



## JRC TECHNICAL REPORT

# PROFICIENCY TESTING SCHEME

## Measurement of inorganic gaseous pollutants ( $\text{SO}_2$ , $\text{CO}$ , $\text{O}_3$ , $\text{NO}$ and $\text{NO}_2$ ) in filtered ambient air

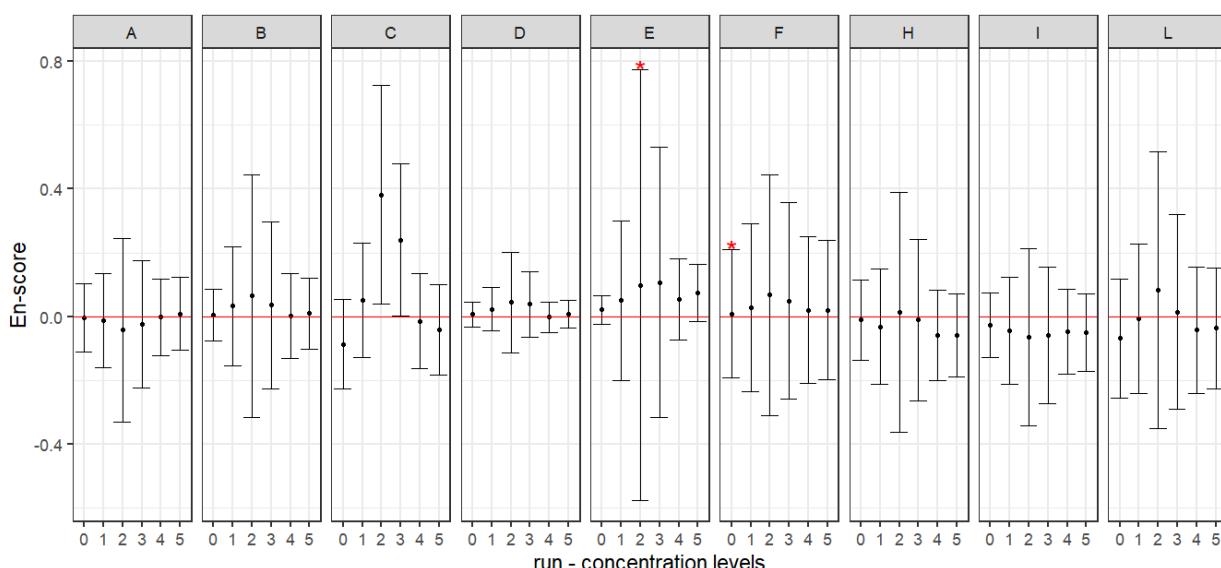
(28-31 March 2022, Ispra-Italy)

*European Commission  
harmonisation programme  
for air quality measurements*

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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).

During the period **28 - 31 of March 2022**, including ERLAP, ten 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, NO<sub>2</sub>, SO<sub>2</sub>, CO and O<sub>3</sub>) covered by the European Air Quality Directive 2008/50 EC [1] and its last amendments 2015/1480/EC [42].

One laboratory (H) didn't report values for NO<sub>2</sub> and some values of NO, due to technical issues with the analytical instrumentation.

The proficiency evaluation, where each participant's bias was compared to two criteria (z/z'-score and En-score), 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, **99.3%** were satisfactory and only two values were found to be questionable (**0.7%**) and none were unsatisfactory.

Considering the repeatability and reproducibility evaluation, the results among AQUILA participants at the highest generated concentration levels are satisfactory for measurements of all pollutants.

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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 (SO<sub>2</sub>), nitrogen dioxide (NO<sub>2</sub>) and nitrogen monoxide (NO), particulate matter, lead, benzene, carbon monoxide (CO) and ozone (O<sub>3</sub>). 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], SO<sub>2</sub> [3], NO-NO<sub>2</sub> [4] and O<sub>3</sub> [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 in the period **28 - 31 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/NO<sub>2</sub>, EN 14212:2012-SO<sub>2</sub>, EN 14625:2012-O<sub>3</sub>, EN 14626:2012-CO) as proved by the certificates 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**

The PT was announced in **September 2021** to the members of the AQUILA network and the WHO CC representative. Registration was opened in **February 2022** and closed the second week of **March 2022**.

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, 28 of March 2022**, for the installation of their equipment. The calibration of NOx and O<sub>3</sub> analysers was carried out the morning of the following day and the generation of NOx and O<sub>3</sub> gas mixtures started at 11:00 on Tuesday.

The calibration of SO<sub>2</sub> and CO analysers was carried out on Wednesday afternoon and the generation of CO and SO<sub>2</sub> 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, Finland, Croatia, Denmark, Czech Republic, Slovak Republic, Belgium and Hungary.

**Table 1:** List of participating organizations.

Acronym	Laboratory	Country	Code
FMI	Finnish Meteorological Institute	Finland	A
EKONERG	Energy and Environmental Protection Institute	Croatia	B
DCE	National Environmental Research Institute	Denmark	C
CHMI AAQCL	Czech Hydrometeorological Institute	Czech Republic	D
CHMI	Czech Hydrometeorological Institute	Czech Republic	E
SHMU	Slovak Hydrometeorological institute	Slovak Republic	F
ERLAP	European Reference Laboratory for Air Pollution	European Commission	G
VMM	Flemish Environmental Agency	Belgium	H
DHZ-CAL	Meteorological and Hydrological Service - CALIBRATION	Croatia	I
HMS	Hungarian Meteorological Service	Hungary	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. This list is used to identify presence of cluster during the data evaluation.

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	Pollutant	Instruments
A	SO <sub>2</sub>	Thermo 43i-TLE
B		not reported
C		Teledyne API T-100
D		Thermo 43i-TLE
E		Teledyne API T-100
F		not reported
G		Thermo 43i TLE, 2015
H		Horiba APSC-370
I		Thermo Scientific 43i TLE, 2014
L		not reported
A		Horiba APMA-360
B		not reported
C	CO	Teledyne API T-300
D		Thermo model 48iTLE
E		Teledyne API T300
F		not reported
G		Horiba, APMA-370, 2010
H		Teledyne API T300
I		Horiba APMA-370, 2010
L		not reported
A		Teledyne T400
B		not reported
C		Teledyne API T-400
D		Thermo 49-i
E	O <sub>3</sub>	Teledyne API T400
F		not reported
G		Thermo, 49-iPS , 2015
H		Envea 42e
I		Teledyne API T400, 2018
L		not reported
A		Horiba APNA-360
B		not reported
C	NO/NO <sub>2</sub>	Teledyne API T-200
D		Thermo TE42i
E		Teledyne API T200
F		not reported
G		Thermo, TE42iTl, 2015
H		Teledyne API T200
I		Teledyne API T200, 2018
L		not reported

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 SO<sub>2</sub>, CO, O<sub>3</sub>, NO and NO<sub>2</sub> 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	NO <sub>2</sub>	O <sub>3</sub>	CO	SO <sub>2</sub>
			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-NO <sub>2</sub> -O <sub>3</sub>		X						
2nd	12:00	2	NO-NO <sub>2</sub>			120					
2nd	14:00	2	NO-NO <sub>2</sub>				70	50			
2nd	16:00	2	O <sub>3</sub>						60		
2nd	18:00	2	NO-NO <sub>2</sub>			25					
2nd	20:00	2	NO-NO <sub>2</sub>				15	10			
2nd	22:00	2	O <sub>3</sub>						15		
3rd	00:00	2	NO-NO <sub>2</sub>			60					
3rd	02:00	2	NO-NO <sub>2</sub>				35	25			
3rd	04:00	2	O <sub>3</sub>						35		
3rd	06:00	2	NO-NO <sub>2</sub>			480					
3rd	08:00	2	NO-NO <sub>2</sub>				380	100			
3rd	10:00	2	O <sub>3</sub>						110		
3rd	12:00	2	NO-NO <sub>2</sub>			300					
3rd	14:00	2	NO-NO <sub>2</sub>				170	130			
3rd	16:00	2	O <sub>3</sub>						130		
3rd	18:00	2	/	X							
3rd	20:00	1	CO-SO <sub>2</sub>		X						
3rd	21:00	2	CO-SO <sub>2</sub>						3	125	
3rd	23:00	2	CO-SO <sub>2</sub>						8	50	
4th	01:00	1	CO-SO <sub>2</sub>		X	Not to be reported					
4th	02:00	2	CO-SO <sub>2</sub>						5	35	
4th	04:00	2	CO-SO <sub>2</sub>						1.5	19	
4th	06:00	2	CO-SO <sub>2</sub>						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, SO<sub>2</sub> or CO using thermal mass flow controllers [8]. O<sub>3</sub> was added using an ozone generator and NO<sub>2</sub> 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 ( $z/z'$ -score and En-score).

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  $u_{X_{pt}} < 0.3\sigma_{pt}$  described in the standard ISO 13528 (par. 9.2) [13], where the uncertainty of the assigned value ( $u_{X_{pt}}$ ) is compared to  $0.3\sigma_{pt}$ . When the criterion is met the  $z$ -score value is applied, in the other case  $z'$ -score is used.

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:

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

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

$z$  =  $z$ -score

$z'$  =  $z'$ -score

$x_i$  = participant average values

$X$  = the assigned/reference value

$u_X$  = uncertainty of the assigned/reference value

$\sigma_{pt}$  = 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' ( $\sigma_{pt}$ ) [13] is calculated in fitness-for-purpose manner from requirements given in European standards.

Over the whole measurement range  $\sigma_{pt}$  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  $\sigma_{pt}$  are given in Table 4.

**Table 4:** Standard deviation for proficiency assessment ( $\sigma_{pt}$ ).

Gas	a	b (nmol/mol)
SO <sub>2</sub>	0.022	1
CO	0.024	100
O <sub>3</sub>	0.020	1
NO	0.024	1
NO <sub>2</sub>	0.020	1

Source: JRC 2022

$\sigma_{pt}$  is a linear function of concentration (c) with parameters: slope “a” and intercept “b”.

$$\sigma_{pt} = (a \cdot X) + b \quad \text{Equation 3}$$

$\sigma_{pt}$  = 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, values between 2 and 3 are considered stragglers and they deserve a specific check. Two values were evaluated as stragglers: level 1 of O<sub>3</sub> for Laboratory H and level 1 of SO<sub>2</sub> for Laboratory C (see Table 5).

No outliers were identified.

**Table 5:** z/z'-score evaluation.

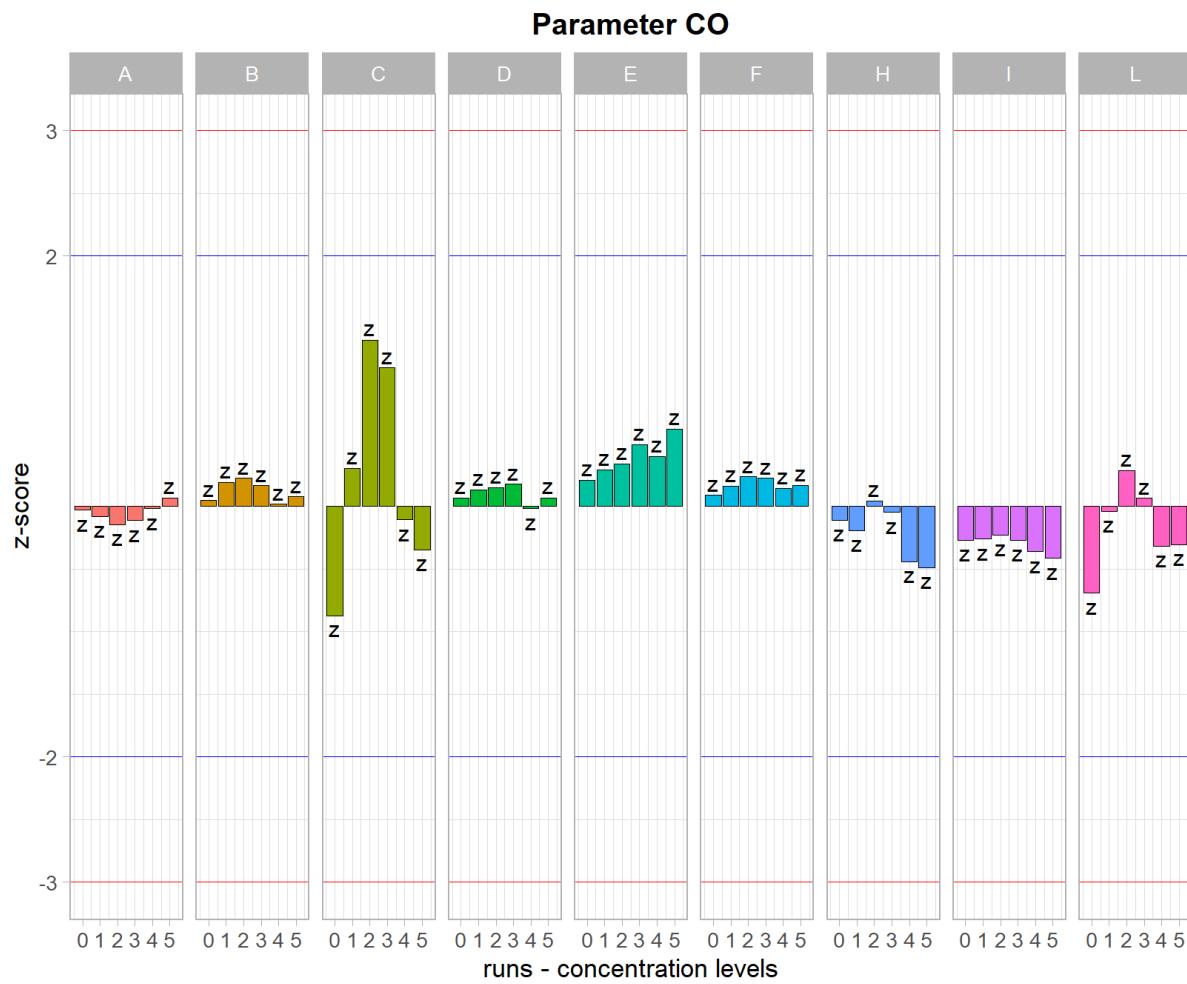
Code	Run	z/z'score value	z/z'-score evaluation
H	O <sub>3</sub> _1	-2.075	questionable
C	SO <sub>2</sub> _1	-2.135	questionable

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  $z/z' = \pm 2$  (blue line) and  $z/z' = \pm 3$  (red line). They represent the limits for the questionable and unsatisfactory results.

**Figure 1:** z-score evaluations of CO measurements in  $\mu\text{mol/mol}$

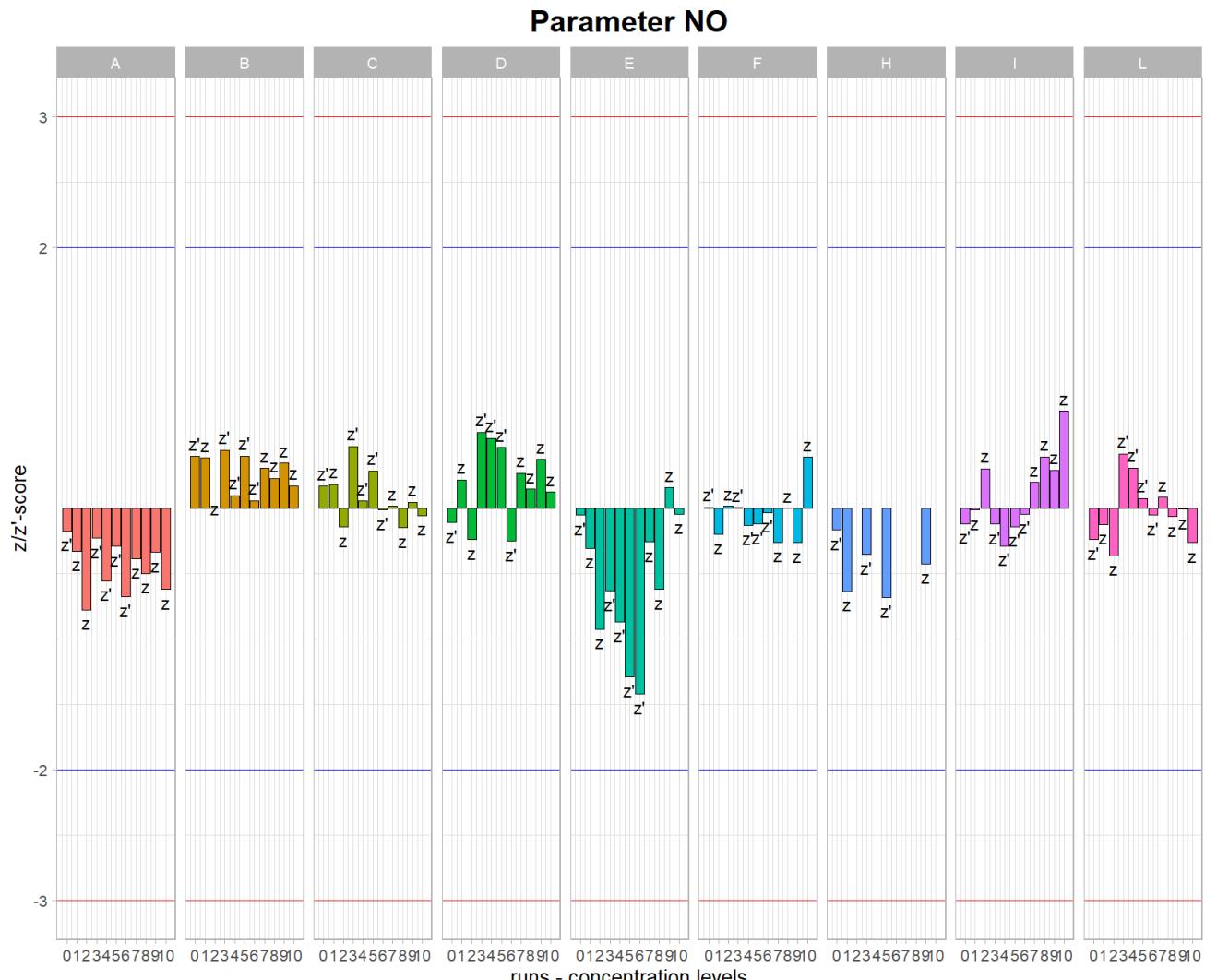


Source: JRC 2022

Scores are given for each participant and each tested concentration level (run). Run numbers order (with nominal concentration) is: 0 (0  $\mu\text{mol/mol}$ ), 1 (3  $\mu\text{mol/mol}$ ), 2 (8  $\mu\text{mol/mol}$ ), 3 (5  $\mu\text{mol/mol}$ ), 4 (1.5  $\mu\text{mol/mol}$ ), 5 (0.9  $\mu\text{mol/mol}$ ).

The assessment criteria limits are presented as  $z = \pm 2$  (blue line) and  $z = \pm 3$  (red line).

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

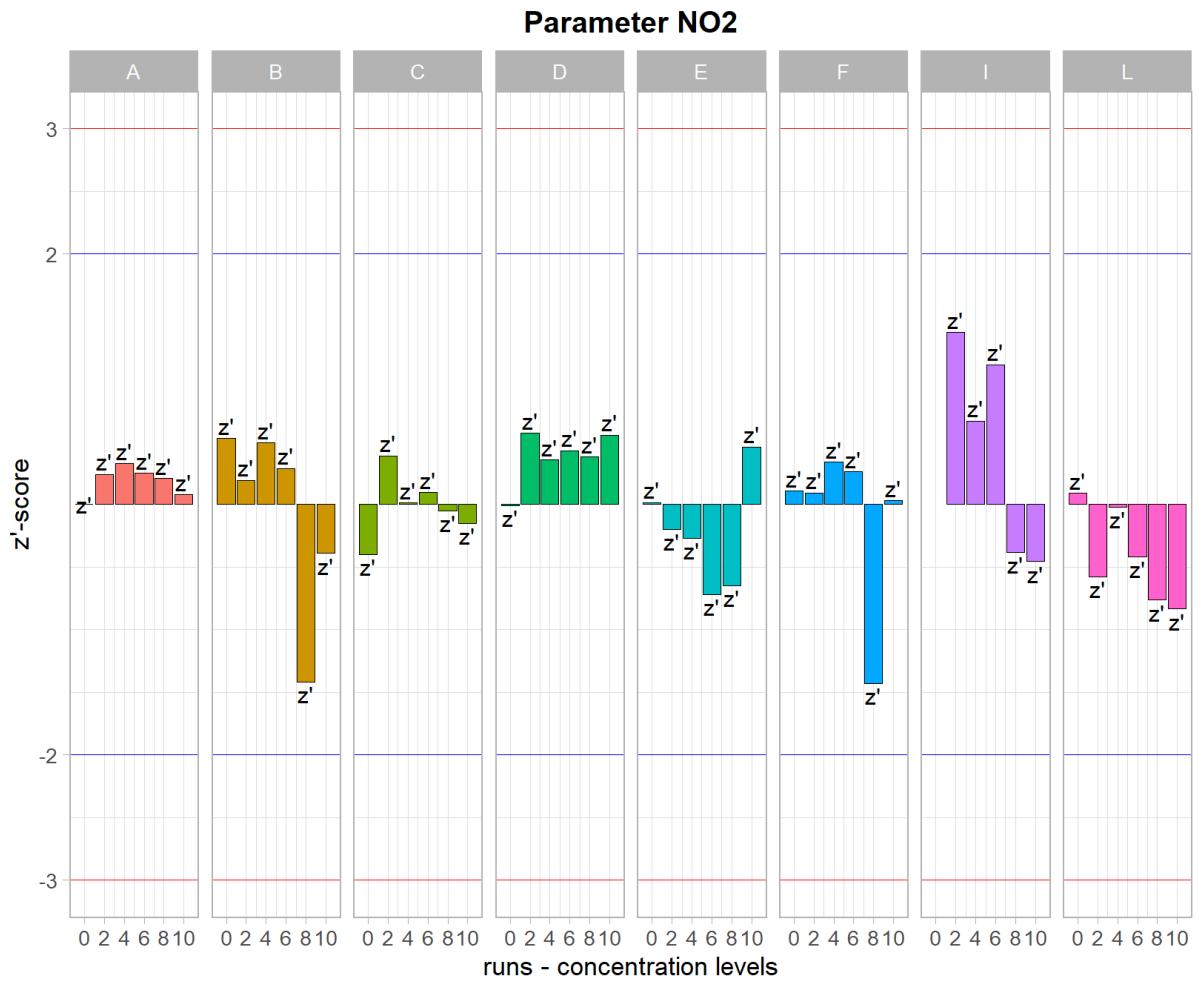


Source: JRC 2022

Scores are given for each participant and each tested concentration level (run). Run numbers 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  $z/z' = \pm 2$  (blue line) and  $z/z' = \pm 3$  (red line).

Laboratories H didn't submit all NO measurement values for technical problems occurred to the instrument during the PT.

**Figure 3:** z'-score evaluations of NO<sub>2</sub> measurements in nmol/mol



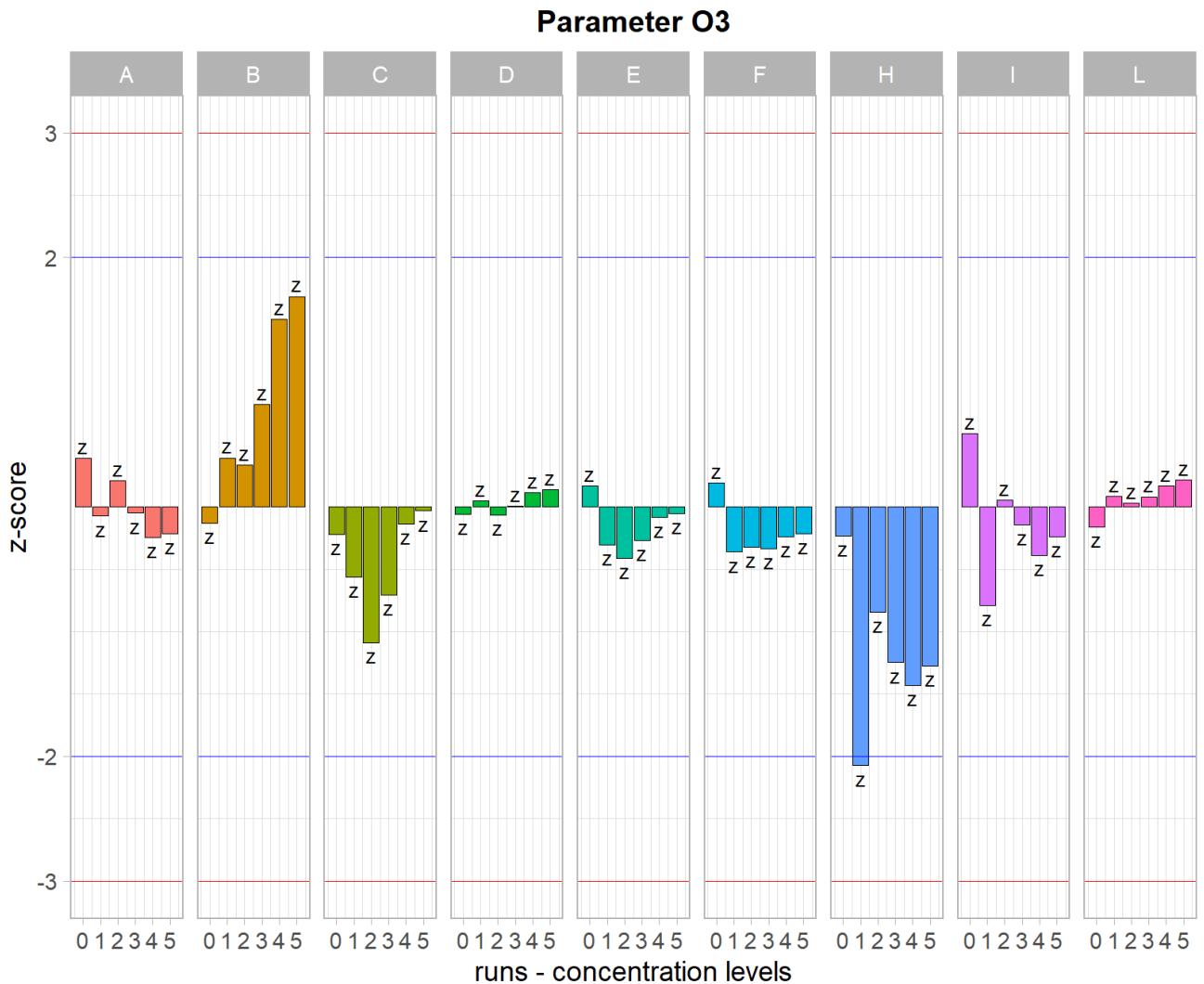
Source: JRC 2022

Scores are given for each participant and each concentration level (run). The run numbers order when NO<sub>2</sub> 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  $z' = \pm 2$  (blue line) and  $z' = \pm 3$  (red line).

