.5	19
4th	06:00	2	CO-SO2							0.9	8
4th	08:00	1	/								
4th	09:00	END									

Source: JRC 2022

The sequence programme of generated test gases is given in Table 3.
The test mixtures were prepared by the dilution of gases from cylinders containing high concentrations of NO, SO2 or CO using thermal mass flow controllers [8]. O3 was added using an ozone generator and NO2 was produced applying the gas phase titration method [19] in a condition of NO excess.
The participants were required to report three half-hour-mean measurements for each concentration level (run) in order to evaluate the repeatability of standardised measurement methods. Zero value concentration levels were generated for one hour and one half-hour-mean measurement was requested to be reported.

5 The evaluation of laboratory's measurement proficiency

To evaluate the participant's measurement proficiency, the methodology described in ISO 13528 [13] was applied and measurement results of ERLAP were used as the assigned/reference values for the whole PT [12].
The traceability of ERLAP's measurement results and the assigned values list are presented in Annex A. In the following proficiency evaluations, the uncertainty of test gas homogeneity (Annex A) was added to the uncertainties of ERLAP's measurement results.
All data reported by participating laboratories are presented in Annex B.
As described in the AQUILA document 37 [12], the proficiency of the participants was assessed by calculating two performance indicators.
The following performance indicators, z-score and z'-score (z/z'-score), verify if the difference between the participants measured value and the assigned/reference value remains within the limits of a common criterion. The choice between z/z'-score is consequence to the meeting of the criterion $u_{Xpt}<0.3\sigma_{pt}$ described in the standard ISO 13528 (par. 9.2) [13], where the uncertainty of the assigned value (u_{Xpt}) is compared to $0.3\sigma_{pt}$. When the criterion is met, the z-score is used, in the other case z'-score is applied. In Annex D a table is showing the values obtained during this evaluation and the selected indicator used for each measurement.
The second performance indicator (En-score) verifies if the difference between the participants measured values and assigned/reference value remains within the limits of a criterion, that is calculated individually for each participant, from the uncertainty of the participant's measurement result and the uncertainty of the assigned/reference value.

5.1 z-score – z'-score

The z/z'- score performance indicators are calculated according to ISO 13528 (par. 9.4 and 9.5) [13] as:

$$z = \frac{(x_i - X)}{\sqrt{\sigma_{pt}^2}} = \frac{(x_i - X)}{\sqrt{(a \cdot X + b)^2}}$$ Equation 1

$$z' = \frac{(x_i - X)}{\sqrt{\sigma_{pt}^2 + u_X^2}} = \frac{(x_i - X)}{\sqrt{(a \cdot X + b)^2 + u_X^2}}$$ Equation 2

z = z-score
z' = z'-score
x_i = participant average values
X = the assigned/reference value
u_X = uncertainty of the assigned/reference value
σ_{pt} = Standard deviation for proficiency assessment
a = slope see table 4
b = intercept see table 4

In the European standards [2], [3], [4] and [5] the uncertainties for calibration gases used in ongoing quality control are prescribed. In fact, it is stated that the maximum permitted expanded uncertainty for calibration gases is 5% and that 'zero gas' shall not give instrument reading higher than the detection limit. As one of the tasks of NRLs is to supply calibration gas mixtures, the 'standard deviation for proficiency assessment' (σ_{pt}) [13] is calculated in fitness-for-purpose manner from requirements given in European standards.
Over the whole measurement range σ_{pt} is calculated by linear interpolation between 2.5% at the calibration point (75% of calibration range) and the limit of detection at zero concentration level. The limits of detection of studied measurement methods were evaluated from the data of previous PT. The linear function parameters of σ_{pt} are given in Table 4.

Table 4: Standard deviation for proficiency assessment (σ_{pt}).

Gas	a	b (nmol/mol)
SO2	0.022	1
CO	0.024	100
O3	0.020	1
NO	0.024	1
NO2	0.020	1

Source: JRC 2022

σ_{pt} is a linear function of concentration (c) with parameters: slope "**a**" and intercept "**b**".

$$\sigma_{pt} = (a \cdot X) + b$$

Equation 3

σ_{pt} = Standard deviation for proficiency assessment
a = slope see table 4
X = reference value
b = intercept see table 4

The assessment of results in z/z'-score evaluation is made according to the following criteria:
$|z/z'| \leq 2$ are considered satisfactory.
$2 < |z/z'| < 3$ are considered questionable.
$|z/z'| \geq 3$ are considered unsatisfactory. Scores falling in this range are very unusual and are taken as evidence that an anomaly has occurred that should be investigated and corrected.
According to z/z'-score calculation, z/z'-score values between |2| and |3| are considered stragglers and they deserve a specific check. Two values were evaluated as stragglers: level 0 of NO and level 8 of NO2 for Laboratory F. Three outliers were identified: level 1,2,3 of SO2 for laboratory L (see Table 5) and these values require an action from the laboratory in order to analyse the process and identify the problem.

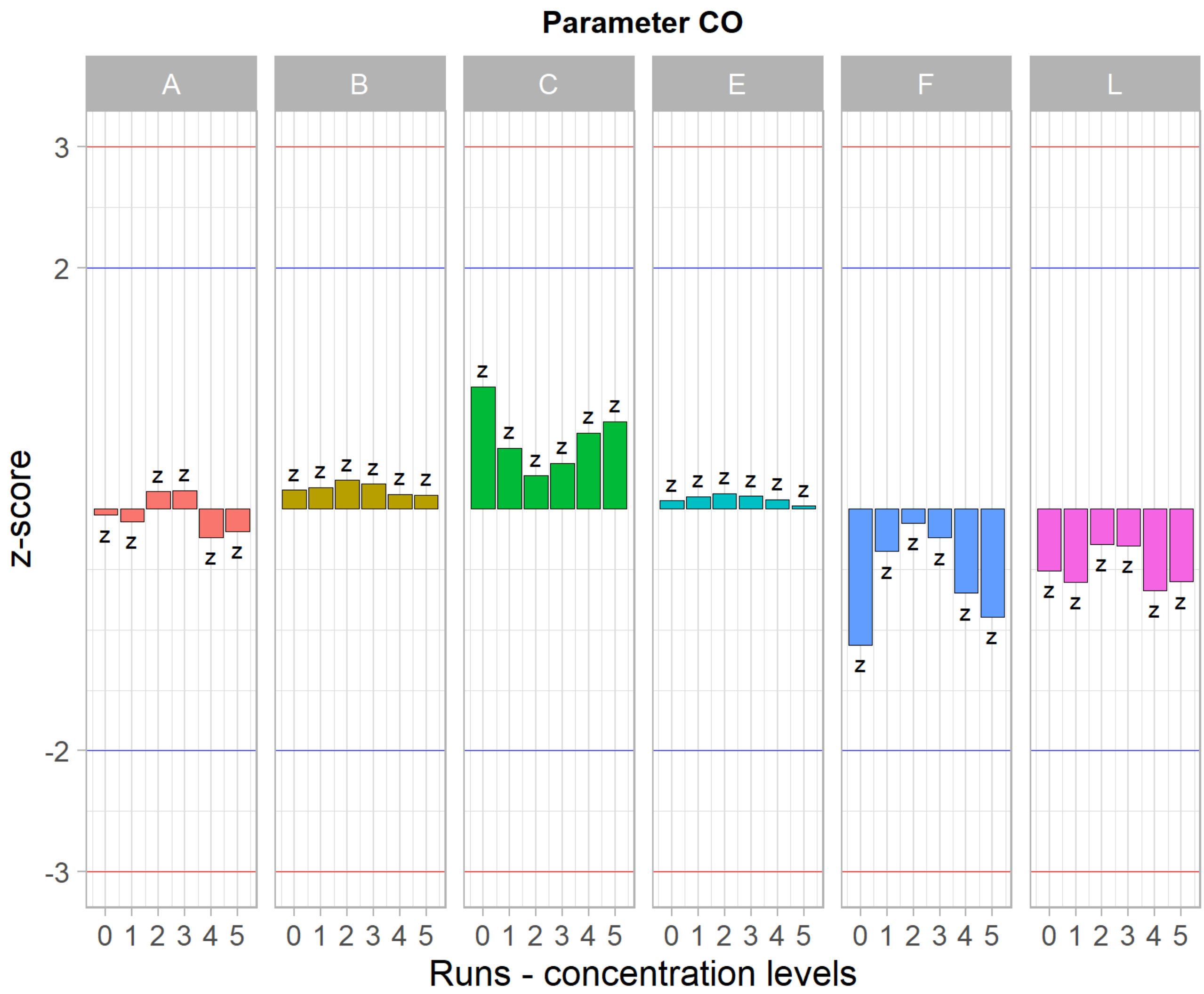
Table 5: z/z'-score evaluation.

Code	Run	z/z'-score value	z/z'-score evaluation
F	NO _0	2.444	questionable
F	NO2 _8	2.378	questionable
L	SO2 _1	-5.604	unsatisfactory
L	SO2 _2	-3.961	unsatisfactory
L	SO2 _3	-3.373	unsatisfactory

Source: JRC 2022

In Annex C, table 13 is showing all z/z'-score values calculated for each participant, parameter and concentration level. The results of z/z'-score evaluation are presented in bar plots (Figure 1 to 5) in which the z/z'-scores of each participant are grouped together. The assessment criteria are presented as z/z'=±2 (blue line) and z/z'=±3 (red line). They represent the limits for the questionable and unsatisfactory results.

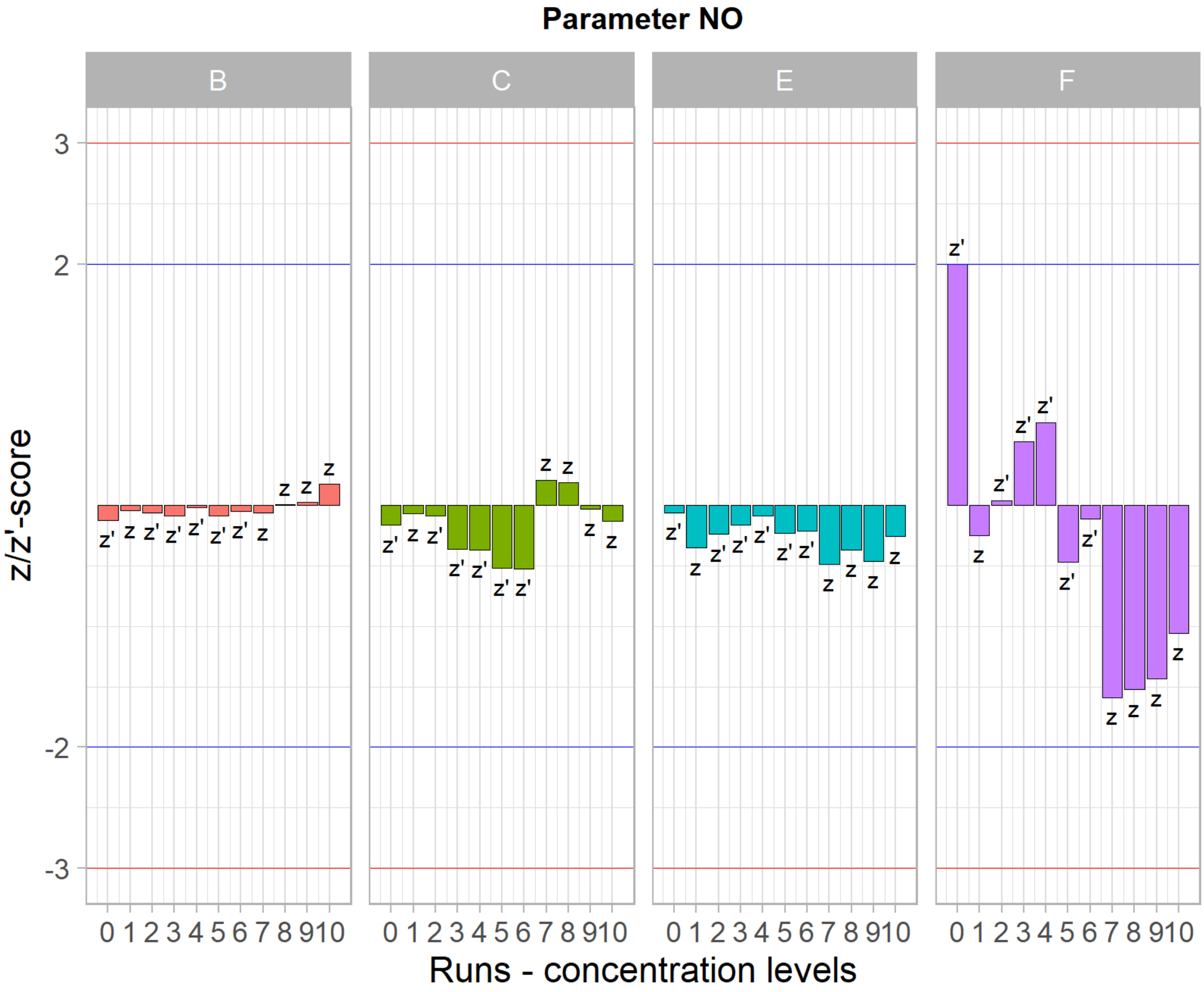
Figure 1: z-score evaluations of CO measurements in µmol/mol



Source: JRC 2022

Scores are given for each participant and each tested concentration level (run). Run number order (with nominal concentration) is: 0 (0 µmol/mol), 1 (3 µmol/mol), 2 (8 µmol/mol), 3 (5 µmol/mol), 4 (1.5 µmol/mol), 5 (0.9 µmol/mol). The assessment criteria limits are presented as z=±2 (blue line) and z=±3 (red line).

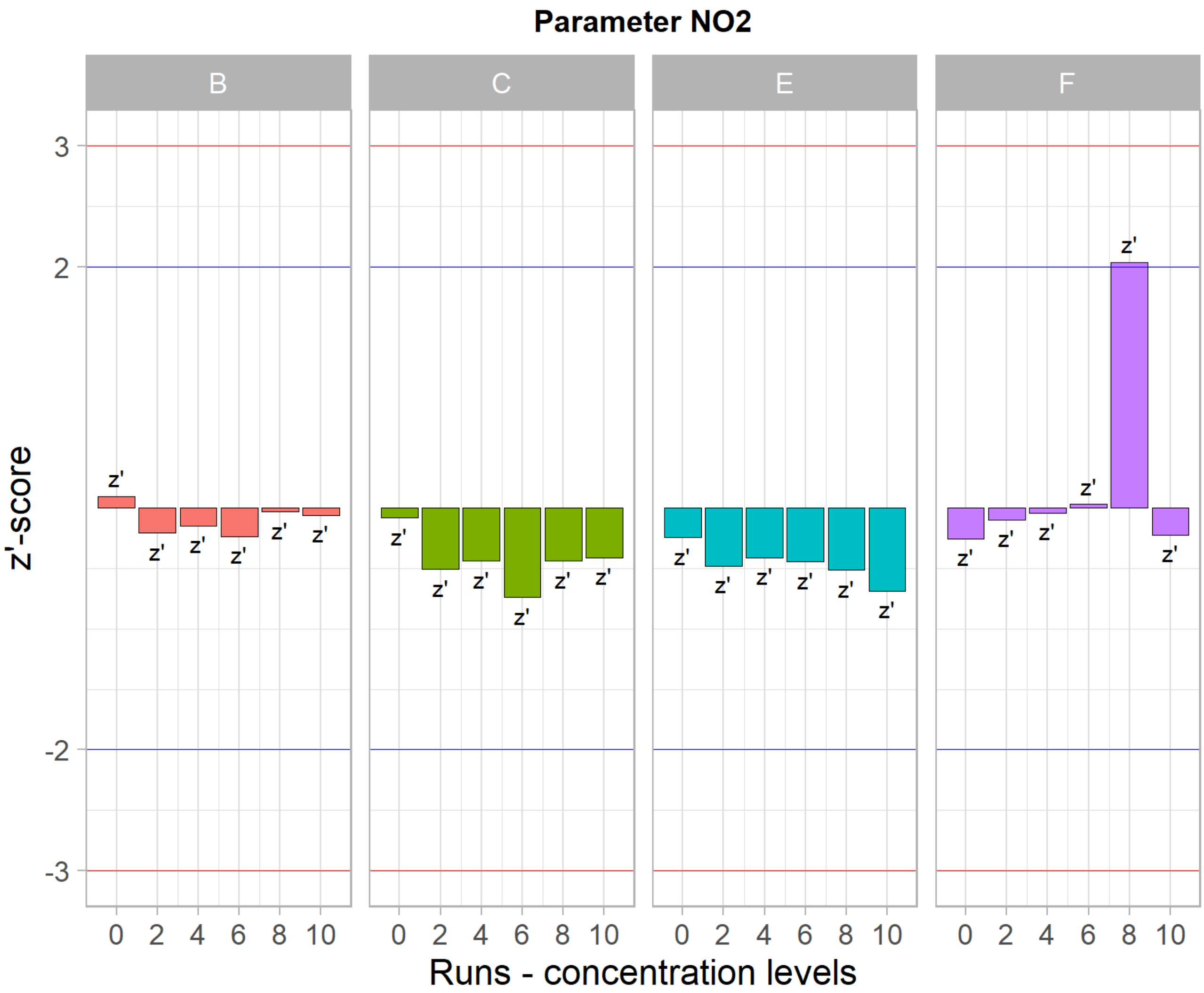
Figure 2: z/z'-score evaluations of NO measurements in nmol/mol



Source: JRC 2022

Scores are given for each participant and each tested concentration level (run). Run number order (with nominal concentration) is: 0 (0 nmol/mol), 1 (120 nmol/mol), 2 (70 nmol/mol), 3 (25 mol/mol), 4 (15 nmol/mol), 5 (60 nmol/mol), 6 (35 nmol/mol), 7 (480 nmol/mol), 8 (380 nmol/mol), 9 (300 nmol/mol), 10 (170 nmol/mol).
The assessment criteria limits are presented as z/z'=±2 (blue line) and z/z'=±3 (red line).
Laboratories A and L didn't submit NO measurement values.

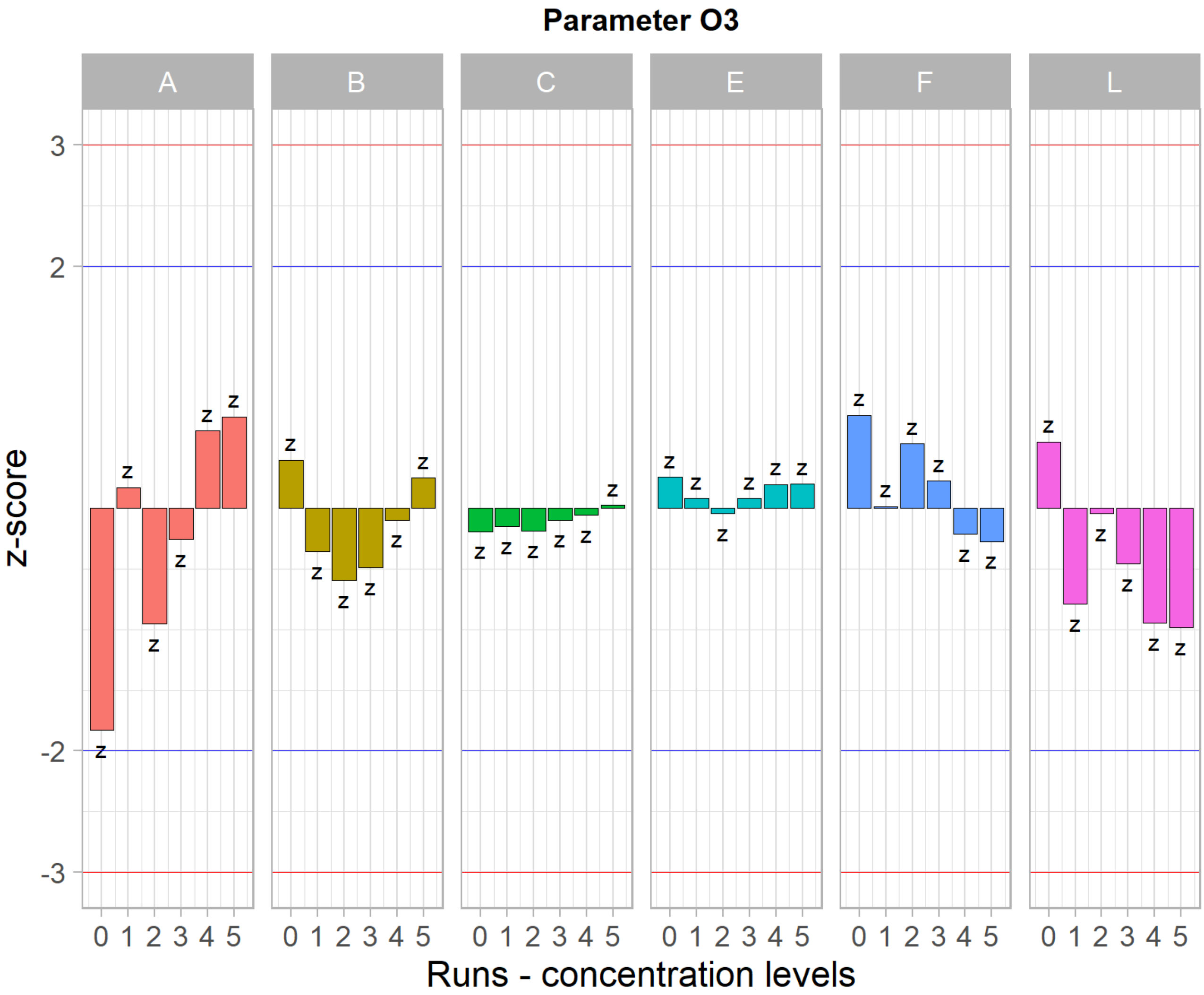
Figure 3: z'-score evaluations of NO2 measurements in nmol/mol



Source: JRC 2022

Scores are given for each participant and each concentration level (run). The order of run numbers when NO2 is generated (with nominal concentration) is: 0 (0 nmol/mol), 2 (50 nmol/mol), 4 (10 nmol/mol), 6 (25 nmol/mol), 8 (100 nmol/mol), 10 (130 nmol/mol).
The assessment criteria limits are presented as z'=±2 (blue line) and z'=±3 (red line).
Laboratories A and L didn't submit NO2 measurement values.

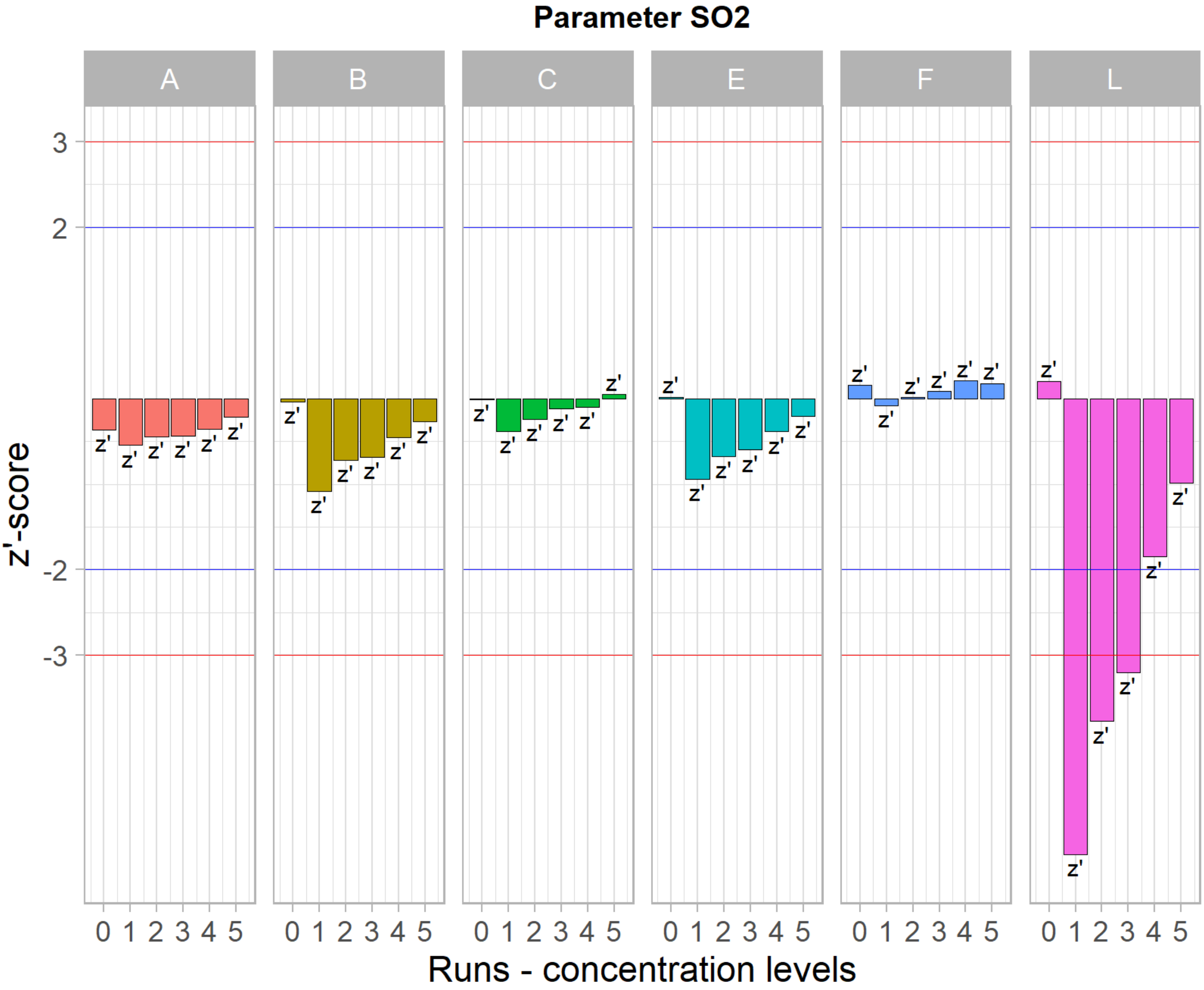
Figure 4: z-score evaluations of O3 measurements in nmol/mol



Source: JRC 2022

Scores are given for each participant and each concentration level (run). Run number order (with nominal concentration) is: 0 (0 nmol/mol), 1 (60 nmol/mol), 2 (15 nmol/mol), 3 (35 nmol/mol), 4 (110 nmol/mol), 5 (130 nmol/mol).
The assessment criteria limits are presented as z=±2 (blue line) and z=±3 (red line)

Figure 5: z'-score evaluations of SO2 measurements in nmol/mol



Source: JRC 2022

Scores are given for each participant and each tested concentration level (run). Run number order (with nominal concentration) is: 0 (0 nmol/mol), 1 (125 nmol/mol), 2 (50 nmol/mol), 3 (35 nmol/mol), 4 (19 nmol/mol), 5 (8 nmol/mol). The assessment criteria limits are presented as z'=±2 (blue line) and z'=±3 (red line)

5.2 **En-score**

In order to evaluate the participant's ability to have results close to the reference values within their reported uncertainties the En-score parameters (En) were calculated according to:

$$En = \frac{x_i - X}{\sqrt{U_{xi}^2 + U_x^2}} \qquad \text{Equation 4}$$

En = En-score
x_i = participant average values
X = assigned/reference value
U_{xi}= expanded uncertainty of the participants
U_X= expanded uncertainty of the assigned/reference value

Satisfactory results are the ones for which |En-score|<1. In Figure 6 to Figure 10 the bias of each participant (xi-X) is plotted and error bars are used to show the value of denominator of equation 4.
These plots represent also the En-score evaluations where, considering the En criterion (|En-score|<1), all results are satisfactory if with the error bars are crossing the x-axis. Reported standard uncertainties (Annex A) that are larger than the "standard deviation for proficiency assessments" (σ_{pt}, Table 4) are considered not fit-for-purpose and are denoted with "*" in the x-axis of each figure.
The En evaluation showed in Figures 6-10 underline few unsatisfactory results for different parameters and concentrations, as reported in table 6.
In Annex D, table 14 is showing all En values calculated for each participant, parameter and concentration level.

