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Evaluation of the Laboratory Comparison Exercise for SO_2, CO, O_3, NO and NO_2 26th- 29th September 2011

EC Harmonization Program for Air Quality Measurements

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Executive Summary

From the 26th to the 29th of September 2011 9 Laboratories of AQUILA (Network of European Air Quality Reference Laboratories) met at an laboratory comparison exercise in Ispra (IT) to evaluate their proficiency in the analysis of inorganic gaseous pollutants (SO_2, CO, NO, NO_2 and O_3) covered by the European Air Quality Directive 2008/50/EC.
The proficiency evaluation, where each participant's bias was compared to two criteria, provides information on compliance with Data Quality Objectives and measurement capabilities of the National Air Quality Laboratories to the European Commission and can be used by participants in their laboratory's quality system.
On the basis of criteria imposed by the European Directive, 86% of the results reported by AQUILA laboratories were good both in terms of measured values and reported uncertainties. Another 13% of the results had good measured values, but the reported uncertainties were either too high (8%) or too small (5%).
The comparability of results among AQUILA participants at the generated concentration levels, excluding outliers, is acceptable for SO_2, NO, NO_2 and O_3 measurements while CO measurements showed less satisfactory results.

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Abbreviations

AQUILA	Network of National Reference Laboratories for Air Quality
CO	Carbon monoxide
DQO	Data Quality Objective
ERLAP	European Reference Laboratory of Air Pollution
EC	European Commission
GPT	Gas Phase Titration
IE	Inter-comparison Exercise
IES	Institute for Environment and Sustainability
ISO	International Organization for Standardization
JRC	Joint Research Centre
NO	Nitrogen monoxide
NO_2	Nitrogen dioxide
NO_X	the oxides of nitrogen, the sum of NO and NO_2
NRL	National Reference Laboratory
O_3	Ozone
SO_2	Sulphur dioxide
WHO CC-EURO	World Health Organization Collaborating Centre for Air Quality Management and Air Pollution Control, Berlin

Mathematical Symbols:

symbol	explanation
α	converter efficiency (EN 14211; [4])
E_n	E_n – number statistic (ISO 13528; [13])
r	repeatability limit (ISO 5725; [14])
R	reproducibility limit (ISO 5725; [14])
σ_p	standard deviation for proficiency assessment (ISO 13528; [13])
x*	robust average (Annex C ISO 13528; [13])
s*	robust standard deviation (Annex C ISO 13528; [13])
s_r	repeatability standard deviation (ISO 5725; [14])
s_R	reproducibility standard deviation (ISO 5725; [14])
$U_{X'}$	expanded uncertainty of the assigned/reference value (ISO 13528; [13])
U_{xi}	expanded uncertainty of the participant's value
$u_{X'}$	standard uncertainty of the assigned/reference value (ISO 13528; [13])
X	assigned/reference value (ISO 13528; [13])
x_i	average of three values reported by the participant i (for particular parameter and concentration level) (ISO 5725; [14])
$x_{i,j}$	j-th reported value of participant i (for particular parameter and concentration level) (ISO 5725; [14])
z'	z'-score statistic (ISO 13528; [13])

1. Introduction

As a result of the revision of the legislation framework on air quality in the CAFÉ (Clean Air for Europe) thematic strategy, former mother and most daughter directives were integrated into a single rule. With the adoption of Directive 2008/50/EC [1] on ambient air quality and cleaner air for Europe, a framework for a harmonized air quality assessment in Europe was set. One important objective of the Directive 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_2), nitrogen dioxide (NO_2) and monoxide (NO), particulate matter, lead, benzene, carbon monoxide (CO) and ozone (O_3). 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_2 [3], NO-NO_2 [4] and O_3 [5] as European standards. Appropriate calibration methods [6], [7] and [8] have been standardized by the International Organization for Standardization (ISO).
As foreseen in the Air Quality Directive, the European Reference Laboratory of Air Pollution (ERLAP) of the Institute for Environment and Sustainability (IES) at the Joint Research Centre (JRC) organizes inter-laboratory comparison exercises (IE) to assess and improve the status of comparability of measurements of National Reference Laboratories (NRL) of each Member State 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], but with a view to obtaining harmonized air quality data for health related studies. Their program 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 optimize resources and have better international harmonization. The following report deals with the IE that took place from 26th to the 29th of September 2011 in Ispra (IT) in joint cooperation of EC/JRC/IES/ERLAP and WHO CC.