Laboratories H didn't submit NO<sub>2</sub> measurement values for technical problems occurred to the instrument during the PT.

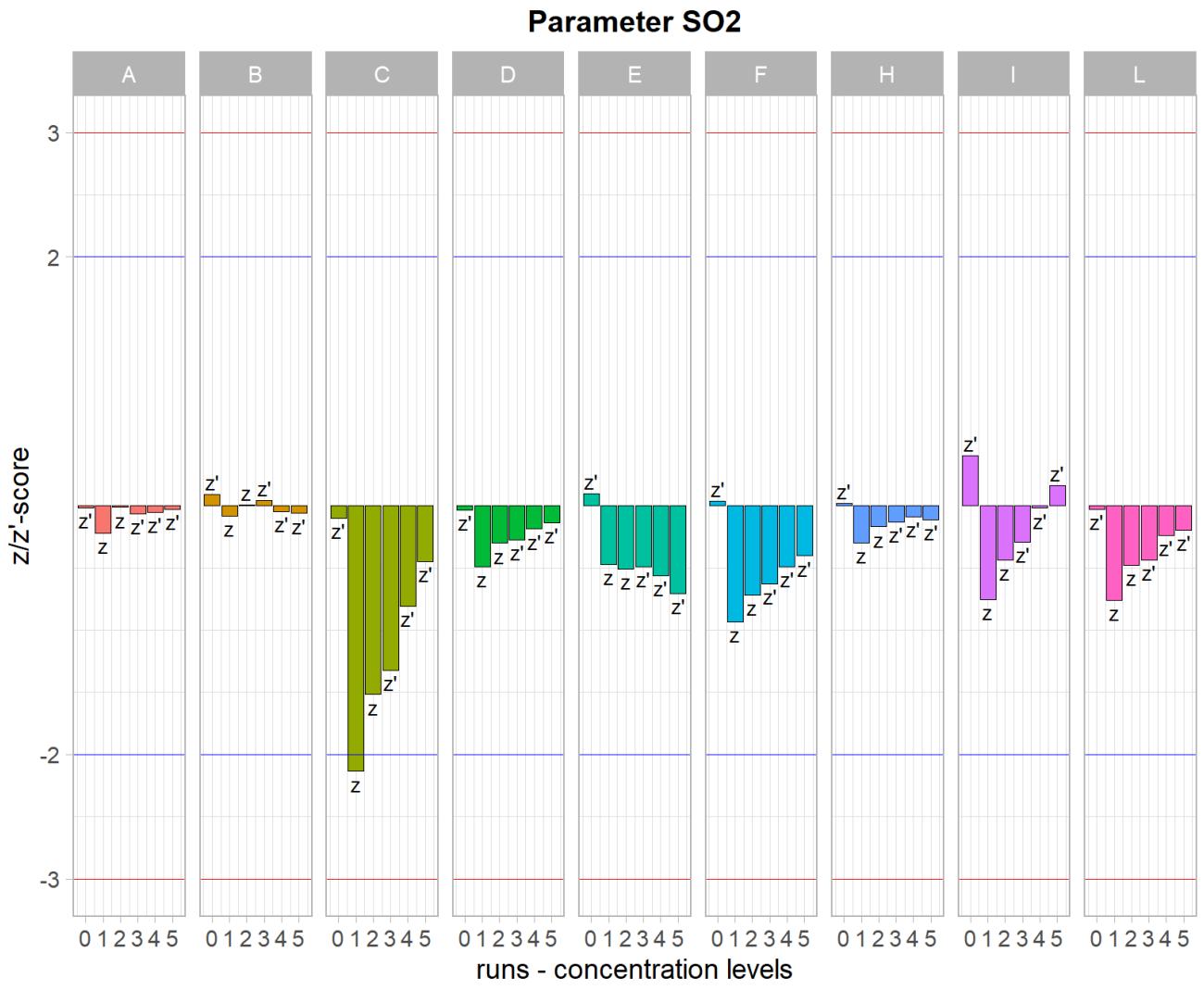
**Figure 4:** z-score evaluations of O<sub>3</sub> measurements in nmol/mol



Scores are given for each participant and each concentration level (run). Run numbers 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  $z=\pm 2$  (blue line) and  $z=\pm 3$  (red line).

**Figure 5:** z'-score evaluations of SO<sub>2</sub> measurements in nmol/mol



Source: JRC 2022

Scores are given for each participant and each tested concentration level (run). Run numbers 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  $z' = \pm 2$  (blue line) and  $z' = \pm 3$  (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:

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

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  $|En\text{-score}|<1$ . In Figures 6 to Figure 10 the bias of each participant ( $x_i-X$ ) and error bars are plotted.

These plots represent also the En-score evaluations where, considering the En criterion ( $|En\text{-score}|<1$ ), 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" ( $\sigma_{pt}$ , 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.

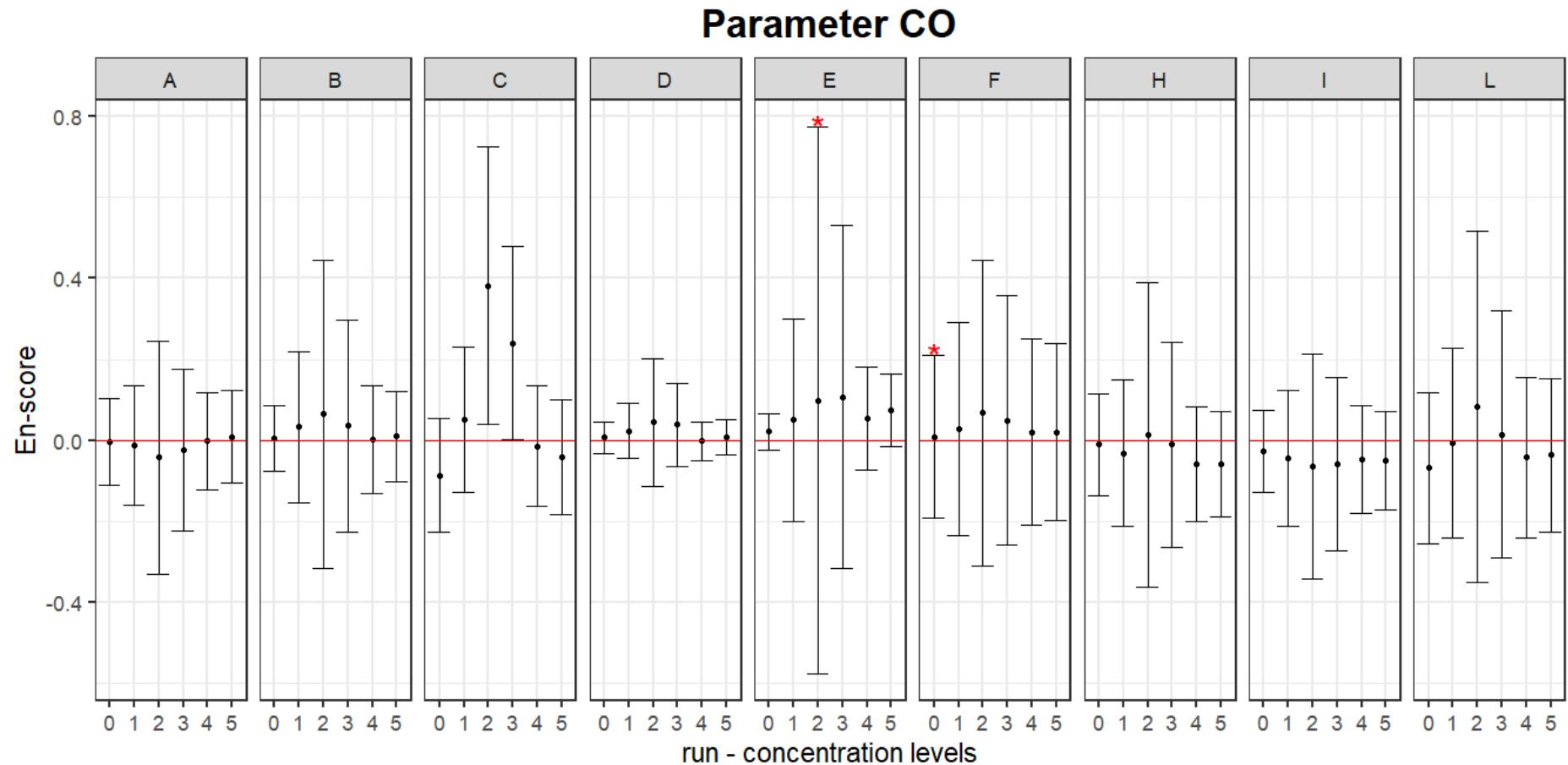
In Annex D, table 14 is showing all En values calculated for each participant, parameter and concentration level.

**Table 6:** Unsatisfactory results according to En-score.

Code	Run	En-score	En evaluation
C	CO_2	1.1	unsatisfactory
H	O3_1	-1.9	unsatisfactory
H	O3_3	-1.1	unsatisfactory
H	O3_4	-1.2	unsatisfactory
C	SO2_1	-1.7	unsatisfactory
C	SO2_2	-1.3	unsatisfactory
C	SO2_3	-1.2	unsatisfactory

Source: JRC 2022

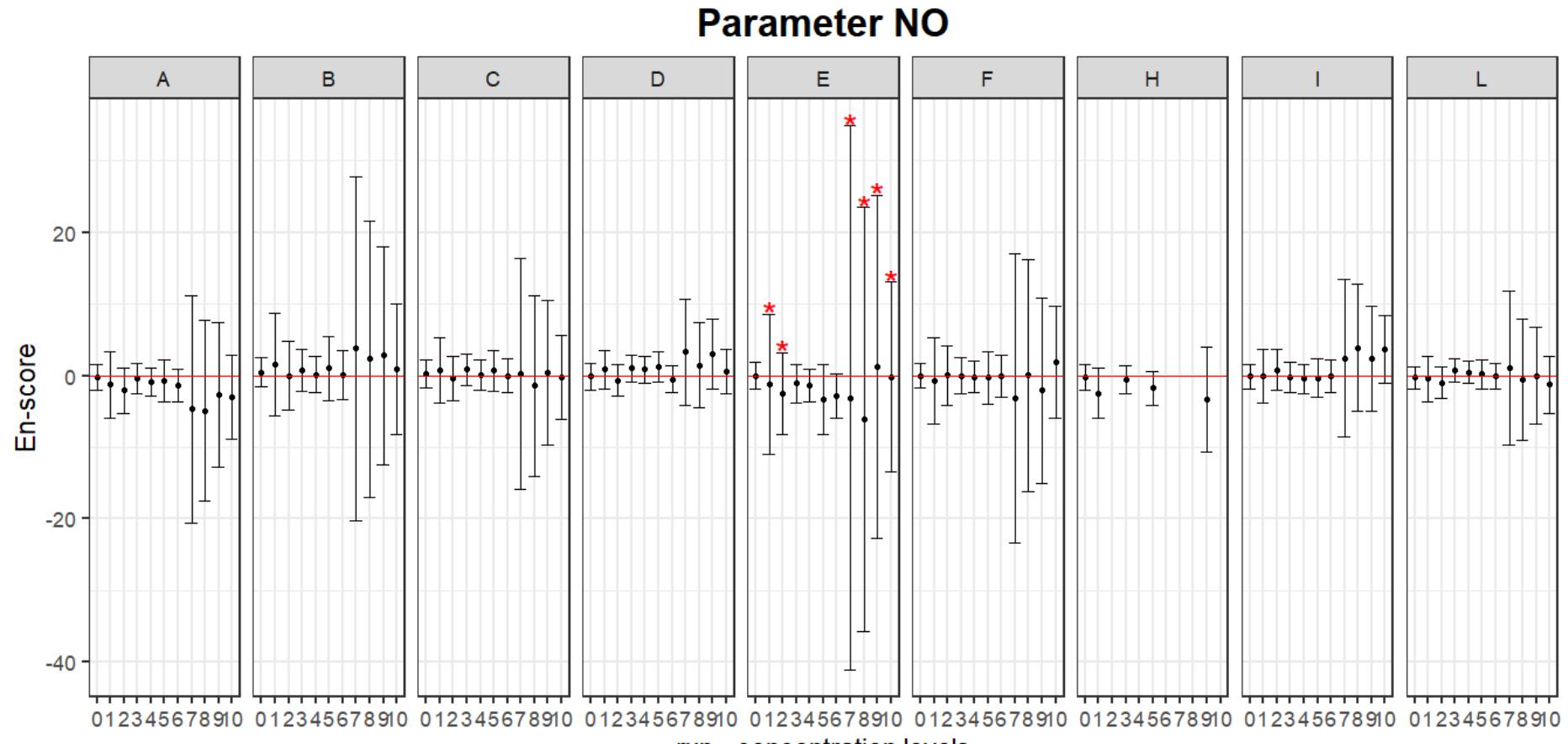
**Figure 6:** Bias of participant's CO measurement results in  $\mu\text{mol/mol}$



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 ( $\mu\text{mol/mol}$ ). The '\*' mark indicates reported standard uncertainties bigger than  $\sigma_{\text{pt}}$ .

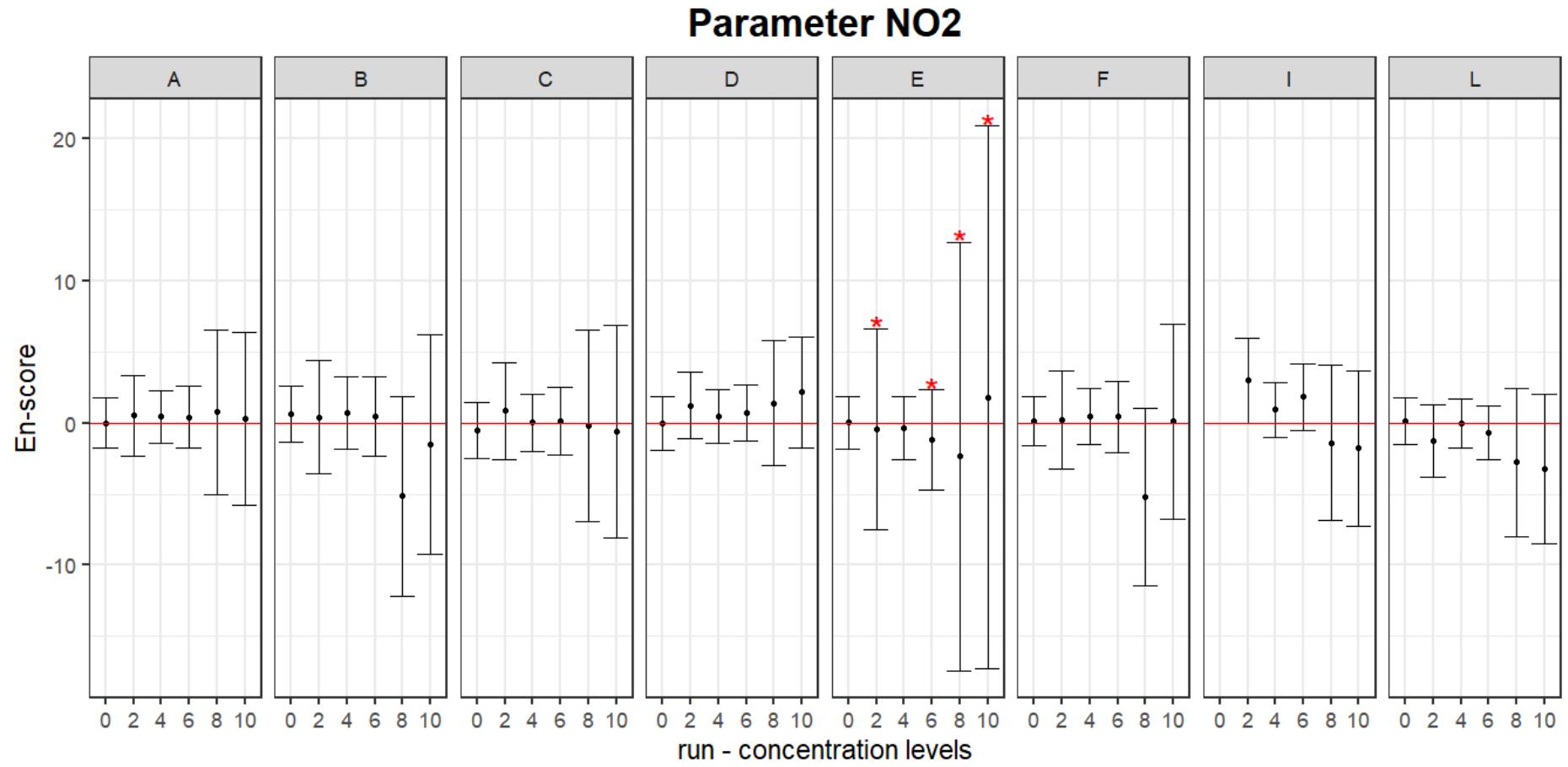
**Figure 7:** Bias of participant's NO measurement results in nmol/mol



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 opt. Laboratories H didn't report all results for this pollutant.

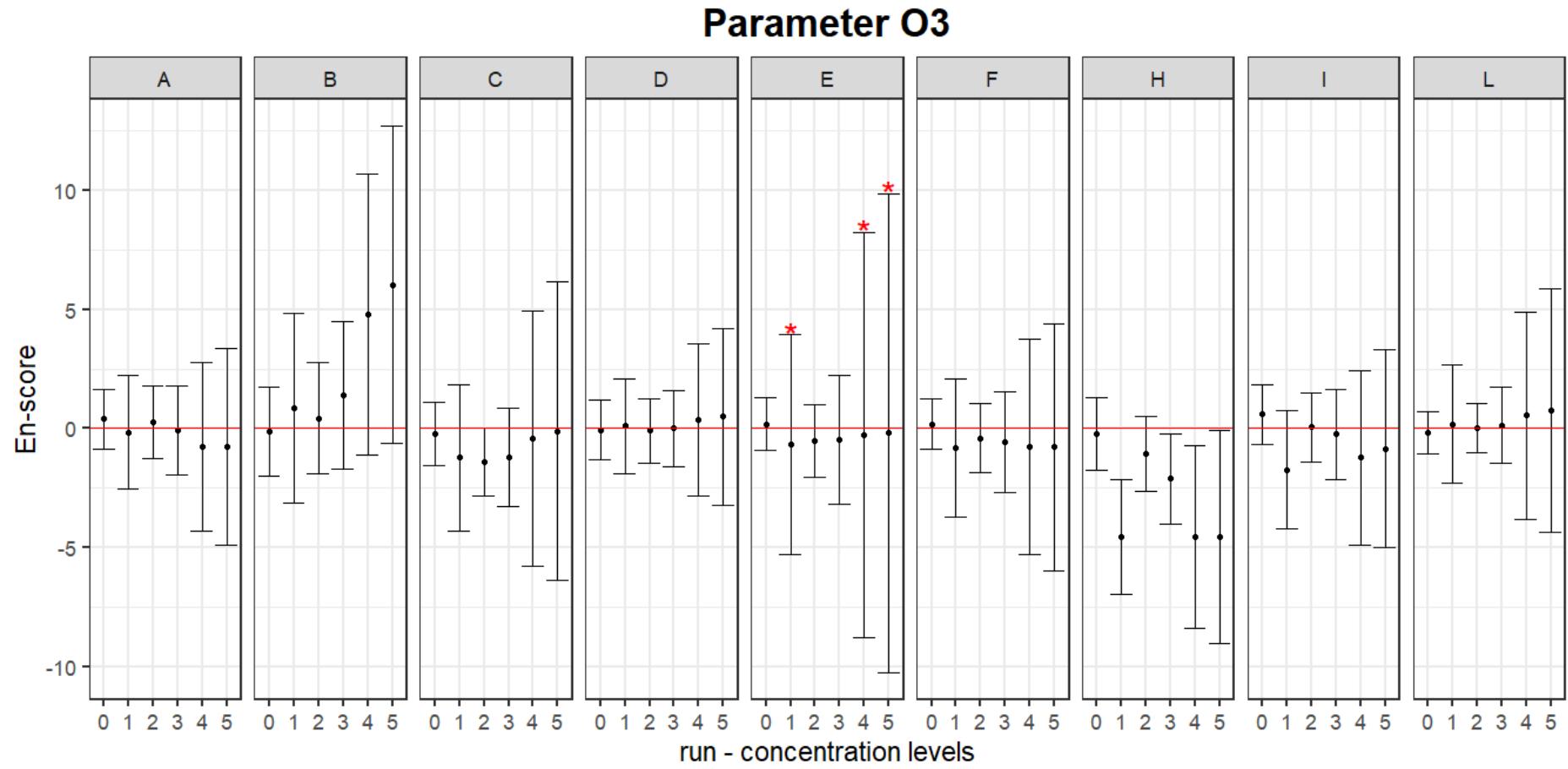
**Figure 8:** Bias of participant's NO<sub>2</sub> measurement results in nmol/mol



Source: JRC 2022

Figure 8 is showing the expanded uncertainty of bias presented as error bar for NO<sub>2</sub> 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  $\sigma_{pt}$ . Laboratories H didn't report results for this pollutant.

**Figure 9:** Bias of participant's O<sub>3</sub> measurement results in nmol/mol

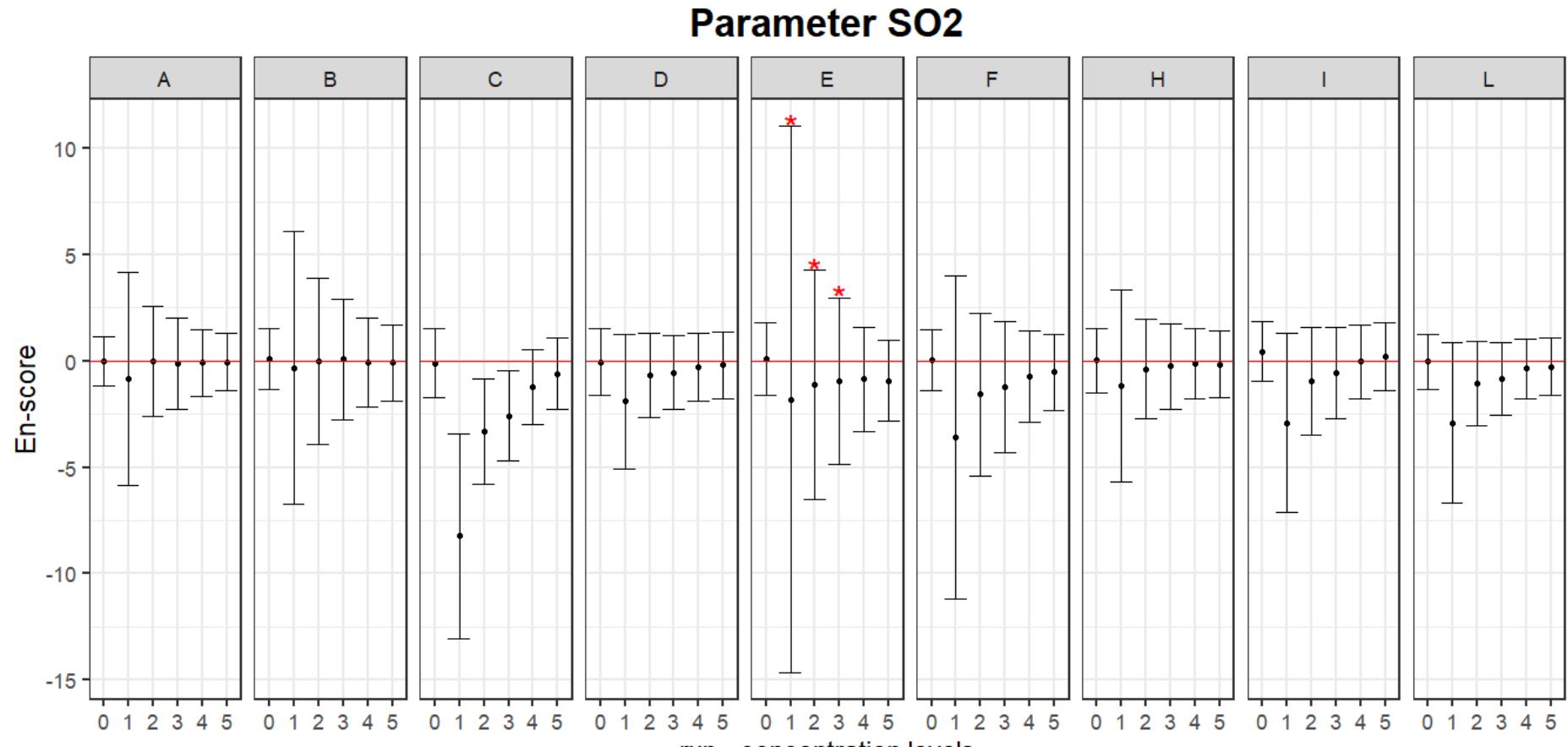


Source: JRC 2022

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  $\sigma_{pt}$ .