Table 6: Unsatisfactory results according to En-score.

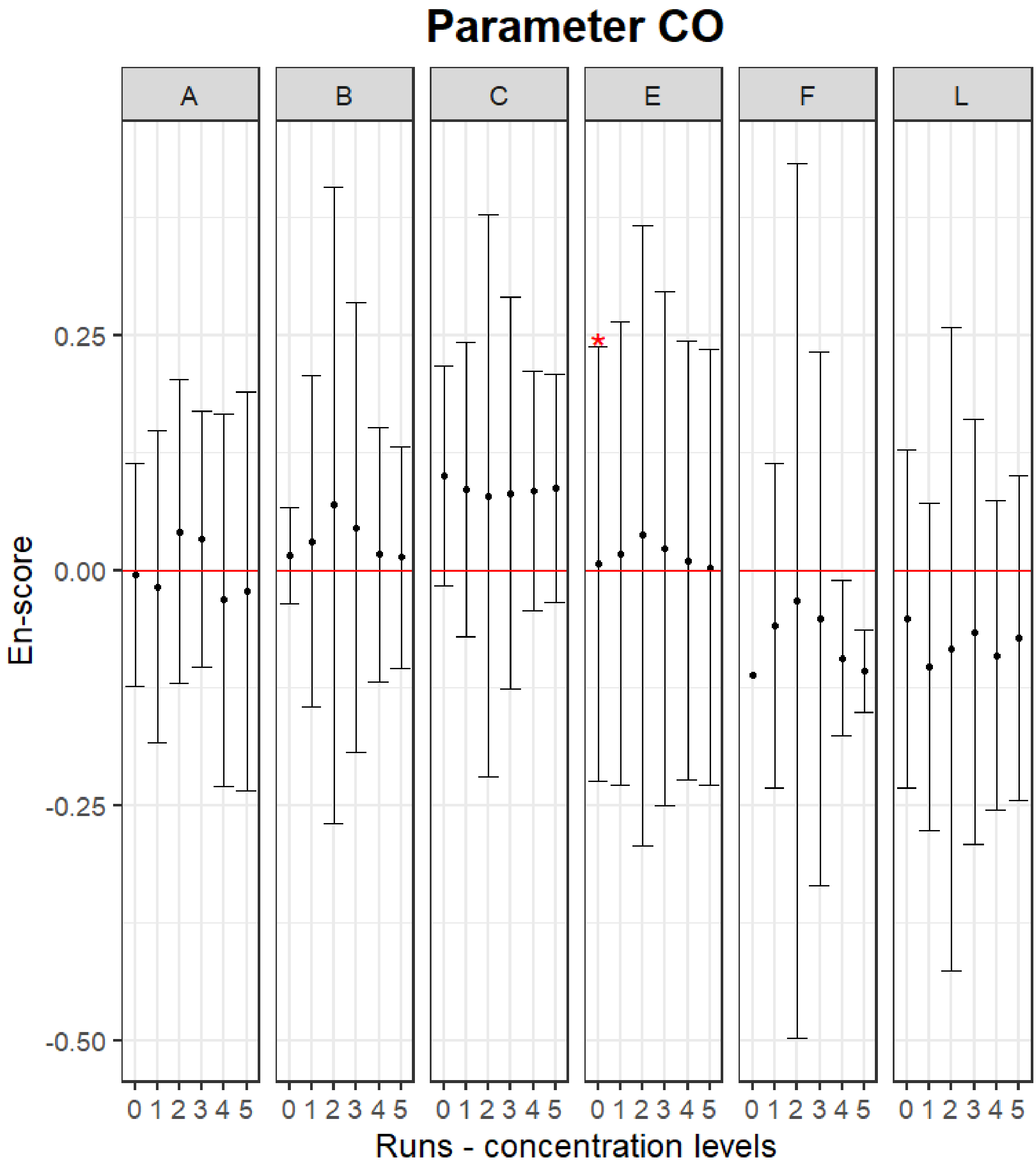
Code	Run	En-score	En evaluation
F	CO _4	-1.1	unsatisfactory
F	CO _5	-2.4	unsatisfactory
L	O3 _0	1.4	unsatisfactory
L	SO2 _1	-3.8	unsatisfactory
L	SO2 _2	-2.8	unsatisfactory
L	SO2 _3	-3.1	unsatisfactory
L	SO2 _4	-1.6	unsatisfactory

Source: JRC 2022

Laboratory F didn't report uncertainty values for Run-0 of all pollutants so the En-score couldn't be evaluated.

(1)

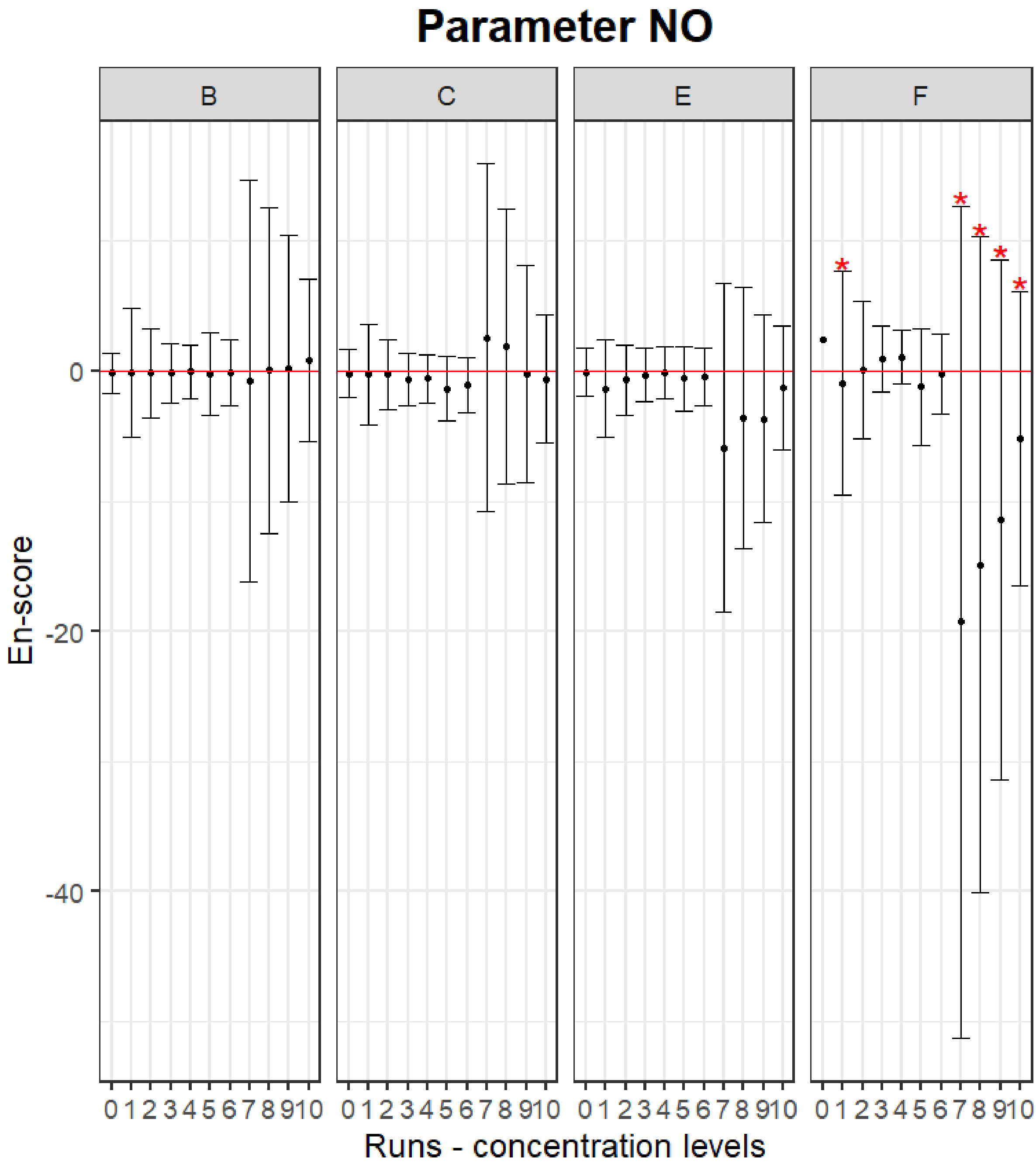
Figure 6: Bias of participant's CO measurement results in µmol/mol



Source: JRC 2022

Figure 6 is showing the expanded uncertainty of bias for each run presented as error bar. For each evaluation is given the run number (from 0 to 5) and the participants rounded run average (µmol/mol). The '*' mark indicates reported standard uncertainties bigger than σ_{pt}.
Laboratory F didn't report uncertainty values for zero concentration level.

Figure 7: Bias of participant's NO measurement results in nmol/mol

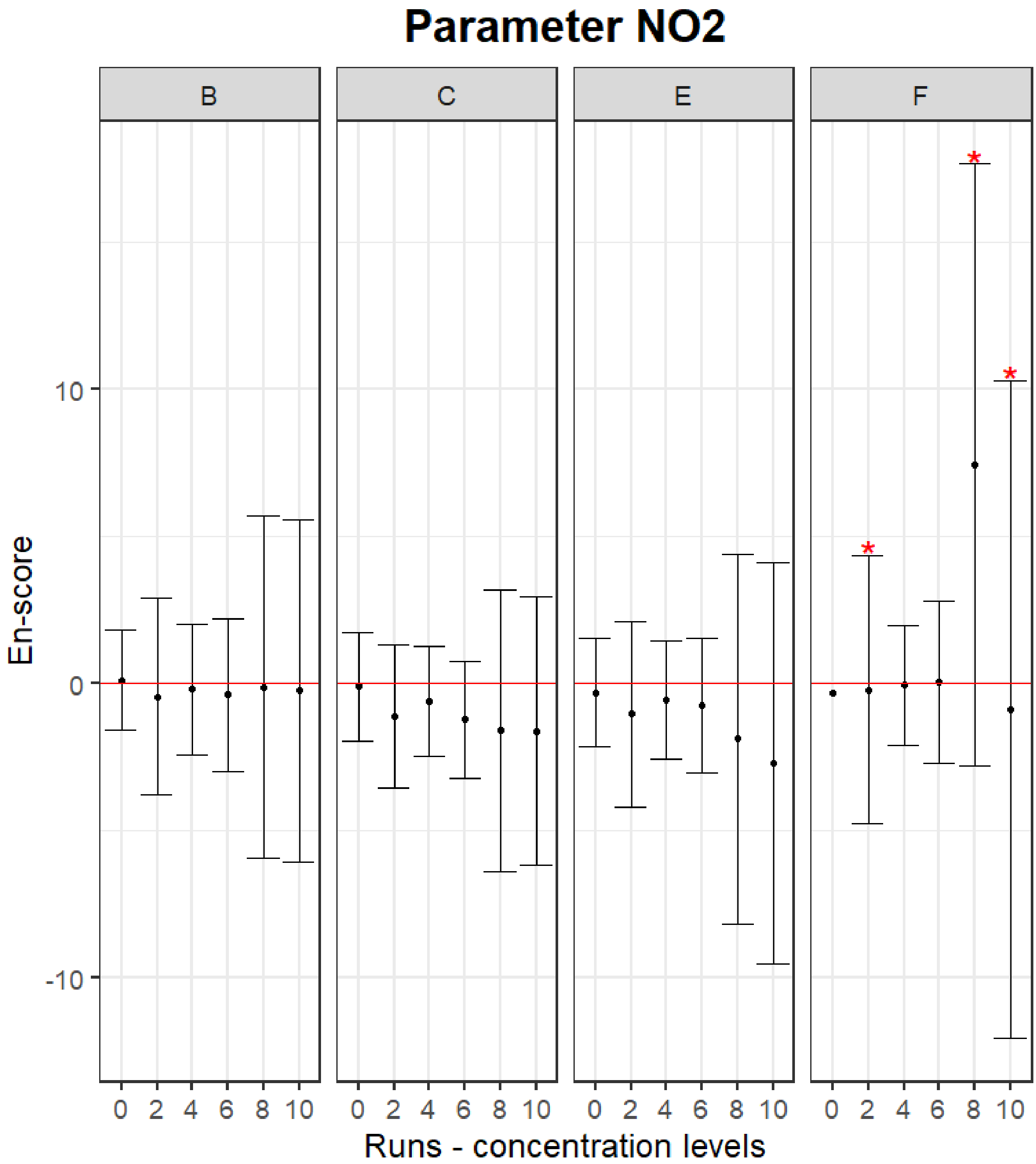


Source: JRC 2022

Figure 7 is showing the expanded uncertainty of bias for each run presented as error bar. For each evaluation is given the run number (from 0 to 10) and the participants rounded run average (nmol/mol). The '*' mark indicates reported standard uncertainties bigger than σpt.

Laboratories A and L didn't report results for this pollutant and laboratory F didn't report uncertainty value for zero concentration level.

Figure 8: Bias of participant's NO2 measurement results in nmol/mol

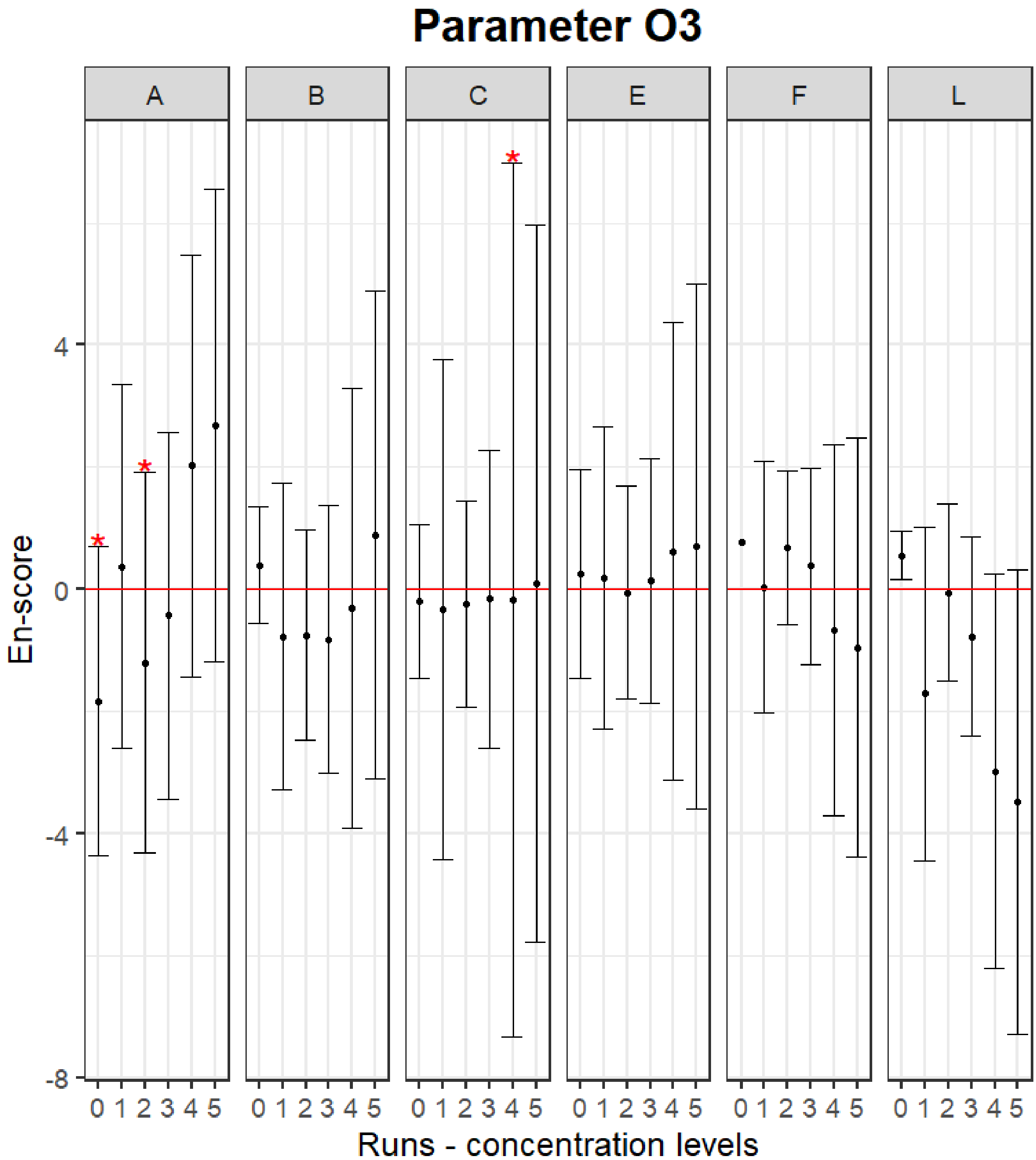


Source: JRC 2022

Figure 8 is showing the expanded uncertainty of bias presented as error bar for NO2 run numbers 0, 2, 4, 6, 8 and 10 (see Table 3). For each evaluation is given the run number and the participants rounded run average (nmol/mol). The '*' mark indicates reported standard uncertainties bigger than σ_{pt}.

Laboratories A and L didn't report results for this pollutant and F didn't report uncertainty value for zero concentration level.

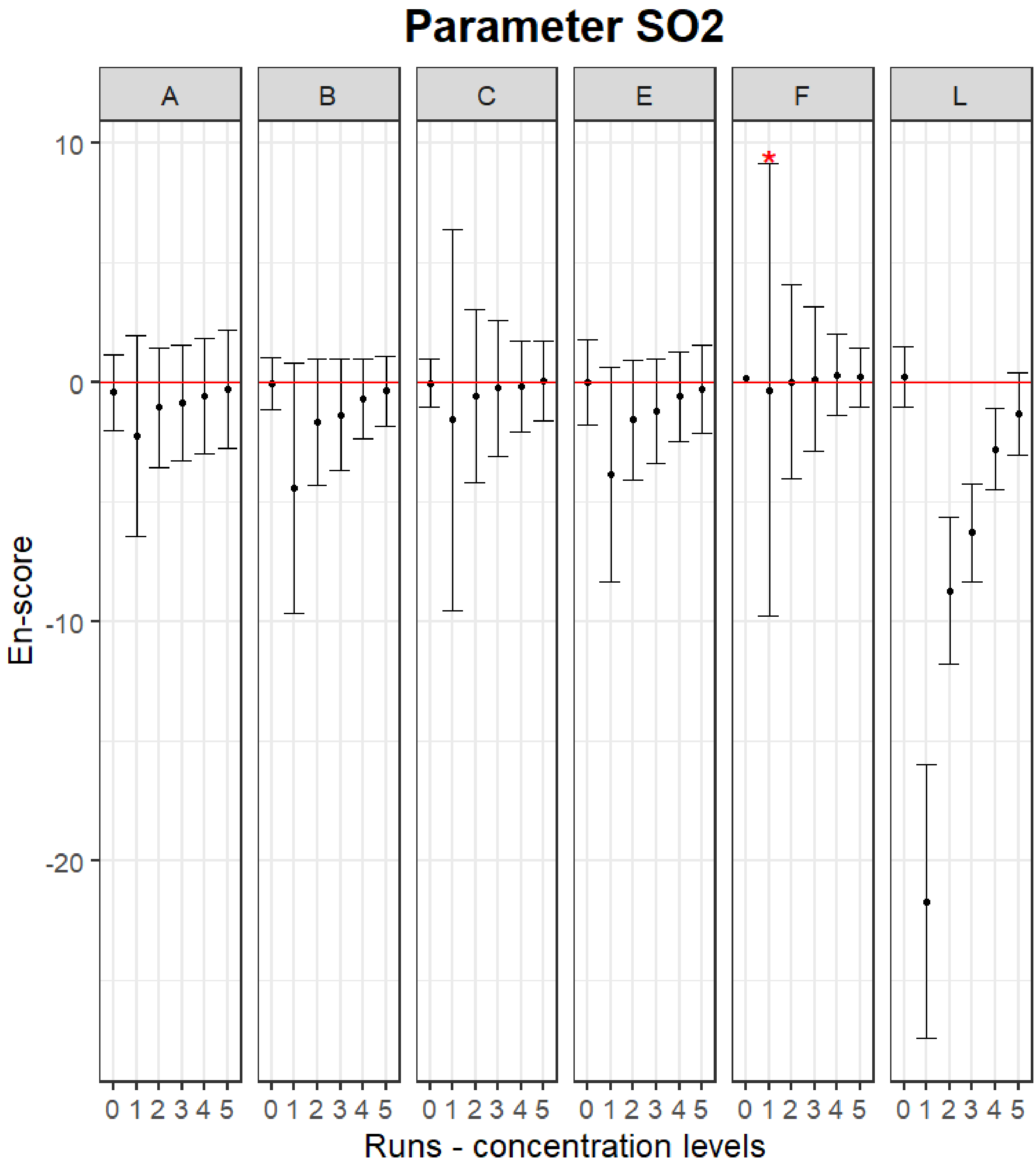
Figure 9: Bias of participant's O3 measurement results in nmol/mol



Source: JRC 2022

Figure 9 is showing the expanded uncertainty of bias for each run presented as error bar. For each evaluation is given the run number (from 0 to 5) and the participants rounded run average (nmol/mol).
The '*' mark indicates reported standard uncertainties bigger than σ_{pt}.
Laboratory F didn't report uncertainty value for zero concentration level.

Figure 10: Bias of participant's SO2 measurement results in nmol/mol



Source: JRC 2022

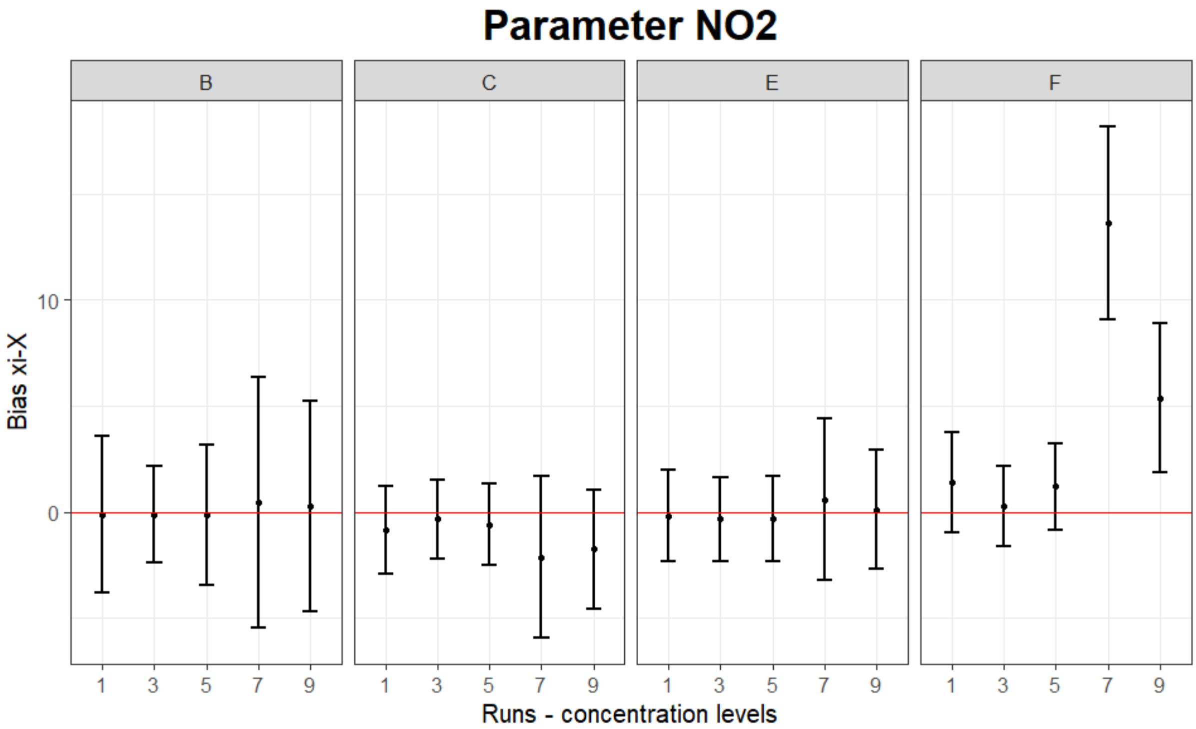
Figure 10 is showing the expanded uncertainty of bias for each run presented as error bar. For each evaluation is given the run number (from 0 to 5) and the participants rounded run average (nmol/mol). The '*' mark indicates reported standard uncertainties bigger than σ_{pt}.
Laboratory F didn't report uncertainty values for zero concentration level.

5.3 Performance characteristics of individual laboratories

The difference between the individual participants' values and the reference values (Bias xi-X) were evaluated and presented in chapter 4.2 (Figure 6 - 10). Since the results of NO2 runs 0, 1, 3, 5, 7 and 9 were not treated in proficiency evaluation the bias of these runs are presented in **Figure 11**.

Also in this figure **laboratories A and L** are not present because they didn't report results for this pollutant.

Figure 11: Bias (in nmol/mol) of participant's NO2 measurements compared to the reference value in concentration levels where it is not applied GPT.



Source: JRC 2022

Within these test gas mixtures there is no Gas Phase Titration (GPT) to produce NO2 (see table 3). For each evaluation is given the run number and the participants rounded run average (nmol/mol).

5.4 Converter efficiencies of NO2-to-NO for NOX analysers

NO and NO2 test gases were measured through a gas phase titration. In order to give an idea of the efficiency of this phase, an estimation of the converter efficiency for each participant's NOX analyser was calculated. The estimation takes each participant's NO and NO2 measurements before and after oxidation by O3. However, possible minor instabilities in the generation of the test gas mixtures were not taken into account. The converter efficiency (Ec) is calculated using Equation 5 [4]:

$$Ec = \left\{\frac{NO2_i - NO2_f}{NO_i - NO_f}\right\} \text{x } 100 \qquad \text{Equation 5}$$

Ec = converter efficiency in %

NO2i = NO2 concentration prior the addition of O3, nmol/mol

NO2f = NO2 concentration remaining after addition of O3, nmol/mol

NOi =original NOX concentration prior to addition of O3, nmol/mol

NOf = NOX concentration remaining after addition of O3, nmol/mol

Ideal value for Ec is 100%. The evaluation of equation 5 for each participant at different concentration levels is given in Table 7. The results are all acceptable according to the method criteria (≥ 98 %).

Table 7: Efficiency of NO2-to-NO converters.