Since 1990 ERLAP organizes IEs aiming at evaluating the comparability of measurements carried out by NRLs and promoting information exchange among the expert laboratories. Currently, a more systematic approach has been adopted, in accordance with the Network of National Reference Laboratories for Air Quality (AQUILA) [11], aiming both at providing an alert mechanism for the purposes of the EC legislation and at supporting the implementation of quality schemes by NRLs. The methodology for the organization of IEs was developed by ERLAP in collaboration with AQUILA and is described in a paper on the organization of laboratory comparison exercises for gaseous air pollutants [12].
This evaluation scheme was adopted in December 2008 and is applied to all IEs 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 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 said document, NRLs with an overall unsatisfactory performance in the z'-score evaluation (one unsatisfactory or two questionable results per parameter) ought to repeat their participation in the following IE 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 compared to the assigned values applying the E_n – number method [13].
Beside the proficiency of participating laboratories, the repeatability and reproducibility of standardized measurement methods [14], [15] and [16] are evaluated as well. These group evaluations are useful indicators of trends in measurement quality over different IEs.

1.1 Communication and time schedule

The IE was announced in March 2011 to the members of the AQUILA network and the WHO CC representative. Registration was opened on March 2011 and due to the number of request ERLAP decided to organize two consecutive sessions of IE exercises.
The participants were required to bring their own measurement instruments, data acquisition equipment and travelling standards (to be used for calibrations or checks during the IE).

The participants were invited to arrive on Monday, 26th September 2011, for the installation of their equipment. The calibration of NOx and O_3 analysers was carried out on Tuesday morning and the generation of NOx and O_3 gas mixtures started at 11:00. The calibration of SO_2 and CO analysers was carried out on Wednesday 18:00 and the generation of CO and SO_2 gas mixtures started at 20:00. The test gases generation finished on Thursday at 9:30.

1.2 Participants

All participants were organizations dealing with the routine ambient air monitoring or institutions involved in public health protection.

The national representatives came from EU member states: Czech Republic, United Kingdom, Denmark, Croatia, Netherland, Bulgaria, Slovak Republic, Belgium and Hungary.

Country	Laboratory	Code
Czech Republic	Czech Hydrometereological Institute (CHMI)	A
United Kingdom	AEA Technology	B
Denmark	National Environmental Research Institute (NERI)	C
Croatia	Energy and Environmental Protection Institute (EKONERG)	D
Netherland	National Institute for Public Health and the Environment (RIVM)	E
Bulgaria	Executive Environmental Agency (EEA)	F
European Commission	European Reference Laboratory for Air Pollution (ERLAP)	G
Slovak Republic	Slovak Hydrometeorological Institute (SHMU)	H
Belgium	Belgian Interregional Environment Agency (IRCEL-CELINE)	I
Hungary	Hungarian Meteorological Service (HMS)	L

Table 1: The list of participating organizations.

In Table 2 are reported the manufacturer and model of the instrumentation used by every participant during the laboratory comparison exercise included those used in the calculation of the assigned values.

As a whole, the instrumentation belongs to 3 producers for all pollutants. The list contains the information reported by participants and by no means can be considered as an implicit or explicit endorsement of the organizers to any specific type of instrumentation.

Gas	Lab Code	Instrument
SO_2	A	Thermo Environmental Instruments, Inc., 1997, model 43C
	B	API 100A 1998
	C	Teledyne, API 100E
	D	HORIBA APSA 370/ 2007.
	E	TE 43i-TLE 2010
	F	Horiba, 2009, analyzer SO2, APSA 370.
	G	Thermo Electrom Corporation, 2009, 43i
	H	Horiba APSA 370/2010
	I	Thermo Fischer scientific 2011, 43i
	L	TEI 43C year 2005
NO_X	A	Thermo Environmental Instruments, Inc., 1997, model 42C
	B	Thermo 42i 2010
	C	Teledyne, API 200E
	D	HORIBA APNA 370 / 2008.
	E	API Teledyne 200E 2008
	F	Horiba, 2009, analyzer NOx, APNA 370
	G	Thermo Electrom Corporation, 2010, 42i
	H	Horiba APNA 370/2010
	I	Thermo Fischer Scientif 42i 2007
	L	API Teledyne M200E 2010
CO	A	Thermo Environmental Instruments, Inc., 1997, model 48C
	B	API 300E 1998
	C	Teledyne, API 300E
	D	HORIBA APMA 370 / 2007.
	E	TE 48i TLE 2010
	F	Horiba, 2009, Analyzer CO, APMA 370.
	G	Thermo Electronic Corporation, 2000, 48C
	H	Horiba APMA 370/2010
	I	HORIBA APMA370 2008
	L	TEI 48C year:2005
O_3	A	Thermo Environmental Instruments, Inc., 1996, model 49C
	B	Thermo 49i 2010
	C	Teledyne, API 400
	D	HORIBA APOA 370 / 2009.
	E	TE 49i 2009
	F	Horiba, 2009, Analyzer O3, APOA 370
	G	Thermo Electronic Corporation, 1996, 49C
	H	Horiba APOA 370/2010
	I	HORIBA APOA 370 2008
	L	TEI 49 C 2005