**Figure 10:** Bias of participant's SO<sub>2</sub> measurement results in nmol/mol



Source: JRC 2022

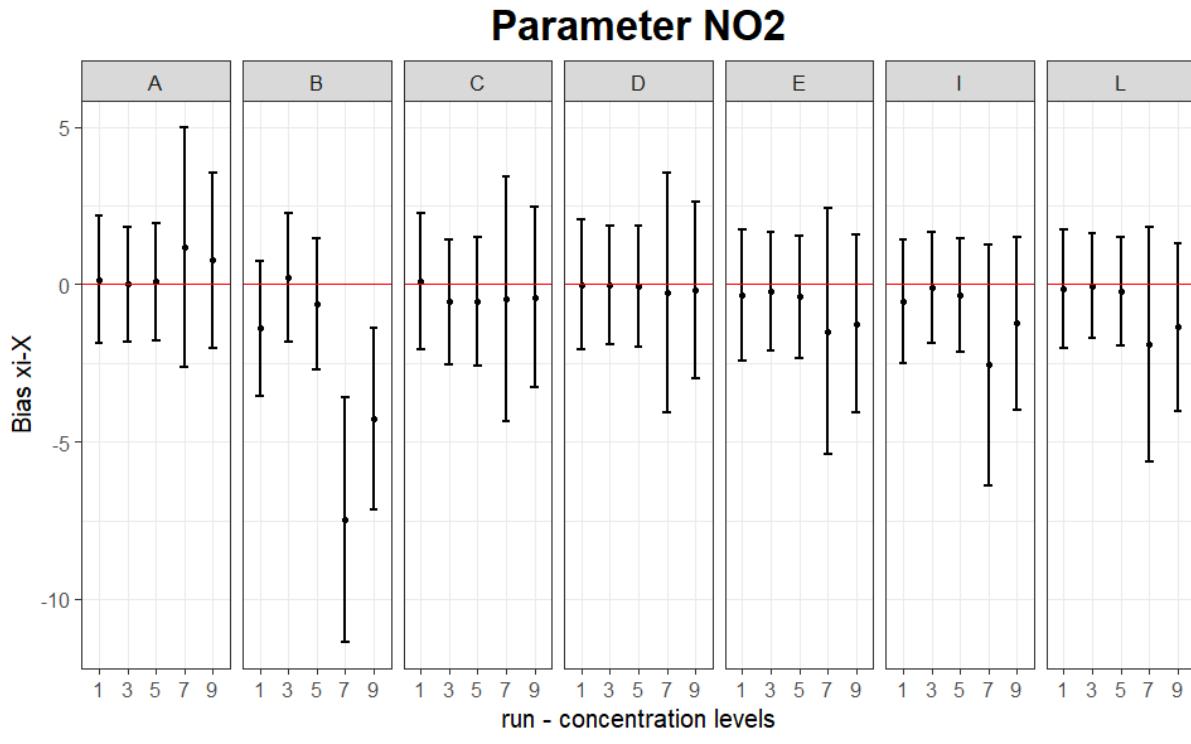
Figure 10 is showing the expanded uncertainty of bias for each run presented as error bar. For each evaluation is given the run number (from 0 to 5) and the participants rounded run average (nmol/mol). The '\*' mark indicates reported standard uncertainties bigger than  $\sigma_{pt}$ .

### 5.3 Performance characteristics of individual laboratories

The difference between individual participants' values and reference values (bias  $\xi_i - X$ ) were evaluated and presented in chapter 4.2 (Figures 6 - 10). Since the results of NO<sub>2</sub> runs 0, 1, 3, 5, 7 and 9 were not treated in proficiency evaluation the bias of these runs are presented in Figure 11.

In this figure **laboratory H** is not included because it didn't report results for this pollutant. **Laboratory F** didn't submit these NO<sub>2</sub> concentration levels.

**Figure 11:** Bias (in nmol/mol) of participant's NO<sub>2</sub> measurements ( $\xi_i$ ) compared to the reference value ( $X$ ) 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 NO<sub>2</sub> (see table 3). For each evaluation is given the run number and the participants rounded run average (nmol/mol).

### 5.4 Converter efficiencies of NO<sub>2</sub>-to-NO for NOX analysers

NO and NO<sub>2</sub> test gases were measured using a gas phase titration technique. 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 NO<sub>2</sub> measurements before and after oxidation by O<sub>3</sub>. 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]:

$$Ec = \left\{ \frac{NO_2i - NO_2f}{NO_i - NO_f} \right\} \times 100 \quad \text{Equation 5}$$

$Ec$  = converter efficiency in %

$NO_2i$  = NO<sub>2</sub> concentration prior the addition of O<sub>3</sub>, nmol/mol

$NO_2f$  = NO<sub>2</sub> concentration remaining after addition of O<sub>3</sub>, nmol/mol

$NO_i$  = original NOX concentration prior to addition of O<sub>3</sub>, nmol/mol

$NO_f$  = NOX concentration remaining after addition of O<sub>3</sub>, nmol/mol

Ideal value for Ec is 100%. The results of equation 5 for each participant at different concentration levels is given in Table 7. The highlighted results are not within the limits foreseen by the EN method ( $\geq 98\%$ ). This evaluation was not carried out for **Laboratory F** and **H** because they didn't report the needed values.

**Table 7:** Efficiency of NO<sub>2</sub>-to-NO converters.

Runs	Laboratories							
	A	B	C	D	E	G	I	L
Run2	99.1	100.6	99.3	99.5	97.3	100.0	109.1	96.8
Run4	99.6	98.1	98.1	103.5	95.3	99.9	108.6	97.4
Run6	99.5	101.4	100.3	97.0	99.1	100.6	111.2	97.4
Run8	99.4	100.9	98.7	99.9	96.3	100.1	102.8	97.6
Run10	99.3	100.6	99.3	99.9	101.1	99.9	100.5	97.6

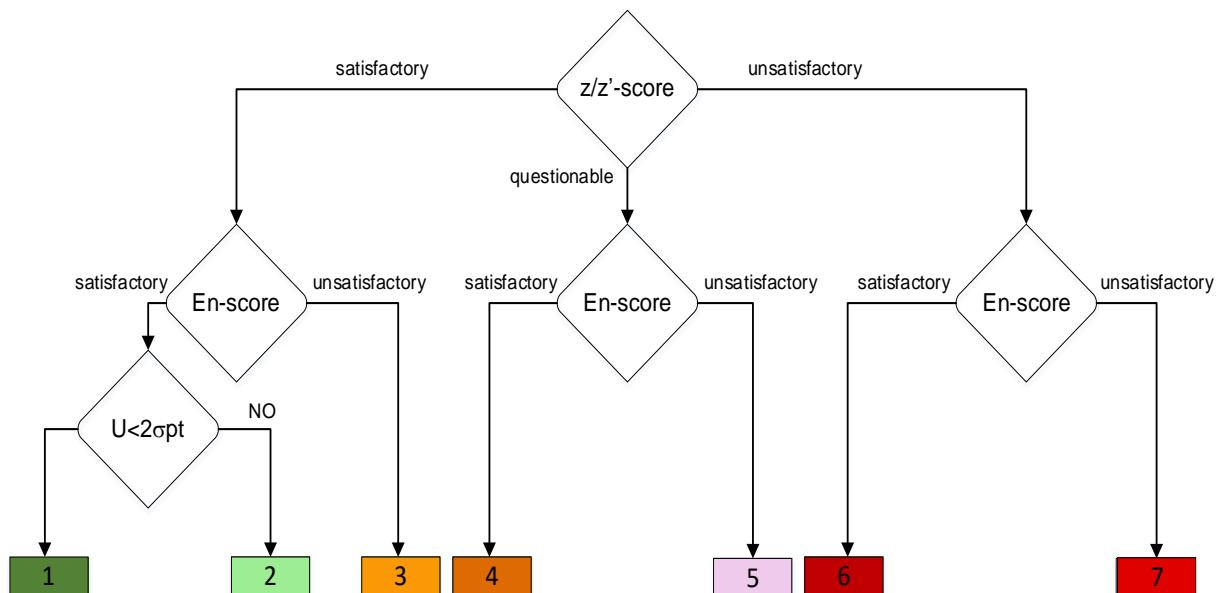
Source: JRC 2022

## 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	Conc. level	Ref. values	A	B	C	D	E	F	H	I	L
CO	0	-0.00	1	1	1	1	1	2	1	1	1
	1	2.90	1	1	1	1	1	1	1	1	1
	2	7.80	1	1	3	1	2	1	1	1	1
	3	4.85	1	1	1	1	1	1	1	1	1
	4	1.43	1	1	1	1	1	1	1	1	1
	5	0.83	1	1	1	1	1	1	1	1	1
NO	0	0.14	1	1	1	1	1	1	1	1	1
	1	119.89	1	1	1	1	2	1	1	1	1
	2	70.56	1	1	1	1	2	1	n.r.	1	1
	3	25.40	1	1	1	1	1	1	1	1	1
	4	16.76	1	1	1	1	1	1	n.r.	1	1
	5	60.02	1	1	1	1	1	1	1	1	1
	6	36.32	1	1	1	1	1	1	n.r.	1	1
	7	468.65	1	1	1	1	2	1	n.r.	1	1
	8	368.95	1	1	1	1	2	1	n.r.	1	1
	9	291.67	1	1	1	1	2	1	1	1	1
	10	162.20	1	1	1	1	2	1	n.r.	1	1
NO <sub>2</sub>	0	0.03	1	1	1	1	1	1	n.r.	n.r.	1
	2	49.67	1	1	1	1	2	1	n.r.	1	1
	4	8.77	1	1	1	1	1	1	n.r.	1	1
	6	24.04	1	1	1	1	2	1	n.r.	1	1
	8	106.88	1	1	1	1	2	1	n.r.	1	1
	10	133.29	1	1	1	1	2	1	n.r.	1	1
O <sub>3</sub>	0	0.07	1	1	1	1	1	1	1	1	1
	1	59.42	1	1	1	1	2	1	5	1	1
	2	13.82	1	1	1	1	1	1	1	1	1
	3	34.66	1	1	1	1	1	1	3	1	1
	4	108.82	1	1	1	1	2	1	3	1	1
	5	128.61	1	1	1	1	2	1	1	1	1
SO <sub>2</sub>	0	0.05	1	1	1	1	1	1	1	1	1
	1	129.86	1	1	5	1	2	1	1	1	1
	2	54.05	1	1	3	1	2	1	1	1	1
	3	38.83	1	1	3	1	2	1	1	1	1
	4	18.27	1	1	1	1	1	1	1	1	1
	5	9.64	1	1	1	1	1	1	1	1	1

"n.r." is referring to values not reported.

Source: JRC 2022

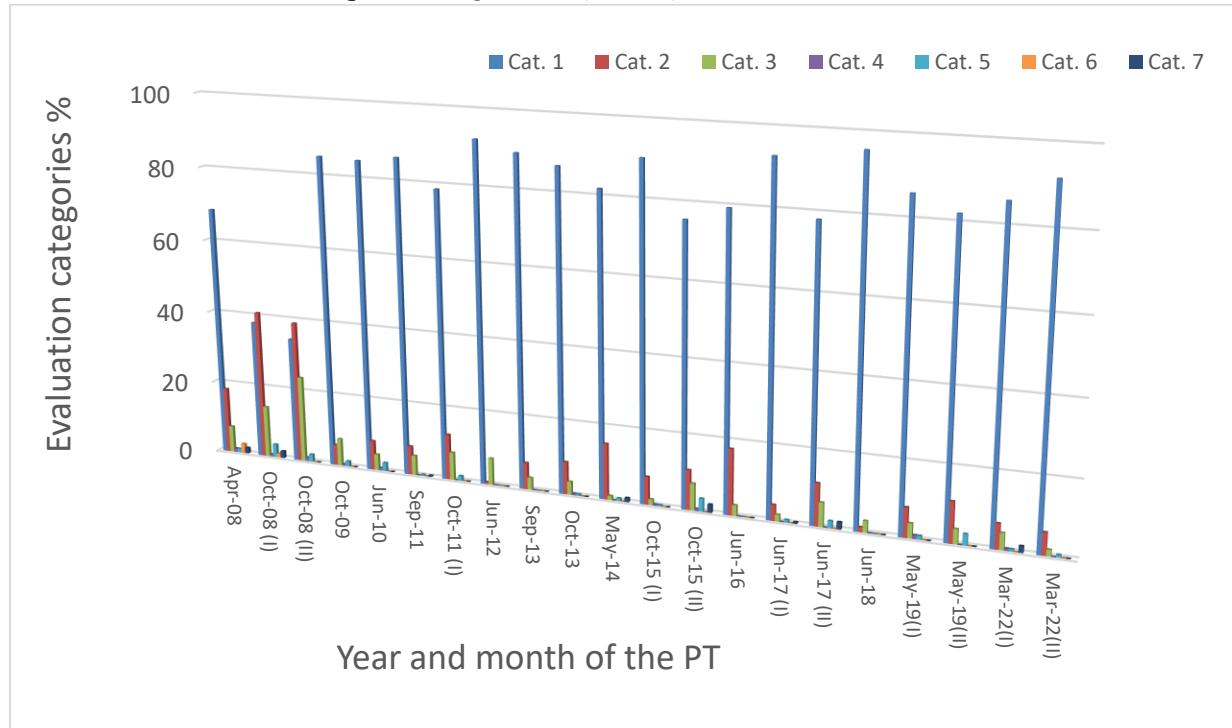
## 7 Conclusions

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 ( $\sigma_{pt}$ ) 91.7% 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’ (6.0%), or too small, ‘category 3’ (1.7%). Two values were found for ‘category 5’ (0.7%) and no values were assigned to ‘categories 4,6,7’.

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



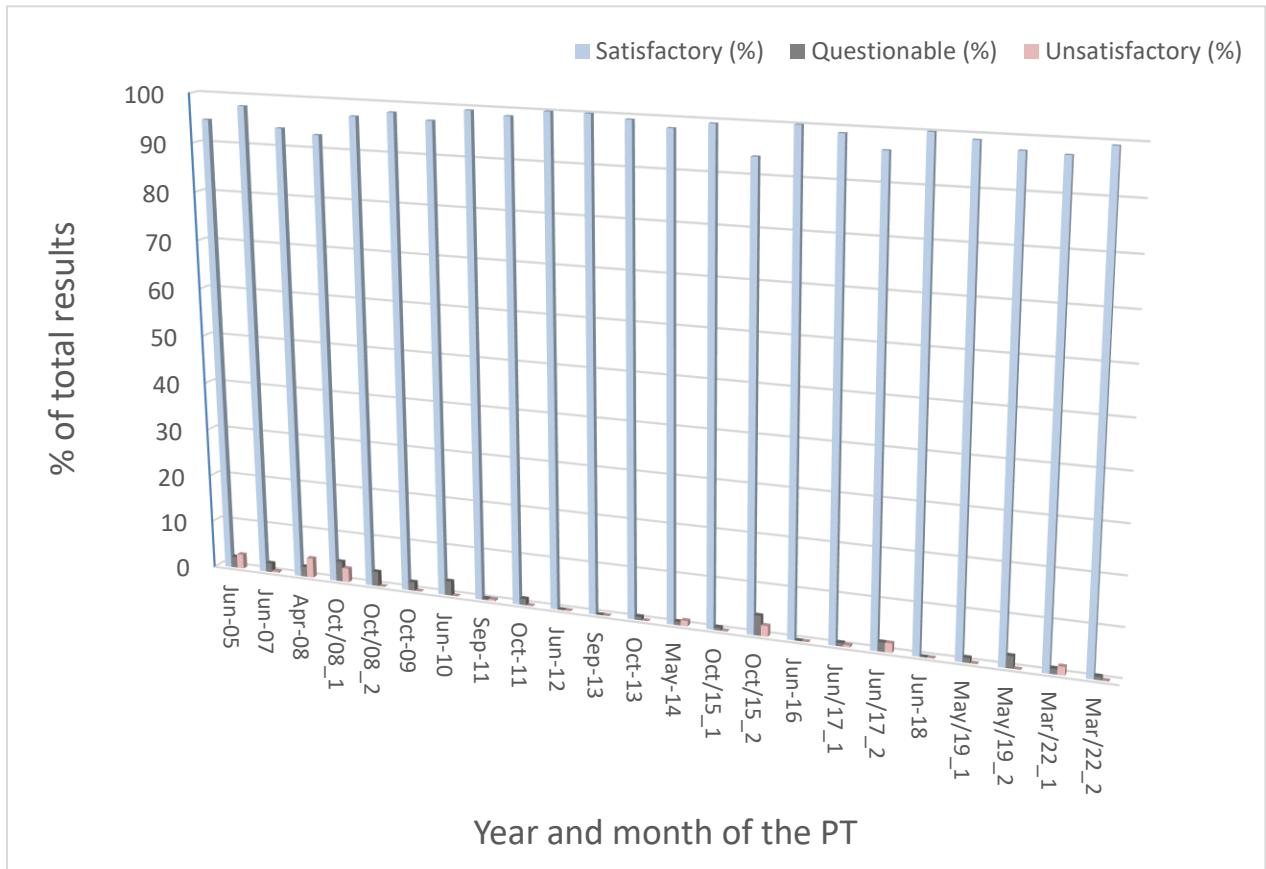
Source: JRC 2022

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], [52] and [53] 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 **99.3%** of the results in the  $z/z'$ -score evaluations were satisfactory, **0.7%** questionable and no results were unsatisfactory. The results of this PT is 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 6% for SO<sub>2</sub>, 5% for CO, 6.4% for O<sub>3</sub>, for NO 2.1% and for NO<sub>2</sub> 4.3% all within the objective derived from criteria imposed by the European Commission ( $\sigma_{pt}$  see Table 4).

During this PT the performance of all NRL was brilliant confirmed by the 99.3% of all values reported that were found satisfactory according to z/z'-score evaluation.

No values were identified as outliers.

In Annex D are reported all the details about the evaluation of this PT and the strugglers 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
NO <sub>2</sub>	Nitrogen dioxide
NOX	The oxides of nitrogen, the sum of NO and NO <sub>2</sub>
NRL	National Reference Laboratory
O <sub>3</sub>	Ozone
PT	Proficiency Test
SO <sub>2</sub>	Sulphur dioxide
VDI	Verein Deutscher Ingenieure
WHO-CC	World Health Organization Collaborating Centre for Air Quality Management and Air Pollution

## **Mathematical Symbols**

$\alpha$	converter efficiency (EN 14211)
$E_c$	Converter efficiency for NO analyser
$En$	En-score statistic (ISO 13528)
$r$	repeatability limit (ISO 5725)
$R$	reproducibility limit (ISO 5725)
$\sigma_{pt}$	standard deviation for proficiency assessment (ISO 13528)
$x^*$	robust average (Annex C ISO 13528)
$s^*$	robust standard deviation (Annex C ISO 13528)
$s_r$	estimate of repeatability variance (ISO 5725)
$s_R$	estimate of reproducibility variance (ISO 5725)
$U_X$	expanded uncertainty of the assigned/reference value (ISO 13528)
$U_{xi}$	expanded uncertainty of the participant's value (ISO 13528)
$u_X$	standard uncertainty of the assigned/reference value (ISO 13528)
$X$	assigned/reference value (ISO 13528)
$x_i$	average of 3 values reported by the participant i (for each parameter and concentration level)
$x_{i,j}$	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 standard ISO 17025 for testing and ISO 17043, both through an audit run by the competent Italian accreditation body (see annex F).

During this PT ERLAP's SO<sub>2</sub>, CO and NO analysers were calibrated according to the methodology described in the standard 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 O<sub>3</sub> 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 NO<sub>2</sub> channel of NOX analyser the GPT test was performed to establish the efficiency of NO<sub>2</sub>-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	-0.005	0.008	0.017
CO_1	µmol/mol	2.895	0.024	0.048
CO_2	µmol/mol	7.802	0.062	0.124
CO_3	µmol/mol	4.854	0.039	0.078
CO_4	µmol/mol	1.425	0.014	0.028
CO_5	µmol/mol	0.834	0.012	0.023
NO_0	nmol/mol	0.140	0.710	1.420
NO_1	nmol/mol	119.89	0.920	1.84
NO_10	nmol/mol	162.19	1.050	2.10
NO_2	nmol/mol	70.56	0.800	1.590
NO_3	nmol/mol	25.40	0.720	1.450
NO_4	nmol/mol	16.76	0.720	1.440
NO_5	nmol/mol	60.02	0.780	1.550
NO_6	nmol/mol	36.32	0.740	1.480
NO_7	nmol/mol	468.64	2.330	4.650
NO_8	nmol/mol	368.94	1.890	3.780
NO_9	nmol/mol	291.67	1.560	3.110
NO2_0	nmol/mol	0.03	0.720	1.43
NO2_1	nmol/mol	0.33	0.840	1.69
NO2_10	nmol/mol	133.29	1.330	2.660
NO2_2	nmol/mol	49.67	0.850	1.700
NO2_3	nmol/mol	0.13	0.720	1.45
NO2_4	nmol/mol	8.77	0.720	1.45
NO2_5	nmol/mol	0.19	0.760	1.52
NO2_6	nmol/mol	24.04	0.760	1.510
NO2_7	nmol/mol	7.11	1.820	3.63
NO2_8	nmol/mol	106.88	1.840	3.680
NO2_9	nmol/mol	3.89	1.260	2.53
O3_0	nmol/mol	0.07	0.180	0.35
O3_1	nmol/mol	59.42	0.440	0.890
O3_2	nmol/mol	13.82	0.180	0.370
O3_3	nmol/mol	34.66	0.290	0.580
O3_4	nmol/mol	108.82	0.780	1.570
O3_5	nmol/mol	128.61	0.920	1.850
SO2_0	nmol/mol	0.05	0.500	1.01
SO2_1	nmol/mol	129.86	1.030	2.060
SO2_2	nmol/mol	54.05	0.640	1.270
SO2_3	nmol/mol	38.83	0.580	1.160
SO2_4	nmol/mol	18.27	0.520	1.050
SO2_5	nmol/mol	9.64	0.510	1.02

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.

$$u_{fx} = \sqrt{u_x^2 + (X \cdot u_{homo})^2} \quad \text{Equation 6}$$

$u_{fx}$  = 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 during 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
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 concentration generated (run), participants were asked to report 3 results representing a measurement of 30 minutes each ( $x_i$ ).

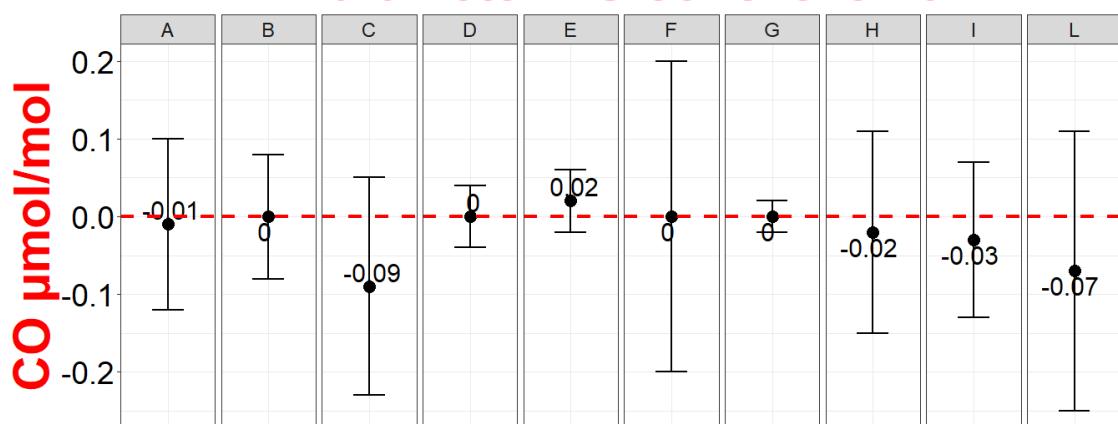
In this annex are presented the reported data and their uncertainty  $u(x_i)$  and  $U(x_i)$  expressed in mol/mol units. For all the runs except concentration levels 0, also average ( $x_{\text{mean}}$ ) and standard deviation (sd) of each participant are presented.

The assigned value is indicated on the graphs with the red line and the individual laboratories expanded uncertainties ( $U_{xi}$ ) are indicated with error bars.