Runs	Laboratory codes				
	B	C	E	F	G
Run2	99.5	99.7	99.8	99.0	100.1
Run4	100.6	97.5	99.1	97.7	100.1
Run6	100.3	99.3	99.7	100.0	100.8
Run8	100.4	100.0	100.1	98.3	100.2
Run10	100.2	99.9	99.8	100.1	100.1

Source: JRC 2022

6 Discussion

For a general assessment of the quality of each result, a decisional diagram was developed (Figure 12) that shows seven categories (1 to 7). The general description of each category is:

1 measurement result is completely satisfactory

2 measurement result is satisfactory for z/z'-score and En-score, but the reported uncertainty is too high according to the criteria $U<2\sigma_{pt}$

3 measured value is satisfactory for z/z'-score but the reported uncertainty is underestimated (En-score unsatisfactory)

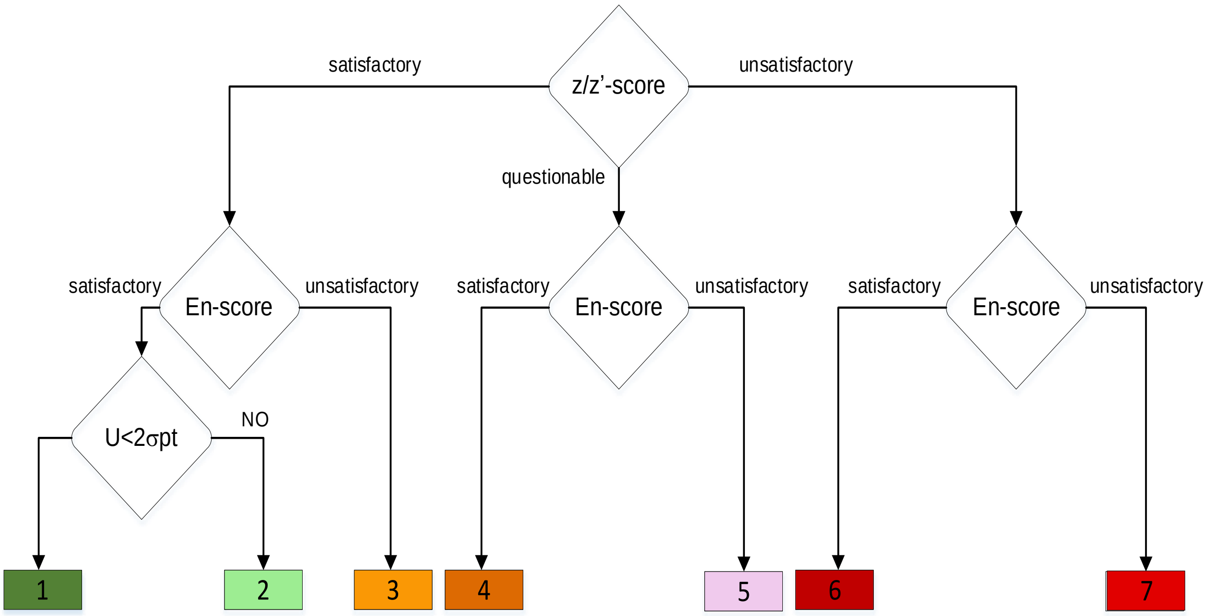
4 measurement result is questionable for z/z'-score, but due to a high reported uncertainty can be considered valid (En-score satisfactory).

5 measurement result is questionable for z/z'-score and unsatisfactory for En-score.

6 measurement result is unsatisfactory for z/z'-score but due to a high reported uncertainty can be considered valid (En-score satisfactory)

7 measurement result is unsatisfactory for z/z'-score and En-score.

Figure 12: Decision diagram for general assessment of proficiency results.



Source: JRC 2022

The results of the PT were assigned to categories according to the diagram given in Figure 12 and are presented in the following table (Table 8). All the results submitted are reported in Annex B.

Table 8: General assessment of proficiency results.

Gas	Concentration Level	Reference values	A	B	C	E	F	L
CO	0	-0.01	1	1	1	2	n.r.	1
	1	2.90	1	1	1	1	1	1
	2	7.82	1	1	1	1	1	1
	3	4.86	1	1	1	1	1	1
	4	1.42	1	1	1	1	3	1
	5	0.83	1	1	1	1	3	1
NO	0	0.11	n.r.	1	1	1	5	n.r.
	1	118.94	n.r.	1	1	1	2	n.r.
	2	69.98	n.r.	1	1	1	1	n.r.
	3	25.17	n.r.	1	1	1	1	n.r.
	4	16.60	n.r.	1	1	1	1	n.r.
	5	59.53	n.r.	1	1	1	1	n.r.
	6	36.01	n.r.	1	1	1	1	n.r.
	7	464.99	n.r.	1	1	1	2	n.r.
	8	366.06	n.r.	1	1	1	2	n.r.
	9	289.38	n.r.	1	1	1	2	n.r.
	10	160.91	n.r.	1	1	1	2	n.r.
NO2	0	0.01	n.r.	1	1	1	n.r.	n.r.
	2	49.40	n.r.	1	1	1	2	n.r.
	4	8.71	n.r.	1	1	1	1	n.r.
	6	23.90	n.r.	1	1	1	1	n.r.
	8	106.43	n.r.	1	1	1	4	n.r.
	10	132.57	n.r.	1	1	1	2	n.r.
O3	0	0.03	2	1	1	1	n.r.	3
	1	58.44	1	1	1	1	1	1
	2	13.22	2	1	1	1	1	1
	3	34.13	1	1	1	1	1	1
	4	107.52	1	1	2	1	1	1
	5	127.13	1	1	1	1	1	1
SO2	0	0.01	1	1	1	1	n.r.	1
	1	130.56	1	1	1	1	2	7
	2	54.30	1	1	1	1	1	7
	3	39.12	1	1	1	1	1	7
	4	18.44	1	1	1	1	1	3
	5	9.68	1	1	1	1	1	1

"n.r." is referring to values not reported.
Source: JRC 2022

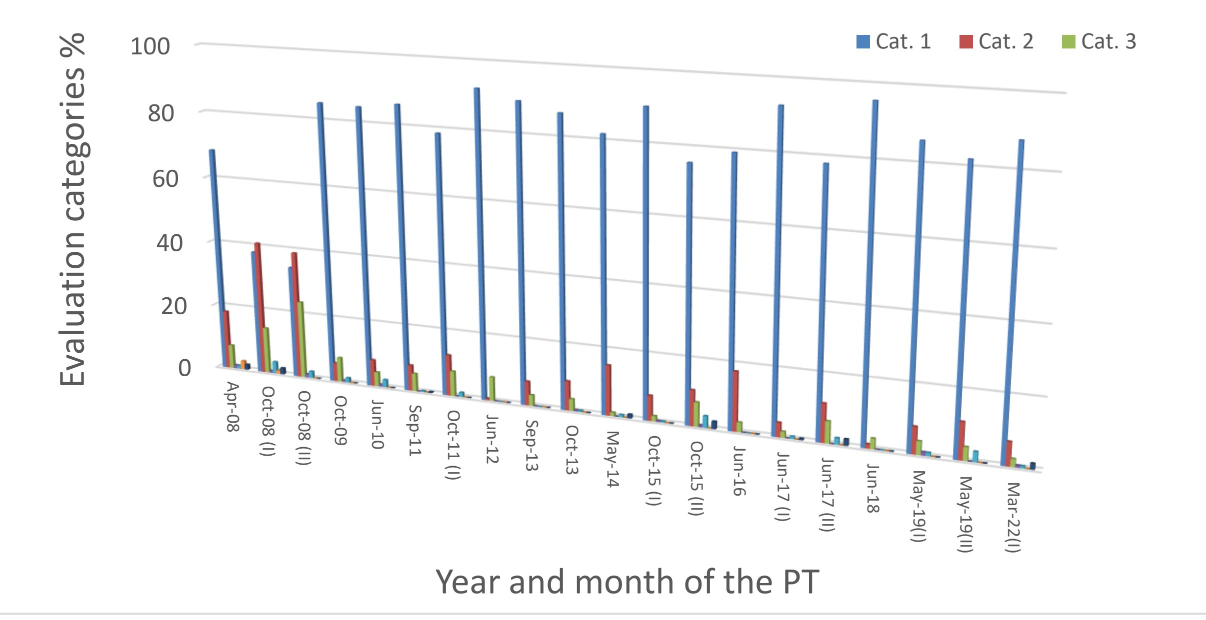
7 Conclusions

The proficiency evaluation scheme has provided an assessment of the participants measured values and their evaluated uncertainties.

In terms of the criteria imposed by the European Directive (σpt) 87.8% of the results reported during this PT (see Table 8) by AQUILA laboratories fall into 'category 1' and are satisfactory both in terms of measured values and evaluated uncertainties. Among the remaining all results presented satisfactory measured values, but the evaluated uncertainties were either too high, 'category 2' (7.0%), or too small, 'category 3' (2.3%). One value was found for 'category 4' (0.6%) and 'category 5' (0.6%). No values were found related to 'category 6' and three values were unsatisfactory for z'-score and En-score ('category 7` - 1.7%).

A summary of the performances registered during the PT organised in Ispra from 2008 till 2022 is presented in Figure 13. The graph is showing how categories 1 and 2 are generally the majority as a sign of consistent satisfactory performances.

Figure 13: Flags summary PT in Ispra from 2008 to 2022



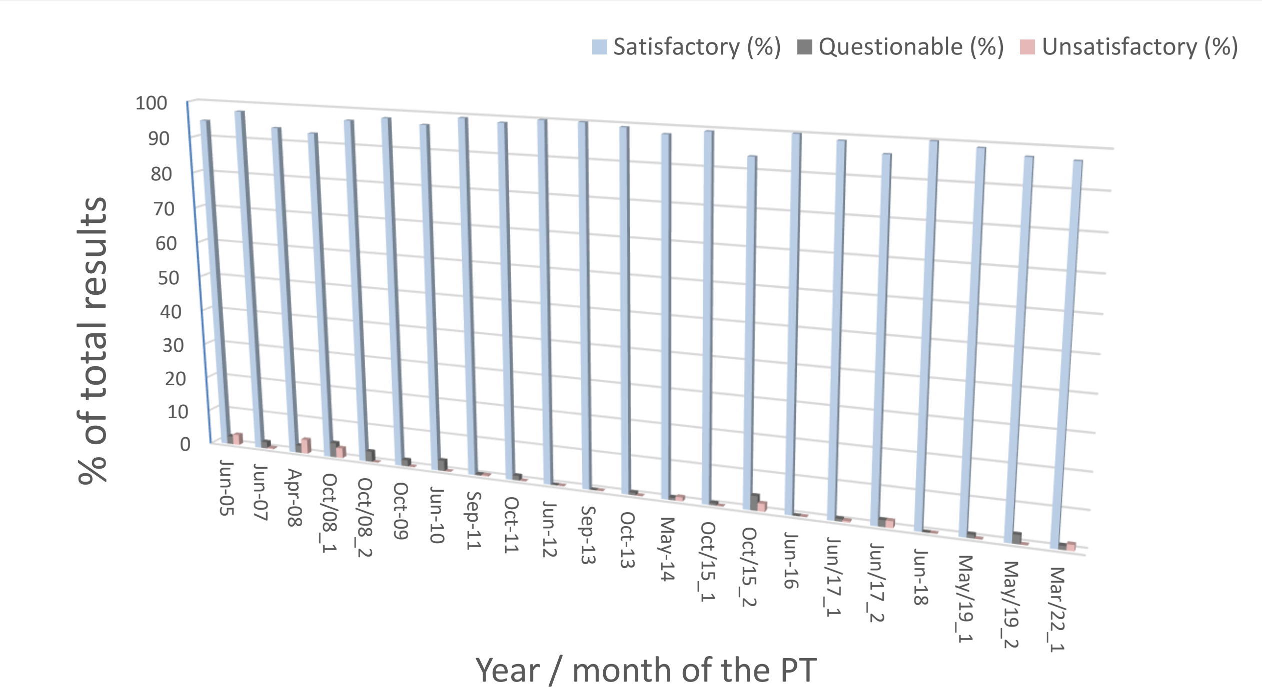
Source: JRC 2022

As in previous PT, the adopted criteria for high concentrations were the standard deviations for proficiency assessment, deriving from the European Standards' uncertainty requirements.

The reproducibility standard deviation obtained at this (Annex C) and previous PT [20], [21], [22], [23], [24], [25], [33], [34], [35], [36], [37], [38], [39], [40], [41], [43], [44], [45], [46], [47], [48], [49], [50], [51] and [52] is comparable to the mentioned criteria. On the other hand, the uncertainty criteria for zero levels were those set in AQUILA's position paper [12].

In this exercise 97.2% of the results in the z/z'-score evaluations were satisfactory, 1.1% questionable and 1.7% unsatisfactory. The results of this PT are in line with the performances of previous years as shown by the following Figure 14.

Figure 14: z/z'-score summary PT in Ispra from 2005 to 2022



Source: JRC 2022

Comparability of results among AQUILA participants at the highest concentration level is acceptable for all pollutant measurements.
The relative reproducibility limits, at the highest studied concentration levels, are 20.9% for SO2, 2.6% for CO, 5.2% for O3, for NO 7.5% and for NO2 3.3% all within the objective derived from criteria imposed by the European Commission (σpt see Table 4).

Three SO2 values of laboratory L were identified as outliers. The outliers have a negative impact on the reproducibility of the PT as shown in Figure 55 were the reproducibility line (blue) is above the reference line (red) from the concentration of 30 nmol/mol onwards.
In Annex D are reported all the details about the strugglers and outliers identified.

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List of abbreviations

AQUILA	Network of National Reference Laboratories for Air Quality
CEN	European Committee for Standardization
CO	Carbon monoxide
CRM	Certified Reference Material
DQO	Data Quality Objective
ERLAP	European Reference Laboratory for Air Pollution
EC	European Commission
GPT	Gas Phase Titration
ILC	Inter-Laboratory Comparison Exercise
ISO	International Organization for Standardization
JRC	Joint Research Centre
NO	Nitrogen monoxide
NO2	Nitrogen dioxide
NOX	The oxides of nitrogen, the sum of NO and NO2
NRL	National Reference Laboratory
O3	Ozone
PT	Proficiency Test
SO2	Sulphur dioxide
VDI	Verein Deutscher Ingenieure
WHO-CC	World Health Organization Collaborating Centre for Air Quality Management and Air Pollution

Mathematical Symbols

α	converter efficiency (EN 14211)
Ec	Converter efficiency for NO analyser
En	En–score statistic (ISO 13528)
r	repeatability limit (ISO 5725)
R	reproducibility limit (ISO 5725)
σ_{pt}	standard deviation for proficiency assessment (ISO 13528)
x*	robust average (Annex C ISO 13528)
s*	robust standard deviation (Annex C ISO 13528)
sr	estimate of repeatability variance (ISO 5725)
sR	estimate of reproducibility variance (ISO 5725)
UX	expanded uncertainty of the assigned/reference value (ISO 13528)
Uxi	expanded uncertainty of the participant's value (ISO 13528)
uX	standard uncertainty of the assigned/reference value (ISO 13528)
X	assigned/reference value (ISO 13528)
xi	average of 3 values reported by the participant i (for each parameter and concentration level)
xi,j	j-the reported value of participant i (for each parameter and concentration level)
z'	z'-score statistic (ISO 13528)
z	z-score statistic (ISO 13528)

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Annex A. Assigned values

The assigned values of tested concentration levels (run) were derived from ERLAP's measurements which are calibrated against the certified reference values of CRMs and are traceable to international standards. In this perspective the assigned values are reference values as defined in the ISO 13528 [13].
To foster its reference function ERLAP is participating regularly to key comparisons of the Gas Analysis Working Group within the framework of BIPM's CCQM and it is yearly confirming the compliance to ISO standard 17025 for testing and ISO 17043, both through an audit run by the competent Italian accreditation body.
During this PT ERLAP's SO2, CO and NO analysers were calibrated according to the methodology described in the ISO 6143 [6]. Reference gas mixtures were produced from the primary reference materials (produced and certified by NMi Van Swinden Laboratorium) by dynamic dilution method using mass flow controllers [8]. All flows were measured with a certified molbloc/molbox1 system. For O3 measurements, the analysers were calibrated using the JRC SRP42 primary standard (constructed by NIST), which has been compared to BIPM primary standard [26]. The photometer absorption cross section uncertainty (1.06%) was included in the uncertainty budget [27], [28].
The reference gas mixture and the calibration experiment evaluation were carried out using two computer applications, the "GUM WORKBENCH" [29] and "B-least" [30] respectively. For extending calibration from the NO to NO2 channel of NOX analyser the GPT test was performed to establish the efficiency of NO2-converter (see table 7).
In table 9 the assigned values are reported together with their uncertainties.

Table 9: Assigned values (X)

Gas	Unit	X	u_ref	U_ref
CO _0	µmol/mol	-0.011	0.008	0.017
CO _1	µmol/mol	2.901	0.015	0.029
CO _2	µmol/mol	7.824	0.034	0.067
CO _3	µmol/mol	4.868	0.022	0.044
CO _4	µmol/mol	1.428	0.010	0.021
CO _5	µmol/mol	0.836	0.010	0.019
NO _0	nmol/mol	0.11	0.71	1.42
NO _1	nmol/mol	118.94	1.09	2.18
NO _2	nmol/mol	69.98	0.86	1.72
NO _3	nmol/mol	25.18	0.73	1.47
NO _4	nmol/mol	16.60	0.72	1.44
NO _5	nmol/mol	59.53	0.82	1.65
NO _6	nmol/mol	36.01	0.76	1.52
NO _7	nmol/mol	464.99	3.29	6.58
NO _8	nmol/mol	366.06	2.63	5.25
NO _9	nmol/mol	289.39	2.12	4.24
NO _10	nmol/mol	160.91	1.32	2.64
NO2 _0	nmol/mol	0.01	0.72	1.43
NO2 _1	nmol/mol	0.37	0.84	1.67
NO2 _2	nmol/mol	49.40	0.88	1.77
NO2 _3	nmol/mol	0.13	0.72	1.45
NO2 _4	nmol/mol	8.71	0.73	1.45
NO2 _5	nmol/mol	0.21	0.76	1.51
NO2 _6	nmol/mol	23.91	0.76	1.53
NO2 _7	nmol/mol	7.30	1.78	3.55
NO2 _8	nmol/mol	106.43	1.89	3.77
NO2 _9	nmol/mol	3.99	1.24	2.48
NO2 _10	nmol/mol	132.58	1.48	2.96
O3 _0	nmol/mol	0.03	0.19	0.38
O3 _1	nmol/mol	58.44	0.48	0.97
O3 _2	nmol/mol	13.22	0.19	0.39
O3 _3	nmol/mol	34.13	0.30	0.60
O3 _4	nmol/mol	107.53	0.86	1.73
O3 _5	nmol/mol	127.14	1.02	2.04
SO2 _0	nmol/mol	0.01	0.50	1.01
SO2 _1	nmol/mol	130.56	1.26	2.52
SO2 _2	nmol/mol	54.30	0.70	1.41
SO2 _3	nmol/mol	39.13	0.63	1.25
SO2 _4	nmol/mol	18.44	0.54	1.08
SO2 _5	nmol/mol	9.68	0.52	1.03

Source: JRC 2022

Homogeneity

The homogeneity of test gas was evaluated from measurements at the beginning and end of the distribution line. The relative differences between beginning and end measurements are calculated.

$$u_{fX} = \sqrt{u_X^2 + (X \cdot u_{homo})^2} \qquad \text{Equation 6}$$

u_{fX} = final reference value combined uncertainty
u_X = reference value uncertainty intermediate
X = reference value
u_{homo} = uncertainty contribution to u_X from homogeneity test

The upper and lower limits of bias due to homogeneity were evaluated to be smaller than 0.5%, which constitutes the relative standard uncertainty of 0.3% of each concentration level assuming a rectangular distribution of the bias. The standard uncertainties of assigned/reference values (u_{fX}) were calculated with Equation 6 and used in the proficiency evaluations of chapter 4.
This type of PT for inorganic gases foresee a generation of gas mixture that is analysed immediately. In this condition, the stability and homogeneity test is not fully applicable. In ERLAP as homogeneity test all sampling ports, used by participants for the PT, are compared with the last port (N20) with a running concentration of ozone and the measurement carried out with 2 different analysers. The test is considered acceptable when the difference of the two measurements is below 0.5%. This test is part of the equipment checks run before a PT organised by ERLAP in Ispra and its result is reported in Table 10.

Table 10: Homogeneity test.

Bench position	Sample Analyzer SN15	Ref Analyzer SN14	Diff. in nmol/mol	Diff<0.5% ?
20a/b	400.5	398.0	0.0	Yes
1a	400.0	398.0	-0.5	Yes
1b	400.5	397.5	0.5	Yes
2a	400.5	397.5	0.5	Yes
2b	400.5	397.5	0.5	Yes
3a	400.5	397.5	0.5	Yes
3b	400.5	397.5	0.5	Yes
4a	400.5	397.5	0.5	Yes
4b	400.5	397.5	0.5	Yes
5a	400.5	397.5	0.5	Yes
5b	400.5	397.5	0.5	Yes
6a	400.5	397.5	0.5	Yes
6b	400.5	397.5	0.5	Yes
7a	400.5	397.5	0.5	Yes
7b	399.0	396.0	0.5	Yes
8a	400.5	397.5	0.5	Yes
8b	400.5	397.5	0.5	Yes
9a	400.5	397.5	0.5	Yes
9b	400.5	397.5	0.5	Yes
10a	400.5	397.5	0.5	Yes
10b	400.5	397.5	0.5	Yes
11a	400.5	397.5	0.5	Yes
11b	400.5	397.5	0.5	Yes
12a	400.5	397.5	0.5	Yes
12b	400.5	397.5	0.5	Yes
13a	399.5	396.0	1.0	Yes

Bench position	Sample Analyzer SN15	Ref Analyzer SN14	Diff. in nmol/mol	Diff<0.5% ?
13b	399.0	397.0	-0.5	Yes
14a	399.0	396.0	0.5	Yes
14b	400.0	396.0	1.5	Yes
15a	399.0	397.0	-0.5	Yes
15b	399.5	396.0	1.0	Yes
16a	399.0	396.0	0.5	Yes
16b	399.0	396.0	0.5	Yes
17a	399.0	396.0	0.5	Yes
17b	399.0	396.0	0.5	Yes
18a	399.0	396.0	0.5	Yes
18b	399.0	396.0	0.5	Yes
19a	399.5	397.0	0.0	Yes
19b	399.5	397.0	0.0	Yes
21a	399.5	397.0	0.0	Yes
21b	399.5	397.0	0.0	Yes
22a	399.0	396.0	0.5	Yes
22b	399.5	397.0	0.0	Yes
22c	399.5	396.0	1.0	Yes
22d	399.5	397.0	0.0	Yes
23a	399.5	397.0	0.0	Yes
23b	399.5	397.0	0.0	Yes
23c	399.5	396.0	1.0	Yes
23d	399.5	396.0	1.0	Yes

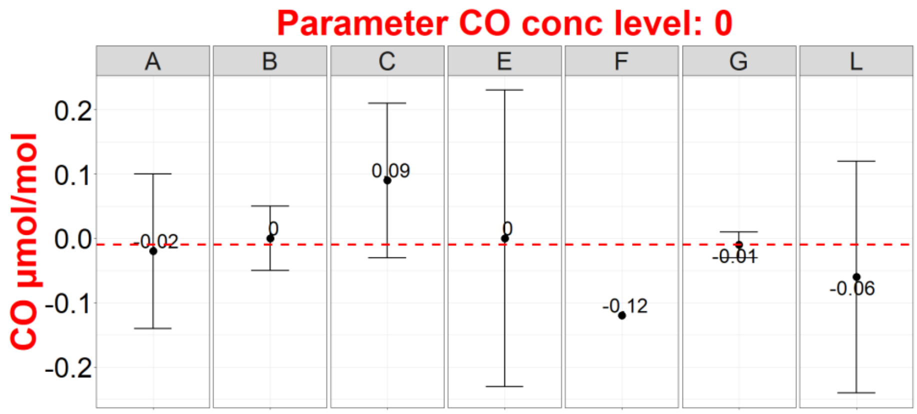
Source: JRC 2022

Annex B: results reported by participants

In this annex are reported participant's results, presented both in tables and graphs. For all mixture concentrations generated (run), participants were asked to report 3 results representing a measurement of 30 minutes each (xi).
In this annex are presented the reported data and their uncertainty u(xi) and U(xi) expressed in mol/mol units.
For all the runs except concentration levels 0, also average (x_mean) and standard deviation (sd) of each participant are presented.
The assigned value is indicated on the graphs with the red line and the individual laboratories expanded uncertainties (Uxi) are indicated with error bars.
When values are not reported they are shown in the tables and graphs. Laboratory F, for zero level concentration, didn't submitted the uncertainty value so in the table they are marked with NA characters.