Table 2: The list of instruments used by participants

1.3 The preparation of test mixtures

The ERLAP IE facility has been described in several reports [17] and [18]. During this IE, gas mixtures were prepared for SO_2, CO, O_3, NO and NO_2 at concentration levels around limit values, critical levels and assessment thresholds set by European Air Quality Directive [1].

The test mixtures were prepared by the dilution of gases from cylinders containing high concentration of NO, SO_2 or CO using thermal mass flow controllers [8]. O_3 was added using an ozone generator and NO_2 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 standardized measurement methods. Zero concentration levels were generated for one hour and one half-hour-mean measurement was reported.
The sequence program of generated test gases is given in Table 3.

day	start time	duration	parameter	installation	calibration	Zero Air	NO	NO2	O3	CO	SO2
		h				nmol/mol	nmol/mol	nmol/mol	nmol/mol	mmol/mol	nmol/mol
26-Sep	12:00	5	/	X							
27-Sep	8:00	3	/		X						
27-Sep	11:00	1	NO-NO2-O3			0					
27-Sep	12:00	2	NO-NO2				520				
27-Sep	14:00	2	NO-NO2				390	130			
27-Sep	16:00	2	O3						130		
27-Sep	18:00	2	NO-NO2				60				
27-Sep	20:00	2	NO-NO2				35	25			
27-Sep	22:00	2	O3						25		
28-Sep	0:00	2	NO-NO2				175				
28-Sep	2:00	2	NO-NO2				120	55			
28-Sep	4:00	2	O3						55		
28-Sep	6:00	2	NO-NO2				260				
28-Sep	8:00	2	NO-NO2				165	95			
28-Sep	10:00	2	O3						95		
28-Sep	12:00	2	NO-NO2				20				
28-Sep	14:00	2	NO-NO2				6	14			
28-Sep	16:00	2	O3						14		
28-Sep	< 18:00	2	calibration		X						
28-Sep	20:00	1	CO-SO2			0					
28-Sep	21:00	2:30	CO-SO2							8	8
28-Sep	23:30	2	CO-SO2							4,5	50
29-Sep	1:30	1	CO-SO2	Zero Air not reported						0	0
29-Sep	2:30	2	CO-SO2							6	20
29-Sep	4:30	2	CO-SO2							3	120
29-Sep	6:30	2	CO-SO2							1	3
29-Sep	8:30	1				0					
29-Sep	9:30	END									

Table 3: The sequence program of generated test gases

2. The evaluation of laboratory's measurement proficiency

To evaluate the participants measurement proficiency the methodology described in ISO 13528 [13] was applied. It has been agreed among the AQUILA members to take the measurement results of ERLAP as the assigned/reference values for the whole IE [12]. The traceability of ERLAP's measurement results and the method applied to validate them 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 it is described in the said position paper [12], the proficiency of the participants was assessed by calculating two performance indicators. The first performance indicator (z'-score) tests whether the difference between the participants measured value and the assigned/reference value remains within the limits of a common criterion. The second performance indicator (E_n-number) tests 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 participants measurement result and the uncertainty of the assigned/reference value.

2.1 z'- score

The z'- score statistic is calculated according to ISO 13528 [13] as:

$$z' = \frac{x_i - X}{\sqrt{\sigma_p^2 + u_X^2}} = \frac{x_i - X}{\sqrt{(a \cdot X + b)^2 + u_X^2}} \quad \textbf{Equation 1}$$

where 'x_i' is a participant's run average value, 'X' is the assigned/reference value, 'σ_p' is the 'standard deviation for proficiency assessment' and 'u_X' is the standard uncertainty of assigned value. For 'a' and 'b' see Table 4.

In the European standards [2], [3], [4] and [5] the uncertainties for calibration gases used in ongoing quality control are prescribed. In fact, it is stated that the maximum permitted expanded uncertainty for calibration gases is 5% and that 'zero gas' shall not give instrument reading higher than the detection limit. As one of the tasks of NRLs is to supply calibration gas mixtures, the 'standard deviation for proficiency assessment' (σ_p) [13] is calculated in fitness-for-purpose manner from requirements given in European standards.