### Reported values for CO

**Figure 15:** Reported values of CO concentration 0 ( $\mu\text{mol/mol}$ )

### Parameter CO conc level: 0

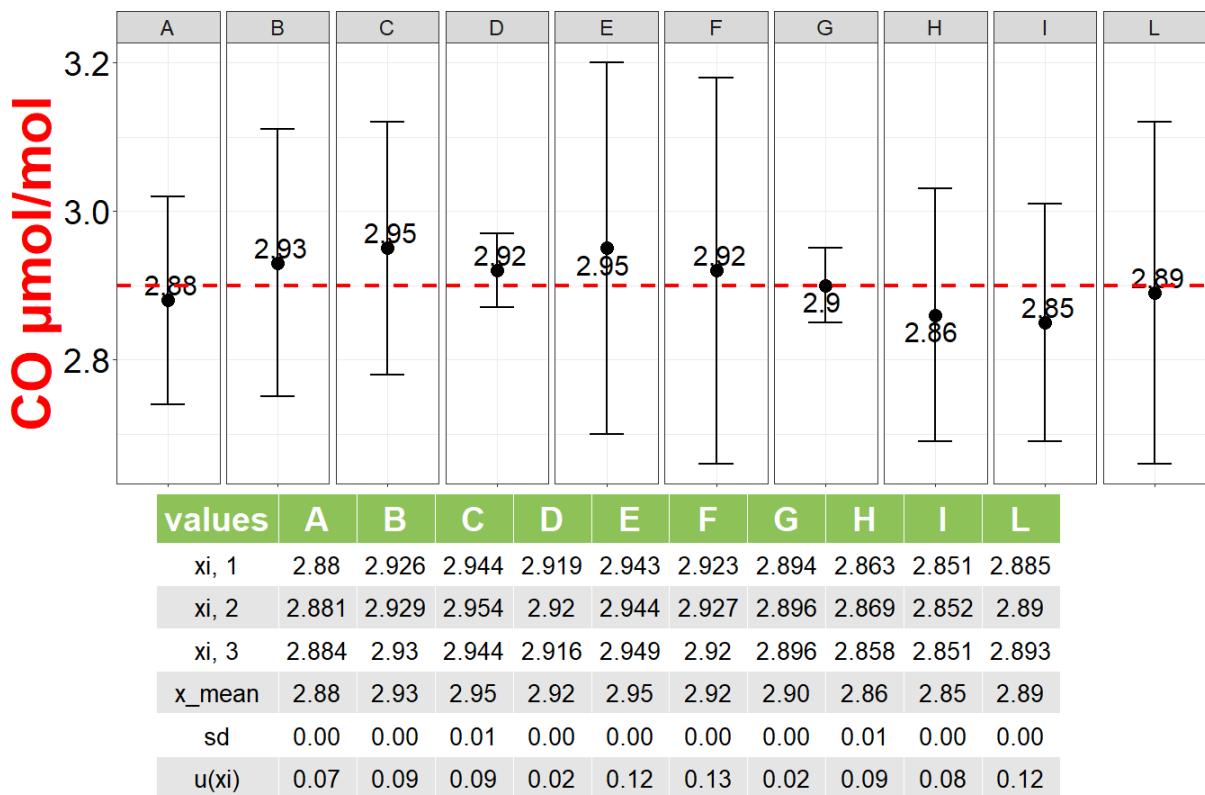


values	A	B	C	D	E	F	G	H	I	L
$x_i, 1$	-0.008	0	-0.092	0.002	0.016	0.004	-0.005	-0.016	-0.032	-0.074
$u(x_i)$	0.05	0.04	0.07	0.02	0.02	0.10	0.01	0.06	0.05	0.09
$U(x_i)$	0.11	0.08	0.14	0.04	0.04	0.20	0.02	0.13	0.10	0.18

Source: JRC 2022

**Figure 16:** Reported values of CO concentration 1 ( $\mu\text{mol/mol}$ )

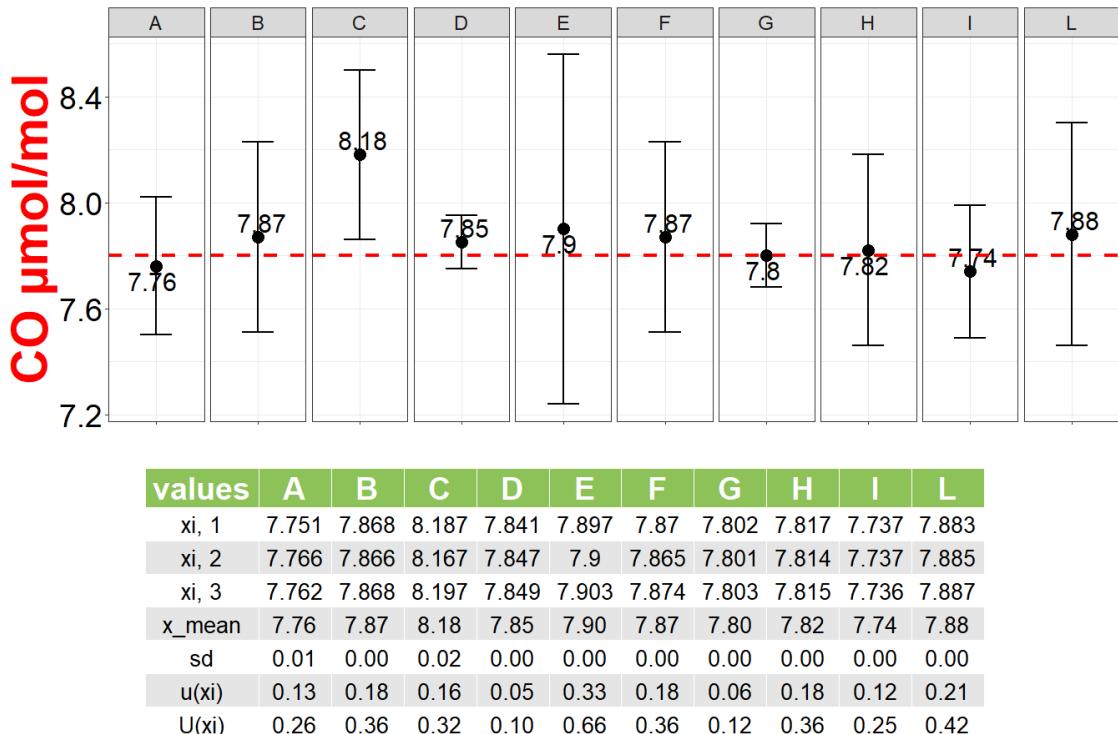
## Parameter CO conc level: 1



Source: JRC 2022

**Figure 17:** Reported values of CO concentration 2 ( $\mu\text{mol/mol}$ )

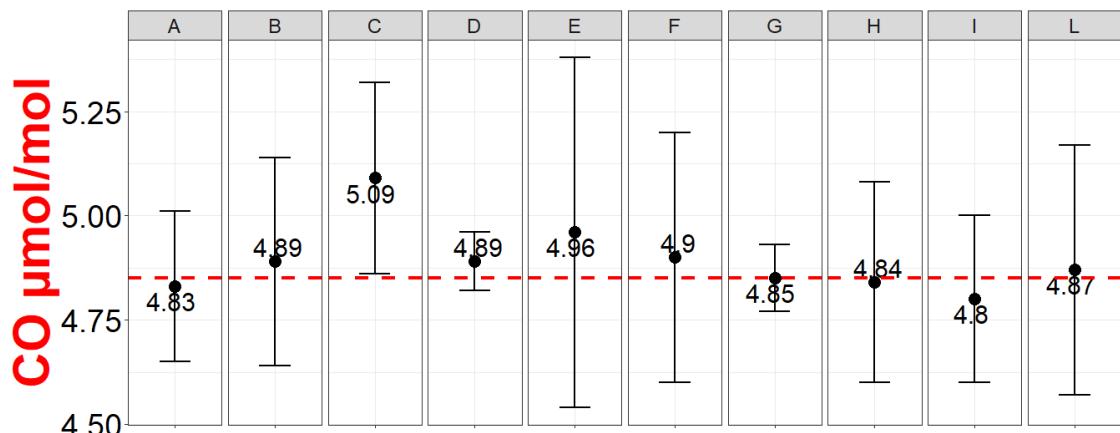
## Parameter CO conc level: 2



Source: JRC 2022

**Figure 18:** Reported values of CO concentration 3 ( $\mu\text{mol/mol}$ )

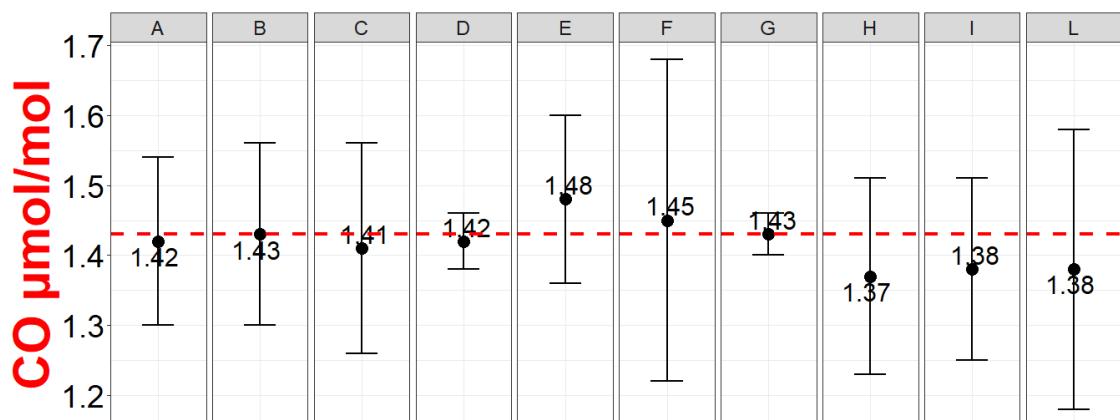
### Parameter CO conc level: 3



Source: JRC 2022

**Figure 19:** Reported values of CO concentration 4 ( $\mu\text{mol/mol}$ )

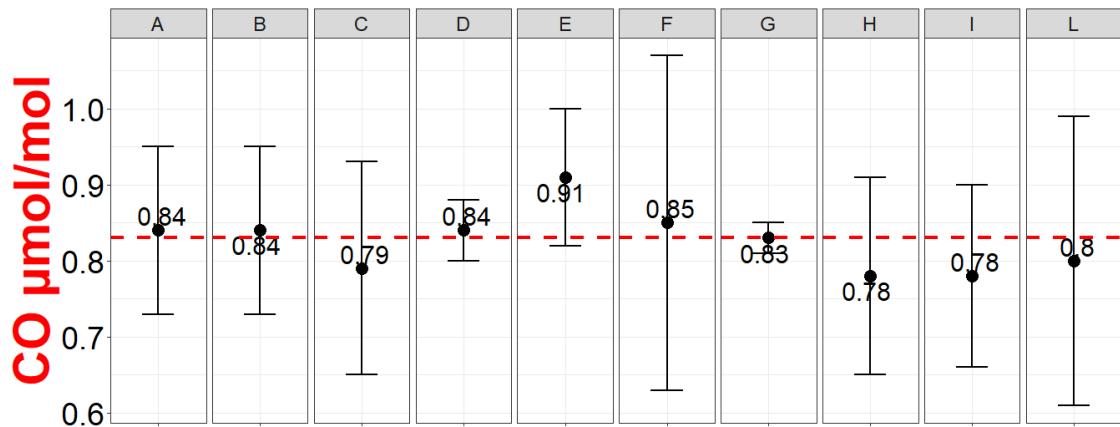
### Parameter CO conc level: 4



Source: JRC 2022

**Figure 20:** Reported values of CO concentration 5 ( $\mu\text{mol/mol}$ )

## Parameter CO conc level: 5



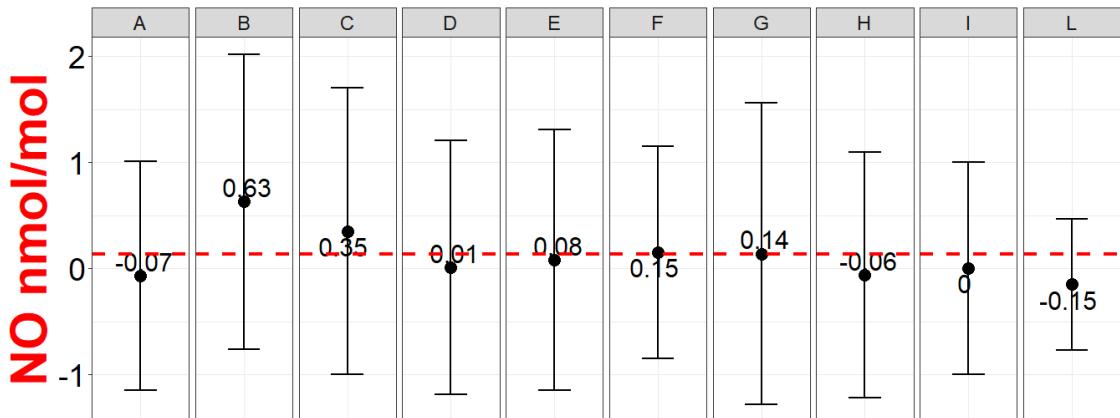
values	A	B	C	D	E	F	G	H	I	L
xi, 1	0.843	0.843	0.788	0.842	0.906	0.859	0.835	0.774	0.785	0.799
xi, 2	0.838	0.841	0.791	0.842	0.906	0.851	0.832	0.773	0.784	0.796
xi, 3	0.845	0.845	0.798	0.841	0.913	0.853	0.834	0.779	0.784	0.796
x_mean	0.84	0.84	0.79	0.84	0.91	0.85	0.83	0.78	0.78	0.80
sd	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
u(xi)	0.06	0.05	0.07	0.02	0.04	0.11	0.01	0.06	0.06	0.09
U(xi)	0.11	0.11	0.14	0.04	0.09	0.22	0.02	0.13	0.12	0.19

Source: JRC 2022

## Reported values for NO

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

**Parameter NO conc level: 0**

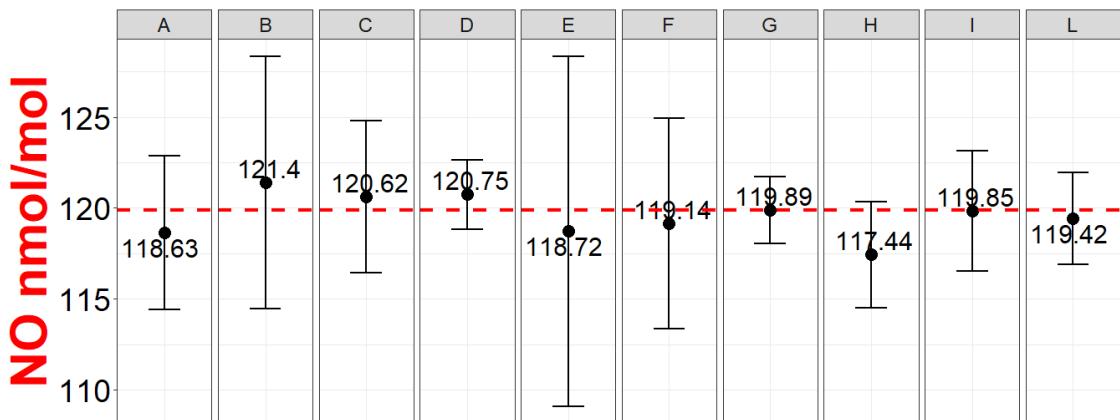


values	A	B	C	D	E	F	G	H	I	L
xi, 1	-0.07	0.63	0.35	0.01	0.08	0.15	0.14	-0.06	0	-0.15
u(xi)	0.54	0.69	0.68	0.58	0.62	0.50	0.71	0.58	0.50	0.31
U(xi)	1.08	1.39	1.35	1.20	1.23	1.00	1.42	1.16	1.00	0.62

Source: JRC 2022

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

**Parameter NO conc level: 1**

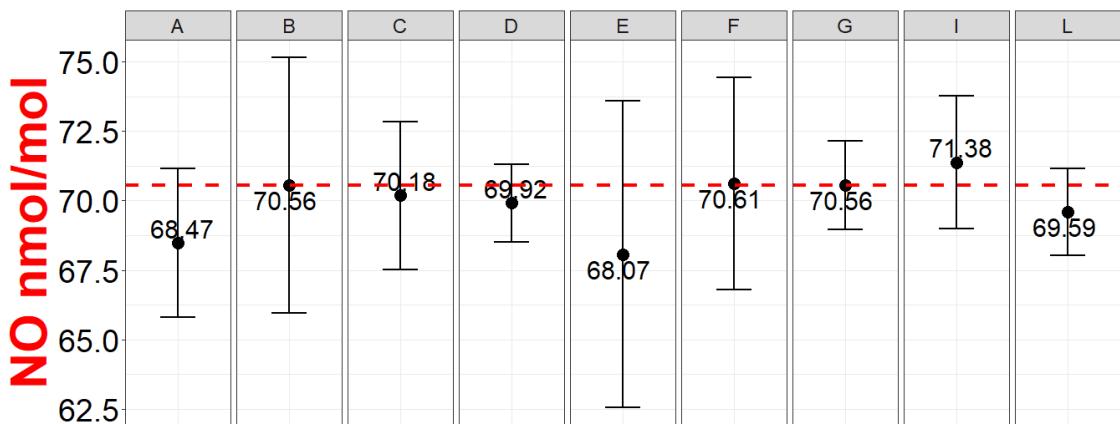


values	A	B	C	D	E	F	G	H	I	L
xi, 1	118.86	121.53	120.9	120.91	119.32	119.46	120.15	117.56	119.95	119.6
xi, 2	118.54	121.31	120.67	120.77	118.6	119.13	119.83	117.34	119.85	119.26
xi, 3	118.48	121.37	120.29	120.58	118.25	118.82	119.7	117.43	119.75	119.4
x_mean	118.63	121.40	120.62	120.75	118.72	119.14	119.89	117.44	119.85	119.42
sd	0.20	0.11	0.31	0.17	0.55	0.32	0.23	0.11	0.10	0.17
u(xi)	2.11	3.47	2.09	0.93	4.81	2.88	0.92	1.45	1.65	1.26
U(xi)	4.22	6.94	4.17	1.90	9.62	5.77	1.84	2.91	3.30	2.53