Reported values for CO

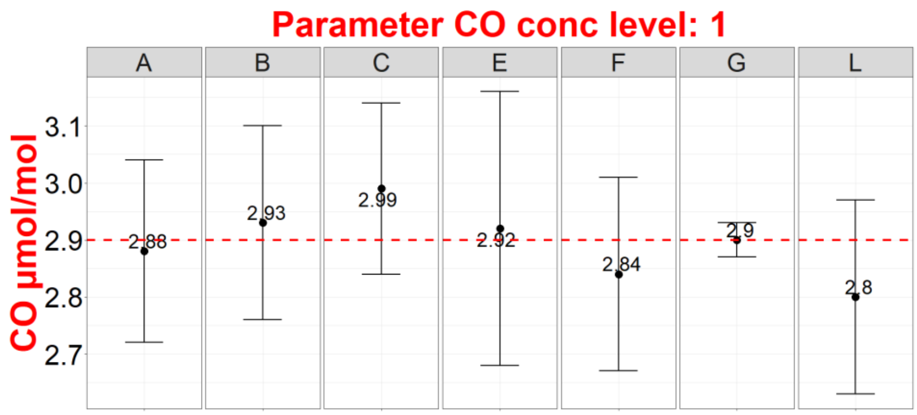
Figure 15: Reported values of CO concentration 0 (µmol/mol)



values	A	B	C	E	F	G	L
xi, 1	-0.016	0.005	0.09	-0.004	-0.123	-0.011	-0.062
u(xi)	0.06	0.02	0.06	0.12	NA	0.01	0.09
U(xi)	0.12	0.05	0.12	0.23	NA	0.02	0.18

Source: JRC 2022

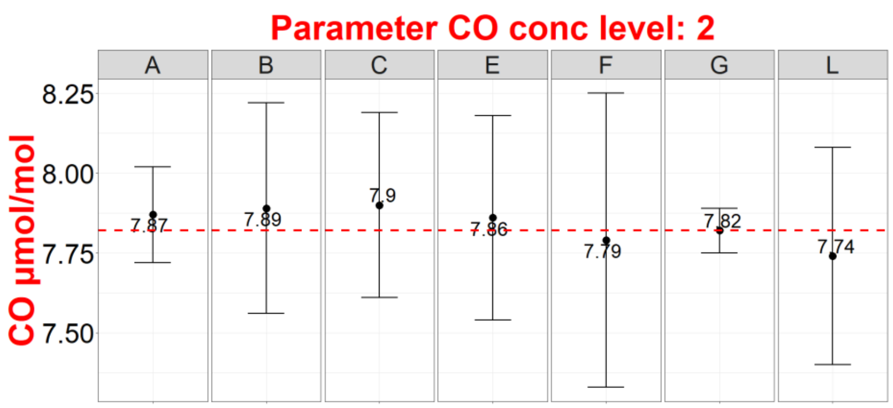
Figure 16: Reported values of CO concentration 1 (µmol/mol)



values	A	B	C	E	F	G	L
xi, 1	2.885	2.929	2.98	2.919	2.842	2.901	2.797
xi, 2	2.883	2.934	2.99	2.919	2.841	2.902	2.798
xi, 3	2.885	2.933	2.99	2.919	2.842	2.901	2.801
x_mean	2.88	2.93	2.99	2.92	2.84	2.90	2.80
sd	0.00	0.00	0.01	0.00	0.00	0.00	0.00
u(xi)	0.08	0.09	0.08	0.12	0.09	0.01	0.09
U(xi)	0.16	0.17	0.15	0.24	0.17	0.03	0.17

Source: JRC 2022

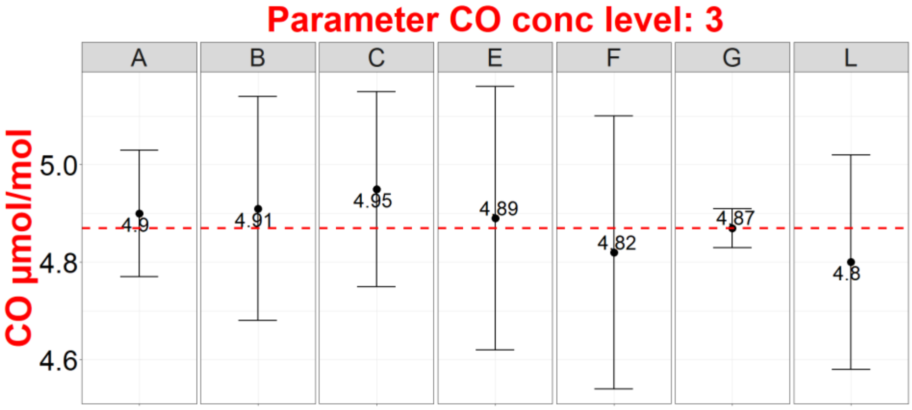
Figure 17: Reported values of CO concentration 2 (µmol/mol)



values	A	B	C	E	F	G	L
xi, 1	7.866	7.892	7.91	7.861	7.791	7.824	7.729
xi, 2	7.867	7.892	7.9	7.861	7.791	7.824	7.742
xi, 3	7.863	7.894	7.9	7.86	7.79	7.823	7.748
x_mean	7.87	7.89	7.90	7.86	7.79	7.82	7.74
sd	0.00	0.00	0.01	0.00	0.00	0.00	0.01
u(xi)	0.07	0.17	0.15	0.16	0.23	0.03	0.17
U(xi)	0.15	0.33	0.29	0.32	0.46	0.07	0.34

Source: JRC 2022

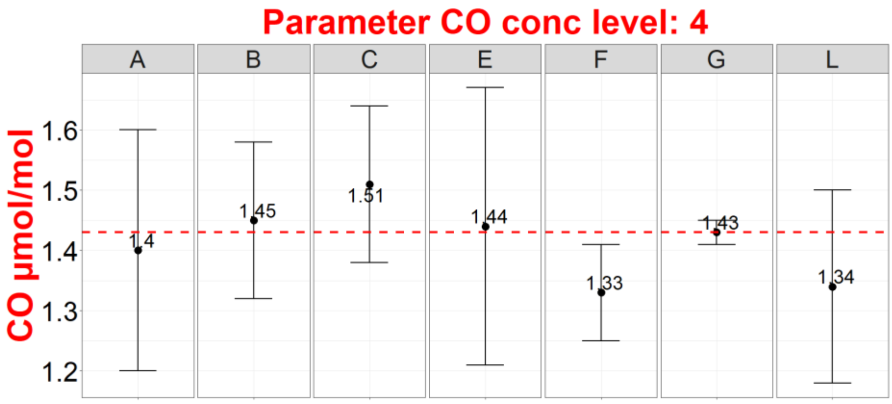
Figure 18: Reported values of CO concentration 3 (µmol/mol)



values	A	B	C	E	F	G	L
xi, 1	4.909	4.912	4.95	4.891	4.816	4.866	4.805
xi, 2	4.9	4.913	4.95	4.891	4.816	4.869	4.801
xi, 3	4.895	4.913	4.95	4.89	4.817	4.868	4.799
x_mean	4.90	4.91	4.95	4.89	4.82	4.87	4.80
sd	0.01	0.00	0.00	0.00	0.00	0.00	0.00
u(xi)	0.06	0.12	0.10	0.14	0.14	0.02	0.11
U(xi)	0.13	0.23	0.20	0.27	0.28	0.04	0.22

Source: JRC 2022

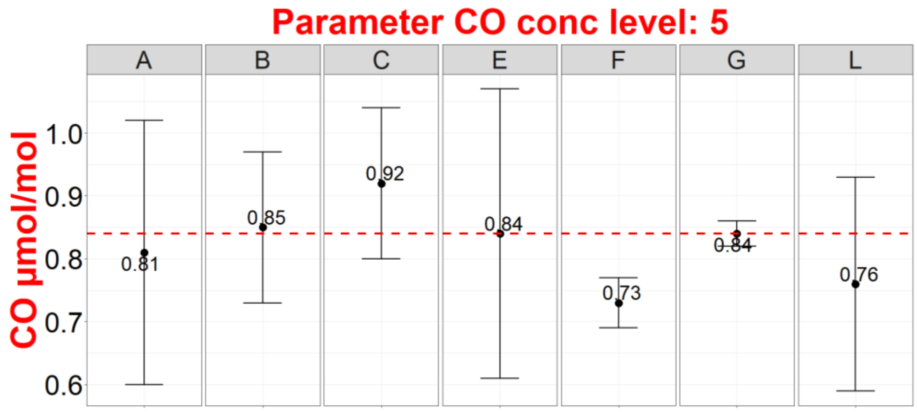
Figure 19: Reported values of CO concentration 4 (µmol/mol)



values	A	B	C	E	F	G	L
xi, 1	1.4	1.444	1.52	1.44	1.335	1.429	1.341
xi, 2	1.398	1.446	1.51	1.439	1.335	1.429	1.338
xi, 3	1.393	1.446	1.51	1.439	1.334	1.427	1.334
x_mean	1.40	1.45	1.51	1.44	1.33	1.43	1.34
sd	0.00	0.00	0.01	0.00	0.00	0.00	0.00
u(xi)	0.10	0.07	0.06	0.12	0.04	0.01	0.08
U(xi)	0.20	0.13	0.13	0.23	0.08	0.02	0.16

Source: JRC 2022

Figure 20: Reported values of CO concentration 5 (µmol/mol)

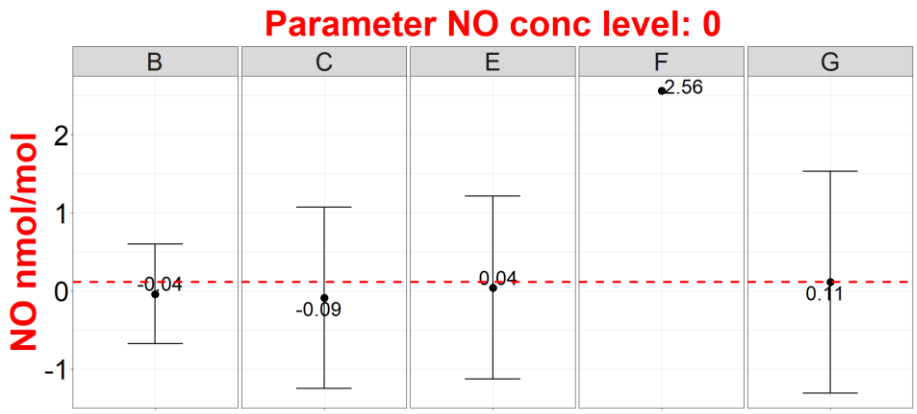


values	A	B	C	E	F	G	L
xi, 1	0.816	0.85	0.92	0.839	0.729	0.835	0.756
xi, 2	0.811	0.85	0.93	0.839	0.729	0.837	0.769
xi, 3	0.814	0.851	0.92	0.839	0.728	0.836	0.767
x_mean	0.81	0.85	0.92	0.84	0.73	0.84	0.76
sd	0.00	0.00	0.01	0.00	0.00	0.00	0.01
u(xi)	0.11	0.06	0.06	0.12	0.02	0.01	0.09
U(xi)	0.21	0.12	0.12	0.23	0.04	0.02	0.17

Source: JRC 2022

Reported values for NO

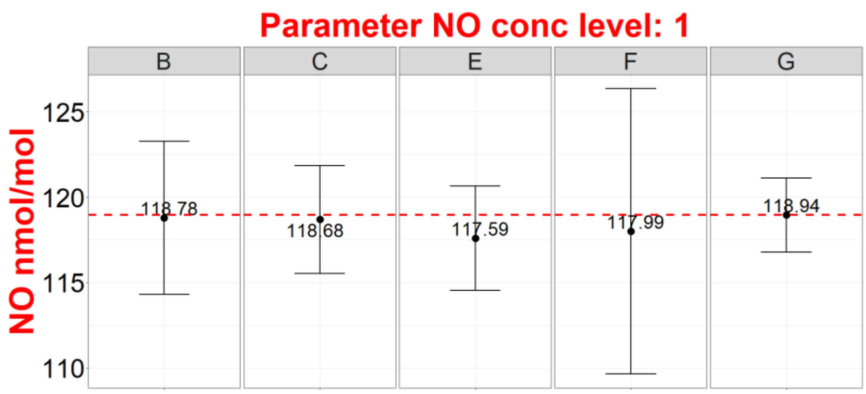
Figure 21: Reported values of NO concentration 0 (nmol/mol)



values	B	C	E	F	G
xi, 1	-0.04	-0.09	0.04	2.56	0.11
u(xi)	0.32	0.58	0.58	NA	0.71
U(xi)	0.64	1.16	1.17	NA	1.42

Source: JRC 2022

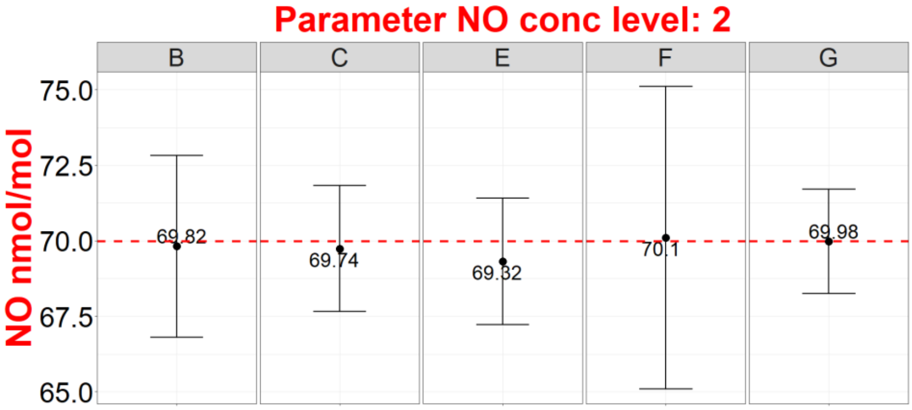
Figure 22: Reported values of NO concentration 1 (nmol/mol)



values	B	C	E	F	G
xi, 1	119.05	118.66	117.9	118.32	119.2
xi, 2	118.68	118.68	117.54	117.81	118.87
xi, 3	118.6	118.71	117.32	117.84	118.75
x_mean	118.78	118.68	117.59	117.99	118.94
sd	0.24	0.03	0.29	0.29	0.23
u(xi)	2.24	1.58	1.52	4.17	1.09
U(xi)	4.47	3.16	3.05	8.34	2.18

Source: JRC 2022

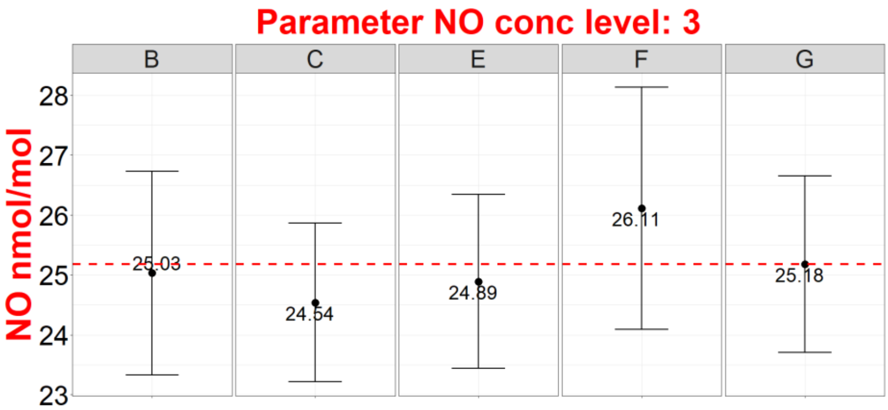
Figure 23: Reported values of NO concentration 2 (nmol/mol)



values	B	C	E	F	G
xi, 1	70.02	70.08	69.48	70.22	70.1
xi, 2	69.83	69.77	69.32	70.2	70.01
xi, 3	69.62	69.38	69.15	69.87	69.84
x_mean	69.82	69.74	69.32	70.10	69.98
sd	0.20	0.35	0.17	0.20	0.13
u(xi)	1.51	1.04	1.05	2.50	0.86
U(xi)	3.01	2.08	2.09	5.00	1.72

Source: JRC 2022

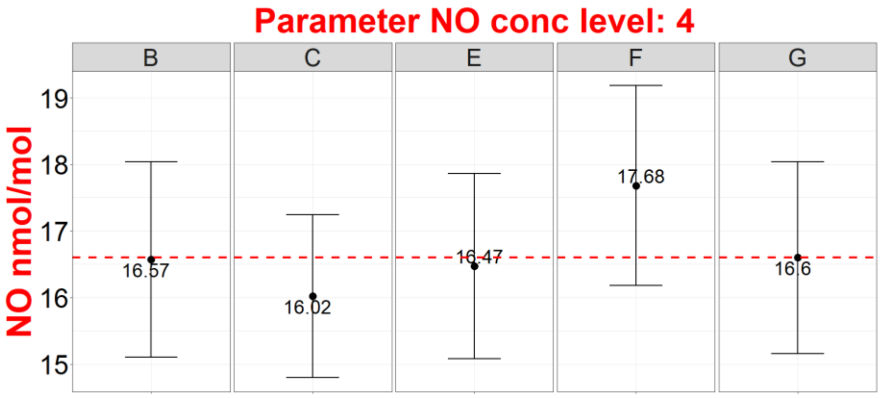
Figure 24: Reported values of NO concentration 3 (nmol/mol)



values	B	C	E	F	G
xi, 1	24.98	24.65	24.87	26.16	25.19
xi, 2	25.07	24.51	24.87	25.88	25.17
xi, 3	25.04	24.47	24.93	26.28	25.17
x_mean	25.03	24.54	24.89	26.11	25.18
sd	0.05	0.09	0.03	0.21	0.01
u(xi)	0.85	0.66	0.73	1.01	0.73
U(xi)	1.70	1.32	1.45	2.02	1.47

Source: JRC 2022

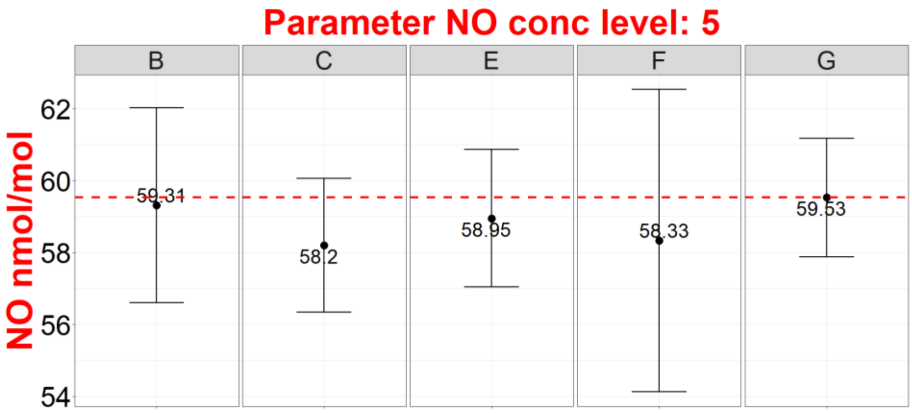
Figure 25: Reported values of NO concentration 4 (nmol/mol)



values	B	C	E	F	G
xi, 1	16.57	16.05	16.4	17.67	16.63
xi, 2	16.56	16.02	16.48	17.73	16.59
xi, 3	16.59	15.98	16.53	17.64	16.58
x_mean	16.57	16.02	16.47	17.68	16.60
sd	0.02	0.04	0.07	0.05	0.03
u(xi)	0.74	0.61	0.69	0.75	0.72
U(xi)	1.47	1.22	1.39	1.50	1.44

Source: JRC 2022

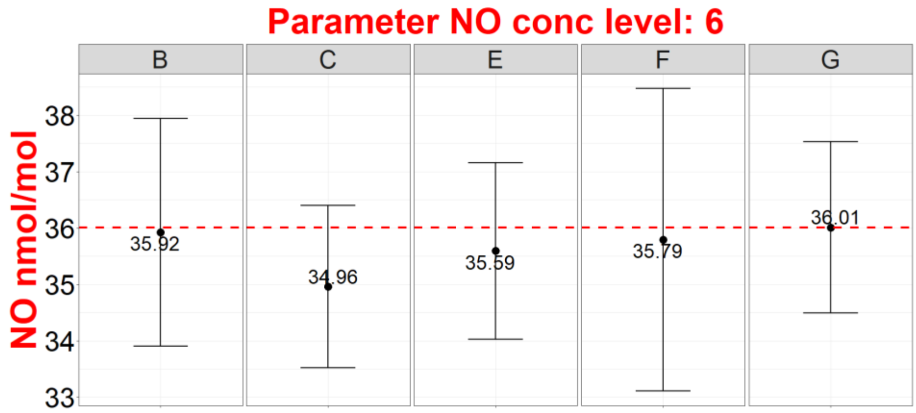
Figure 26: Reported values of NO concentration 5 (nmol/mol)



values	B	C	E	F	G
xi, 1	59.32	58.18	58.94	58.36	59.49
xi, 2	59.32	58.26	58.93	58.3	59.55
xi, 3	59.29	58.15	58.97	58.34	59.56
x_mean	59.31	58.20	58.95	58.33	59.53
sd	0.02	0.06	0.02	0.03	0.04
u(xi)	1.36	0.93	0.96	2.10	0.82
U(xi)	2.71	1.86	1.91	4.20	1.65

Source: JRC 2022

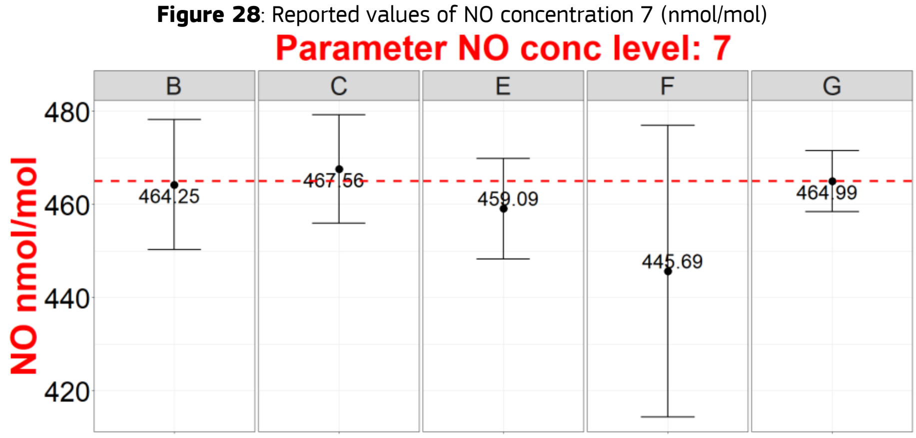
Figure 27: Reported values of NO concentration 6 (nmol/mol)



values	B	C	E	F	G
xi, 1	35.96	35.01	35.57	35.68	36.07
xi, 2	35.85	34.91	35.63	35.89	35.97
xi, 3	35.95	34.96	35.58	35.8	36
x_mean	35.92	34.96	35.59	35.79	36.01
sd	0.06	0.05	0.03	0.11	0.05
u(xi)	1.01	0.72	0.79	1.34	0.76
U(xi)	2.02	1.44	1.57	2.68	1.52

Source: JRC 2022

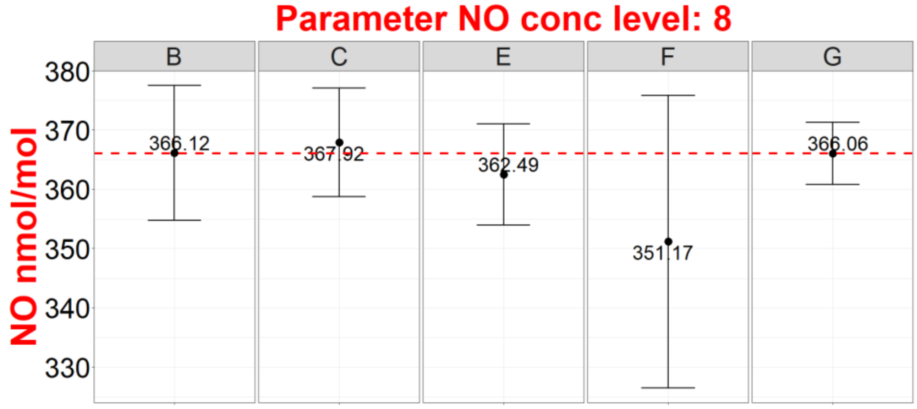
Figure 28: Reported values of NO concentration 7 (nmol/mol)



values	B	C	E	F	G
xi, 1	463.73	467.13	458.72	445.58	464.67
xi, 2	464.55	467.68	459.17	445.72	465.11
xi, 3	464.48	467.88	459.38	445.77	465.2
x_mean	464.25	467.56	459.09	445.69	464.99
sd	0.45	0.39	0.34	0.10	0.28
u(xi)	6.96	5.81	5.39	15.65	3.29
U(xi)	13.92	11.62	10.78	31.30	6.58

Source: JRC 2022

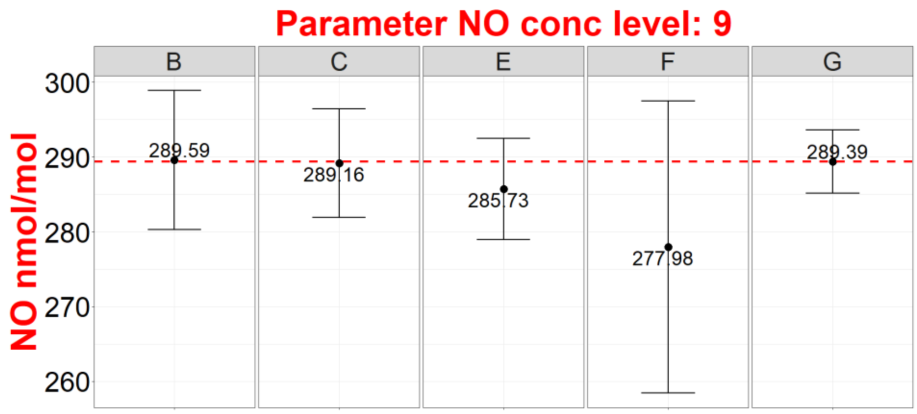
Figure 29: Reported values of NO concentration 8 (nmol/mol)



values	B	C	E	F	G
xi, 1	366.14	368.68	362.4	350.78	365.9
xi, 2	365.97	367.66	362.61	351.24	365.85
xi, 3	366.26	367.43	362.46	351.48	366.43
x_mean	366.12	367.92	362.49	351.17	366.06
sd	0.15	0.67	0.11	0.36	0.32
u(xi)	5.67	4.59	4.27	12.33	2.63
U(xi)	11.35	9.18	8.55	24.66	5.25

Source: JRC 2022

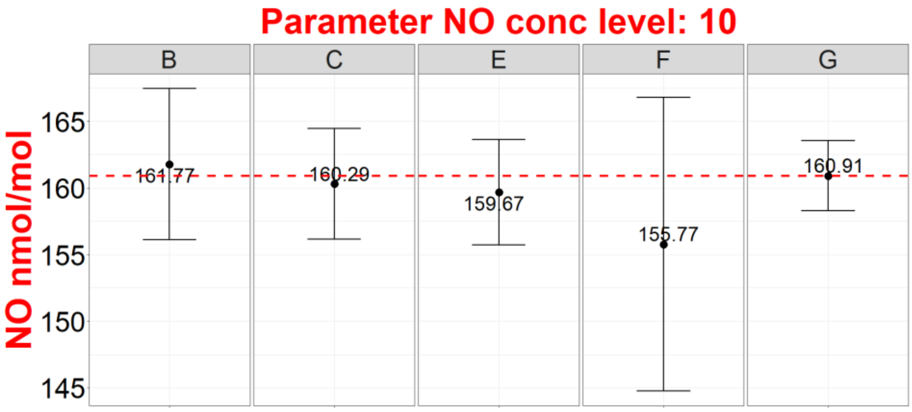
Figure 30: Reported values of NO concentration 9 (nmol/mol)



values	B	C	E	F	G
xi, 1	289.35	288.94	285.77	277.82	289.25
xi, 2	289.66	289.13	285.77	277.96	289.44
xi, 3	289.77	289.4	285.66	278.17	289.47
x_mean	289.59	289.16	285.73	277.98	289.39
sd	0.22	0.23	0.06	0.18	0.12
u(xi)	4.64	3.62	3.99	9.77	2.12
U(xi)	9.28	7.24	6.79	19.54	4.24

Source: JRC 2022

Figure 31: Reported values of NO concentration 10 (nmol/mol)

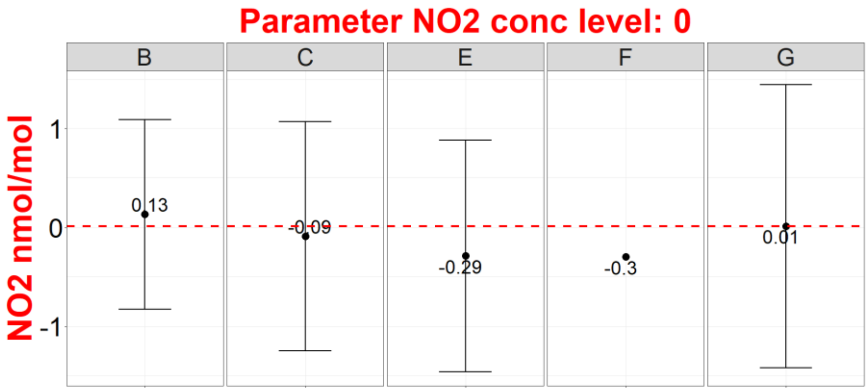


values	B	C	E	F	G
xi, 1	161.87	160.55	159.65	155.83	160.96
xi, 2	161.73	160.27	159.69	155.78	160.9
xi, 3	161.72	160.05	159.67	155.7	160.87
x_mean	161.77	160.29	159.67	155.77	160.91
sd	0.08	0.25	0.02	0.07	0.05
u(xi)	2.84	2.08	1.98	5.50	1.32
U(xi)	5.67	4.16	3.95	11.00	2.64