Source: JRC 2022

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

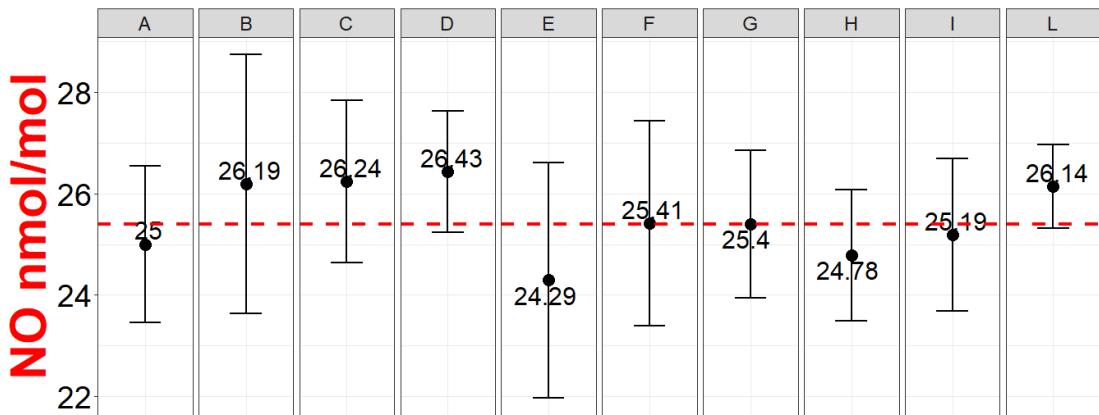
## Parameter NO conc level: 2



Source: JRC 2022

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

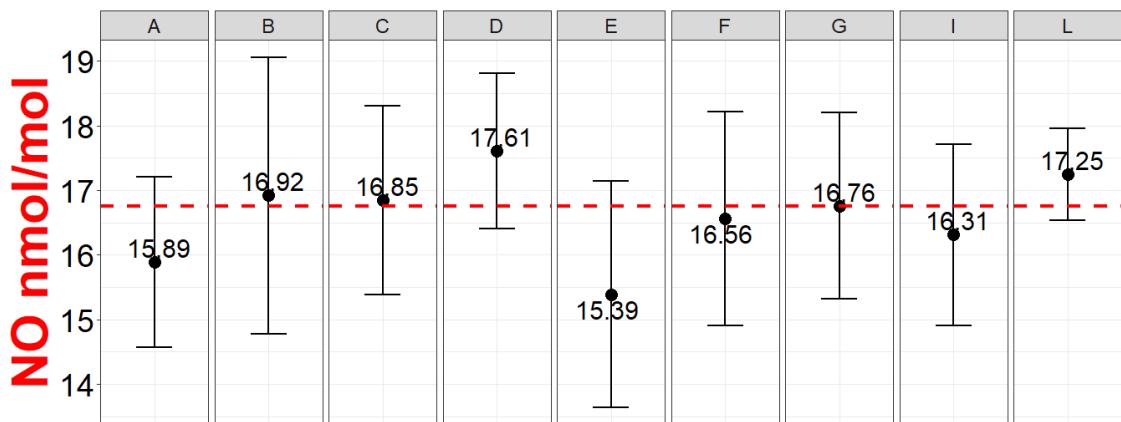
## Parameter NO conc level: 3



Source: JRC 2022

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

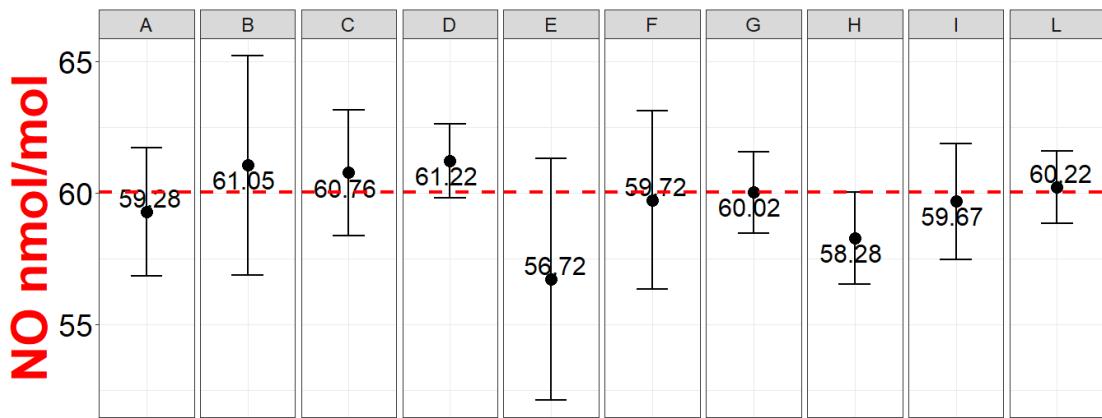
### Parameter NO conc level: 4



Source: JRC 2022

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

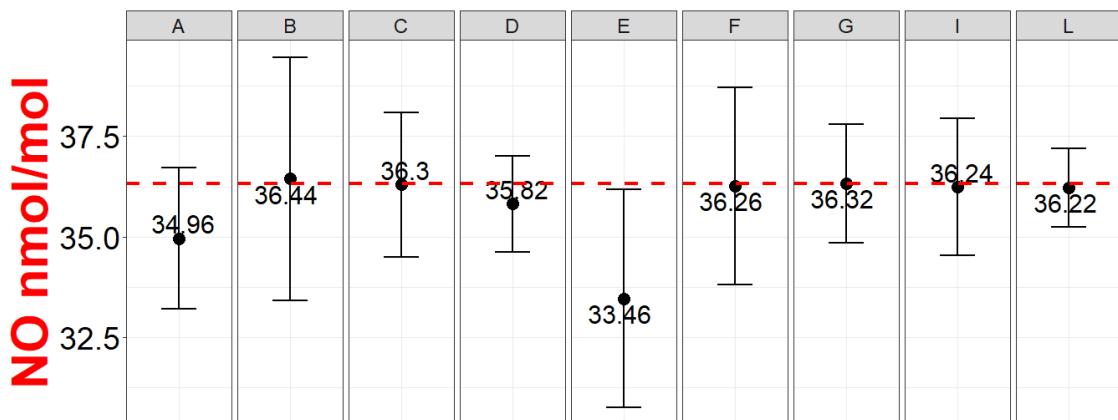
### Parameter NO conc level: 5



Source: JRC 2022

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

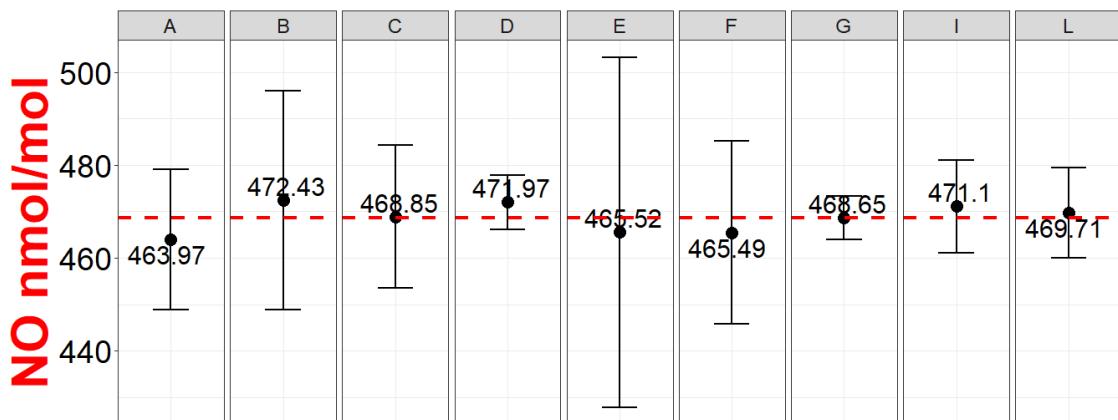
### Parameter NO conc level: 6



Source: JRC 2022

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

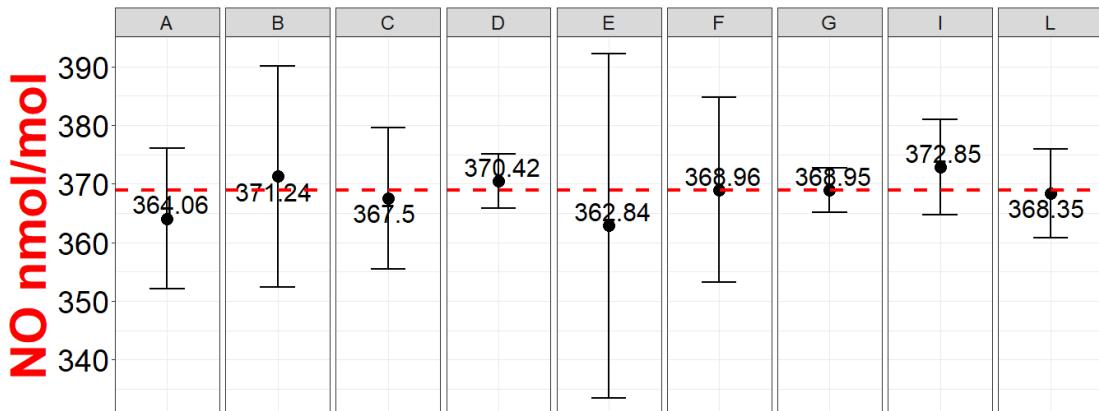
### Parameter NO conc level: 7



Source: JRC 2022

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

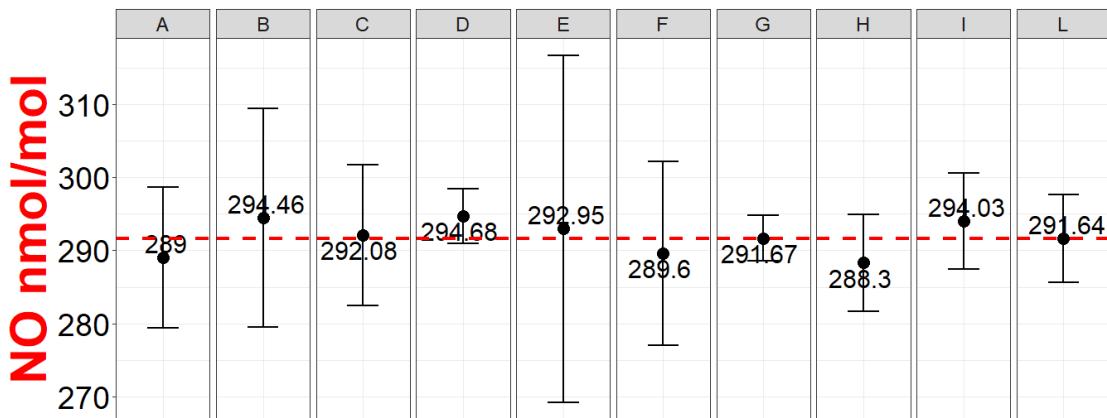
### Parameter NO conc level: 8



Source: JRC 2022

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

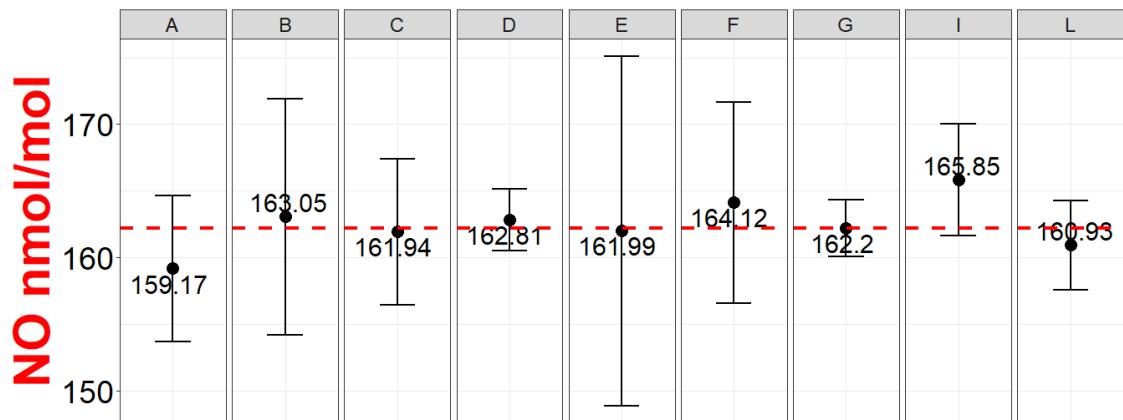
### Parameter NO conc level: 9



Source: JRC 2022

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

### Parameter NO conc level: 10



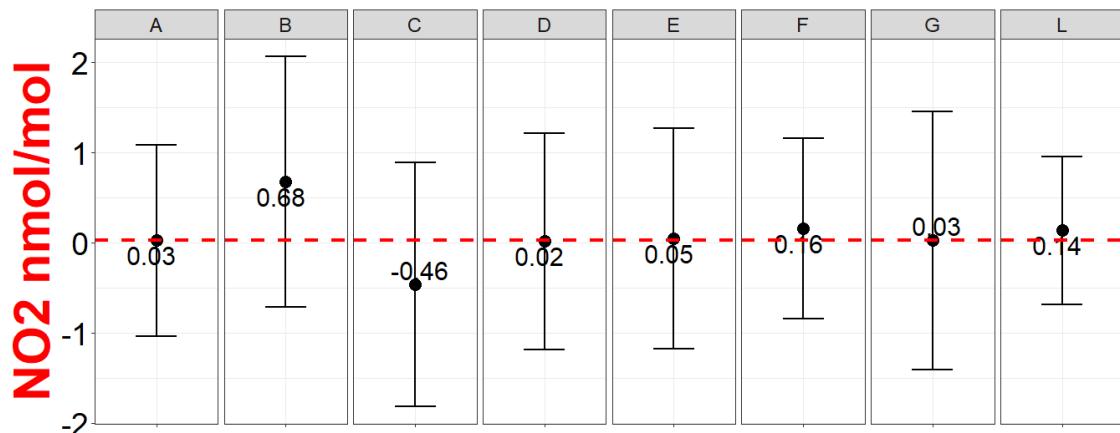
values	A	B	C	D	E	F	G	I	L
xi, 1	159.29	163.05	162.04	162.88	161.83	164.21	162.25	165.97	160.99
xi, 2	159.13	163.02	161.83	162.7	162.07	164.08	162.19	165.74	160.86
xi, 3	159.08	163.08	161.95	162.85	162.08	164.06	162.15	165.85	160.93
x_mean	159.17	163.05	161.94	162.81	161.99	164.12	162.20	165.85	160.93
sd	0.11	0.03	0.11	0.10	0.14	0.08	0.05	0.12	0.07
u(xi)	2.74	4.43	2.74	1.14	6.56	3.78	1.05	2.10	1.68
U(xi)	5.48	8.86	5.47	2.30	13.12	7.56	2.10	4.20	3.36

Source: JRC 2022

## Reported values for NO<sub>2</sub>

**Figure 32:** Reported values of NO<sub>2</sub> concentration 0 (nmol/mol)

**Parameter NO<sub>2</sub> conc level: 0**

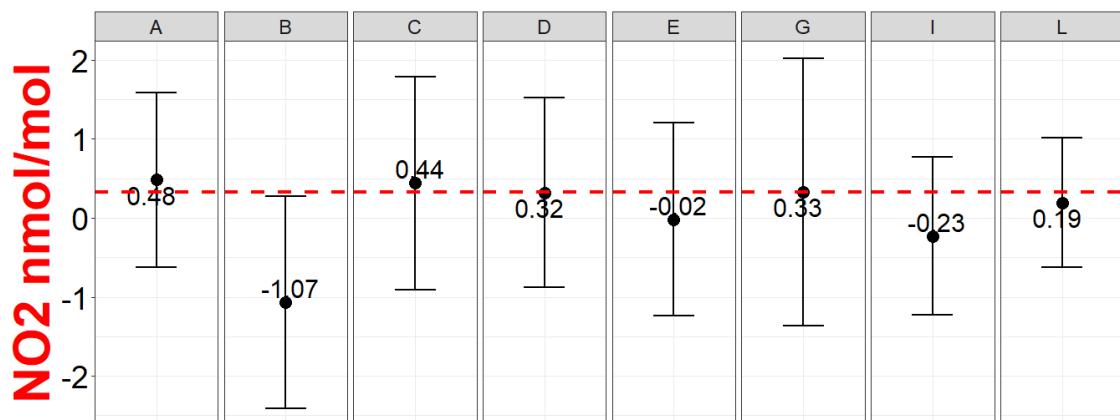


values	A	B	C	D	E	F	G	L
xi, 1	0.03	0.68	-0.46	0.02	0.05	0.16	0.03	0.14
u(xi)	0.53	0.71	0.68	0.60	0.61	0.50	0.71	0.41
U(xi)	1.06	1.39	1.35	1.20	1.22	1.00	1.43	0.82

Source: JRC 2022

**Figure 33:** Reported values of NO<sub>2</sub> concentration 1 (nmol/mol)

**Parameter NO<sub>2</sub> conc level: 1**

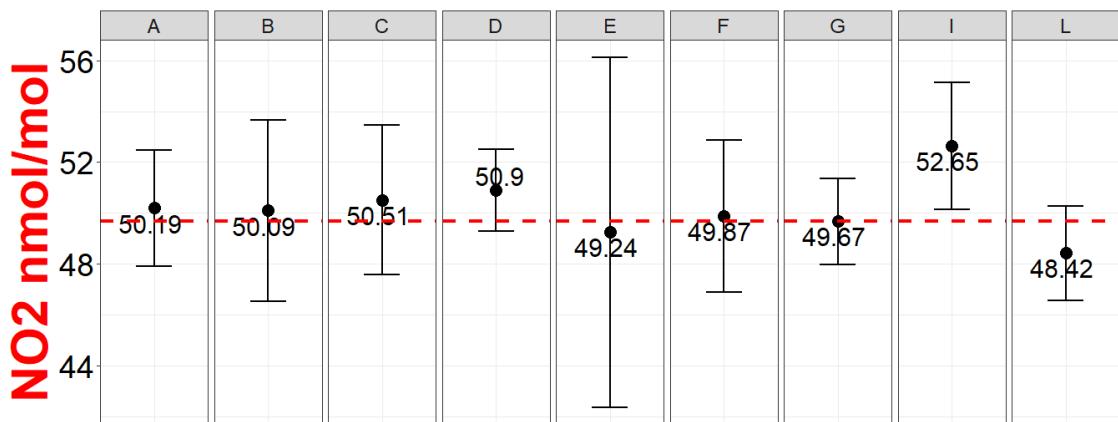


values	A	B	C	D	E	G	I	L
xi, 1	0.38	-1.13	0.37	0.36	0.01	0.33	-0.13	0.25
xi, 2	0.5	-0.97	0.23	0.27	0.05	0.31	0.04	0.29
xi, 3	0.55	-1.12	0.73	0.32	-0.12	0.35	-0.61	0.02
x_mean	0.48	-1.07	0.44	0.32	-0.02	0.33	-0.23	0.19
sd	0.09	0.09	0.26	0.05	0.09	0.02	0.34	0.15
u(xi)	0.55	0.67	0.68	0.60	0.61	0.84	0.50	0.41
U(xi)	1.10	1.34	1.35	1.20	1.22	1.69	1.00	0.82

Source: JRC 2022

**Figure 34:** Reported values of NO<sub>2</sub> concentration 2 (nmol/mol)

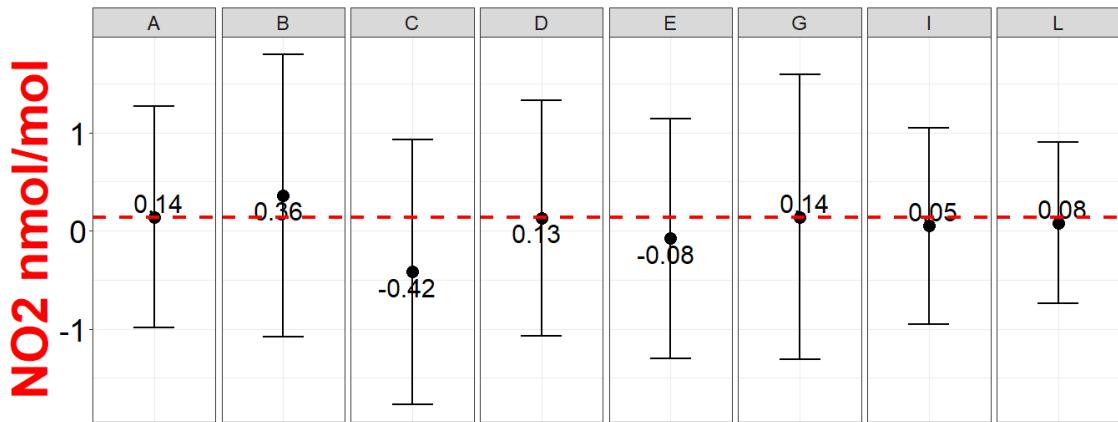
## Parameter NO<sub>2</sub> conc level: 2



Source: JRC 2022

**Figure 35:** Reported values of NO<sub>2</sub> concentration 3 (nmol/mol)

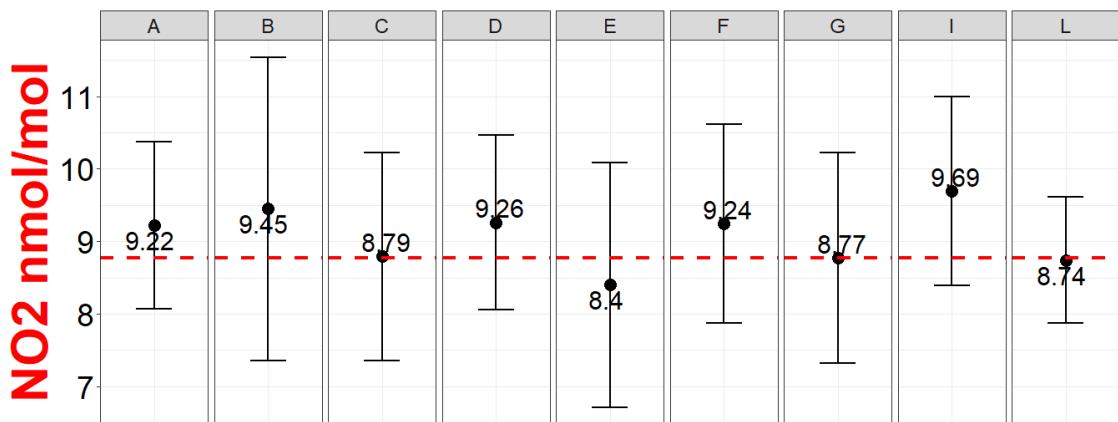
## Parameter NO<sub>2</sub> conc level: 3



Source: JRC 2022

**Figure 36:** Reported values of NO<sub>2</sub> concentration 4 (nmol/mol)

## Parameter NO<sub>2</sub> conc level: 4

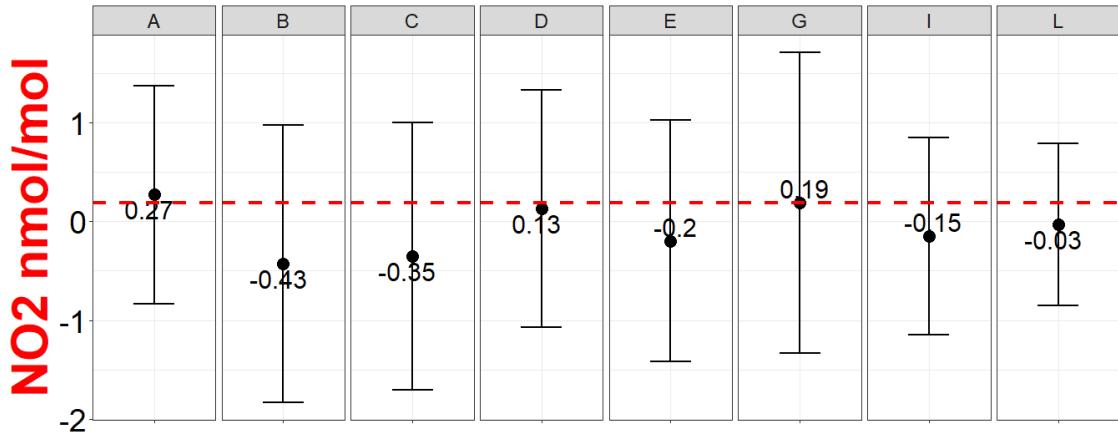


values	A	B	C	D	E	F	G	I	L
xi, 1	9.23	9.39	8.87	9.29	8.4	9.15	8.74	9.74	8.77
xi, 2	9.16	9.38	8.66	9.26	8.43	9.28	8.78	9.7	8.71
xi, 3	9.26	9.58	8.85	9.24	8.36	9.3	8.79	9.63	8.75
x_mean	9.22	9.45	8.79	9.26	8.40	9.24	8.77	9.69	8.74
sd	0.05	0.11	0.12	0.03	0.04	0.08	0.03	0.06	0.03
u(xi)	0.57	1.04	0.71	0.61	0.85	0.68	0.73	0.65	0.44
U(xi)	1.15	2.09	1.43	1.20	1.69	1.37	1.45	1.30	0.87

Source: JRC 2022

**Figure 37:** Reported values of NO<sub>2</sub> concentration 5 (nmol/mol)

## Parameter NO<sub>2</sub> conc level: 5

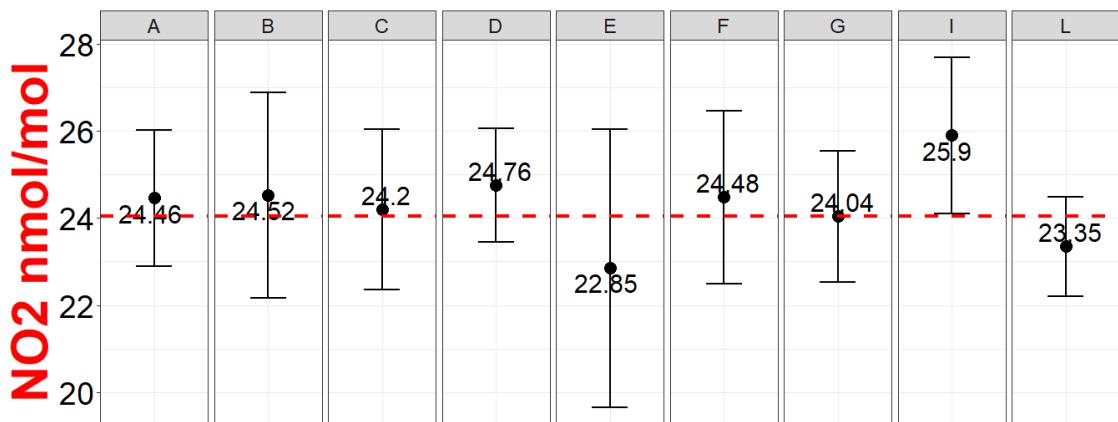


values	A	B	C	D	E	G	I	L
xi, 1	0.28	-0.3	-0.05	0.1	-0.26	0.18	-0.05	-0.06
xi, 2	0.29	-0.45	-0.43	0.17	-0.22	0.17	-0.33	0.04
xi, 3	0.24	-0.54	-0.57	0.11	-0.13	0.22	-0.06	-0.06
x_mean	0.27	-0.43	-0.35	0.13	-0.20	0.19	-0.15	-0.03
sd	0.03	0.12	0.27	0.04	0.07	0.03	0.16	0.06
u(xi)	0.55	0.70	0.68	0.60	0.61	0.76	0.50	0.41
U(xi)	1.10	1.40	1.35	1.20	1.22	1.52	1.00	0.82

Source: JRC 2022

**Figure 38:** Reported values of NO<sub>2</sub> concentration 6 (nmol/mol)

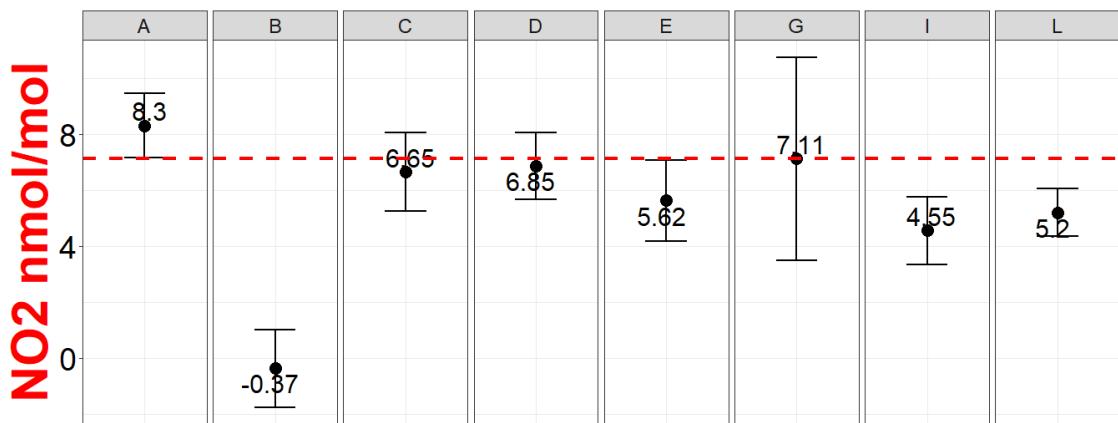
### Parameter NO<sub>2</sub> conc level: 6



Source: JRC 2022

**Figure 39:** Reported values of NO<sub>2</sub> concentration 7 (nmol/mol)

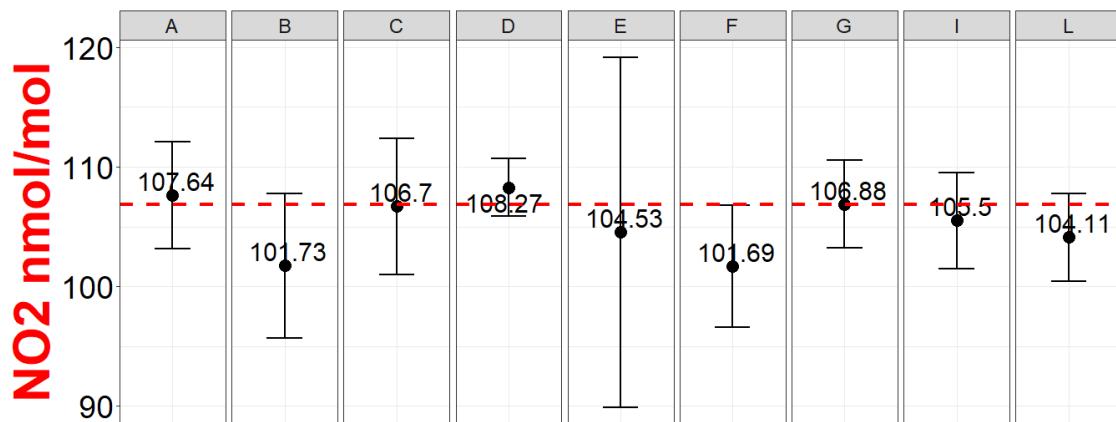
### Parameter NO<sub>2</sub> conc level: 7



Source: JRC 2022

**Figure 40:** Reported values of NO<sub>2</sub> concentration 8 (nmol/mol)

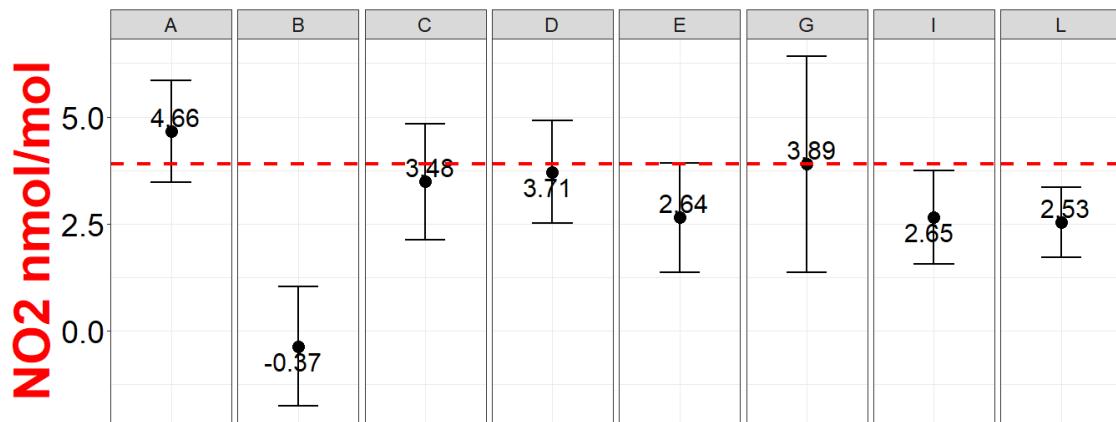
### Parameter NO<sub>2</sub> conc level: 8



Source: JRC 2022

**Figure 41:** Reported values of NO<sub>2</sub> concentration 9 (nmol/mol)

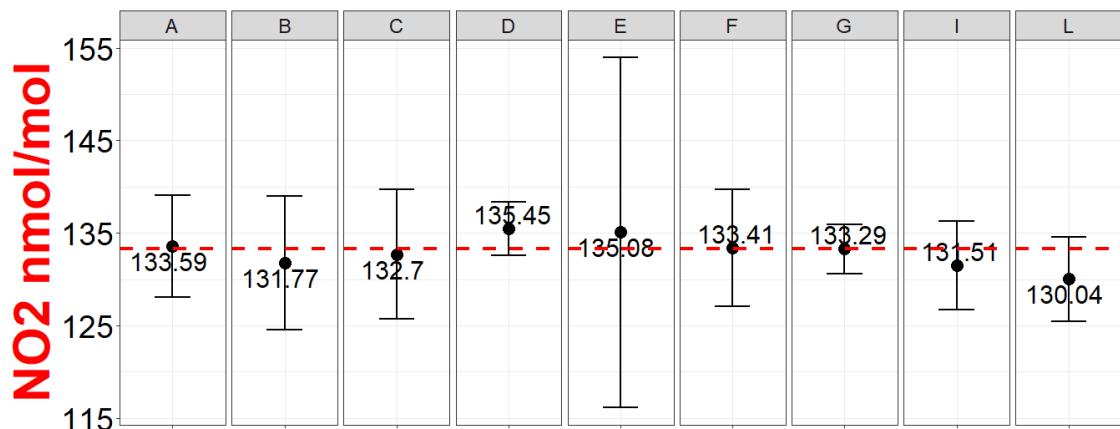
### Parameter NO<sub>2</sub> conc level: 9



Source: JRC 2022

**Figure 42:** Reported values of NO<sub>2</sub> concentration 10 (nmol/mol)

## Parameter NO<sub>2</sub> conc level: 10



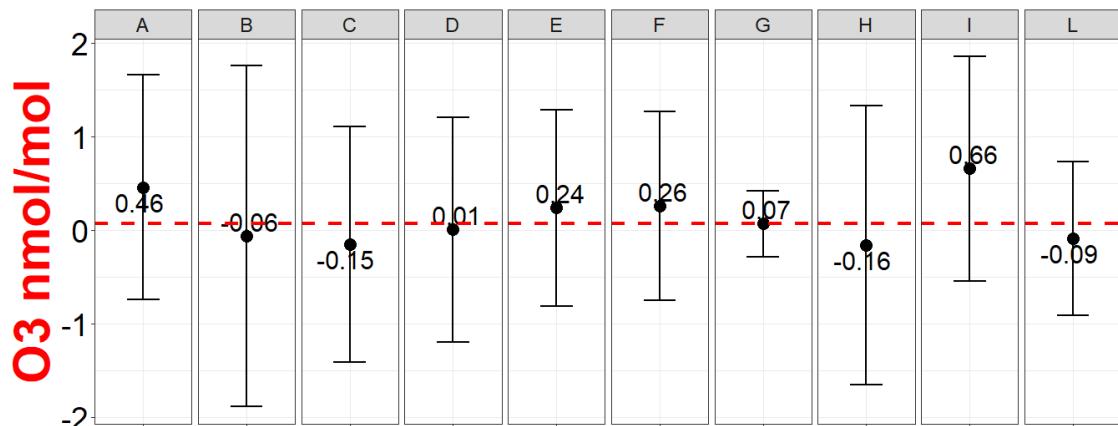
values	A	B	C	D	E	F	G	I	L
xi, 1	133.6	131.76	132.68	135.41	134.74	133.38	133.19	132.7	129.89
xi, 2	133.55	131.73	132.98	135.5	134.96	133.31	133.38	131.22	130.08
xi, 3	133.62	131.83	132.44	135.43	135.53	133.54	133.3	130.61	130.14
x_mean	133.59	131.77	132.70	135.45	135.08	133.41	133.29	131.51	130.04
sd	0.04	0.05	0.27	0.05	0.41	0.12	0.10	1.07	0.13
u(xi)	2.75	3.63	3.50	1.45	9.46	3.17	1.33	2.40	2.28
U(xi)	5.49	7.26	6.99	2.90	18.91	6.34	2.66	4.80	4.55

Source: JRC 2022

## Reported values for O3

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

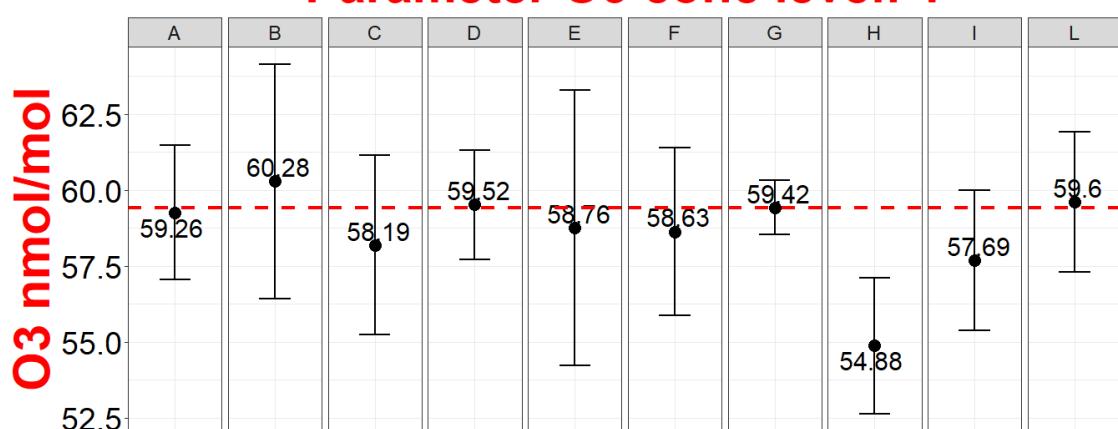
**Parameter O3 conc level: 0**



Source: JRC 2022

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

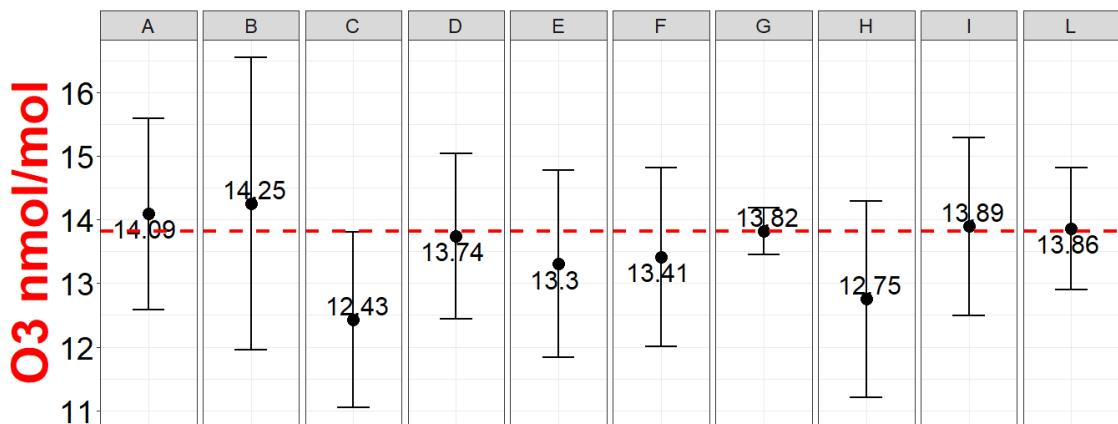
**Parameter O3 conc level: 1**



Source: JRC 2022

**Figure 45:** Reported values of O<sub>3</sub> concentration 2 (nmol/mol)

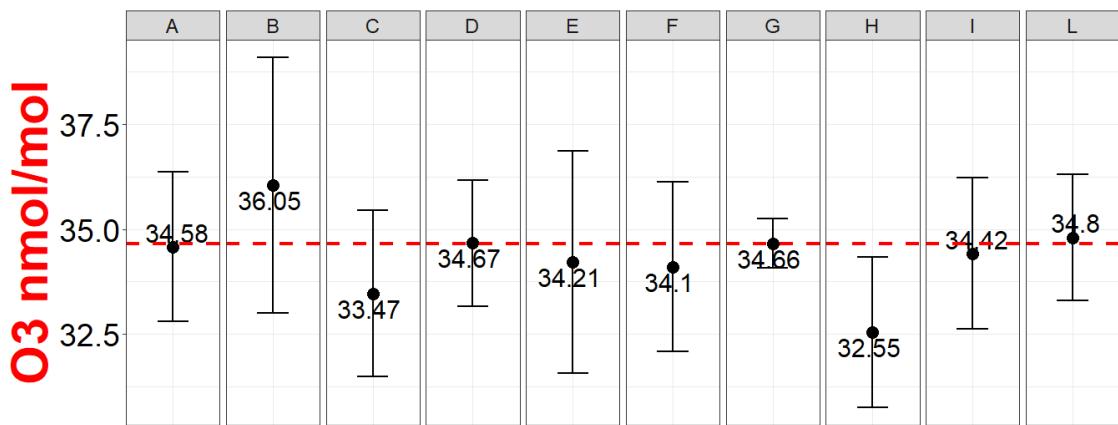
### Parameter O<sub>3</sub> conc level: 2



Source: JRC 2022

**Figure 46:** Reported values of O<sub>3</sub> concentration 3 (nmol/mol)

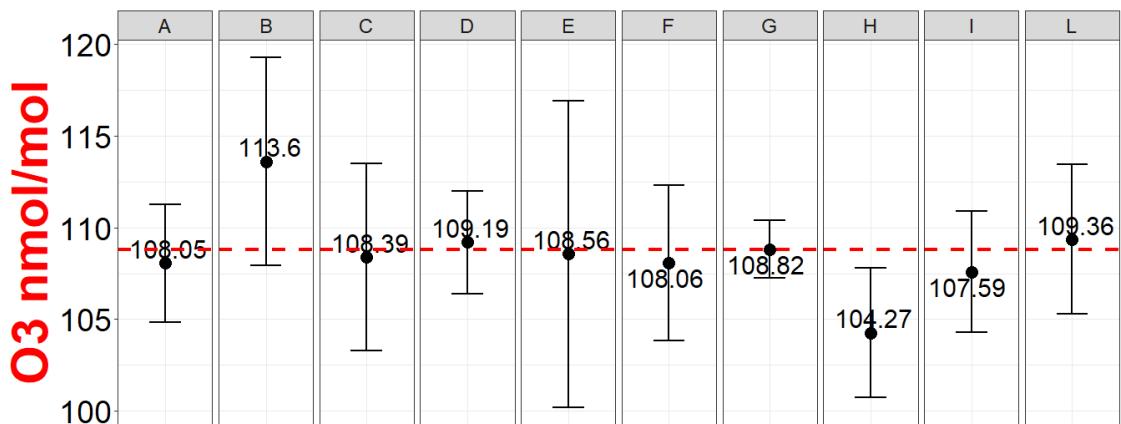
### Parameter O<sub>3</sub> conc level: 3



Source: JRC 2022

**Figure 47:** Reported values of O<sub>3</sub> concentration 4 (nmol/mol)

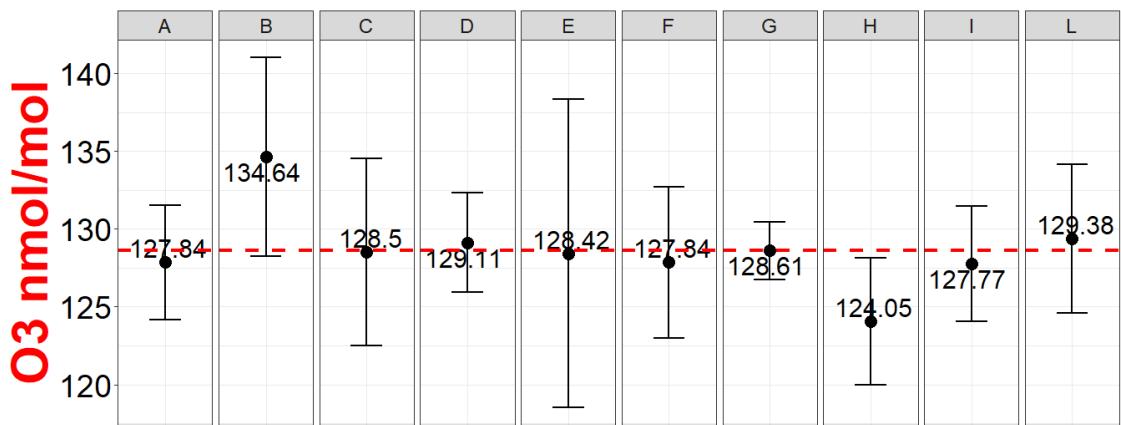
### Parameter O<sub>3</sub> conc level: 4



Source: JRC 2022

**Figure 48:** Reported values of O<sub>3</sub> concentration 5 (nmol/mol)

### Parameter O<sub>3</sub> conc level: 5

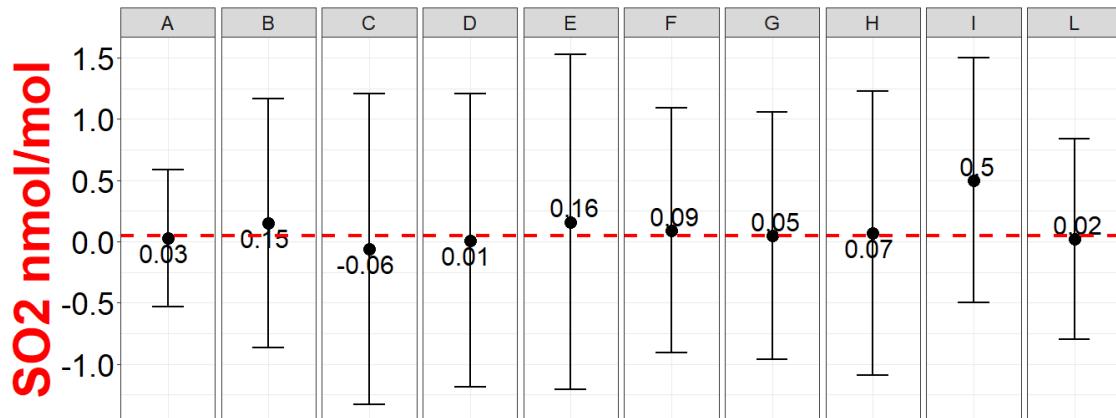


Source: JRC 2022

## Reported values for SO<sub>2</sub>

**Figure 49:** Reported values of SO<sub>2</sub> concentration 0 (nmol/mol)

**Parameter SO<sub>2</sub> conc level: 0**

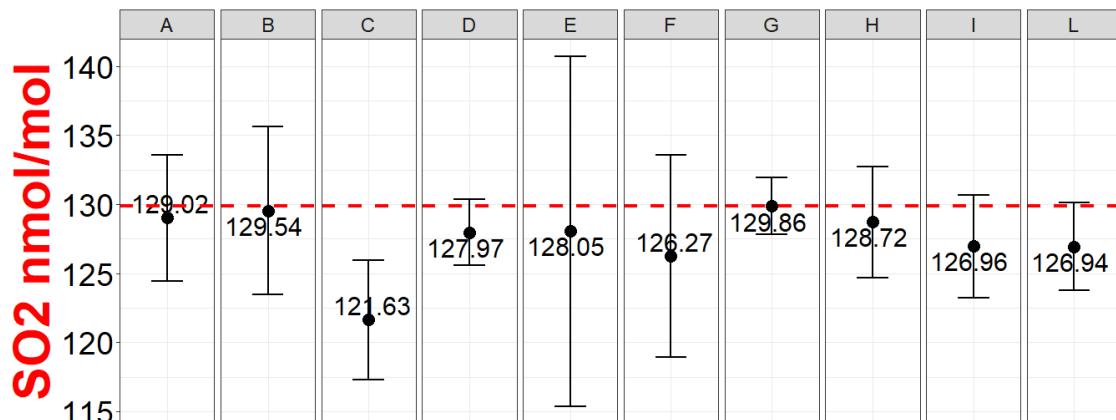


values	A	B	C	D	E	F	G	H	I	L
xi, 1	0.03	0.15	-0.06	0.01	0.16	0.09	0.05	0.07	0.5	0.02
u(xi)	0.28	0.51	0.64	0.58	0.69	0.50	0.51	0.58	0.50	0.41
U(xi)	0.56	1.02	1.27	1.20	1.37	1.00	1.01	1.16	1.00	0.82

Source: JRC 2022

**Figure 50:** Reported values of SO<sub>2</sub> concentration 1 (nmol/mol)

**Parameter SO<sub>2</sub> conc level: 1**

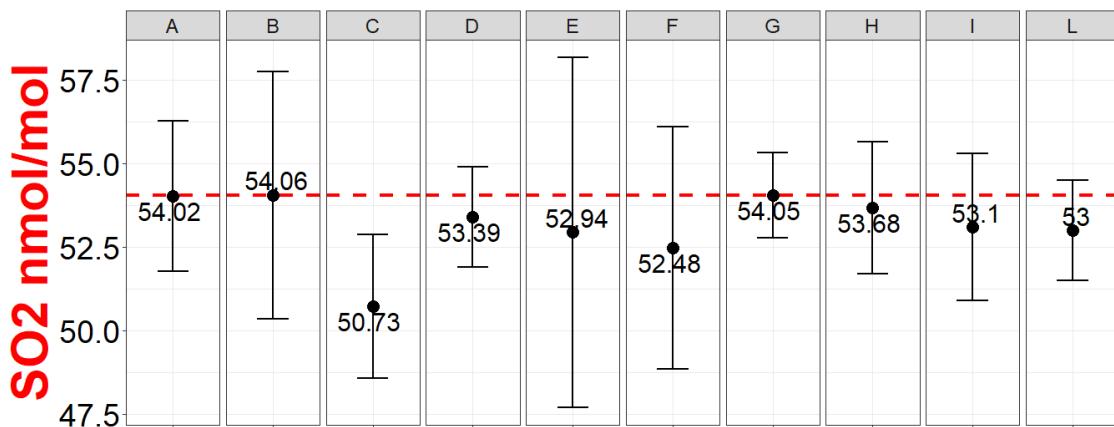


values	A	B	C	D	E	F	G	H	I	L
xi, 1	128.94	129.44	121.58	127.8	128.02	125.97	129.75	128.44	126.85	126.94
xi, 2	128.96	129.52	121.52	128	127.94	126.34	129.81	128.8	126.96	127.05
xi, 3	129.16	129.66	121.79	128.1	128.2	126.49	130.03	128.93	127.07	126.84
x_mean	129.02	129.54	121.63	127.97	128.05	126.27	129.86	128.72	126.96	126.94
sd	0.12	0.11	0.14	0.15	0.13	0.27	0.15	0.25	0.11	0.11
u(xi)	2.27	3.04	2.18	1.21	6.34	3.66	1.03	2.01	1.85	1.58
U(xi)	4.55	6.08	4.35	2.40	12.68	7.31	2.06	4.02	3.70	3.16

Source: JRC 2022

**Figure 51:** Reported values of SO<sub>2</sub> concentration 2 (nmol/mol)

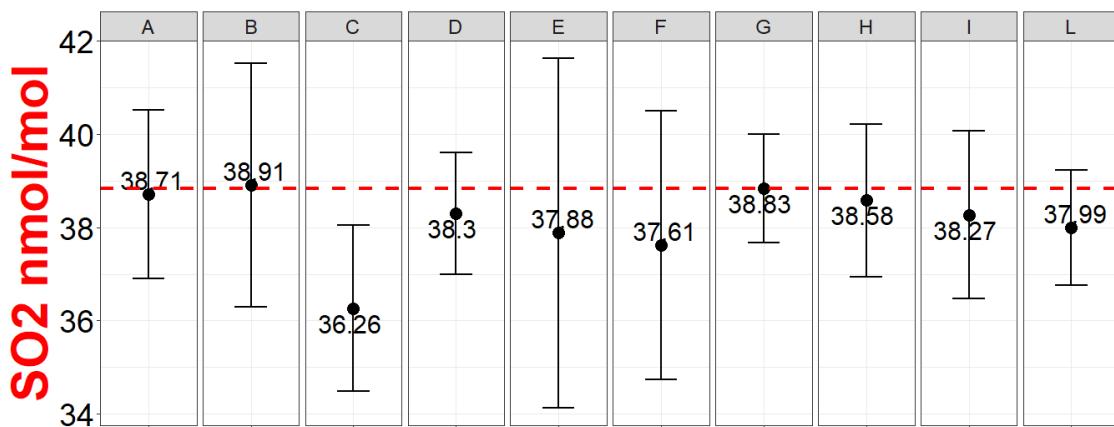
## Parameter SO<sub>2</sub> conc level: 2



Source: JRC 2022

**Figure 52:** Reported values of SO<sub>2</sub> concentration 3 (nmol/mol)

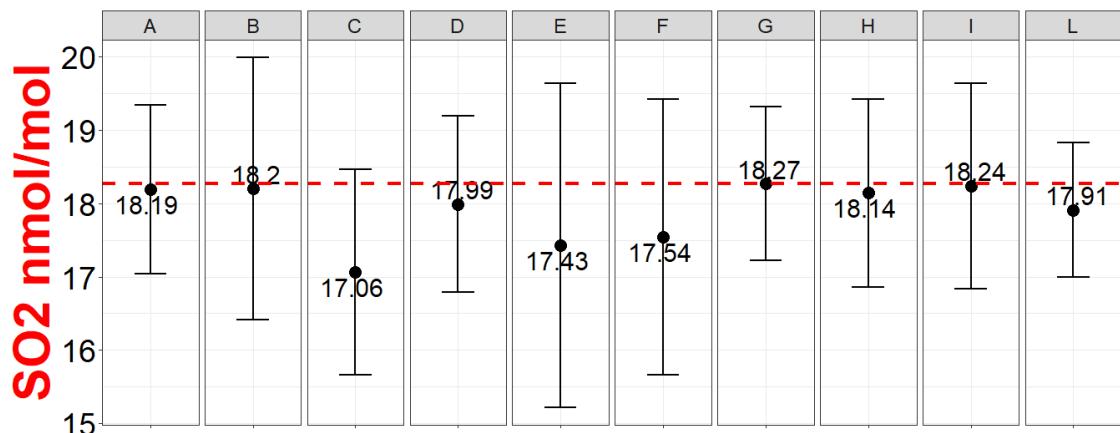
## Parameter SO<sub>2</sub> conc level: 3



Source: JRC 2022

**Figure 53:** Reported values of SO<sub>2</sub> concentration 4 (nmol/mol)

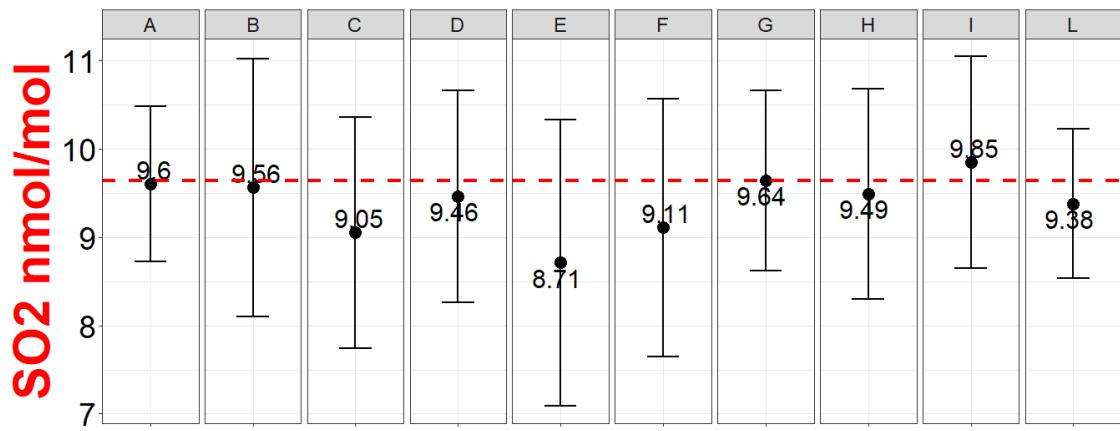
### Parameter SO<sub>2</sub> conc level: 4



Source: JRC 2022

**Figure 54:** Reported values of SO<sub>2</sub> concentration 5 (nmol/mol)

### Parameter SO<sub>2</sub> conc level: 5



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 SO<sub>2</sub>, CO, O<sub>3</sub> and NO<sub>x</sub> 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 ( $p_j$ ) 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 O<sub>3</sub>, CO, SO<sub>2</sub> and NO<sub>2</sub>, 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 -  $\alpha$ ) probability level.

The repeatability standard deviation ( $s_r$ ) 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].

$$r = t_{v/\alpha} \cdot \sqrt{2} \cdot s_r \quad \text{Equation 7}$$

r = repeatability limit

$t_{v/\alpha}$  = 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 ( $\alpha$ ). The reproducibility limit (R) is calculated using Equation 8 [16].

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

R = reproducibility limit

$t_{v/\alpha}$  = t Student distribution value

SR = estimate of reproducibility variance

The repeatability standard deviation was evaluated with ( $p_j * (3-1)$ ) degrees of freedom (v) and reproducibility standard deviation with ( $p_j-1$ ) degrees of freedom (v).

The critical range Student factors, for r and R, corresponding to defined confidence level ( $\alpha$ ) and degree of freedom (v) are reported in Table 11.

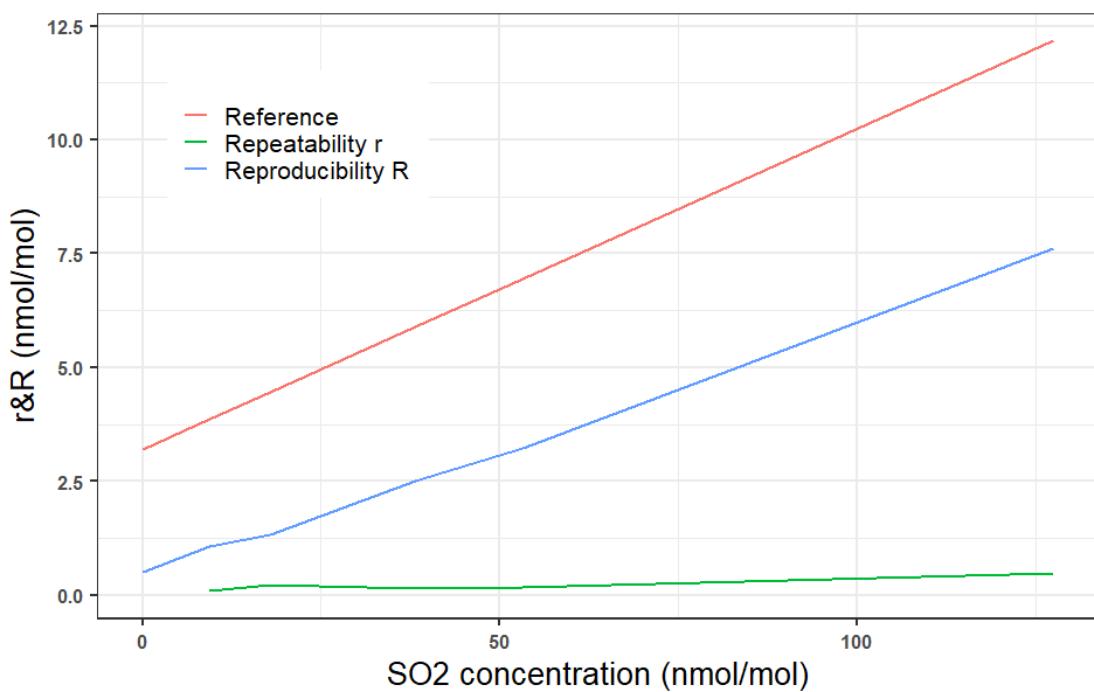
**Table 11:** Critical values of t used in the repeatability (r) and reproducibility (R) evaluation.

parameter	run	$p_j$	t critical value 95% for r	t critical value 95% for R
CO	1,2,3,4,5	10	2,086	2,262
NO	1,3,5,9	10	2,086	2,262
NO	2,4,6,7,8,10	9	2.101	2.306
NO <sub>2</sub>	2,4,6,8,10	9	2.101	2.306
O <sub>3</sub>	1,2,3,4,5	10	2,086	2,262
SO <sub>2</sub>	1,2,3,4,5	10	2,086	2,262

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  $\sigma_{pt}$  is realistic [13] or from the other point of view, that the general methodology implemented by NRLs is appropriate for  $\sigma_{pt}$ .

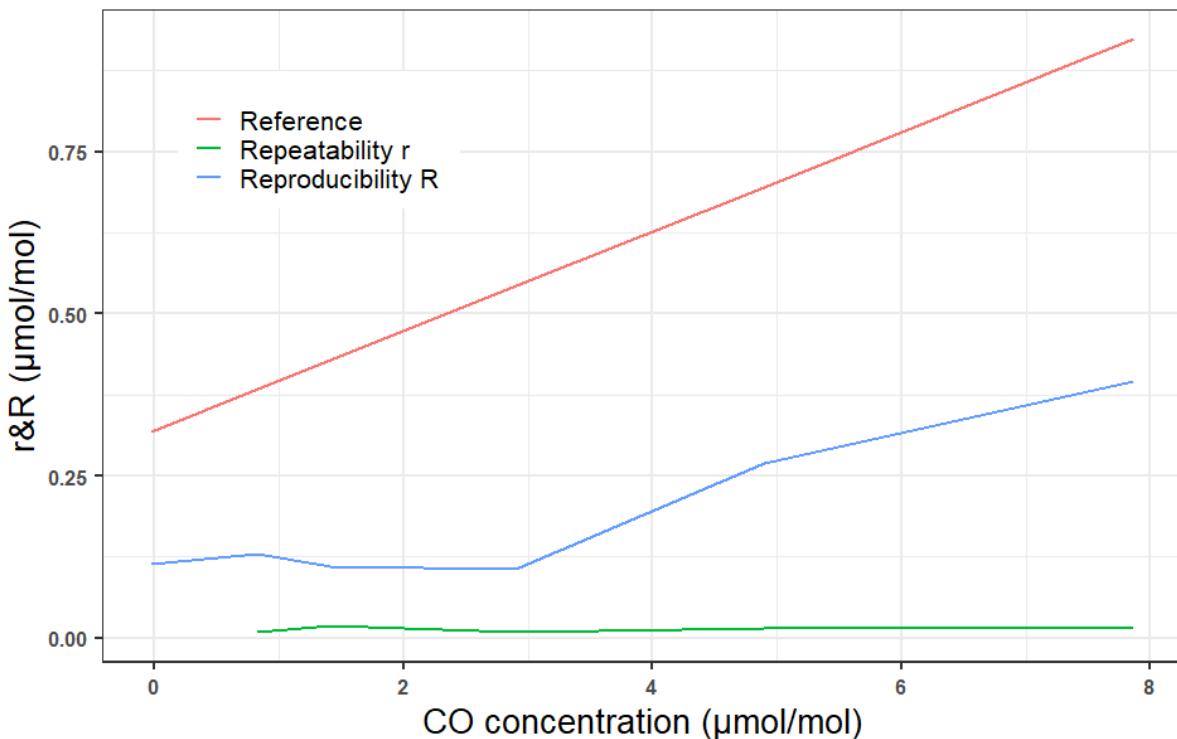
**Figure 55:** The R and r of SO<sub>2</sub> standard measurement method as a function of concentration.