Source: JRC 2022

Reported values for NO2

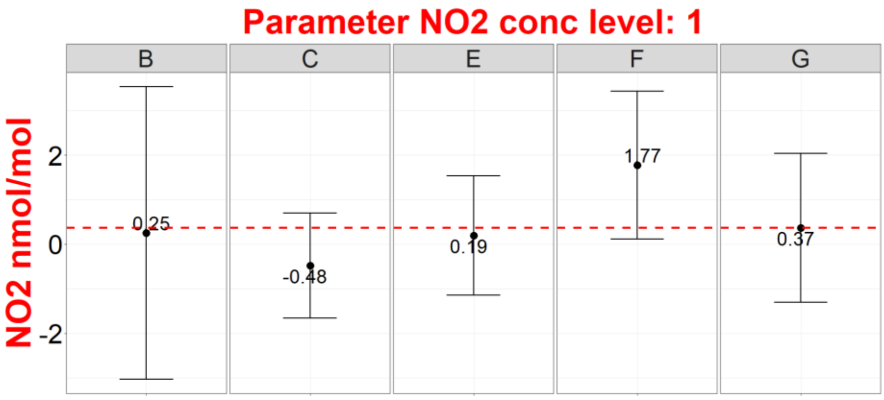
Figure 32: Reported values of NO2 concentration 0 (nmol/mol)



values	B	C	E	F	G
xi, 1	0.13	-0.09	-0.29	-0.3	0.01
u(xi)	0.48	0.58	0.58	NA	0.72
U(xi)	0.96	1.16	1.17	NA	1.43

Source: JRC 2022

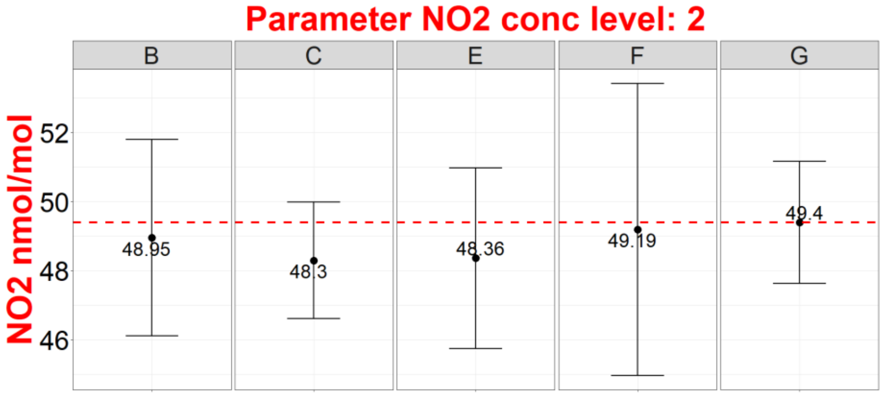
Figure 33: Reported values of NO2 concentration 1 (nmol/mol)



values	B	C	E	F	G
xi, 1	0.14	-0.39	0.21	1.86	0.37
xi, 2	0.32	-0.53	0.13	1.84	0.36
xi, 3	0.3	-0.53	0.24	1.61	0.39
x_mean	0.25	-0.48	0.19	1.77	0.37
sd	0.10	0.08	0.06	0.14	0.02
u(xi)	1.64	0.59	0.67	0.83	0.84
U(xi)	3.28	1.18	1.34	1.66	1.67

Source: JRC 2022

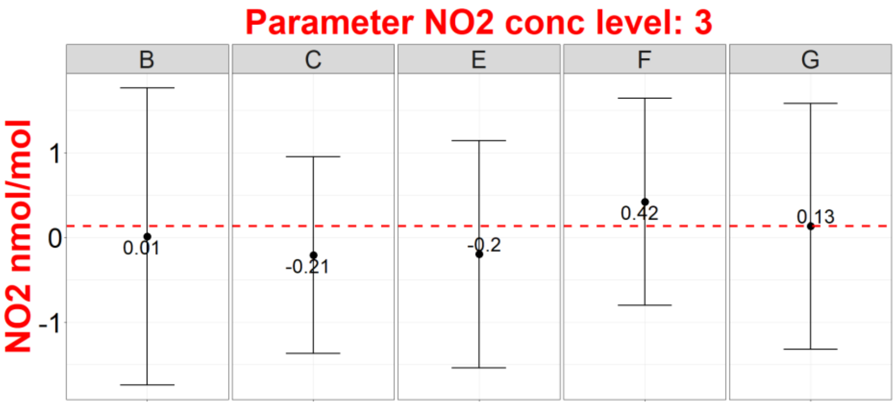
Figure 34: Reported values of NO2 concentration 2 (nmol/mol)



values	B	C	E	F	G
xi, 1	48.76	48.13	48.13	49.27	49.23
xi, 2	48.95	48.2	48.43	49.11	49.34
xi, 3	49.13	48.57	48.52	49.19	49.63
x_mean	48.95	48.30	48.36	49.19	49.40
sd	0.19	0.24	0.20	0.08	0.21
u(xi)	1.42	0.84	1.30	2.11	0.88
U(xi)	2.84	1.68	2.61	4.22	1.77

Source: JRC 2022

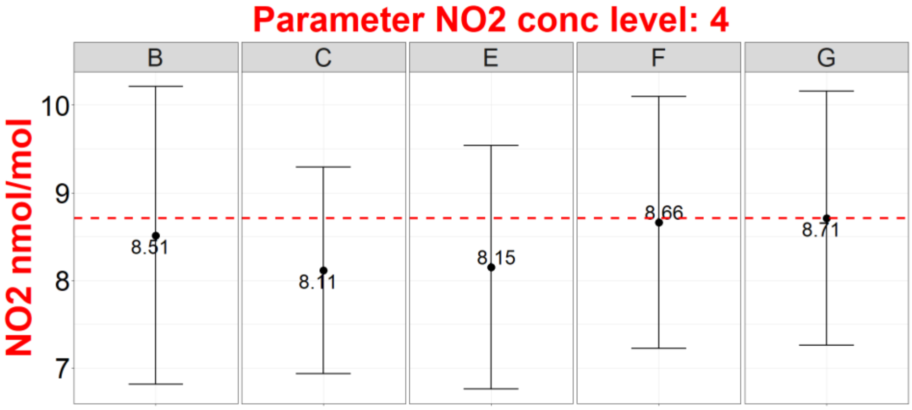
Figure 35: Reported values of NO2 concentration 3 (nmol/mol)



values	B	C	E	F	G
xi, 1	0	-0.23	-0.11	0.36	0.13
xi, 2	0	-0.24	-0.19	0.63	0.13
xi, 3	0.02	-0.15	-0.29	0.28	0.12
x_mean	0.01	-0.21	-0.20	0.42	0.13
sd	0.01	0.05	0.09	0.18	0.01
u(xi)	0.88	0.58	0.67	0.61	0.72
U(xi)	1.75	1.16	1.34	1.22	1.45

Source: JRC 2022

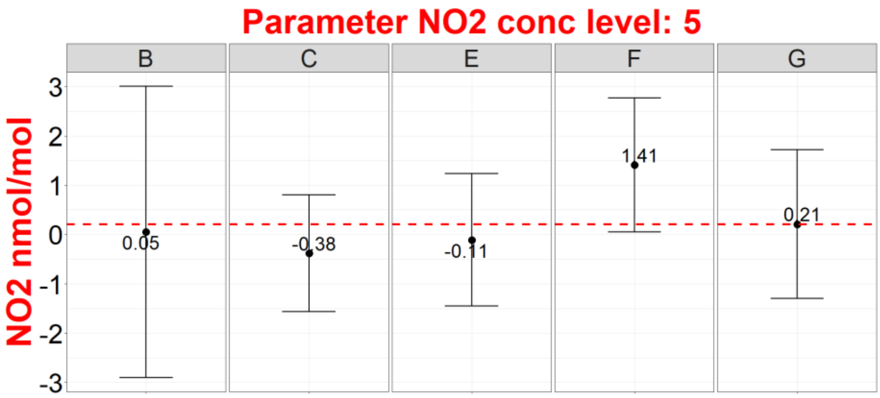
Figure 36: Reported values of NO2 concentration 4 (nmol/mol)



values	B	C	E	F	G
xi, 1	8.51	8.11	8.18	8.71	8.69
xi, 2	8.57	8.12	8.14	8.54	8.72
xi, 3	8.46	8.1	8.12	8.73	8.73
x_mean	8.51	8.11	8.15	8.66	8.71
sd	0.06	0.01	0.03	0.10	0.02
u(xi)	0.85	0.59	0.69	0.72	0.73
U(xi)	1.70	1.18	1.39	1.44	1.45

Source: JRC 2022

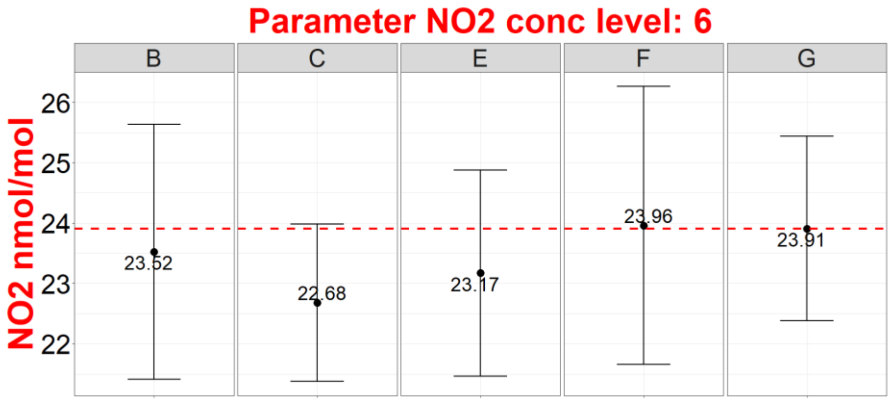
Figure 37: Reported values of NO2 concentration 5 (nmol/mol)



values	B	C	E	F	G
xi, 1	0	-0.43	-0.07	1.34	0.2
xi, 2	0.07	-0.38	-0.12	1.43	0.19
xi, 3	0.09	-0.34	-0.14	1.47	0.24
x_mean	0.05	-0.38	-0.11	1.41	0.21
sd	0.05	0.05	0.04	0.07	0.03
u(xi)	1.48	0.59	0.67	0.68	0.76
U(xi)	2.95	1.18	1.34	1.36	1.51

Source: JRC 2022

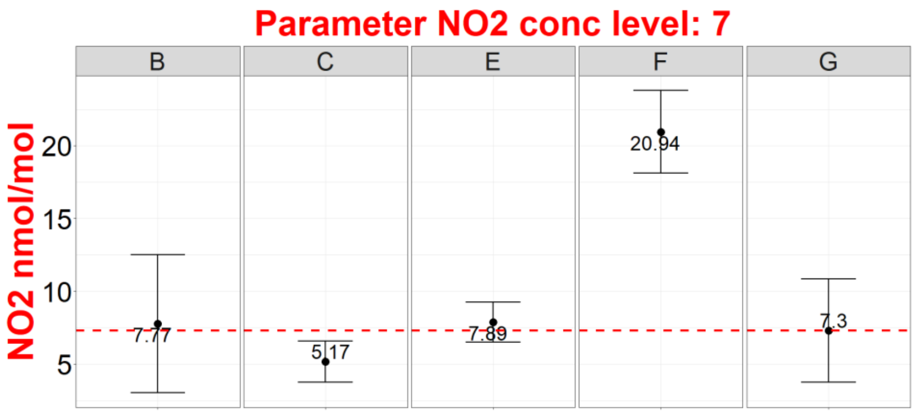
Figure 38: Reported values of NO2 concentration 6 (nmol/mol)



values	B	C	E	F	G
xi, 1	23.51	22.61	23.15	24.07	23.88
xi, 2	23.55	22.83	23.19	23.82	23.93
xi, 3	23.49	22.61	23.18	24	23.91
x_mean	23.52	22.68	23.17	23.96	23.91
sd	0.03	0.13	0.02	0.13	0.03
u(xi)	1.06	0.65	0.86	1.15	0.76
U(xi)	2.11	1.30	1.71	2.30	1.53

Source: JRC 2022

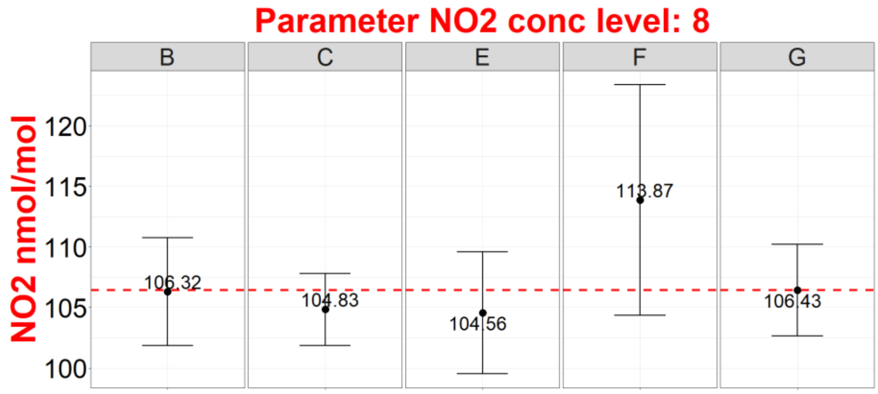
Figure 39: Reported values of NO2 concentration 7 (nmol/mol)



values	B	C	E	F	G
xi, 1	7.76	4.96	8.14	20.74	7.57
xi, 2	7.74	5.35	7.84	21.32	7.17
xi, 3	7.82	5.19	7.68	20.76	7.15
x_mean	7.77	5.17	7.89	20.94	7.30
sd	0.04	0.20	0.23	0.33	0.24
u(xi)	2.37	0.70	0.69	1.42	1.78
U(xi)	4.73	1.40	1.38	2.84	3.55

Source: JRC 2022

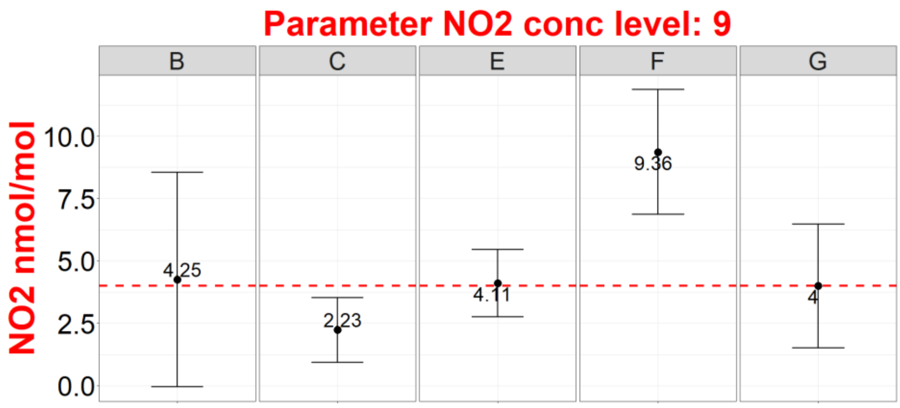
Figure 40: Reported values of NO2 concentration 8 (nmol/mol)



values	B	C	E	F	G
xi, 1	106.15	105.12	104.5	115.31	106.3
xi, 2	106.32	104.82	104.73	113.69	106.56
xi, 3	106.48	104.55	104.44	112.6	106.43
x_mean	106.32	104.83	104.56	113.87	106.43
sd	0.17	0.29	0.15	1.36	0.13
u(xi)	2.23	1.48	2.51	4.75	1.89
U(xi)	4.45	2.96	5.02	9.50	3.77

Source: JRC 2022

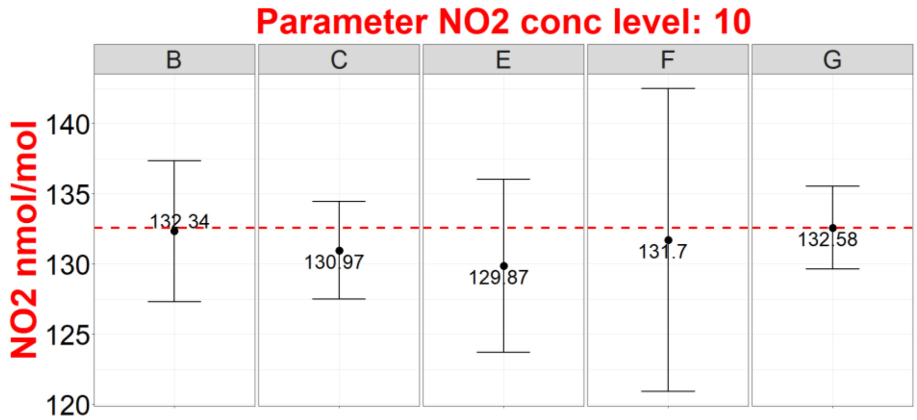
Figure 41: Reported values of NO2 concentration 9 (nmol/mol)



values	B	C	E	F	G
xi, 1	4.24	2.38	4.19	9.62	4.12
xi, 2	4.23	2.17	4.09	8.83	3.95
xi, 3	4.28	2.14	4.06	9.63	3.92
x_mean	4.25	2.23	4.11	9.36	4.00
sd	0.03	0.13	0.07	0.46	0.11
u(xi)	2.15	0.65	0.67	1.25	1.24
U(xi)	4.29	1.30	1.35	2.50	2.48

Source: JRC 2022

Figure 42: Reported values of NO2 concentration 10 (nmol/mol)

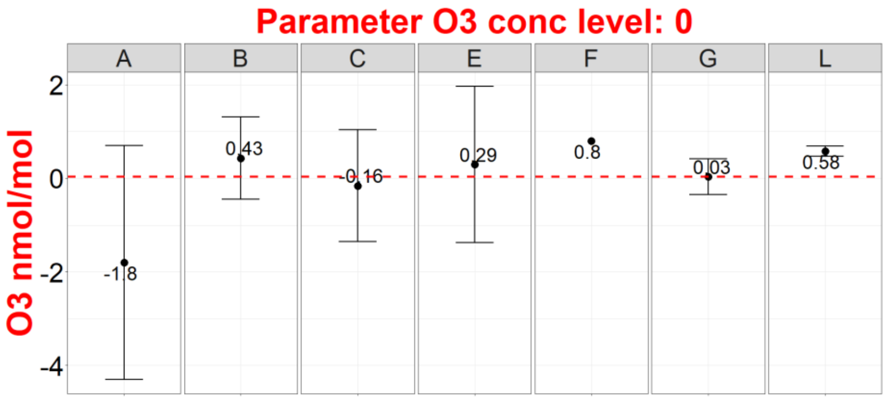


values	B	C	E	F	G
xi, 1	132.23	130.84	129.85	131.8	132.49
xi, 2	132.38	130.97	129.98	131.9	132.66
xi, 3	132.4	131.11	129.77	131.41	132.58
x_mean	132.34	130.97	129.87	131.70	132.58
sd	0.09	0.14	0.11	0.26	0.09
u(xi)	2.51	1.74	3.08	5.39	1.48
U(xi)	5.02	3.48	6.16	10.78	2.96

Source: JRC 2022

Reported values for O3

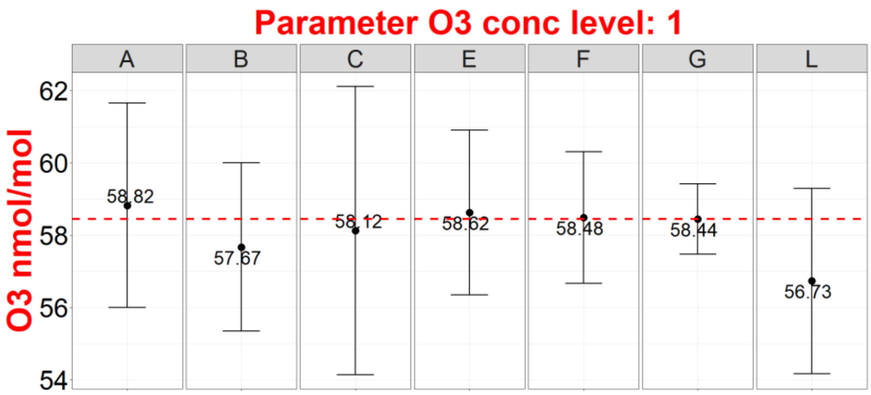
Figure 43: Reported values of O3 concentration 0 (nmol/mol)



values	A	B	C	E	F	G	L
xi, 1	-1.8	0.43	-0.16	0.29	0.8	0.03	0.58
u(xi)	1.25	0.44	0.59	0.83	NA	0.19	0.06
U(xi)	2.50	0.88	1.20	1.67	NA	0.38	0.11

Source: JRC 2022

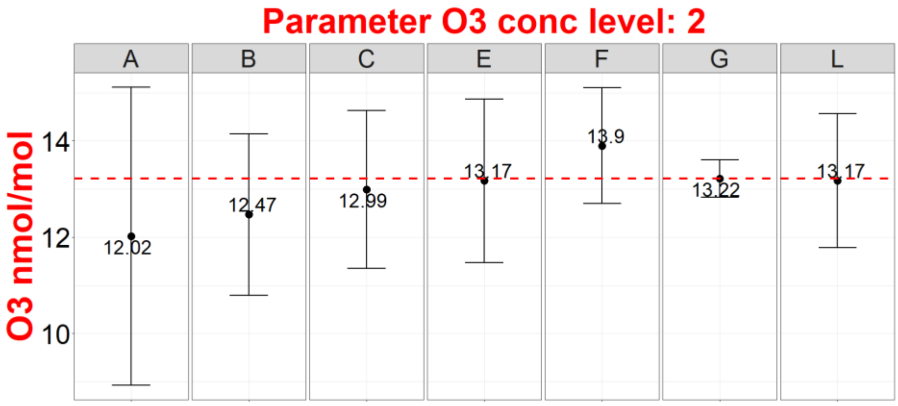
Figure 44: Reported values of O3 concentration 1 (nmol/mol)



values	A	B	C	E	F	G	L
xi, 1	58.71	57.51	57.95	58.48	58.31	58.3	56.46
xi, 2	58.74	57.7	58.09	58.65	58.51	58.47	56.79
xi, 3	59.01	57.8	58.31	58.74	58.62	58.56	56.94
x_mean	58.82	57.67	58.12	58.62	58.48	58.44	56.73
sd	0.17	0.15	0.18	0.13	0.16	0.13	0.25
u(xi)	1.41	1.16	1.59	1.14	0.91	0.48	1.28
U(xi)	2.83	2.32	3.98	2.28	1.82	0.97	2.56

Source: JRC 2022

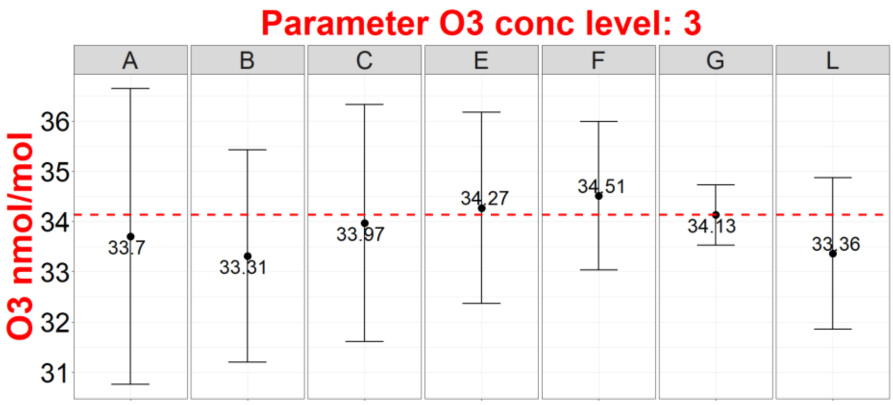
Figure 45: Reported values of O3 concentration 2 (nmol/mol)



values	A	B	C	E	F	G	L
xi, 1	11.99	12.49	13.01	13.14	13.87	13.17	13.08
xi, 2	12.01	12.43	13.02	13.17	13.9	13.24	13.09
xi, 3	12.06	12.48	12.93	13.19	13.92	13.26	13.35
x_mean	12.02	12.47	12.99	13.17	13.90	13.22	13.17
sd	0.04	0.03	0.05	0.03	0.03	0.05	0.15
u(xi)	1.55	0.84	0.69	0.85	0.60	0.19	0.69
U(xi)	3.09	1.68	1.64	1.70	1.20	0.39	1.39

Source: JRC 2022

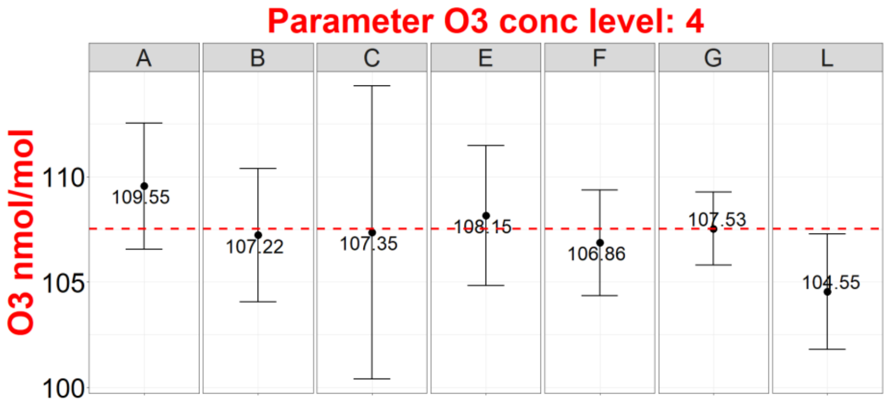
Figure 46: Reported values of O3 concentration 3 (nmol/mol)



values	A	B	C	E	F	G	L
xi, 1	33.65	33.25	33.95	34.24	34.46	34.08	33.21
xi, 2	33.63	33.38	33.93	34.3	34.51	34.17	33.37
xi, 3	33.81	33.3	34.03	34.27	34.57	34.14	33.51
x_mean	33.70	33.31	33.97	34.27	34.51	34.13	33.36
sd	0.10	0.07	0.05	0.03	0.06	0.05	0.15
u(xi)	1.47	1.06	1.05	0.95	0.74	0.30	0.76
U(xi)	2.94	2.11	2.36	1.90	1.48	0.60	1.51

Source: JRC 2022

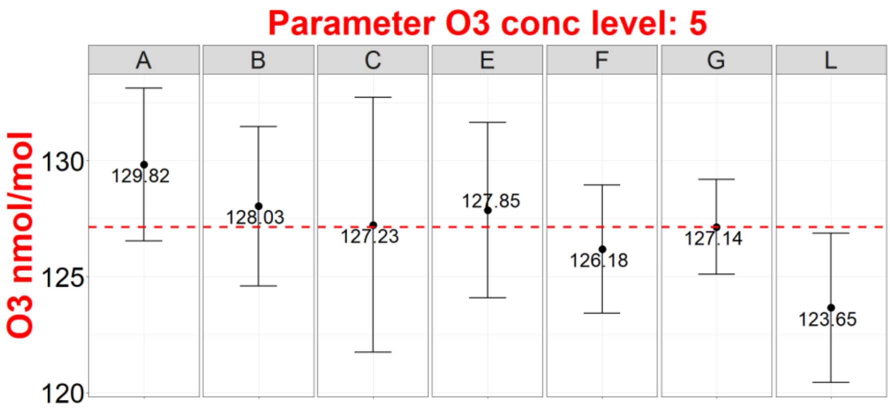
Figure 47: Reported values of O3 concentration 4 (nmol/mol)



alues	A	B	C	E	F	G	L
xi, 1	109.43	107.07	107.29	108.11	106.77	107.46	104.4
xi, 2	109.72	107.27	107.32	108.18	106.88	107.53	104.5
xi, 3	109.49	107.32	107.43	108.17	106.92	107.59	104.6
_mean	109.55	107.22	107.35	108.15	106.86	107.53	104.5
sd	0.15	0.13	0.07	0.04	0.08	0.07	0.09
u(xi)	1.50	1.58	2.78	1.66	1.25	0.86	1.37
U(xi)	2.99	3.17	6.94	3.32	2.50	1.73	2.74