Parameter	Conc.(nmol/mol)	r(nmol/mol)	R(nmol/mol)	R (%)	Reference
SO <sub>2</sub>	0.102		0.493		3.206
SO <sub>2</sub>	9.385	0.094	1.081		3.859
SO <sub>2</sub>	17.897	0.212	1.337		4.458
SO <sub>2</sub>	38.135	0.156	2.514		5.883
SO <sub>2</sub>	53.144	0.162	3.221		6.939
SO <sub>2</sub>	127.497	0.484	7.601	6	12.172

Source: JRC 2022

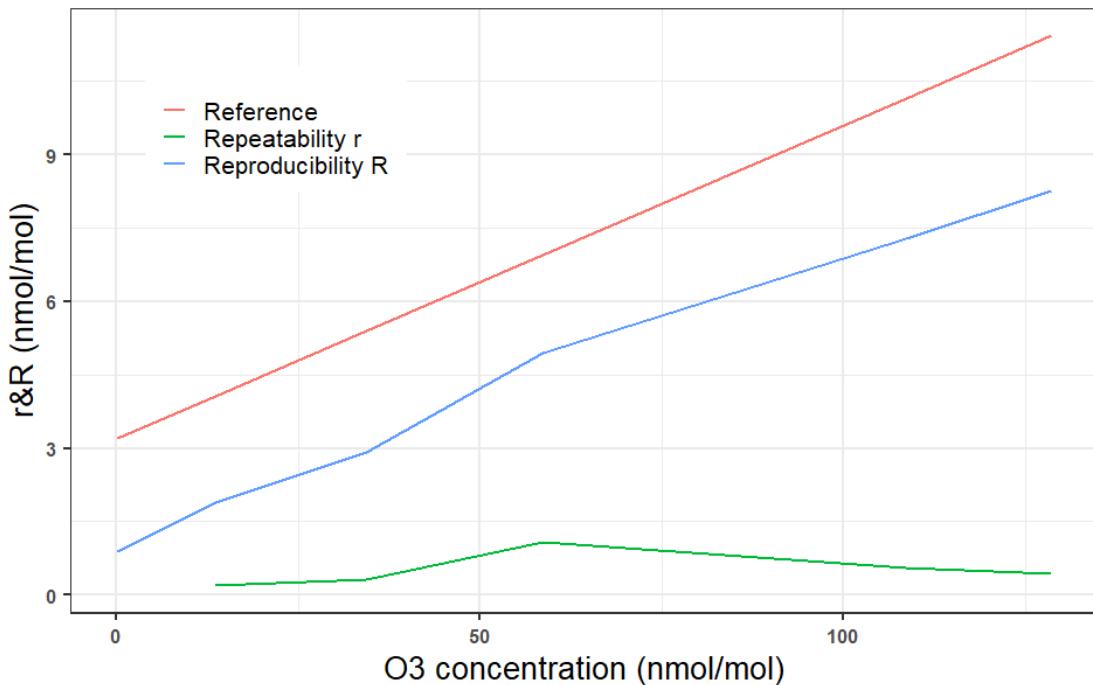
**Figure 56:** The R and r of CO standard measurement method as a function of concentration.



Parameter	Conc. ( $\mu\text{mol/mol}$ )	$r$ ( $\mu\text{mol/mol}$ )	$R$ ( $\mu\text{mol/mol}$ )	R (%)	Reference
CO	-0.0205		0.1139		0.3183
CO	0.8272	0.0091	0.1296		0.3834
CO	1.4160	0.0195	0.1094		0.4286
CO	2.9043	0.01	0.1068		0.5429
CO	4.8934	0.0148	0.2687		0.6956
CO	7.8665	0.0174	0.3957	5	0.9238

Source: JRC 2022

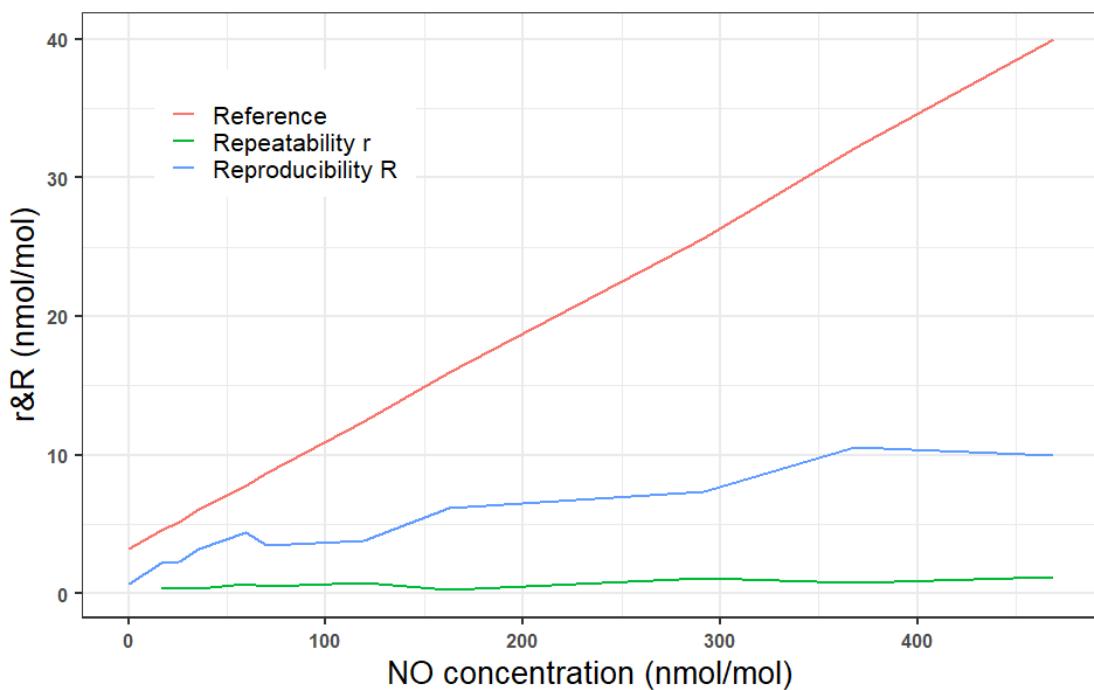
**Figure 57:** The R and r of O<sub>3</sub> standard measurement method as a function of concentration.



Parameter	Conc.(nmol/mol)	r(nmol/mol)	R(nmol/mol)	R (%)	Reference
O3	0.124		0.883		3.207
O3	13.554	0.198	1.881		4.066
O3	34.352	0.307	2.924		5.397
O3	58.622	1.074	4.936		6.950
O3	108.589	0.561	7.274		10.146
O3	128.618	0.428	8.263	6.4	11.428

Source: JRC 2022

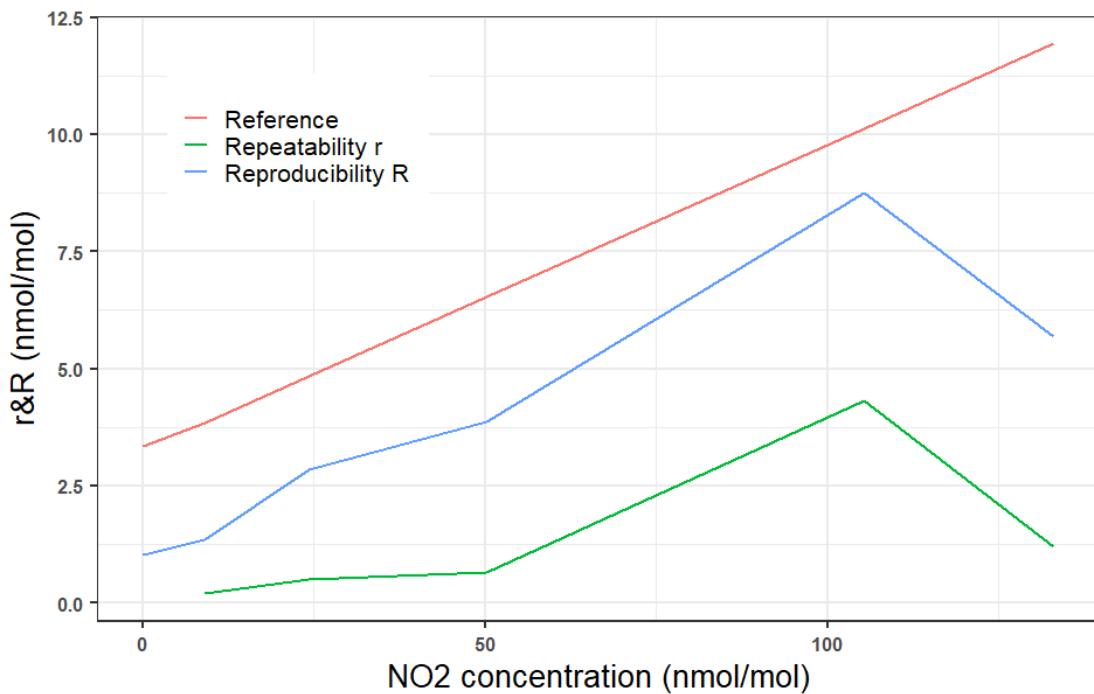
**Figure 58:** The R and r of NO standard measurement method as a function of concentration.



Parameter	Conc.(nmol/mol)	r(nmol/mol)	R(nmol/mol)	R (%)	Reference
NO	0.108		0.742		3.207
NO	16.616	0.336	2.231		4.562
NO	25.508	0.36	2.319		5.157
NO	35.780	0.362	3.212		6.062
NO	59.696	0.708	4.399		7.782
NO	69.927	0.547	3.519		8.734
NO	119.587	0.77	3.813		12.380
NO	162.450	0.279	6.157		15.976
NO	291.840	1.112	7.351		25.605
NO	368.353	0.778	10.537		32.092
NO	468.632	1.239	9.986	2.1	39.940

Source: JRC 2022

**Figure 59:** The R and r of NO<sub>2</sub> standard measurement method as a function of concentration.



Parameter	Conc.(nmol/mol)	r(nmol/mol)	R(nmol/mol)	R (%)	Reference
NO <sub>2</sub>	0.081		1.037		3.350
NO <sub>2</sub>	9.063	0.202	1.350		3.852
NO <sub>2</sub>	24.284	0.511	2.850		4.845
NO <sub>2</sub>	50.171	0.645	3.874		6.534
NO <sub>2</sub>	105.228	4.305	8.763		10.125
NO <sub>2</sub>	132.982	1.189	5.691	4.3	11.935

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.

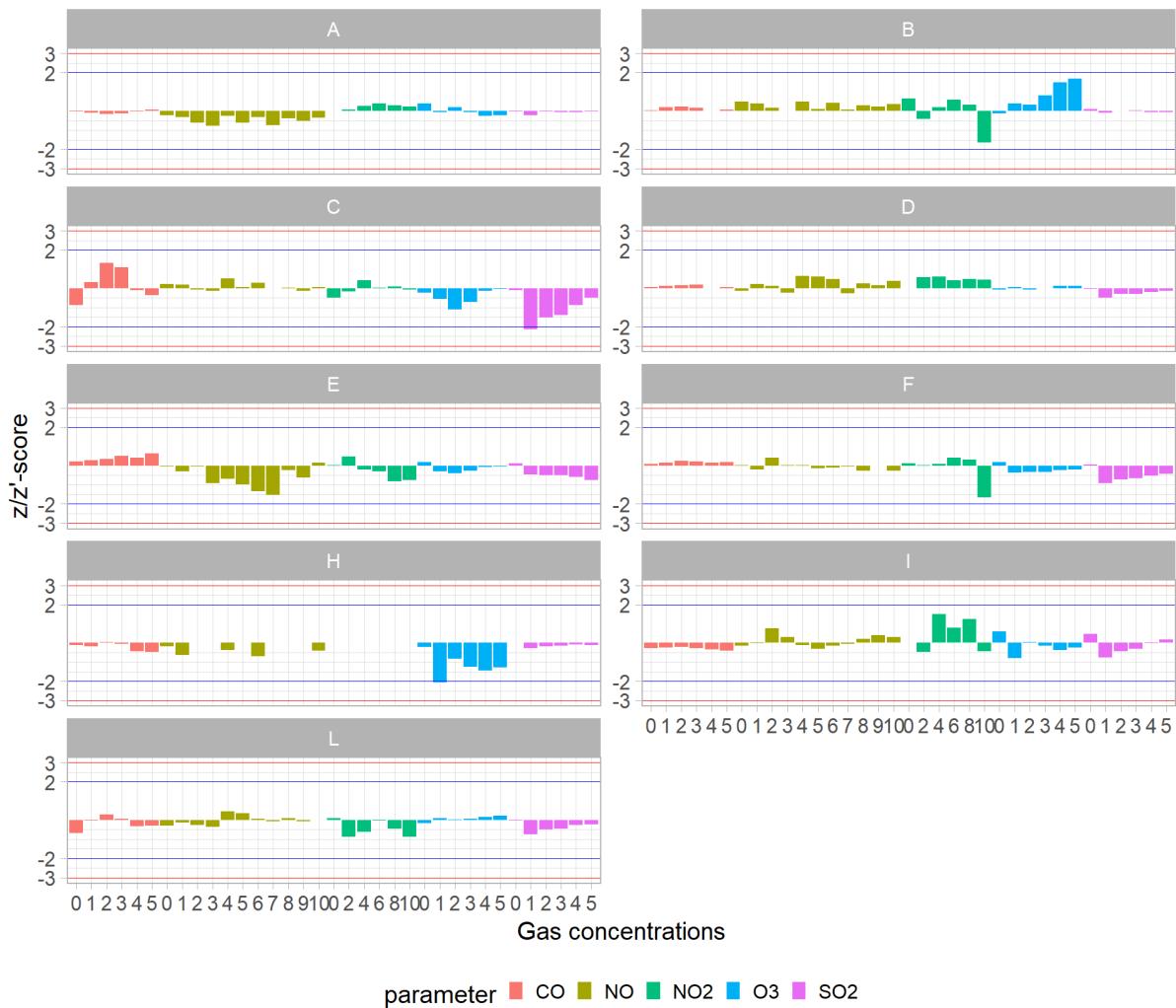
For that reason, a procedure for the detection of exceptional errors (error during typing, slip in performing the measurement or the calculation, wrong averaging interval, malfunction of instrumentation, etc.) was applied. In this procedure were carried out tests for data consistency and statistical 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, but 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 without outliers. Figure 60 is summarizing the  $z$ -score evaluation of each participant for all parameters.

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

**$z/z'$ -score overview**



Source: JRC 2022

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

<b>Gas</b>	<b>Unit</b>	<b>Ref</b>	<b>u_ref</b>	<b>p</b>	<b>0.3*opt</b>	<b>z/z'</b>
CO_0	µmol/mol	-0.005	0.008	9	0.030	z
CO_1	µmol/mol	2.895	0.024	9	0.051	z
CO_2	µmol/mol	7.802	0.062	9	0.086	z
CO_3	µmol/mol	4.854	0.039	9	0.065	z
CO_4	µmol/mol	1.425	0.014	9	0.040	z
CO_5	µmol/mol	0.834	0.012	9	0.036	z
NO_0	nmol/mol	0.140	0.710	9	0.301	z'
NO_1	nmol/mol	119.893	0.920	9	1.163	z
NO_2	nmol/mol	70.560	0.800	8	0.808	z
NO_3	nmol/mol	25.400	0.720	9	0.483	z'
NO_4	nmol/mol	16.760	0.720	8	0.421	z'
NO_5	nmol/mol	60.023	0.780	9	0.732	z'
NO_6	nmol/mol	36.320	0.740	8	0.562	z'
NO_7	nmol/mol	468.647	2.330	8	3.674	z
NO_8	nmol/mol	368.947	1.890	8	2.956	z
NO_9	nmol/mol	291.673	1.560	9	2.400	z
NO_10	nmol/mol	162.197	1.050	8	1.468	z
NO2_0	nmol/mol	0.030	0.720	7	0.300	z'
NO2_1	nmol/mol	0.330	0.840	7	0.302	z'
NO2_2	nmol/mol	49.670	0.850	8	0.598	z'
NO2_3	nmol/mol	0.137	0.720	7	0.301	z'
NO2_4	nmol/mol	8.770	0.720	8	0.353	z'
NO2_5	nmol/mol	0.190	0.760	7	0.301	z'
NO2_6	nmol/mol	24.043	0.760	8	0.444	z'
NO2_7	nmol/mol	7.113	1.820	7	0.343	z'
NO2_8	nmol/mol	106.883	1.840	8	0.941	z'
NO2_9	nmol/mol	3.890	1.260	7	0.323	z'
NO2_10	nmol/mol	133.290	1.330	8	1.100	z'
O3_0	nmol/mol	0.070	0.180	9	0.300	z
O3_1	nmol/mol	59.420	0.440	9	0.657	z
O3_2	nmol/mol	13.823	0.180	9	0.383	z
O3_3	nmol/mol	34.663	0.290	9	0.508	z
O3_4	nmol/mol	108.820	0.780	9	0.953	z
O3_5	nmol/mol	128.613	0.920	9	1.072	z
SO2_0	nmol/mol	0.050	0.500	9	0.300	z'
SO2_1	nmol/mol	129.863	1.030	9	1.157	z
SO2_2	nmol/mol	54.050	0.640	9	0.657	z
SO2_3	nmol/mol	38.833	0.580	9	0.556	z'
SO2_4	nmol/mol	18.270	0.520	9	0.421	z'
SO2_5	nmol/mol	9.640	0.510	9	0.364	z'

Source: JRC 2022

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

<b>Gas</b>	<b>Code</b>	<b>Unit</b>	<b>Ref</b>	<b>u_ref</b>	<b>uref&lt;0.3*opt</b>	<b>z_value</b>
CO _0	A	µmol/mol	-5.00	0.01	z	-0.030
CO _1	A	µmol/mol	2,895.30	0.02	z	-0.078
CO _2	A	µmol/mol	7,802.00	0.06	z	-0.146
CO _3	A	µmol/mol	4,854.00	0.04	z	-0.111
CO _4	A	µmol/mol	1,425.30	0.01	z	-0.017
CO _5	A	µmol/mol	833.70	0.01	z	0.069
NO _0	A	nmol/mol	0.14	0.71	z'	-0.171
NO _1	A	nmol/mol	119.89	0.92	z	-0.326
NO _2	A	nmol/mol	70.56	0.80	z	-0.776
NO _3	A	nmol/mol	25.40	0.72	z'	-0.227
NO _4	A	nmol/mol	16.76	0.72	z'	-0.552
NO _5	A	nmol/mol	60.02	0.78	z'	-0.290
NO _6	A	nmol/mol	36.32	0.74	z'	-0.676
NO _7	A	nmol/mol	468.65	2.33	z	-0.382
NO _8	A	nmol/mol	368.95	1.89	z	-0.496
NO _9	A	nmol/mol	291.67	1.56	z	-0.334
NO _10	A	nmol/mol	162.20	1.05	z	-0.619
NO2 _0	A	nmol/mol	0.03	0.72	z'	0.000
NO2 _2	A	nmol/mol	49.67	0.85	z'	0.240
NO2 _4	A	nmol/mol	8.77	0.72	z'	0.326
NO2 _6	A	nmol/mol	24.04	0.76	z'	0.251
NO2 _8	A	nmol/mol	106.88	1.84	z'	0.208
NO2 _10	A	nmol/mol	133.29	1.33	z'	0.077
O3 _0	A	nmol/mol	0.07	0.18	z	0.389
O3 _1	A	nmol/mol	59.42	0.44	z	-0.073
O3 _2	A	nmol/mol	13.82	0.18	z	0.209
O3 _3	A	nmol/mol	34.66	0.29	z	-0.049
O3 _4	A	nmol/mol	108.82	0.78	z	-0.242
O3 _5	A	nmol/mol	128.61	0.92	z	-0.216
SO2 _0	A	nmol/mol	0.05	0.50	z'	-0.018
SO2 _1	A	nmol/mol	129.86	1.03	z	-0.219
SO2 _2	A	nmol/mol	54.05	0.64	z	-0.014
SO2 _3	A	nmol/mol	38.83	0.58	z'	-0.063
SO2 _4	A	nmol/mol	18.27	0.52	z'	-0.053
SO2 _5	A	nmol/mol	9.64	0.51	z'	-0.030
CO _0	B	µmol/mol	-5.00	0.01	z	0.050
CO _1	B	µmol/mol	2,895.30	0.02	z	0.193
CO _2	B	µmol/mol	7,802.00	0.06	z	0.226
CO _3	B	µmol/mol	4,854.00	0.04	z	0.166
CO _4	B	µmol/mol	1,425.30	0.01	z	0.020
CO _5	B	µmol/mol	833.70	0.01	z	0.077
NO _0	B	nmol/mol	0.14	0.71	z'	0.399
NO _1	B	nmol/mol	119.89	0.92	z	0.389
NO _2	B	nmol/mol	70.56	0.80	z	0.000
NO _3	B	nmol/mol	25.40	0.72	z'	0.448
NO _4	B	nmol/mol	16.76	0.72	z'	0.102
NO _5	B	nmol/mol	60.02	0.78	z'	0.401

<b>Gas</b>	<b>Code</b>	<b>Unit</b>	<b>Ref</b>	<b>u_ref</b>	<b>uref&lt;0.3*opt</b>	<b>z_value</b>
NO_6	B	nmol/mol	36.32	0.74	z'	0.060
NO_7	B	nmol/mol	468.65	2.33	z	0.309
NO_8	B	nmol/mol	368.95	1.89	z	0.233
NO_9	B	nmol/mol	291.67	1.56	z	0.348
NO_10	B	nmol/mol	162.20	1.05	z	0.174
NO2_0	B	nmol/mol	0.03	0.72	z'	0.529
NO2_2	B	nmol/mol	49.67	0.85	z'	0.194
NO2_4	B	nmol/mol	8.77	0.72	z'	0.492
NO2_6	B	nmol/mol	24.04	0.76	z'	0.287
NO2_8	B	nmol/mol	106.88	1.84	z'	-1.417
NO2_10	B	nmol/mol	133.29	1.33	z'	-0.390
O3_0	B	nmol/mol	0.07	0.18	z	-0.130
O3_1	B	nmol/mol	59.42	0.44	z	0.393
O3_2	B	nmol/mol	13.82	0.18	z	0.335
O3_3	B	nmol/mol	34.66	0.29	z	0.819
O3_4	B	nmol/mol	108.82	0.78	z	1.505
O3_5	B	nmol/mol	128.61	0.92	z	1.687
SO2_0	B	nmol/mol	0.05	0.50	z'	0.089
SO2_1	B	nmol/mol	129.86	1.03	z	-0.084
SO2_2	B	nmol/mol	54.05	0.64	z	0.005
SO2_3	B	nmol/mol	38.83	0.58	z'	0.040
SO2_4	B	nmol/mol	18.27	0.52	z'	-0.047
SO2_5	B	nmol/mol	9.64	0.51	z'	-0.061
CO_0	C	µmol/mol	-5.00	0.01	z	-0.871
CO_1	C	µmol/mol	2,895.30	0.02	z	0.305
CO_2	C	µmol/mol	7,802.00	0.06	z	1.330
CO_3	C	µmol/mol	4,854.00	0.04	z	1.109
CO_4	C	µmol/mol	1,425.30	0.01	z	-0.107
CO_5	C	µmol/mol	833.70	0.01	z	-0.347
NO_0	C	nmol/mol	0.14	0.71	z'	0.171
NO_1	C	nmol/mol	119.89	0.92	z	0.187
NO_2	C	nmol/mol	70.56	0.80	z	-0.141
NO_3	C	nmol/mol	25.40	0.72	z'	0.476
NO_4	C	nmol/mol	16.76	0.72	z'	0.057
NO_5	C	nmol/mol	60.02	0.78	z'	0.288
NO_6	C	nmol/mol	36.32	0.74	z'	-0.010
NO_7	C	nmol/mol	468.65	2.33	z	0.017
NO_8	C	nmol/mol	368.95	1.89	z	-0.147
NO_9	C	nmol/mol	291.67	1.56	z	0.051
NO_10	C	nmol/mol	162.20	1.05	z	-0.053
NO2_0	C	nmol/mol	0.03	0.72	z'	-0.398
NO2_2	C	nmol/mol	49.67	0.85	z'	0.388
NO2_4	C	nmol/mol	8.77	0.72	z'	0.014
NO2_6	C	nmol/mol	24.04	0.76	z'	0.094
NO2_8	C	nmol/mol	106.88	1.84	z'	-0.050
NO2_10	C	nmol/mol	133.29	1.33	z'	-0.151
O3_0	C	nmol/mol	0.07	0.18	z	-0.220
O3_1	C	nmol/mol	59.42	0.44	z	-0.562