Source: JRC 2022

Figure 48: Reported values of O3 concentration 5 (nmol/mol)

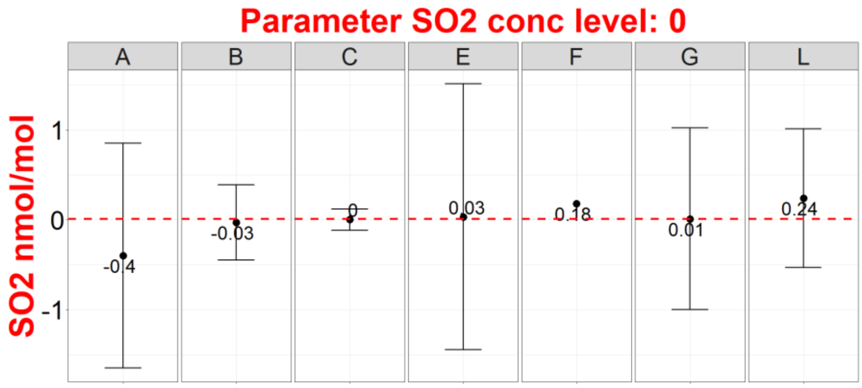


alues	A	B	C	E	F	G	L
xi, 1	129.86	127.34	127.14	127.87	126.07	127.11	123.5
xi, 2	129.71	127.91	127.23	127.83	126.18	127.17	123.5
xi, 3	129.88	128.85	127.31	127.86	126.3	127.13	123.7
_mean	129.82	128.03	127.23	127.85	126.18	127.14	123.6
sd	0.09	0.76	0.09	0.02	0.12	0.03	0.13
u(xi)	1.64	1.71	3.27	1.89	1.38	1.02	1.60
U(xi)	3.29	3.43	5.50	3.78	2.76	2.04	3.2

Source: JRC 2022

Reported values for SO2

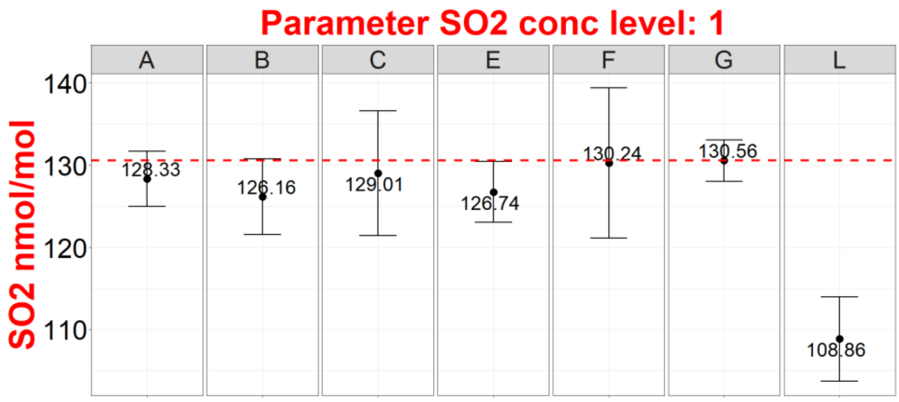
Figure 49: Reported values of SO2 concentration 0 (nmol/mol)



values	A	B	C	E	F	G	L
xi, 1	-0.4	-0.03	0	0.03	0.18	0.01	0.24
u(xi)	0.63	0.21	0.06	0.74	NA	0.50	0.39
U(xi)	1.25	0.42	0.12	1.48	NA	1.01	0.77

Source: JRC 2022

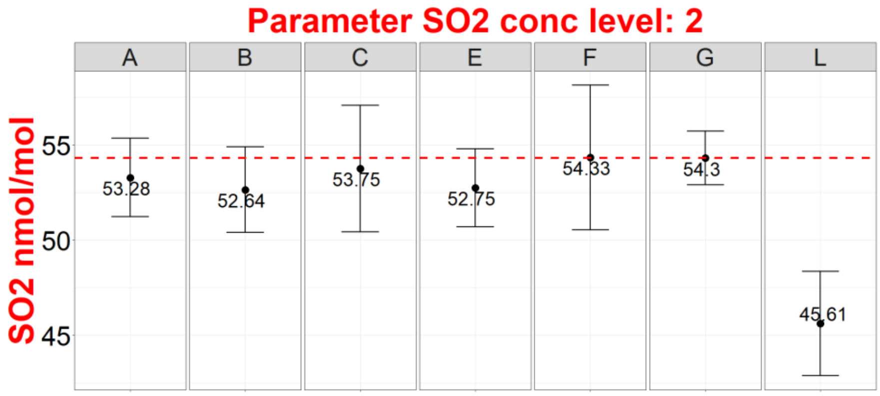
Figure 50: Reported values of SO2 concentration 1 (nmol/mol)



alues	A	B	C	E	F	G	L
xi, 1	128.29	126.09	128.86	126.55	130.32	130.42	108.
xi, 2	128.29	126.05	128.89	126.75	130.04	130.56	109.
xi, 3	128.4	126.33	129.27	126.93	130.36	130.7	109.
_mean	128.33	126.16	129.01	126.74	130.24	130.56	108.
sd	0.06	0.15	0.23	0.19	0.17	0.14	0.2
u(xi)	1.68	2.29	3.78	1.86	4.56	1.26	2.5
U(xi)	3.36	4.59	7.56	3.72	9.12	2.52	5.1

Source: JRC 2022

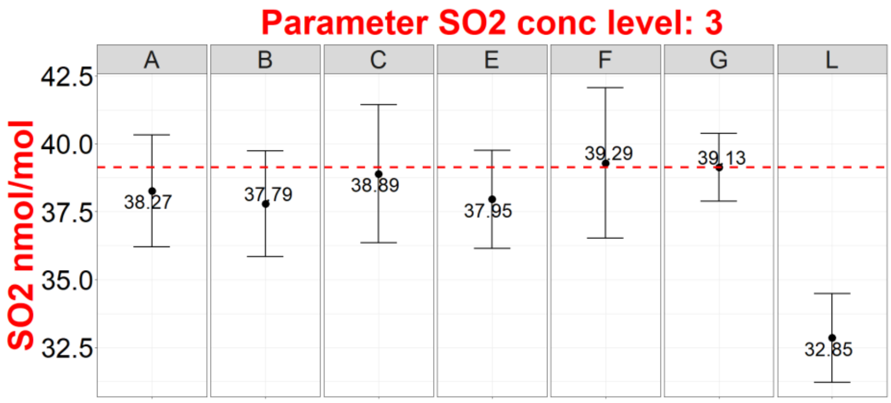
Figure 51: Reported values of SO2 concentration 2 (nmol/mol)



values	A	B	C	E	F	G	L
xi, 1	53.23	52.69	53.79	52.79	54.48	54.32	45.57
xi, 2	53.31	52.64	53.7	52.71	54.37	54.28	45.67
xi, 3	53.31	52.58	53.76	52.74	54.14	54.31	45.6
x_mean	53.28	52.64	53.75	52.75	54.33	54.30	45.61
sd	0.05	0.06	0.05	0.04	0.17	0.02	0.05
u(xi)	1.03	1.12	1.66	1.02	1.90	0.70	1.36
U(xi)	2.06	2.25	3.32	2.05	3.80	1.41	2.73

Source: JRC 2022

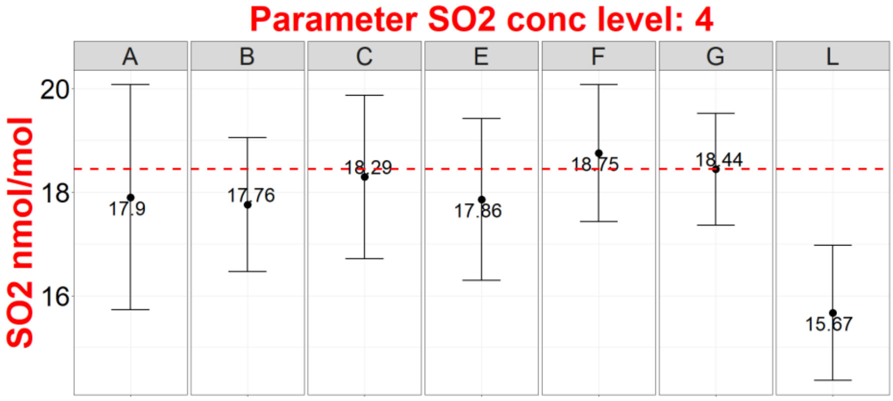
Figure 52: Reported values of SO2 concentration 3 (nmol/mol)



values	A	B	C	E	F	G	L
xi, 1	38.3	37.71	38.75	37.93	39.4	39.07	32.89
xi, 2	38.05	37.81	38.98	37.94	39.46	39.18	32.74
xi, 3	38.46	37.86	38.95	37.98	39.01	39.13	32.92
x_mean	38.27	37.79	38.89	37.95	39.29	39.13	32.85
sd	0.21	0.08	0.13	0.03	0.24	0.06	0.10
u(xi)	1.03	0.97	1.27	0.90	1.38	0.63	0.82
U(xi)	2.06	1.94	2.54	1.80	2.76	1.25	1.63

Source: JRC 2022

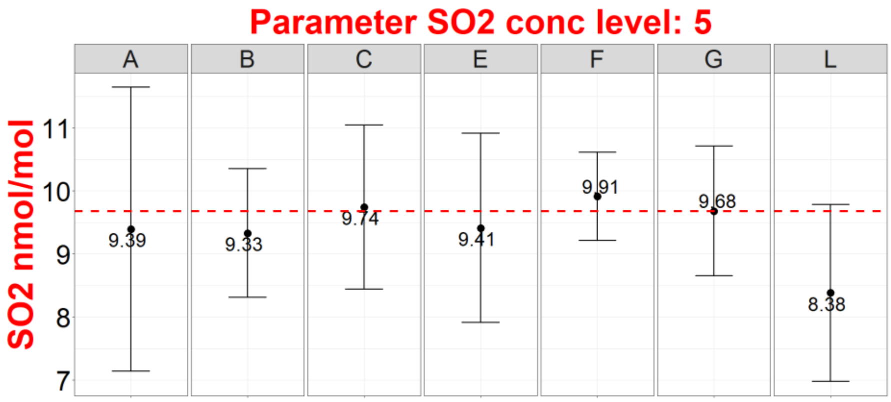
Figure 53: Reported values of SO2 concentration 4 (nmol/mol)



values	A	B	C	E	F	G	L
xi, 1	17.92	17.72	18.24	17.82	18.48	18.38	15.63
xi, 2	17.88	17.81	18.29	17.88	18.97	18.48	15.73
xi, 3	17.89	17.76	18.33	17.89	18.79	18.46	15.64
x_mean	17.90	17.76	18.29	17.86	18.75	18.44	15.67
sd	0.02	0.05	0.05	0.04	0.25	0.05	0.06
u(xi)	1.09	0.65	0.79	0.78	0.66	0.54	0.65
U(xi)	2.17	1.29	1.58	1.56	1.32	1.08	1.30

Source: JRC 2022

Figure 54: Reported values of SO2 concentration 5 (nmol/mol)



values	A	B	C	E	F	G	L
xi, 1	9.5	9.33	9.77	9.4	10.01	9.67	8.35
xi, 2	9.38	9.31	9.75	9.41	9.87	9.67	8.43
xi, 3	9.29	9.35	9.71	9.41	9.84	9.7	8.35
x_mean	9.39	9.33	9.74	9.41	9.91	9.68	8.38
sd	0.11	0.02	0.03	0.01	0.09	0.02	0.05
u(xi)	1.13	0.51	0.65	0.75	0.35	0.52	0.70
U(xi)	2.25	1.02	1.30	1.50	0.70	1.03	1.40

Source: JRC 2022

Annex C: repeatability and reproducibility

For the main purpose of monitoring trends between different PT undertaken by ERLAP, the precision of standardized SO2, CO, O3 and NOX measurement methods [2], [3], [4] and [5] as implemented by NRLs, was evaluated. Applied methodology is described in ISO 5725-1, 5725-2 and 5725-6 [14], [15] and [16]. The precision experiment has involved a total of seven laboratories, the actual number of laboratories (pj) is listed in Table 11 according to the data reported.
Six concentration levels (for run 0 only one value is requested so repeatability cannot be evaluated) were tested for O3, CO, SO2 and NO2, and eleven for NO. Outlier tests were performed and results are reported in Annex D.
In ISO 5725 repeatability (r) and reproducibility (R) limits are defined. These limits are the values less than or equal to which the absolute difference between two test results, obtained under either repeatability or reproducibility conditions, may be expected to be with (1 - α) probability level.
The repeatability standard deviation (Sr) was calculated as the square root of average within-laboratory variance at the 95% confidence level. The repeatability limit (r) is calculated using Equation 7 [16].

$$r = t_{\nu/\alpha} \cdot \sqrt{2} \cdot Sr \qquad \text{Equation 7}$$

r = repeatability limit
$t_{\nu/\alpha}$ = *t* Student distribution value
S_r = estimate of repeatability variance

The reproducibility standard deviation (SR) was calculated as the square root of sum of repeatability and between-laboratory variance at the 95% confidence level (α). The reproducibility limit (R) is calculated using Equation 8 [16].

$$R = t_{\nu/\alpha} \cdot \sqrt{2} \cdot SR \qquad \text{Equation 8}$$

R = reproducibility limit
$t_{\nu/\alpha}$ = *t* Student distribution value
S_R = estimate of reproducibility variance

The repeatability standard deviation was evaluated with (pj *(3-1)) degrees of freedom (ν) and reproducibility standard deviation with (pj-1) degrees of freedom (ν).
The critical range Student factors, for r and R, corresponding to defined confidence level (α) and degree of freedom (ν) are reported in Table 11.

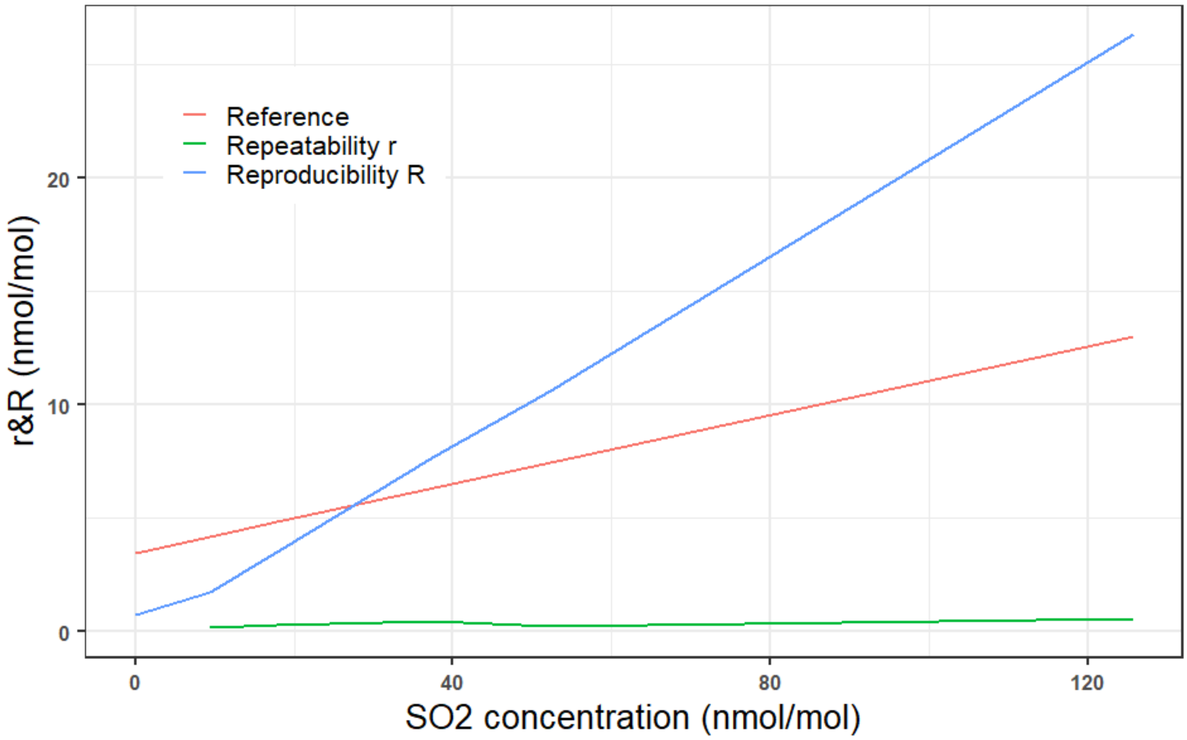
Table 11: Critical values of t used in the repeatability (r) and reproducibility (R) evaluation.

parameter	run	p_j	t critical value 95% for r	t critical value 95% for R
CO	1,2,3,4,5	7	2,145	2,447
NO	1,2,3,4,5,6,7,8,9,10	5	2,228	2,776
NO_2	2,4,6,8,10	5	2,228	2,776
O_3	1,2,3,4,5	7	2,145	2,447
SO_2	1,2,3,4,5	7	2,145	2,447

Source: JRC 2022

The repeatability (r) and reproducibility (R) limits of measurement methods are presented from Figure 55 to Figure 59. It is reported also the ‘reproducibility from common criteria (Reference)’ calculated by substituting SR in Equation 8 with a ‘standard deviation for proficiency assessment’ (see Table 4). Comparison between R and Reference serves to indicate that σ_{pt} is realistic [13] or from the other point of view, that the general methodology implemented by NRLs is appropriate for σ_{pt}.

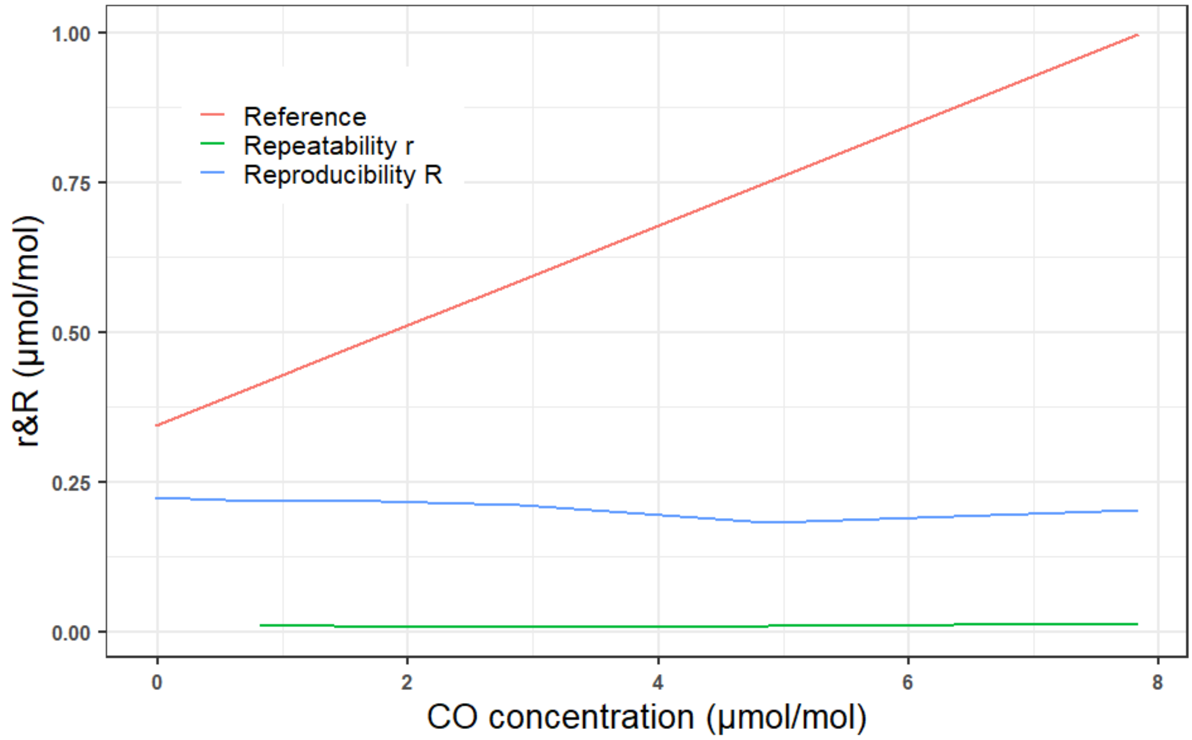
Figure 55: The R and r of SO_2 standard measurement method as a function of concentration.



Parameter	Conc.(nmol/mol)	r(nmol/mol)	R(nmol/mol)	R (%)	Reference
SO2	0.004		0.709		3.461
SO2	9.405	0.173	1.741		4.177
SO2	17.809	0.309	3.502		4.816
SO2	37.739	0.425	7.734		6.334
SO2	52.380	0.237	10.593		7.448
SO2	125.699	0.57	26.321	20.9	13.030

Source: JRC 2022

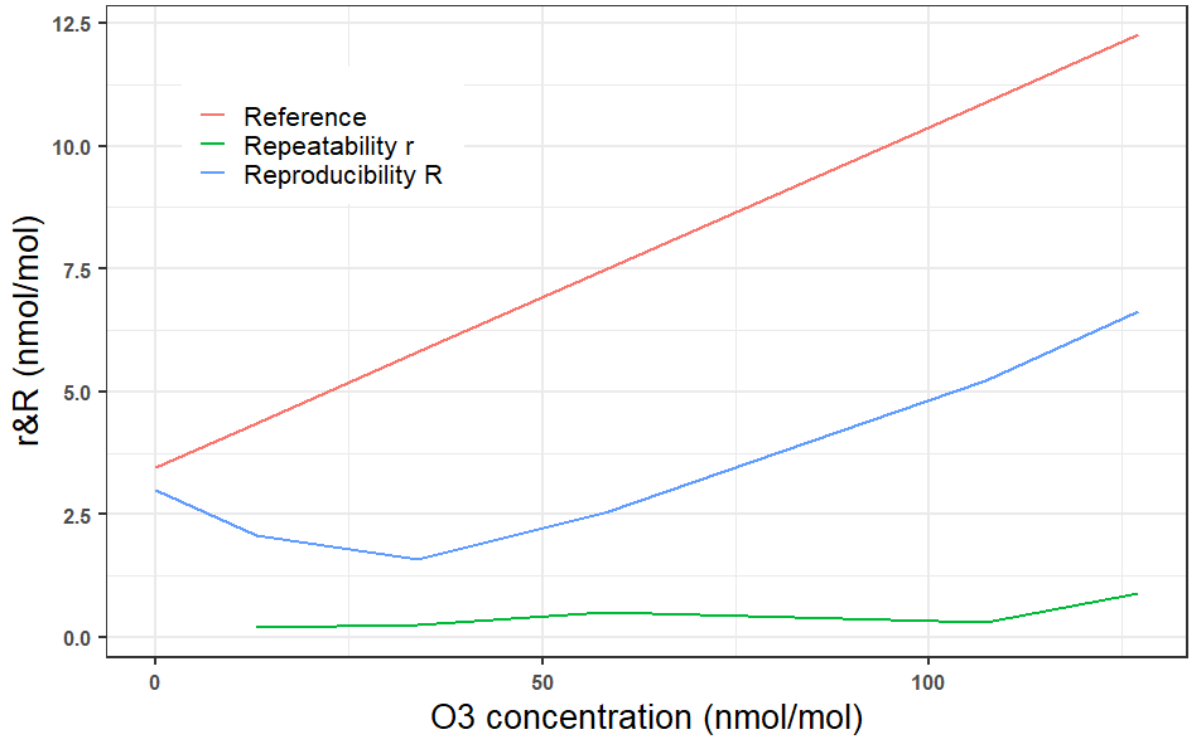
Figure 56: The R and r of CO standard measurement method as a function of concentration.



Parameter	Conc.(µmol/mol)	r(µmol/mol)	R(µmol/mol)	R (%)	Reference
CO	-0.0173		0.2253		0.3446
CO	0.8221	0.0109	0.2177		0.4143
CO	1.4137	0.0091	0.2194		0.4635
CO	2.8948	0.0079	0.2125		0.5865
CO	4.8772	0.0091	0.1834		0.7511
CO	7.8394	0.0133	0.2031	2.6	0.9972

Source: JRC 2022

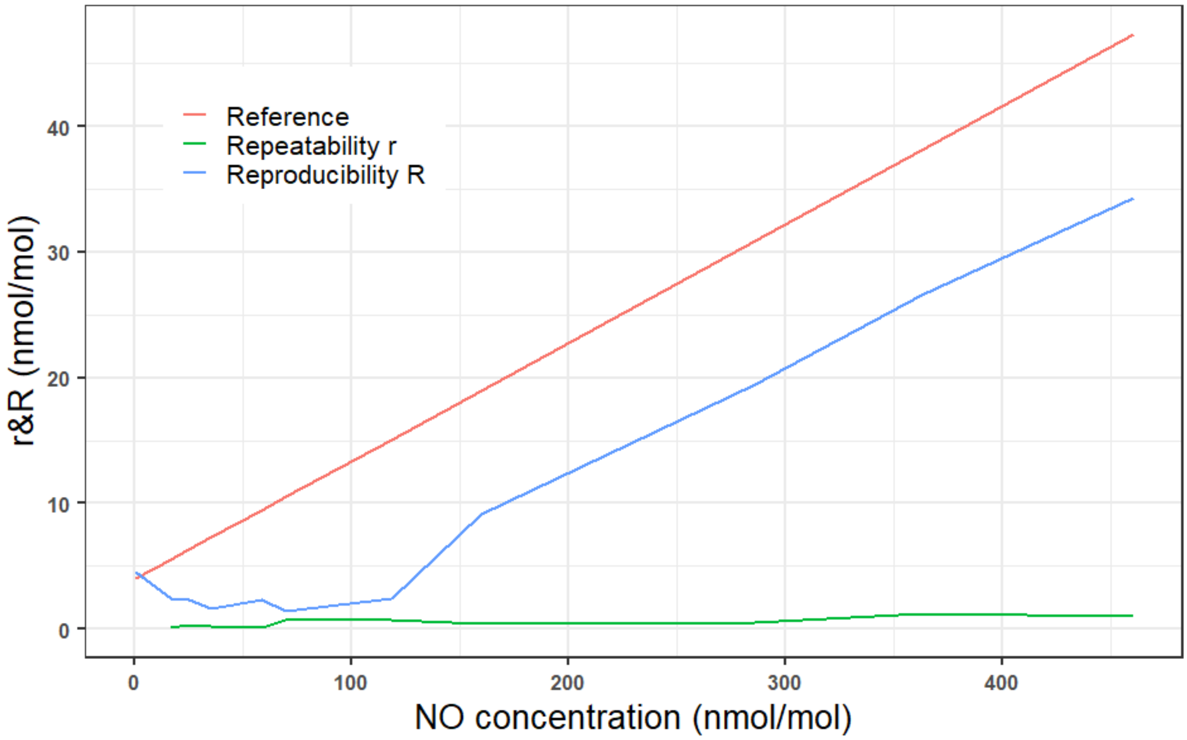
Figure 57: The R and r of O_3 standard measurement method as a function of concentration.