<b>Gas</b>	<b>Code</b>	<b>Unit</b>	<b>Ref</b>	<b>u_ref</b>	<b>uref&lt;0.3*opt</b>	<b>z_value</b>
O3 _2	C	nmol/mol	13.82	0.18	z	-1.091
O3 _3	C	nmol/mol	34.66	0.29	z	-0.705
O3 _4	C	nmol/mol	108.82	0.78	z	-0.135
O3 _5	C	nmol/mol	128.61	0.92	z	-0.032
SO2 _0	C	nmol/mol	0.05	0.50	z'	-0.098
SO2 _1	C	nmol/mol	129.86	1.03	z	-2.135
SO2 _2	C	nmol/mol	54.05	0.64	z	-1.517
SO2 _3	C	nmol/mol	38.83	0.58	z'	-1.324
SO2 _4	C	nmol/mol	18.27	0.52	z'	-0.808
SO2 _5	C	nmol/mol	9.64	0.51	z'	-0.449
CO _0	D	µmol/mol	-5.00	0.01	z	0.070
CO _1	D	µmol/mol	2,895.30	0.02	z	0.134
CO _2	D	µmol/mol	7,802.00	0.06	z	0.153
CO _3	D	µmol/mol	4,854.00	0.04	z	0.180
CO _4	D	µmol/mol	1,425.30	0.01	z	-0.017
CO _5	D	µmol/mol	833.70	0.01	z	0.069
NO _0	D	nmol/mol	0.14	0.71	z'	-0.106
NO _1	D	nmol/mol	119.89	0.92	z	0.221
NO _2	D	nmol/mol	70.56	0.80	z	-0.238
NO _3	D	nmol/mol	25.40	0.72	z'	0.583
NO _4	D	nmol/mol	16.76	0.72	z'	0.539
NO _5	D	nmol/mol	60.02	0.78	z'	0.467
NO _6	D	nmol/mol	36.32	0.74	z'	-0.248
NO _7	D	nmol/mol	468.65	2.33	z	0.271
NO _8	D	nmol/mol	368.95	1.89	z	0.149
NO _9	D	nmol/mol	291.67	1.56	z	0.376
NO _10	D	nmol/mol	162.20	1.05	z	0.125
NO2 _0	D	nmol/mol	0.03	0.72	z'	-0.008
NO2 _2	D	nmol/mol	49.67	0.85	z'	0.568
NO2 _4	D	nmol/mol	8.77	0.72	z'	0.355
NO2 _6	D	nmol/mol	24.04	0.76	z'	0.431
NO2 _8	D	nmol/mol	106.88	1.84	z'	0.381
NO2 _10	D	nmol/mol	133.29	1.33	z'	0.554
O3 _0	D	nmol/mol	0.07	0.18	z	-0.060
O3 _1	D	nmol/mol	59.42	0.44	z	0.046
O3 _2	D	nmol/mol	13.82	0.18	z	-0.065
O3 _3	D	nmol/mol	34.66	0.29	z	0.004
O3 _4	D	nmol/mol	108.82	0.78	z	0.116
O3 _5	D	nmol/mol	128.61	0.92	z	0.139
SO2 _0	D	nmol/mol	0.05	0.50	z'	-0.036
SO2 _1	D	nmol/mol	129.86	1.03	z	-0.491
SO2 _2	D	nmol/mol	54.05	0.64	z	-0.301
SO2 _3	D	nmol/mol	38.83	0.58	z'	-0.274
SO2 _4	D	nmol/mol	18.27	0.52	z'	-0.187
SO2 _5	D	nmol/mol	9.64	0.51	z'	-0.137
CO _0	E	µmol/mol	-5.00	0.01	z	0.210
CO _1	E	µmol/mol	2,895.30	0.02	z	0.293
CO _2	E	µmol/mol	7,802.00	0.06	z	0.341

<b>Gas</b>	<b>Code</b>	<b>Unit</b>	<b>Ref</b>	<b>u_ref</b>	<b>uref&lt;0.3*opt</b>	<b>z_value</b>
CO_3	E	µmol/mol	4,854.00	0.04	z	0.494
CO_4	E	µmol/mol	1,425.30	0.01	z	0.400
CO_5	E	µmol/mol	833.70	0.01	z	0.619
NO_0	E	nmol/mol	0.14	0.71	z'	-0.049
NO_1	E	nmol/mol	119.89	0.92	z	-0.303
NO_2	E	nmol/mol	70.56	0.80	z	-0.924
NO_3	E	nmol/mol	25.40	0.72	z'	-0.629
NO_4	E	nmol/mol	16.76	0.72	z'	-0.869
NO_5	E	nmol/mol	60.02	0.78	z'	-1.290
NO_6	E	nmol/mol	36.32	0.74	z'	-1.421
NO_7	E	nmol/mol	468.65	2.33	z	-0.255
NO_8	E	nmol/mol	368.95	1.89	z	-0.620
NO_9	E	nmol/mol	291.67	1.56	z	0.160
NO_10	E	nmol/mol	162.20	1.05	z	-0.042
NO2_0	E	nmol/mol	0.03	0.72	z'	0.016
NO2_2	E	nmol/mol	49.67	0.85	z'	-0.198
NO2_4	E	nmol/mol	8.77	0.72	z'	-0.268
NO2_6	E	nmol/mol	24.04	0.76	z'	-0.718
NO2_8	E	nmol/mol	106.88	1.84	z'	-0.647
NO2_10	E	nmol/mol	133.29	1.33	z'	0.459
O3_0	E	nmol/mol	0.07	0.18	z	0.170
O3_1	E	nmol/mol	59.42	0.44	z	-0.302
O3_2	E	nmol/mol	13.82	0.18	z	-0.410
O3_3	E	nmol/mol	34.66	0.29	z	-0.268
O3_4	E	nmol/mol	108.82	0.78	z	-0.082
O3_5	E	nmol/mol	128.61	0.92	z	-0.054
SO2_0	E	nmol/mol	0.05	0.50	z'	0.098
SO2_1	E	nmol/mol	129.86	1.03	z	-0.470
SO2_2	E	nmol/mol	54.05	0.64	z	-0.507
SO2_3	E	nmol/mol	38.83	0.58	z'	-0.490
SO2_4	E	nmol/mol	18.27	0.52	z'	-0.561
SO2_5	E	nmol/mol	9.64	0.51	z'	-0.707
CO_0	F	µmol/mol	-5.00	0.01	z	0.090
CO_1	F	µmol/mol	2,895.30	0.02	z	0.163
CO_2	F	µmol/mol	7,802.00	0.06	z	0.237
CO_3	F	µmol/mol	4,854.00	0.04	z	0.226
CO_4	F	µmol/mol	1,425.30	0.01	z	0.147
CO_5	F	µmol/mol	833.70	0.01	z	0.169
NO_0	F	nmol/mol	0.14	0.71	z'	0.008
NO_1	F	nmol/mol	119.89	0.92	z	-0.194
NO_2	F	nmol/mol	70.56	0.80	z	0.019
NO_3	F	nmol/mol	25.40	0.72	z'	0.006
NO_4	F	nmol/mol	16.76	0.72	z'	-0.127
NO_5	F	nmol/mol	60.02	0.78	z'	-0.118
NO_6	F	nmol/mol	36.32	0.74	z'	-0.030
NO_7	F	nmol/mol	468.65	2.33	z	-0.258
NO_8	F	nmol/mol	368.95	1.89	z	0.001
NO_9	F	nmol/mol	291.67	1.56	z	-0.259

<b>Gas</b>	<b>Code</b>	<b>Unit</b>	<b>Ref</b>	<b>u_ref</b>	<b>uref&lt;0.3*opt</b>	<b>z_value</b>
NO_10	F	nmol/mol	162.20	1.05	z	0.393
NO2_0	F	nmol/mol	0.03	0.72	z'	0.106
NO2_2	F	nmol/mol	49.67	0.85	z'	0.092
NO2_4	F	nmol/mol	8.77	0.72	z'	0.340
NO2_6	F	nmol/mol	24.04	0.76	z'	0.263
NO2_8	F	nmol/mol	106.88	1.84	z'	-1.428
NO2_10	F	nmol/mol	133.29	1.33	z'	0.031
O3_0	F	nmol/mol	0.07	0.18	z	0.190
O3_1	F	nmol/mol	59.42	0.44	z	-0.361
O3_2	F	nmol/mol	13.82	0.18	z	-0.324
O3_3	F	nmol/mol	34.66	0.29	z	-0.332
O3_4	F	nmol/mol	108.82	0.78	z	-0.239
O3_5	F	nmol/mol	128.61	0.92	z	-0.216
SO2_0	F	nmol/mol	0.05	0.50	z'	0.036
SO2_1	F	nmol/mol	129.86	1.03	z	-0.932
SO2_2	F	nmol/mol	54.05	0.64	z	-0.717
SO2_3	F	nmol/mol	38.83	0.58	z'	-0.629
SO2_4	F	nmol/mol	18.27	0.52	z'	-0.488
SO2_5	F	nmol/mol	9.64	0.51	z'	-0.403
CO_0	H	µmol/mol	-5.00	0.01	z	-0.110
CO_1	H	µmol/mol	2,895.30	0.02	z	-0.191
CO_2	H	µmol/mol	7,802.00	0.06	z	0.045
CO_3	H	µmol/mol	4,854.00	0.04	z	-0.046
CO_4	H	µmol/mol	1,425.30	0.01	z	-0.442
CO_5	H	µmol/mol	833.70	0.01	z	-0.489
NO_0	H	nmol/mol	0.14	0.71	z'	-0.163
NO_1	H	nmol/mol	119.89	0.92	z	-0.633
NO_3	H	nmol/mol	25.40	0.72	z'	-0.351
NO_5	H	nmol/mol	60.02	0.78	z'	-0.681
NO_9	H	nmol/mol	291.67	1.56	z	-0.422
O3_0	H	nmol/mol	0.07	0.18	z	-0.230
O3_1	H	nmol/mol	59.42	0.44	z	-2.075
O3_2	H	nmol/mol	13.82	0.18	z	-0.841
O3_3	H	nmol/mol	34.66	0.29	z	-1.248
O3_4	H	nmol/mol	108.82	0.78	z	-1.432
O3_5	H	nmol/mol	128.61	0.92	z	-1.277
SO2_0	H	nmol/mol	0.05	0.50	z'	0.018
SO2_1	H	nmol/mol	129.86	1.03	z	-0.296
SO2_2	H	nmol/mol	54.05	0.64	z	-0.169
SO2_3	H	nmol/mol	38.83	0.58	z'	-0.130
SO2_4	H	nmol/mol	18.27	0.52	z'	-0.087
SO2_5	H	nmol/mol	9.64	0.51	z'	-0.114
CO_0	I	µmol/mol	-5.00	0.01	z	-0.270
CO_1	I	µmol/mol	2,895.30	0.02	z	-0.261
CO_2	I	µmol/mol	7,802.00	0.06	z	-0.226
CO_3	I	µmol/mol	4,854.00	0.04	z	-0.268
CO_4	I	µmol/mol	1,425.30	0.01	z	-0.360
CO_5	I	µmol/mol	833.70	0.01	z	-0.414

<b>Gas</b>	<b>Code</b>	<b>Unit</b>	<b>Ref</b>	<b>u_ref</b>	<b>uref&lt;0.3*opt</b>	<b>z_value</b>
NO _0	I	nmol/mol	0.14	0.71	z'	-0.114
NO _1	I	nmol/mol	119.89	0.92	z	-0.011
NO _2	I	nmol/mol	70.56	0.80	z	0.304
NO _3	I	nmol/mol	25.40	0.72	z'	-0.119
NO _4	I	nmol/mol	16.76	0.72	z'	-0.285
NO _5	I	nmol/mol	60.02	0.78	z'	-0.138
NO _6	I	nmol/mol	36.32	0.74	z'	-0.040
NO _7	I	nmol/mol	468.65	2.33	z	0.200
NO _8	I	nmol/mol	368.95	1.89	z	0.396
NO _9	I	nmol/mol	291.67	1.56	z	0.295
NO _10	I	nmol/mol	162.20	1.05	z	0.747
NO2 _2	I	nmol/mol	49.67	0.85	z'	1.375
NO2 _4	I	nmol/mol	8.77	0.72	z'	0.666
NO2 _6	I	nmol/mol	24.04	0.76	z'	1.117
NO2 _8	I	nmol/mol	106.88	1.84	z'	-0.380
NO2 _10	I	nmol/mol	133.29	1.33	z'	-0.456
O3 _0	I	nmol/mol	0.07	0.18	z	0.589
O3 _1	I	nmol/mol	59.42	0.44	z	-0.791
O3 _2	I	nmol/mol	13.82	0.18	z	0.052
O3 _3	I	nmol/mol	34.66	0.29	z	-0.144
O3 _4	I	nmol/mol	108.82	0.78	z	-0.387
O3 _5	I	nmol/mol	128.61	0.92	z	-0.236
SO2 _0	I	nmol/mol	0.05	0.50	z'	0.401
SO2 _1	I	nmol/mol	129.86	1.03	z	-0.753
SO2 _2	I	nmol/mol	54.05	0.64	z	-0.434
SO2 _3	I	nmol/mol	38.83	0.58	z'	-0.290
SO2 _4	I	nmol/mol	18.27	0.52	z'	-0.020
SO2 _5	I	nmol/mol	9.64	0.51	z'	0.160
CO _0	L	µmol/mol	-5.00	0.01	z	-0.691
CO _1	L	µmol/mol	2,895.30	0.02	z	-0.037
CO _2	L	µmol/mol	7,802.00	0.06	z	0.289
CO _3	L	µmol/mol	4,854.00	0.04	z	0.065
CO _4	L	µmol/mol	1,425.30	0.01	z	-0.315
CO _5	L	µmol/mol	833.70	0.01	z	-0.306
NO _0	L	nmol/mol	0.14	0.71	z'	-0.236
NO _1	L	nmol/mol	119.89	0.92	z	-0.122
NO _2	L	nmol/mol	70.56	0.80	z	-0.360
NO _3	L	nmol/mol	25.40	0.72	z'	0.419
NO _4	L	nmol/mol	16.76	0.72	z'	0.311
NO _5	L	nmol/mol	60.02	0.78	z'	0.077
NO _6	L	nmol/mol	36.32	0.74	z'	-0.050
NO _7	L	nmol/mol	468.65	2.33	z	0.087
NO _8	L	nmol/mol	368.95	1.89	z	-0.061
NO _9	L	nmol/mol	291.67	1.56	z	-0.004
NO _10	L	nmol/mol	162.20	1.05	z	-0.259
NO2 _0	L	nmol/mol	0.03	0.72	z'	0.089
NO2 _2	L	nmol/mol	49.67	0.85	z'	-0.577
NO2 _4	L	nmol/mol	8.77	0.72	z'	-0.022

<b>Gas</b>	<b>Code</b>	<b>Unit</b>	<b>Ref</b>	<b>u_ref</b>	<b>uref&lt;0.3*opt</b>	<b>z_value</b>
NO2_6	L	nmol/mol	24.04	0.76	z'	-0.417
NO2_8	L	nmol/mol	106.88	1.84	z'	-0.762
NO2_10	L	nmol/mol	133.29	1.33	z'	-0.833
O3_0	L	nmol/mol	0.07	0.18	z	-0.160
O3_1	L	nmol/mol	59.42	0.44	z	0.082
O3_2	L	nmol/mol	13.82	0.18	z	0.029
O3_3	L	nmol/mol	34.66	0.29	z	0.081
O3_4	L	nmol/mol	108.82	0.78	z	0.170
O3_5	L	nmol/mol	128.61	0.92	z	0.215
SO2_0	L	nmol/mol	0.05	0.50	z'	-0.027
SO2_1	L	nmol/mol	129.86	1.03	z	-0.758
SO2_2	L	nmol/mol	54.05	0.64	z	-0.480
SO2_3	L	nmol/mol	38.83	0.58	z'	-0.434
SO2_4	L	nmol/mol	18.27	0.52	z'	-0.240
SO2_5	L	nmol/mol	9.64	0.51	z'	-0.198

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	-0.1
A	CO	3	-0.1
A	CO	4	0.0
A	CO	5	0.1
A	NO	0	-0.1
A	NO	1	-0.3
A	NO	2	-0.7
A	NO	3	-0.2
A	NO	4	-0.4
A	NO	5	-0.3
A	NO	6	-0.6
A	NO	7	-0.3
A	NO	8	-0.4
A	NO	9	-0.3
A	NO	10	-0.5
A	NO <sub>2</sub>	0	0.0
A	NO <sub>2</sub>	1	0.1
A	NO <sub>2</sub>	2	0.2
A	NO <sub>2</sub>	3	0.0
A	NO <sub>2</sub>	4	0.2
A	NO <sub>2</sub>	5	0.0
A	NO <sub>2</sub>	6	0.2
A	NO <sub>2</sub>	7	0.3
A	NO <sub>2</sub>	8	0.1
A	NO <sub>2</sub>	9	0.3
A	NO <sub>2</sub>	10	0.0
A	O <sub>3</sub>	0	0.3
A	O <sub>3</sub>	1	-0.1
A	O <sub>3</sub>	2	0.2
A	O <sub>3</sub>	3	0.0
A	O <sub>3</sub>	4	-0.2
A	O <sub>3</sub>	5	-0.2
A	SO <sub>2</sub>	0	0.0
A	SO <sub>2</sub>	1	-0.2
A	SO <sub>2</sub>	2	0.0
A	SO <sub>2</sub>	3	-0.1
A	SO <sub>2</sub>	4	-0.1
A	SO <sub>2</sub>	5	0.0
B	CO	0	0.1
B	CO	1	0.2
B	CO	2	0.2
B	CO	3	0.1
B	CO	4	0.0
B	CO	5	0.1
B	NO	0	0.2

Code	Parameter	Concentrations	En
B	NO	1	0.2
B	NO	2	0.0
B	NO	3	0.3
B	NO	4	0.1
B	NO	5	0.2
B	NO	6	0.0
B	NO	7	0.2
B	NO	8	0.1
B	NO	9	0.2
B	NO	10	0.1
B	NO <sub>2</sub>	0	0.3
B	NO <sub>2</sub>	1	-0.6
B	NO <sub>2</sub>	2	0.1
B	NO <sub>2</sub>	3	0.1
B	NO <sub>2</sub>	4	0.3
B	NO <sub>2</sub>	5	-0.3
B	NO <sub>2</sub>	6	0.2
B	NO <sub>2</sub>	7	-1.9
B	NO <sub>2</sub>	8	-0.7
B	NO <sub>2</sub>	9	-1.5
B	NO <sub>2</sub>	10	-0.2
B	O <sub>3</sub>	0	-0.1
B	O <sub>3</sub>	1	0.2
B	O <sub>3</sub>	2	0.2
B	O <sub>3</sub>	3	0.4
B	O <sub>3</sub>	4	0.8
B	O <sub>3</sub>	5	0.9
B	SO <sub>2</sub>	0	0.1
B	SO <sub>2</sub>	1	-0.1
B	SO <sub>2</sub>	2	0.0
B	SO <sub>2</sub>	3	0.0
B	SO <sub>2</sub>	4	0.0
B	SO <sub>2</sub>	5	0.0
C	CO	0	-0.6
C	CO	1	0.3
C	CO	2	1.1
C	CO	3	1.0
C	CO	4	-0.1
C	CO	5	-0.3
C	NO	0	0.1
C	NO	1	0.2
C	NO	2	-0.1
C	NO	3	0.4
C	NO	4	0.0
C	NO	5	0.3
C	NO	6	0.0
C	NO	7	0.0
C	NO	8	-0.1

Code	Parameter	Concentrations	En
C	NO	9	0.0
C	NO	10	0.0
C	NO2	0	-0.2
C	NO2	1	0.1
C	NO2	2	0.2
C	NO2	3	-0.3
C	NO2	4	0.0
C	NO2	5	-0.3
C	NO2	6	0.1
C	NO2	7	-0.1
C	NO2	8	0.0
C	NO2	9	-0.1
C	NO2	10	-0.1
C	O3	0	-0.2
C	O3	1	-0.4
C	O3	2	-1.0
C	O3	3	-0.6
C	O3	4	-0.1
C	O3	5	0.0
C	SO2	0	-0.1
C	SO2	1	-1.7
C	SO2	2	-1.3
C	SO2	3	-1.2
C	SO2	4	-0.7
C	SO2	5	-0.4
D	CO	0	0.2
D	CO	1	0.3
D	CO	2	0.3
D	CO	3	0.4
D	CO	4	0.0
D	CO	5	0.2
D	NO	0	-0.1
D	NO	1	0.3
D	NO	2	-0.3
D	NO	3	0.5
D	NO	4	0.5
D	NO	5	0.6
D	NO	6	-0.3
D	NO	7	0.4
D	NO	8	0.2
D	NO	9	0.6
D	NO	10	0.2
D	NO2	0	0.0
D	NO2	1	0.0
D	NO2	2	0.5
D	NO2	3	0.0
D	NO2	4	0.3
D	NO2	5	0.0

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

Code	Parameter	Concentrations	En
E	O3	3	-0.2
E	O3	4	0.0
E	O3	5	0.0
E	SO2	0	0.1
E	SO2	1	-0.1
E	SO2	2	-0.2
E	SO2	3	-0.2
E	SO2	4	-0.3
E	SO2	5	-0.5
F	CO	0	0.0
F	CO	1	0.1
F	CO	2	0.2
F	CO	3	0.2
F	CO	4	0.1
F	CO	5	0.1
F	NO	0	0.0
F	NO	1	-0.1
F	NO	2	0.0
F	NO	3	0.0
F	NO	4	-0.1
F	NO	5	-0.1
F	NO	6	0.0
F	NO	7	-0.2
F	NO	8	0.0
F	NO	9	-0.2
F	NO	10	0.2
F	NO2	0	0.1
F	NO2	2	0.1
F	NO2	4	0.2
F	NO2	6	0.2
F	NO2	8	-0.8
F	NO2	10	0.0
F	O3	0	0.2
F	O3	1	-0.3
F	O3	2	-0.3
F	O3	3	-0.3
F	O3	4	-0.2
F	O3	5	-0.1
F	SO2	0	0.0
F	SO2	1	-0.5
F	SO2	2	-0.4
F	SO2	3	-0.4
F	SO2	4	-0.3
F	SO2	5	-0.3
H	CO	0	-0.1
H	CO	1	-0.2
H	CO	2	0.0
H	CO	3	0.0

Code	Parameter	Concentrations	En
H	CO	4	-0.4
H	CO	5	-0.4
H	NO	0	-0.1
H	NO	1	-0.7
H	NO	3	-0.3
H	NO	5	-0.7
H	NO	9	-0.5
H	O3	0	-0.2
H	O3	1	-1.9
H	O3	2	-0.7
H	O3	3	-1.1
H	O3	4	-1.2
H	O3	5	-1.0
H	SO2	0	0.0
H	SO2	1	-0.3
H	SO2	2	-0.2
H	SO2	3	-0.1
H	SO2	4	-0.1
H	SO2	5	-0.1
I	CO	0	-0.3
I	CO	1	-0.3
I	CO	2	-0.2
I	CO	3	-0.3
I	CO	4	-0.4
I	CO	5	-0.4
I	NO	0	-0.1
I	NO	1	0.0
I	NO	2	0.3
I	NO	3	-0.1
I	NO	4	-0.2
I	NO	5	-0.1
I	NO	6	0.0
I	NO	7	0.2
I	NO	8	0.4
I	NO	9	0.3
I	NO	10	0.8
I	NO2	1	-0.3
I	NO2	2	1.0
I	NO2	3	0.0
I	NO2	4	0.5
I	NO2	5	-0.2
I	NO2	6	0.8
I	NO2	7	-0.7
I	NO2	8	-0.3
I	NO2	9	-0.4
I	NO2	10	-0.3
I	O3	0	0.5
I	O3	1	-0.7

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

Code	Parameter	Concentrations	En
L	SO2	4	-0.3
L	SO2	5	-0.2

*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



### 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**

QUALE

**Organizzatori di prove valutative interlaboratorio**

**Proficiency Testing Provider**

Data di 1<sup>a</sup> emissione  
*1st Issue date*  
**17-01-2019**

Data di modifica  
*Modification date*  
**17-01-2019**

Data di scadenza  
*Expiring date*  
**16-01-2023**

*Silvia Tramontin*  
Dott.ssa Silvia Tramontin  
Il Direttore di Dipartimento  
The Department Director

*Filippo Trifiletti*  
Dott. Filippo Trifiletti  
Il Direttore Generale  
The General Director

*Giuseppe Rossi*  
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 validità dell'accreditamento può essere verificata sul sito web ([www.accredia.it](http://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](http://www.accredia.it) or by contacting the relevant Department.

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ACCREDIA

Sede operativa e legale: Via Guglielmo Saliceto, 7/9 | 00161 Roma - Italy | Tel. +39 06 8440991 | Fax +39 06 8841199  
[info@accredia.it](mailto:info@accredia.it) | [www.accredia.it](http://www.accredia.it) | Partita IVA - Codice Fiscale 10566361001

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

**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.acredia.it](http://www.acredia.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



Membro degli Accordi di Mutuo Riconoscimento EA, IAF e ILAC  
Signatory of EA, IAF and ILAC Mutual Recognition Agreements



## CERTIFICATO DI ACCREDITAMENTO Accreditation Certificate

ACCREDITAMENTO N.  
ACCREDITATION N.

**1362L REV. 03**

EMESSO DA  
ISSUED BY

**DIPARTIMENTO LABORATORI DI PROVA**

SI DICHIARA CHE  
WE DECLARE THAT

**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

MID-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<sup>a</sup> emissione  
*1st issue date*  
**19-06-2013**

Data di revisione  
*Review date*  
**22-06-2021**

Data di scadenza  
*Expiring date*  
**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 Probe allegato al presente certificato di accreditamento.

Il presente certificato non è da ritenersi valido se non accompagnato dagli Elenchi Probe, 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.

La validità dell'accreditamento può essere verificata sul sito web ([www.accredia.it](http://www.accredia.it)) o richiesta al Dipartimento di competenza.

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.

Confirmation of the validity of accreditation can be verified on the website ([www.accredia.it](http://www.accredia.it)) or by contacting the relevant Department.

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](http://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](http://www.accredia.it), sezione "Documenti".

The QRcode links directly to the website [www.accredia.it](http://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](http://www.accredia.it), 'Documents' section.

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

ACCREDIA is the sole national Accreditation Body, appointed by the Italian government in compliance with the application of REGULATION (EC) No 765/2008.

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ACCREDIA - 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  Via E. Fermi 2749	UNI CEI EN ISO/IEC 17025:2018
Revisione: 5	Data: 22/06/2021
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**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](http://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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