Parameter	Conc.(nmol/mol)	r(nmol/mol)	R(nmol/mol)	R (%)	Reference
O3	0.024		3.000		3.462
O3	12.991	0.203	2.083		4.360
O3	33.893	0.246	1.595		5.806
O3	58.126	0.516	2.537		7.484
O3	107.314	0.297	5.219		10.888
O3	127.128	0.907	6.620	5.2	12.259

Source: JRC 2022

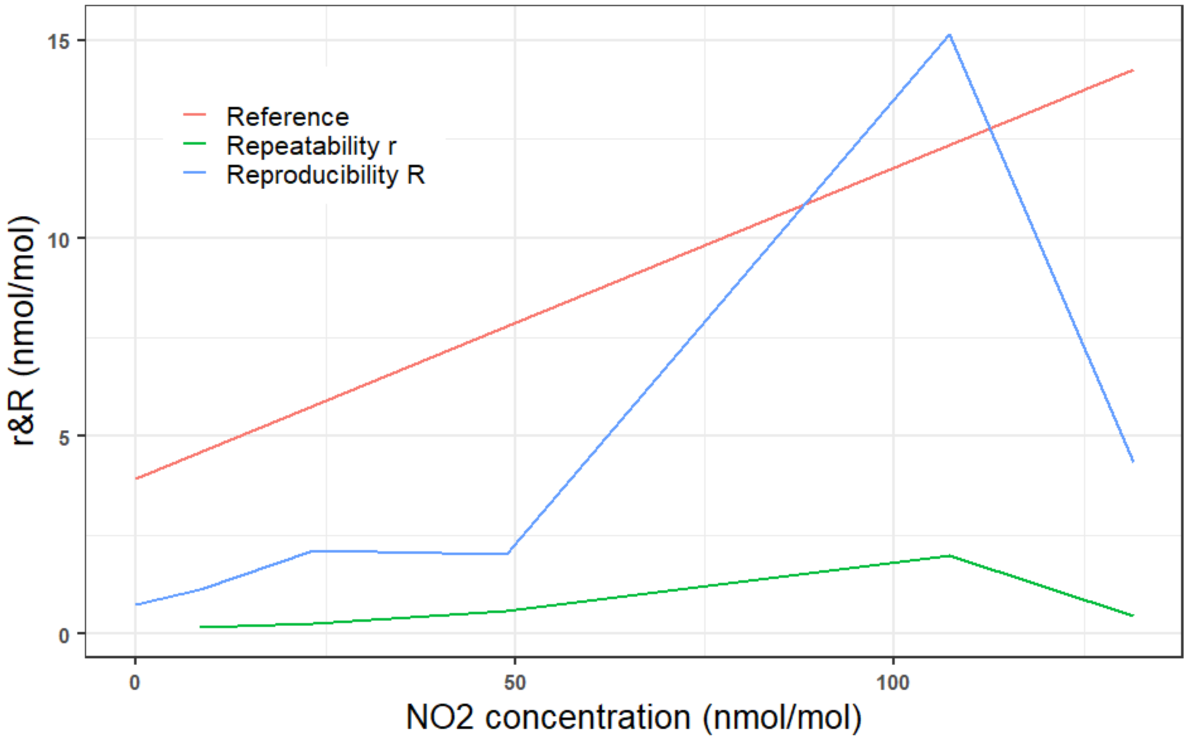
Figure 58: The R and r of NO standard measurement method as a function of concentration.



Parameter	Conc.(nmol/mol)	r(nmol/mol)	R(nmol/mol)	R (%)	Reference
NO	0.516		4.495		3.974
NO	16.668	0.129	2.407		5.496
NO	25.149	0.328	2.320		6.295
NO	35.655	0.205	1.661		7.285
NO	58.864	0.113	2.308		9.472
NO	69.793	0.699	1.374		10.502
NO	118.395	0.747	2.399		15.081
NO	159.683	0.391	9.124		18.971
NO	286.371	0.545	19.441		30.908
NO	362.753	1.185	26.606		38.105
NO	460.318	1.056	34.316	7.5	47.297

Source: JRC 2022

Figure 59: The R and r of NO_2 standard measurement method as a function of concentration.



Parameter	Conc.(nmol/mol)	r(nmol/mol)	R(nmol/mol)	R (%)	Reference
NO2	-0.108		0.738		3.917
NO2	8.429	0.173	1.127		4.588
NO2	23.449	0.262	2.116		5.767
NO2	48.839	0.599	2.026		7.761
NO2	107.200	1.998	15.142		12.343
NO2	131.491	0.473	4.346	3.3	14.250

Source: JRC 2022

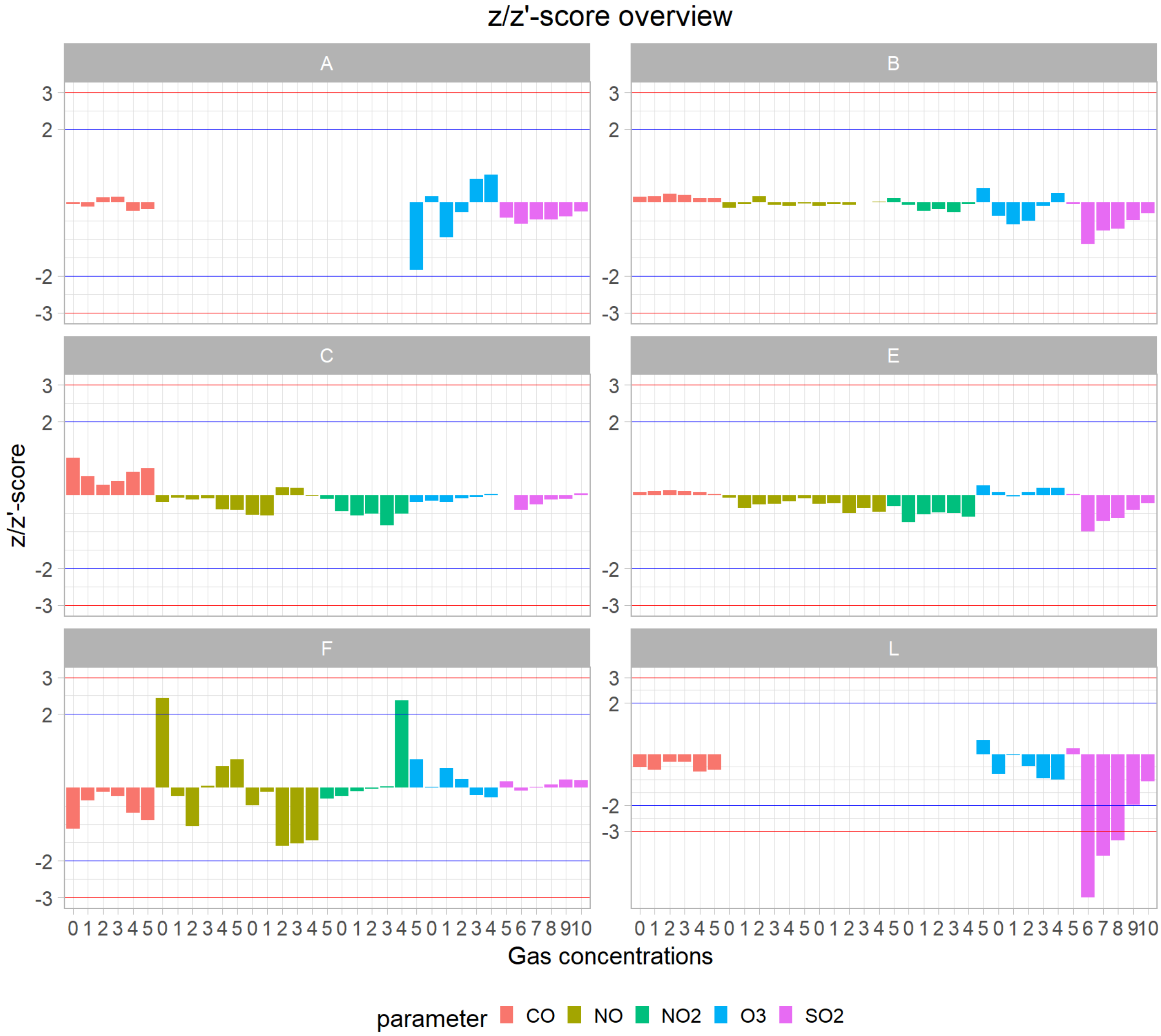
Annex D: scrutiny of results for consistency and outlier test

The precision evaluation (Annex C) focuses on data that are as much as possible the reflection of every day work of NRLs and thus represents the comparability of participant's standard operating procedures. For that reason, a procedure for the detection of exceptional errors (error during typing, slip in performing the measurement or the calculation, wrong averaging interval, malfunction of instrumentation, etc.) was applied. In this procedure were carried out tests for data consistency and statistical outliers as described in ISO 13528 [13].

Laboratories showing some form of statistical inconsistency were requested to investigate the cause of discrepancies before the release of the draft report. Laboratories were allowed to correct their results in case of identification of exceptional errors, none of the laboratories contacted has modified the values submitted. Subsequently, data were considered definitive and z/z'-scores calculation was performed to estimate outliers. Statistical outliers obtained at this stage are not considered as extraordinary errors but due to significant difference in participant's standard operating procedure.

The precision of standardised measurement methods reported in Annex D are calculated using the data pool with outliers. Figure 60 is summarizing the z-score evaluation of each participant for all parameters.

Figure 60: Overview about z/z'-score final evaluation.



Source: JRC 2022

Table 12: z/z'-score selected according to the criteria uref<0.3 σpt.

Gas	Unit	Ref	u_ref	p	0.3*σpt	z/z'
CO _0	µmol/mol	-0.011	0.008	6	0.030	z
CO _1	µmol/mol	2.901	0.015	6	0.051	z
CO _2	µmol/mol	7.824	0.034	6	0.086	z
CO _3	µmol/mol	4.868	0.022	6	0.065	z
CO _4	µmol/mol	1.428	0.011	6	0.040	z
CO _5	µmol/mol	0.836	0.009	6	0.036	z
NO _0	nmol/mol	0.110	0.710	4	0.301	z'
NO _1	nmol/mol	118.940	1.090	4	1.156	z
NO _2	nmol/mol	69.983	0.860	4	0.804	z'
NO _3	nmol/mol	25.177	0.730	4	0.481	z'
NO _4	nmol/mol	16.600	0.720	4	0.420	z'
NO _5	nmol/mol	59.533	0.820	4	0.729	z'
NO _6	nmol/mol	36.013	0.760	4	0.559	z'
NO _7	nmol/mol	464.993	3.290	4	3.648	z
NO _8	nmol/mol	366.060	2.630	4	2.936	z
NO _9	nmol/mol	289.387	2.120	4	2.384	z
NO _10	nmol/mol	160.910	1.320	4	1.459	z
NO2 _0	nmol/mol	0.010	0.720	4	0.300	z'
NO2 _1	nmol/mol	0.373	0.840	4	0.302	z'
NO2 _2	nmol/mol	49.400	0.880	4	0.596	z'
NO2 _3	nmol/mol	0.127	0.720	4	0.301	z'
NO2 _4	nmol/mol	8.713	0.730	4	0.352	z'
NO2 _5	nmol/mol	0.210	0.760	4	0.301	z'
NO2 _6	nmol/mol	23.907	0.760	4	0.443	z'
NO2 _7	nmol/mol	7.297	1.780	4	0.344	z'
NO2 _8	nmol/mol	106.430	1.890	4	0.939	z'

Gas	Unit	Ref	u_ref	p	0.3*σpt	z/z'
NO2 _9	nmol/mol	3.997	1.240	4	0.324	z'
NO2 _10	nmol/mol	132.577	1.480	4	1.095	z'
O3 _0	nmol/mol	0.030	0.190	6	0.300	z
O3 _1	nmol/mol	58.443	0.480	6	0.651	z
O3 _2	nmol/mol	13.223	0.190	6	0.379	z
O3 _3	nmol/mol	34.130	0.300	6	0.505	z
O3 _4	nmol/mol	107.527	0.860	6	0.945	z
O3 _5	nmol/mol	127.137	1.020	6	1.063	z
SO2 _0	nmol/mol	0.010	0.500	6	0.300	z'
SO2 _1	nmol/mol	130.560	1.260	6	1.162	z'
SO2 _2	nmol/mol	54.303	0.700	6	0.658	z'
SO2 _3	nmol/mol	39.127	0.630	6	0.558	z'
SO2 _4	nmol/mol	18.440	0.540	6	0.422	z'
SO2 _5	nmol/mol	9.680	0.520	6	0.364	z'

Source: JRC 2022

Table 13: z/z'-score participants calculated values.

Gas	Code	Unit	Ref	u_ref	uref<0.3*σpt	z_value
CO _0	A	µmol/mol	-11.00	0.008	z	-0.050
CO _1	A	µmol/mol	2,901.30	0.015	z	-0.102
CO _2	A	µmol/mol	7,823.70	0.034	z	0.144
CO _3	A	µmol/mol	4,867.70	0.022	z	0.154
CO _4	A	µmol/mol	1,428.30	0.011	z	-0.233
CO _5	A	µmol/mol	836.00	0.009	z	-0.183
O3 _0	A	nmol/mol	0.03	0.190	z	-1.829
O3 _1	A	nmol/mol	58.44	0.480	z	0.174
O3 _2	A	nmol/mol	13.22	0.190	z	-0.951
O3 _3	A	nmol/mol	34.13	0.300	z	-0.256
O3 _4	A	nmol/mol	107.527	0.860	z	0.642
O3 _5	A	nmol/mol	127.137	1.020	z	0.757
SO2 _0	A	nmol/mol	0.010	0.500	z'	-0.366
SO2 _1	A	nmol/mol	130.560	1.260	z'	-0.548
SO2 _2	A	nmol/mol	54.303	0.700	z'	-0.444
SO2 _3	A	nmol/mol	39.127	0.630	z'	-0.437
SO2 _4	A	nmol/mol	18.440	0.540	z'	-0.359
SO2 _5	A	nmol/mol	9.680	0.520	z'	-0.220
CO _0	B	µmol/mol	-11.000	0.008	z	0.160
CO _1	B	µmol/mol	2,901.300	0.015	z	0.181
CO _2	B	µmol/mol	7,823.700	0.034	z	0.241
CO _3	B	µmol/mol	4,867.700	0.022	z	0.209
CO _4	B	µmol/mol	1,428.300	0.011	z	0.124
CO _5	B	µmol/mol	836.000	0.009	z	0.117
NO _0	B	nmol/mol	0.110	0.710	z'	-0.122
NO _1	B	nmol/mol	118.940	1.090	z	-0.042
NO _2	B	nmol/mol	69.983	0.860	z'	-0.058
NO _3	B	nmol/mol	25.177	0.730	z'	-0.083
NO _4	B	nmol/mol	16.600	0.720	z'	-0.019
NO _5	B	nmol/mol	59.533	0.820	z'	-0.087
NO _6	B	nmol/mol	36.013	0.760	z'	-0.046
NO _7	B	nmol/mol	464.993	3.290	z	-0.061
NO _8	B	nmol/mol	366.060	2.630	z	0.006
NO _9	B	nmol/mol	289.387	2.120	z	0.026
NO _10	B	nmol/mol	160.910	1.320	z	0.177
NO2 _0	B	nmol/mol	0.010	0.720	z'	0.098
NO2 _2	B	nmol/mol	49.400	0.880	z'	-0.207

Gas	Code	Unit	Ref	u_ref	uref<0.3*σpt	z_value
NO2 _4	B	nmol/mol	8.713	0.730	z'	-0.147
NO2 _6	B	nmol/mol	23.907	0.760	z'	-0.233
NO2 _8	B	nmol/mol	106.430	1.890	z'	-0.030
NO2 _10	B	nmol/mol	132.577	1.480	z'	-0.060
O3 _0	B	nmol/mol	0.030	0.190	z	0.400
O3 _1	B	nmol/mol	58.443	0.480	z	-0.356
O3 _2	B	nmol/mol	13.223	0.190	z	-0.596
O3 _3	B	nmol/mol	34.130	0.300	z	-0.487
O3 _4	B	nmol/mol	107.527	0.860	z	-0.097
O3 _5	B	nmol/mol	127.137	1.020	z	0.252
SO2 _0	B	nmol/mol	0.010	0.500	z'	-0.036
SO2 _1	B	nmol/mol	130.560	1.260	z'	-1.081
SO2 _2	B	nmol/mol	54.303	0.700	z'	-0.721
SO2 _3	B	nmol/mol	39.127	0.630	z'	-0.681
SO2 _4	B	nmol/mol	18.440	0.540	z'	-0.452
SO2 _5	B	nmol/mol	9.680	0.520	z'	-0.266
CO _0	C	µmol/mol	-11.000	0.008	z	1.013
CO _1	C	µmol/mol	2,901.300	0.015	z	0.505
CO _2	C	µmol/mol	7,823.700	0.034	z	0.276
CO _3	C	µmol/mol	4,867.700	0.022	z	0.380
CO _4	C	µmol/mol	1,428.300	0.011	z	0.631
CO _5	C	µmol/mol	836.000	0.009	z	0.725
NO _0	C	nmol/mol	0.110	0.710	z'	-0.163
NO _1	C	nmol/mol	118.940	1.090	z	-0.067
NO _2	C	nmol/mol	69.983	0.860	z'	-0.086
NO _3	C	nmol/mol	25.177	0.730	z'	-0.361
NO _4	C	nmol/mol	16.600	0.720	z'	-0.369
NO _5	C	nmol/mol	59.533	0.820	z'	-0.520
NO _6	C	nmol/mol	36.013	0.760	z'	-0.523
NO _7	C	nmol/mol	464.993	3.290	z	0.211
NO _8	C	nmol/mol	366.060	2.630	z	0.190
NO _9	C	nmol/mol	289.387	2.120	z	-0.029
NO _10	C	nmol/mol	160.910	1.320	z	-0.128
NO2 _0	C	nmol/mol	0.010	0.720	z'	-0.081
NO2 _2	C	nmol/mol	49.400	0.880	z'	-0.505
NO2 _4	C	nmol/mol	8.713	0.730	z'	-0.437
NO2 _6	C	nmol/mol	23.907	0.760	z'	-0.737
NO2 _8	C	nmol/mol	106.430	1.890	z'	-0.438

Gas	Code	Unit	Ref	u_ref	uref<0.3*σpt	z_value
NO2 _10	C	nmol/mol	132.577	1.480	z'	-0.408
O3 _0	C	nmol/mol	0.030	0.190	z	-0.190
O3 _1	C	nmol/mol	58.443	0.480	z	-0.149
O3 _2	C	nmol/mol	13.223	0.190	z	-0.184
O3 _3	C	nmol/mol	34.130	0.300	z	-0.095
O3 _4	C	nmol/mol	107.527	0.860	z	-0.056
O3 _5	C	nmol/mol	127.137	1.020	z	0.026
SO2 _0	C	nmol/mol	0.010	0.500	z'	-0.009
SO2 _1	C	nmol/mol	130.560	1.260	z'	-0.381
SO2 _2	C	nmol/mol	54.303	0.700	z'	-0.240
SO2 _3	C	nmol/mol	39.127	0.630	z'	-0.121
SO2 _4	C	nmol/mol	18.440	0.540	z'	-0.100
SO2 _5	C	nmol/mol	9.680	0.520	z'	0.046
CO _0	E	μmol/mol	-11.000	0.008	z	0.070
CO _1	E	μmol/mol	2,901.300	0.015	z	0.104
CO _2	E	μmol/mol	7,823.700	0.034	z	0.130
CO _3	E	μmol/mol	4,867.700	0.022	z	0.107
CO _4	E	μmol/mol	1,428.300	0.011	z	0.080
CO _5	E	μmol/mol	836.000	0.009	z	0.025
NO _0	E	nmol/mol	0.110	0.710	z'	-0.057
NO _1	E	nmol/mol	118.940	1.090	z	-0.350
NO _2	E	nmol/mol	69.983	0.860	z'	-0.236
NO _3	E	nmol/mol	25.177	0.730	z'	-0.163
NO _4	E	nmol/mol	16.600	0.720	z'	-0.083
NO _5	E	nmol/mol	59.533	0.820	z'	-0.227
NO _6	E	nmol/mol	36.013	0.760	z'	-0.210
NO _7	E	nmol/mol	464.993	3.290	z	-0.485
NO _8	E	nmol/mol	366.060	2.630	z	-0.365
NO _9	E	nmol/mol	289.387	2.120	z	-0.460
NO _10	E	nmol/mol	160.910	1.320	z	-0.255
NO2 _0	E	nmol/mol	0.010	0.720	z'	-0.244
NO2 _2	E	nmol/mol	49.400	0.880	z'	-0.478
NO2 _4	E	nmol/mol	8.713	0.730	z'	-0.408
NO2 _6	E	nmol/mol	23.907	0.760	z'	-0.443
NO2 _8	E	nmol/mol	106.430	1.890	z'	-0.512
NO2 _10	E	nmol/mol	132.577	1.480	z'	-0.687
O3 _0	E	nmol/mol	0.030	0.190	z	0.260
O3 _1	E	nmol/mol	58.443	0.480	z	0.082

Gas	Code	Unit	Ref	u_ref	uref<0.3*σpt	z_value
O3 _2	E	nmol/mol	13.223	0.190	z	-0.042
O3 _3	E	nmol/mol	34.130	0.300	z	0.083
O3 _4	E	nmol/mol	107.527	0.860	z	0.198
O3 _5	E	nmol/mol	127.137	1.020	z	0.201
SO2 _0	E	nmol/mol	0.010	0.500	z'	0.018
SO2 _1	E	nmol/mol	130.560	1.260	z'	-0.938
SO2 _2	E	nmol/mol	54.303	0.700	z'	-0.674
SO2 _3	E	nmol/mol	39.127	0.630	z'	-0.600
SO2 _4	E	nmol/mol	18.440	0.540	z'	-0.385
SO2 _5	E	nmol/mol	9.680	0.520	z'	-0.205
CO _0	F	µmol/mol	-11.000	0.008	z	-1.123
CO _1	F	µmol/mol	2,901.300	0.015	z	-0.350
CO _2	F	µmol/mol	7,823.700	0.034	z	-0.114
CO _3	F	µmol/mol	4,867.700	0.022	z	-0.238
CO _4	F	µmol/mol	1,428.300	0.011	z	-0.695
CO _5	F	µmol/mol	836.000	0.009	z	-0.891
NO _0	F	nmol/mol	0.110	0.710	z'	1.994
NO _1	F	nmol/mol	118.940	1.090	z	-0.246
NO _2	F	nmol/mol	69.983	0.860	z'	0.042
NO _3	F	nmol/mol	25.177	0.730	z'	0.529
NO _4	F	nmol/mol	16.600	0.720	z'	0.687
NO _5	F	nmol/mol	59.533	0.820	z'	-0.469
NO _6	F	nmol/mol	36.013	0.760	z'	-0.111
NO _7	F	nmol/mol	464.993	3.290	z	-1.587
NO _8	F	nmol/mol	366.060	2.630	z	-1.522
NO _9	F	nmol/mol	289.387	2.120	z	-1.436
NO _10	F	nmol/mol	160.910	1.320	z	-1.057
NO2 _0	F	nmol/mol	0.010	0.720	z'	-0.252
NO2 _2	F	nmol/mol	49.400	0.880	z'	-0.097
NO2 _4	F	nmol/mol	8.713	0.730	z'	-0.038
NO2 _6	F	nmol/mol	23.907	0.760	z'	0.032
NO2 _8	F	nmol/mol	106.430	1.890	z'	2.037
NO2 _10	F	nmol/mol	132.577	1.480	z'	-0.223
O3 _0	F	nmol/mol	0.030	0.190	z	0.770
O3 _1	F	nmol/mol	58.443	0.480	z	0.017
O3 _2	F	nmol/mol	13.223	0.190	z	0.535
O3 _3	F	nmol/mol	34.130	0.300	z	0.226
O3 _4	F	nmol/mol	107.527	0.860	z	-0.212

Gas	Code	Unit	Ref	u_ref	uref<0.3*σpt	z_value
O3 _5	F	nmol/mol	127.137	1.020	z	-0.270
SO2 _0	F	nmol/mol	0.010	0.500	z'	0.152
SO2 _1	F	nmol/mol	130.560	1.260	z'	-0.079
SO2 _2	F	nmol/mol	54.303	0.700	z'	0.012
SO2 _3	F	nmol/mol	39.127	0.630	z'	0.083
SO2 _4	F	nmol/mol	18.440	0.540	z'	0.206
SO2 _5	F	nmol/mol	9.680	0.520	z'	0.175
CO _0	L	μmol/mol	-11.000	0.008	z	-0.511
CO _1	L	μmol/mol	2,901.300	0.015	z	-0.603
CO _2	L	μmol/mol	7,823.700	0.034	z	-0.291
CO _3	L	μmol/mol	4,867.700	0.022	z	-0.303
CO _4	L	μmol/mol	1,428.300	0.011	z	-0.672
CO _5	L	μmol/mol	836.000	0.009	z	-0.600
O3 _0	L	nmol/mol	0.030	0.190	z	0.550
O3 _1	L	nmol/mol	58.443	0.480	z	-0.790
O3 _2	L	nmol/mol	13.223	0.190	z	-0.042
O3 _3	L	nmol/mol	34.130	0.300	z	-0.458
O3 _4	L	nmol/mol	107.527	0.860	z	-0.945
O3 _5	L	nmol/mol	127.137	1.020	z	-0.984
SO2 _0	L	nmol/mol	0.010	0.500	z'	0.205
SO2 _1	L	nmol/mol	130.560	1.260	z'	-5.329
SO2 _2	L	nmol/mol	54.303	0.700	z'	-3.771
SO2 _3	L	nmol/mol	39.127	0.630	z'	-3.198
SO2 _4	L	nmol/mol	18.440	0.540	z'	-1.840
SO2 _5	L	nmol/mol	9.680	0.520	z'	-0.987
CO _0	A	μmol/mol	-11.000	0.008	z	-0.050
CO _1	A	μmol/mol	2,901.300	0.015	z	-0.102
CO _2	A	μmol/mol	7,823.700	0.034	z	0.144
CO _3	A	μmol/mol	4,867.700	0.022	z	0.154
CO _4	A	μmol/mol	1,428.300	0.011	z	-0.233
CO _5	A	μmol/mol	836.000	0.009	z	-0.183
O3 _0	A	nmol/mol	0.030	0.190	z	-1.829
O3 _1	A	nmol/mol	58.443	0.480	z	0.174
O3 _2	A	nmol/mol	13.223	0.190	z	-0.951
O3 _3	A	nmol/mol	34.130	0.300	z	-0.256
O3 _4	A	nmol/mol	107.527	0.860	z	0.642
O3 _5	A	nmol/mol	127.137	1.020	z	0.757
SO2 _0	A	nmol/mol	0.010	0.500	z'	-0.366

Gas	Code	Unit	Ref	u_ref	uref<0.3*σpt	z_value
SO2 _1	A	nmol/mol	130.560	1.260	z'	-0.548
SO2 _2	A	nmol/mol	54.303	0.700	z'	-0.444
SO2 _3	A	nmol/mol	39.127	0.630	z'	-0.437
SO2 _4	A	nmol/mol	18.440	0.540	z'	-0.359
SO2 _5	A	nmol/mol	9.680	0.520	z'	-0.220
CO _0	B	μmol/mol	-11.000	0.008	z	0.160
CO _1	B	μmol/mol	2,901.300	0.015	z	0.181
CO _2	B	μmol/mol	7,823.700	0.034	z	0.241
CO _3	B	μmol/mol	4,867.700	0.022	z	0.209
CO _4	B	μmol/mol	1,428.300	0.011	z	0.124
CO _5	B	μmol/mol	836.000	0.009	z	0.117
NO _0	B	nmol/mol	0.110	0.710	z'	-0.122
NO _1	B	nmol/mol	118.940	1.090	z	-0.042
NO _2	B	nmol/mol	69.983	0.860	z'	-0.058
NO _3	B	nmol/mol	25.177	0.730	z'	-0.083
NO _4	B	nmol/mol	16.600	0.720	z'	-0.019
NO _5	B	nmol/mol	59.533	0.820	z'	-0.087
NO _6	B	nmol/mol	36.013	0.760	z'	-0.046
NO _7	B	nmol/mol	464.993	3.290	z	-0.061
NO _8	B	nmol/mol	366.060	2.630	z	0.006
NO _9	B	nmol/mol	289.387	2.120	z	0.026
NO _10	B	nmol/mol	160.910	1.320	z	0.177
NO2 _0	B	nmol/mol	0.010	0.720	z'	0.098
NO2 _2	B	nmol/mol	49.400	0.880	z'	-0.207
NO2 _4	B	nmol/mol	8.713	0.730	z'	-0.147
NO2 _6	B	nmol/mol	23.907	0.760	z'	-0.233
NO2 _8	B	nmol/mol	106.430	1.890	z'	-0.030
NO2 _10	B	nmol/mol	132.577	1.480	z'	-0.060
O3 _0	B	nmol/mol	0.030	0.190	z	0.400
O3 _1	B	nmol/mol	58.443	0.480	z	-0.356
O3 _2	B	nmol/mol	13.223	0.190	z	-0.596
O3 _3	B	nmol/mol	34.130	0.300	z	-0.487
O3 _4	B	nmol/mol	107.527	0.860	z	-0.097
O3 _5	B	nmol/mol	127.137	1.020	z	0.252
SO2 _0	B	nmol/mol	0.010	0.500	z'	-0.036
SO2 _1	B	nmol/mol	130.560	1.260	z'	-1.081
SO2 _2	B	nmol/mol	54.303	0.700	z'	-0.721
SO2 _3	B	nmol/mol	39.127	0.630	z'	-0.681

Gas	Code	Unit	Ref	u_ref	uref<0.3*σpt	z_value
SO2 _4	B	nmol/mol	18.440	0.540	z'	-0.452
SO2 _5	B	nmol/mol	9.680	0.520	z'	-0.266
CO _0	C	µmol/mol	-11.000	0.008	z	1.013
CO _1	C	µmol/mol	2,901.300	0.015	z	0.505
CO _2	C	µmol/mol	7,823.700	0.034	z	0.276
CO _3	C	µmol/mol	4,867.700	0.022	z	0.380
CO _4	C	µmol/mol	1,428.300	0.011	z	0.631
CO _5	C	µmol/mol	836.000	0.009	z	0.725
NO _0	C	nmol/mol	0.110	0.710	z'	-0.163
NO _1	C	nmol/mol	118.940	1.090	z	-0.067
NO _2	C	nmol/mol	69.983	0.860	z'	-0.086
NO _3	C	nmol/mol	25.177	0.730	z'	-0.361
NO _4	C	nmol/mol	16.600	0.720	z'	-0.369
NO _5	C	nmol/mol	59.533	0.820	z'	-0.520
NO _6	C	nmol/mol	36.013	0.760	z'	-0.523
NO _7	C	nmol/mol	464.993	3.290	z	0.211
NO _8	C	nmol/mol	366.060	2.630	z	0.190
NO _9	C	nmol/mol	289.387	2.120	z	-0.029
NO _10	C	nmol/mol	160.910	1.320	z	-0.128
NO2 _0	C	nmol/mol	0.010	0.720	z'	-0.081
NO2 _2	C	nmol/mol	49.400	0.880	z'	-0.505
NO2 _4	C	nmol/mol	8.713	0.730	z'	-0.437
NO2 _6	C	nmol/mol	23.907	0.760	z'	-0.737
NO2 _8	C	nmol/mol	106.430	1.890	z'	-0.438
NO2 _10	C	nmol/mol	132.577	1.480	z'	-0.408
O3 _0	C	nmol/mol	0.030	0.190	z	-0.190
O3 _1	C	nmol/mol	58.443	0.480	z	-0.149
O3 _2	C	nmol/mol	13.223	0.190	z	-0.184
O3 _3	C	nmol/mol	34.130	0.300	z	-0.095
O3 _4	C	nmol/mol	107.527	0.860	z	-0.056
O3 _5	C	nmol/mol	127.137	1.020	z	0.026
SO2 _0	C	nmol/mol	0.010	0.500	z'	-0.009
SO2 _1	C	nmol/mol	130.560	1.260	z'	-0.381
SO2 _2	C	nmol/mol	54.303	0.700	z'	-0.240
SO2 _3	C	nmol/mol	39.127	0.630	z'	-0.121
SO2 _4	C	nmol/mol	18.440	0.540	z'	-0.100
SO2 _5	C	nmol/mol	9.680	0.520	z'	0.046
CO _0	E	µmol/mol	-11.000	0.008	z	0.070

Gas	Code	Unit	Ref	u_ref	uref<0.3*σpt	z_value
CO _1	E	µmol/mol	2,901.300	0.015	z	0.104
CO _2	E	µmol/mol	7,823.700	0.034	z	0.130
CO _3	E	µmol/mol	4,867.700	0.022	z	0.107
CO _4	E	µmol/mol	1,428.300	0.011	z	0.080
CO _5	E	µmol/mol	836.000	0.009	z	0.025
NO _0	E	nmol/mol	0.110	0.710	z'	-0.057
NO _1	E	nmol/mol	118.940	1.090	z	-0.350
NO _2	E	nmol/mol	69.983	0.860	z'	-0.236
NO _3	E	nmol/mol	25.177	0.730	z'	-0.163
NO _4	E	nmol/mol	16.600	0.720	z'	-0.083
NO _5	E	nmol/mol	59.533	0.820	z'	-0.227
NO _6	E	nmol/mol	36.013	0.760	z'	-0.210
NO _7	E	nmol/mol	464.993	3.290	z	-0.485
NO _8	E	nmol/mol	366.060	2.630	z	-0.365
NO _9	E	nmol/mol	289.387	2.120	z	-0.460
NO _10	E	nmol/mol	160.910	1.320	z	-0.255
NO2 _0	E	nmol/mol	0.010	0.720	z'	-0.244
NO2 _2	E	nmol/mol	49.400	0.880	z'	-0.478
NO2 _4	E	nmol/mol	8.713	0.730	z'	-0.408
NO2 _6	E	nmol/mol	23.907	0.760	z'	-0.443
NO2 _8	E	nmol/mol	106.430	1.890	z'	-0.512
NO2 _10	E	nmol/mol	132.577	1.480	z'	-0.687
O3 _0	E	nmol/mol	0.030	0.190	z	0.260
O3 _1	E	nmol/mol	58.443	0.480	z	0.082
O3 _2	E	nmol/mol	13.223	0.190	z	-0.042
O3 _3	E	nmol/mol	34.130	0.300	z	0.083
O3 _4	E	nmol/mol	107.527	0.860	z	0.198
O3 _5	E	nmol/mol	127.137	1.020	z	0.201
SO2 _0	E	nmol/mol	0.010	0.500	z'	0.018
SO2 _1	E	nmol/mol	130.560	1.260	z'	-0.938
SO2 _2	E	nmol/mol	54.303	0.700	z'	-0.674
SO2 _3	E	nmol/mol	39.127	0.630	z'	-0.600
SO2 _4	E	nmol/mol	18.440	0.540	z'	-0.385
SO2 _5	E	nmol/mol	9.680	0.520	z'	-0.205
CO _0	F	µmol/mol	-11.000	0.008	z	-1.123
CO _1	F	µmol/mol	2,901.300	0.015	z	-0.350
CO _2	F	µmol/mol	7,823.700	0.034	z	-0.114
CO _3	F	µmol/mol	4,867.700	0.022	z	-0.238

Gas	Code	Unit	Ref	u_ref	uref<0.3*σpt	z_value
CO _4	F	µmol/mol	1,428.300	0.011	z	-0.695
CO _5	F	µmol/mol	836.000	0.009	z	-0.891
NO _0	F	nmol/mol	0.110	0.710	z'	1.994
NO _1	F	nmol/mol	118.940	1.090	z	-0.246
NO _2	F	nmol/mol	69.983	0.860	z'	0.042
NO _3	F	nmol/mol	25.177	0.730	z'	0.529
NO _4	F	nmol/mol	16.600	0.720	z'	0.687
NO _5	F	nmol/mol	59.533	0.820	z'	-0.469
NO _6	F	nmol/mol	36.013	0.760	z'	-0.111
NO _7	F	nmol/mol	464.993	3.290	z	-1.587
NO _8	F	nmol/mol	366.060	2.630	z	-1.522
NO _9	F	nmol/mol	289.387	2.120	z	-1.436
NO _10	F	nmol/mol	160.910	1.320	z	-1.057
NO2 _0	F	nmol/mol	0.010	0.720	z'	-0.252
NO2 _2	F	nmol/mol	49.400	0.880	z'	-0.097
NO2 _4	F	nmol/mol	8.713	0.730	z'	-0.038
NO2 _6	F	nmol/mol	23.907	0.760	z'	0.032
NO2 _8	F	nmol/mol	106.430	1.890	z'	2.037
NO2 _10	F	nmol/mol	132.577	1.480	z'	-0.223
O3 _0	F	nmol/mol	0.030	0.190	z	0.770
O3 _1	F	nmol/mol	58.443	0.480	z	0.017
O3 _2	F	nmol/mol	13.223	0.190	z	0.535
O3 _3	F	nmol/mol	34.130	0.300	z	0.226
O3 _4	F	nmol/mol	107.527	0.860	z	-0.212
O3 _5	F	nmol/mol	127.137	1.020	z	-0.270
SO2 _0	F	nmol/mol	0.010	0.500	z'	0.152
SO2 _1	F	nmol/mol	130.560	1.260	z'	-0.079
SO2 _2	F	nmol/mol	54.303	0.700	z'	0.012
SO2 _3	F	nmol/mol	39.127	0.630	z'	0.083
SO2 _4	F	nmol/mol	18.440	0.540	z'	0.206
SO2 _5	F	nmol/mol	9.680	0.520	z'	0.175
CO _0	L	µmol/mol	-11.000	0.008	z	-0.511
CO _1	L	µmol/mol	2,901.300	0.015	z	-0.603
CO _2	L	µmol/mol	7,823.700	0.034	z	-0.291
CO _3	L	µmol/mol	4,867.700	0.022	z	-0.303
CO _4	L	µmol/mol	1,428.300	0.011	z	-0.672
CO _5	L	µmol/mol	836.000	0.009	z	-0.600
O3 _0	L	nmol/mol	0.030	0.190	z	0.550

Gas	Code	Unit	Ref	u_ref	uref<0.3*σpt	z_value
O3 _1	L	nmol/mol	58.443	0.480	z	-0.790
O3 _2	L	nmol/mol	13.223	0.190	z	-0.042
O3 _3	L	nmol/mol	34.130	0.300	z	-0.458
O3 _4	L	nmol/mol	107.527	0.860	z	-0.945
O3 _5	L	nmol/mol	127.137	1.020	z	-0.984
SO2 _0	L	nmol/mol	0.010	0.500	z'	0.205
SO2 _1	L	nmol/mol	130.560	1.260	z'	-5.329
SO2 _2	L	nmol/mol	54.303	0.700	z'	-3.771
SO2 _3	L	nmol/mol	39.127	0.630	z'	-3.198
SO2 _4	L	nmol/mol	18.440	0.540	z'	-1.840
SO2 _5	L	nmol/mol	9.680	0.520	z'	-0.987

Source: JRC 2022

Table 14: En-score participants calculated values.

Code	Parameter	Concentrations	En
A	CO	0	0.0
A	CO	1	-0.1
A	CO	2	0.3
A	CO	3	0.2
A	CO	4	-0.2
A	CO	5	-0.1
A	O3	0	-0.7
A	O3	1	0.1
A	O3	2	-0.4
A	O3	3	-0.1
A	O3	4	0.6
A	O3	5	0.7
A	SO2	0	-0.3
A	SO2	1	-0.5
A	SO2	2	-0.4
A	SO2	3	-0.4
A	SO2	4	-0.2
A	SO2	5	-0.1
B	CO	0	0.3
B	CO	1	0.2
B	CO	2	0.2
B	CO	3	0.2
B	CO	4	0.1
B	CO	5	0.1
B	NO	0	-0.1
B	NO	1	0.0
B	NO	2	0.0
B	NO	3	-0.1
B	NO	4	0.0
B	NO	5	-0.1
B	NO	6	0.0
B	NO	7	0.0
B	NO	8	0.0
B	NO	9	0.0
B	NO	10	0.1
B	NO2	0	0.1
B	NO2	1	0.0

Code	Parameter	Concentrations	En
B	NO2	2	-0.1
B	NO2	3	-0.1
B	NO2	4	-0.1
B	NO2	5	0.0
B	NO2	6	-0.1
B	NO2	7	0.1
B	NO2	8	0.0
B	NO2	9	0.1
B	NO2	10	0.0
B	O3	0	0.4
B	O3	1	-0.3
B	O3	2	-0.4
B	O3	3	-0.4
B	O3	4	-0.1
B	O3	5	0.2
B	SO2	0	0.0
B	SO2	1	-0.8
B	SO2	2	-0.6
B	SO2	3	-0.6
B	SO2	4	-0.4
B	SO2	5	-0.2
C	CO	0	0.9
C	CO	1	0.5
C	CO	2	0.3
C	CO	3	0.4
C	CO	4	0.7
C	CO	5	0.7
C	NO	0	-0.1
C	NO	1	-0.1
C	NO	2	-0.1
C	NO	3	-0.3
C	NO	4	-0.3
C	NO	5	-0.5
C	NO	6	-0.5
C	NO	7	0.2
C	NO	8	0.2
C	NO	9	0.0
C	NO	10	-0.1

Code	Parameter	Concentrations	En
C	NO2	0	-0.1
C	NO2	1	-0.4
C	NO2	2	-0.5
C	NO2	3	-0.2
C	NO2	4	-0.3
C	NO2	5	-0.3
C	NO2	6	-0.6
C	NO2	7	-0.6
C	NO2	8	-0.3
C	NO2	9	-0.6
C	NO2	10	-0.4
C	O3	0	-0.2
C	O3	1	-0.1
C	O3	2	-0.1
C	O3	3	-0.1
C	O3	4	0.0
C	O3	5	0.0
C	SO2	0	0.0
C	SO2	1	-0.2
C	SO2	2	-0.2
C	SO2	3	-0.1
C	SO2	4	-0.1
C	SO2	5	0.0
E	CO	0	0.0
E	CO	1	0.1
E	CO	2	0.1
E	CO	3	0.1
E	CO	4	0.0
E	CO	5	0.0
E	NO	0	0.0
E	NO	1	-0.4
E	NO	2	-0.2
E	NO	3	-0.1
E	NO	4	-0.1
E	NO	5	-0.2
E	NO	6	-0.2
E	NO	7	-0.5
E	NO	8	-0.4

Code	Parameter	Concentrations	En
E	NO	9	-0.5
E	NO	10	-0.3
E	NO2	0	-0.2
E	NO2	1	-0.1
E	NO2	2	-0.3
E	NO2	3	-0.2
E	NO2	4	-0.3
E	NO2	5	-0.2
E	NO2	6	-0.3
E	NO2	7	0.2
E	NO2	8	-0.3
E	NO2	9	0.0
E	NO2	10	-0.4
E	O3	0	0.2
E	O3	1	0.1
E	O3	2	0.0
E	O3	3	0.1
E	O3	4	0.2
E	O3	5	0.2
E	SO2	0	0.0
E	SO2	1	-0.9
E	SO2	2	-0.6
E	SO2	3	-0.5
E	SO2	4	-0.3
E	SO2	5	-0.1
F	CO	0	
F	CO	1	-0.3
F	CO	2	-0.1
F	CO	3	-0.2
F	CO	4	-1.1
F	CO	5	-2.4
F	NO	0	
F	NO	1	-0.1
F	NO	2	0.0
F	NO	3	0.4
F	NO	4	0.5
F	NO	5	-0.3
F	NO	6	-0.1

Code	Parameter	Concentrations	En
F	NO	7	-0.6
F	NO	8	-0.6
F	NO	9	-0.6
F	NO	10	-0.5
F	NO2	0	
F	NO2	1	0.6
F	NO2	2	0.0
F	NO2	3	0.2
F	NO2	4	0.0
F	NO2	5	0.6
F	NO2	6	0.0
F	NO2	7	3.0
F	NO2	8	0.7
F	NO2	9	1.5
F	NO2	10	-0.1
F	O3	0	
F	O3	1	0.0
F	O3	2	0.5
F	O3	3	0.2
F	O3	4	-0.2
F	O3	5	-0.3
F	SO2	0	
F	SO2	1	0.0
F	SO2	2	0.0
F	SO2	3	0.1
F	SO2	4	0.2
F	SO2	5	0.2
L	CO	0	-0.3
L	CO	1	-0.6
L	CO	2	-0.2
L	CO	3	-0.3
L	CO	4	-0.5
L	CO	5	-0.4
L	O3	0	1.4
L	O3	1	-0.6
L	O3	2	0.0
L	O3	3	-0.5
L	O3	4	-0.9

Code	Parameter	Concentrations	En
L	O3	5	-0.9
L	SO2	0	0.2
L	SO2	1	-3.8
L	SO2	2	-2.8
L	SO2	3	-3.1
L	SO2	4	-1.6
L	SO2	5	-0.7

Source: JRC 2022

Annex E: Confidentiality

Results of the PT are published according to the agreements included in the document AQUILA-N37 [12] approved by all NRL of the AQUILA network.
In order to ensure confidentiality of the laboratories information, ERLAP guarantees the submitted data as follows:
Any administrative information provided by the laboratory is confidential and cannot be communicated to a third party.
Access to ERLAP facilities is allowed only to members of the Unit JRC-C5 and authorized persons (cleaning staff, maintenance staff, safety and security staff etc.)
Confidential passwords to access the web application for data submission are sent once the registration to PT is completed. Confidential passwords allow access to the WEB interface and to on-line questionnaire. Passwords are valid until the PT is closed. Laboratories can change their password online.

The form LAB-REC-2000 (Confidentiality involvement form) is asked to be signed by the participants during their first participation to a PT organized by ERLAP.

Annex F: Accreditation certificates

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CERTIFICATO DI ACCREDITAMENTO
Accreditation Certificate

ACCREDITAMENTO N. / *ACCREDITATION N.* **0018P** REV. **00**

EMESSO DA / ISSUED BY **DIPARTIMENTO LABORATORI DI PROVA**

SI DICHIARA CHE / *WE DECLARE THAT*

European Reference Laboratory for air Pollution (ERLAP)
Sede/Headquarters:
- Via E. Fermi 2749 - 21027 Ispra VA

È CONFORME AI REQUISITI DELLA NORMA UNI CEI EN ISO/IEC 17043:2010

MEETS THE REQUIREMENTS OF THE STANDARD *ISO/IEC 17043:2010*

MD-CA-01 rev. 03

QUALE **Organizzatori di prove valutative interlaboratorio**

AS ***Proficiency Testing Provider***

Data di 1° emissione *1st issue date* **17-01-2019**	Data di modifica *Modification date* **17-01-2019**	Data di scadenza *Expiring date* **16-01-2023**
Dott.ssa Silvia Tramontin Il Direttore di Dipartimento *The Department Director*	Dott. Filippo Trifiletti Il Direttore Generale *The General Director*	Ing. Giuseppe Rossi Il Presidente *The President*

L'accreditamento attesta la competenza tecnica dell'Organizzazione relativamente al campo di accreditamento riportato nell'Elenco Schemi allegato al presente certificato di accreditamento.
Il presente certificato non è da ritenersi valido se non accompagnato dagli Elenchi Schemi, che possono variare nel tempo.
La vigenza dell'accreditamento può essere verificata sul sito web (www.accredia.it) o richiesta al Dipartimento di competenza.

The accreditation certifies the technical competence of the organisation limited to the scope detailed in the attached Enclosure.
The present certificate is valid only if associated to the annexed schedule, that may vary in the time.
Confirmation of the validity of accreditation can be verified on website www.accredia.it or by contacting the relevant Department.

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ACCREDIA

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info@accredia.it | www.accredia.it | Partita IVA - Codice Fiscale 10566361001

Allegato al certificato di accreditamento n. **0018P** rev. **2** del **13/09/2022**

European Reference Laboratory for air Pollution (ERLAP) Via E. Fermi 2749 21027 Ispra VA	UNI CEI EN ISO/IEC 17043:2010	
	Revisione: **1**	Data: **13/09/2022**
	Sede **A**	pag. **1** di **1**

ELENCO SCHEMI ACCREDITATI - CON CAMPO FISSO IN CATEGORIA: 0

Codice identificativo	*Settore*	*Oggetto /Materiale/ Prodotto/Matrice*	*Misurando/ Proprietà misurata/ Grandezza*	*Tipologia*
	ambientale	Synthetic mixture gas	carbon monoxide	schema quantitativo
	ambientale	Synthetic mixture gas	nitrogen oxides	schema quantitativo
	ambientale	Synthetic mixture gas	ozone	schema quantitativo
	ambientale	Synthetic mixture gas	sulphur dioxide	schema quantitativo

Il QRcode consente di accedere direttamente al sito www.accredia.it per verificare la validità dell'elenco schemi e del certificato di accreditamento rilasciato al PTP.

L'eventuale simbolo (*) indica che è attiva una sospensione dell'accreditamento per la specifica attività riportata a fianco

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DL1362L/003

CERTIFICATO DI ACCREDITAMENTO
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ACCREDITAMENTO N. / *ACCREDITATION N.* **1362L** REV. **03**

EMESSO DA / ISSUED BY **DIPARTIMENTO LABORATORI DI PROVA**

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European Reference Laboratory for Air Pollution (ERLAP) Air and Climate Unit Directorate C.Energy, Transport and Climate Joint Research Centre -European Commission

Sede/Headquarters:
- Via E. Fermi 2749 - 21027 Ispra VA

MD-CA-01 rev. 05

È CONFORME AI REQUISITI DELLA NORMA UNI CEI EN ISO/IEC 17025:2018

MEETS THE REQUIREMENTS OF THE STANDARD *ISO/IEC 17025:2017*

QUALE **Laboratorio di Prova**

AS ***Testing Laboratory***

Data di 1° emissione	Data di revisione	Data di scadenza
1st issue date	*Review date*	*Expiring date*
19-06-2013	**22-06-2021**	**16-06-2025**

L'accreditamento attesta la competenza tecnica, l'imparzialità e il costante e coerente funzionamento del Laboratorio relativamente al campo di accreditamento riportato nell'Elenco Prove allegato al presente certificato di accreditamento.
Il presente certificato non è da ritenersi valido se non accompagnato dagli Elenchi Prove, che possono variare nel tempo e può essere sospeso o revocato o ridotto in qualsiasi momento nel caso di inadempienza accertata da parte di ACCREDIA.
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I requisiti di sistema della ISO/IEC 17025 sono scritti in un linguaggio attinente alle attività di laboratorio e sono generalmente in accordo con i principi della norma ISO 9001 (si veda comunicato congiunto ISO-ILAC-IAF dell'Aprile 2017).
The accreditation attests competence, impartiality and consistent operation in performing laboratory activities, limited to the scope detailed in the attached Enclosure.
The present certificate is valid only if associated to the annexed Lists and can be suspended, withdrawn or reduced at any time in the event of non fulfilment as ascertained by ACCREDIA.
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The management system requirements in ISO/IEC 17025 are written in language relevant to laboratories operations and generally operate in accordance with the principles of ISO 9001 (refer joint ISO-ILAC-IAF Communiqué dated April 2017).

Il QRcode consente di accedere direttamente al sito www.accredia.it per verificare la validità del certificato di accreditamento rilasciato al CAB.
La data di revisione riportata sul certificato corrisponde alla data di aggiornamento / di delibera del pertinente Comitato Settoriale di Accreditamento. L'atto di delibera, firmato dal Presidente di ACCREDIA, è scaricabile dal sito www.accredia.it, sezione 'Documenti'
The QRcode links directly to the website www.accredia.it to check the validity of the accreditation certificate issued to the CAB.
The revision date shown on the certificate refers to the update / resolution date of the Sector Accreditation Committee. The Resolution, signed by the President of ACCREDIA, can be downloaded from the website www.accredia.it, 'Documents' section.

ACCREDIA è l'Ente Unico nazionale di accreditamento designato dal governo italiano, in applicazione del Regolamento Europeo 765/2008.
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ACCREDIA - Dipartimento Laboratori di prova

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Allegato al certificato di accreditamento n. **1362L** rev. 3 del **22/06/2021**

European Reference Laboratory for Air Pollution (ERLAP) **Air and Climate Unit** **Directorate C.Energy, Transport and Climate** **Joint Research Centre -European Commission**	UNI CEI EN ISO/IEC 17025:2018	
	Revisione: **5**	Data: **22/06/2021**
Via E. Fermi 2749	Sede **A**	pag. **1** di **1**

ELENCO PROVE ACCREDITATE - CON CAMPO FISSO IN CATEGORIA: 0

Aria ambiente/Ambient air

Denominazione della prova / Campi di prova	*Metodo di prova*	*Tecnica di prova*	*O&I*
Carbonio elementare/Elemental carbon, Carbonio organico/Organic carbon	EN 12341:2014 + EN 16909:2017	Thermal-optical analysis (TOA)	
Diossido di azoto/Nitrogen dioxide, Monossido di azoto/Nitrogen monoxide	UNI EN 14211:2012	Chemiluminescenza	
Diossido di zolfo/Sulfur dioxide	EN 14212:2012	Spettrofotometria UV fluorescenza	
Monossido di carbonio/Carbon monoxide	UNI EN 14626:2012	Spettrofotometria IR	
Ozono/Ozone	UNI EN 14625:2012	Spettrofotometria UV-VIS	
Particolato sospeso PM10/Suspended particulate matter PM10, Particolato sospeso PM2.5/Suspended particulate matter PM2.5	UNI EN 12341:2014	Gravimetria	

Legenda

L'eventuale simbolo (1) in corrispondenza della matrice indica:matrice non prevista dal metodo ma assimilabile/matrix not provided for by the method but acceptable

Il QRcode consente di accedere direttamente al sito www.accredia.it per verificare la validità dell'elenco prove e del certificato di accreditamento rilasciato al laboratorio.

L'eventuale simbolo "X" riportato nella colonna "O&I" indica che il laboratorio è accreditato anche per fornire opinioni e interpretazioni basate sui risultati delle specifiche prove contrassegnate.

L'eventuale simbolo (*) indica che è attiva una sospensione dell'accreditamento per la specifica attività riportata a fianco

End of report

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