Over the whole measurement range σ_p 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 IEs. The linear function parameters of σ_p are given in Table 4:

	σ_p=a·c+b	
Gas	**a**	**b** nmol/mol
SO_2	0.022	1
CO	0.024	100
O_3	0.020	1
NO	0.024	1
NO_2	0.020	1

Table 4: The standard deviation for proficiency assessment (σ_p).
σ_p is a linear function of concentration (c) with parameters: slope (a) and intercept (b).

The assessment of results in the z‘-score evaluation is made according to the following criteria:
$|z'| \leq 2$ are considered satisfactory.
$2 < |z'| \leq 3$ are considered questionable.
$|z'| > 3$ 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.
The results of z'-score evaluation are presented in bar plots (Figure 1 to Figure 5) in which the z'-scores of each participant are grouped together, and assessment criteria are presented as z'=±2 and z'=±3 lines.

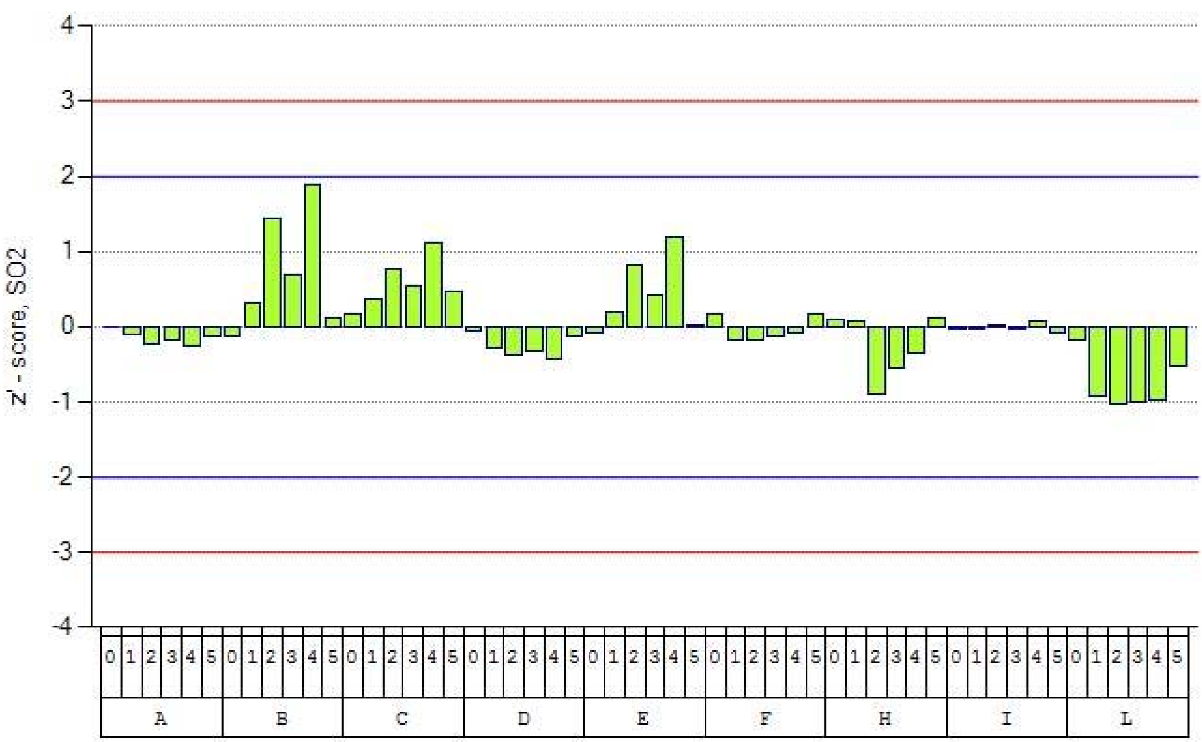

Figure 1: The z'-score evaluations of SO_2 measurements
Scores are given for each participant and each tested concentration level (run). Run number order (with nominal concentration) is: 0 (0 nmol/mol), 1 (8 nmol/mol), 2 (50 nmol/mol), 3 (20 nmol/mol), 4 (120 nmol/mol), 5 (3 nmol/mol). The assessment criteria are presented as z'=±2 (blue line) and z'=±3 (red line). They represent the limits for the questionable and unsatisfactory results.

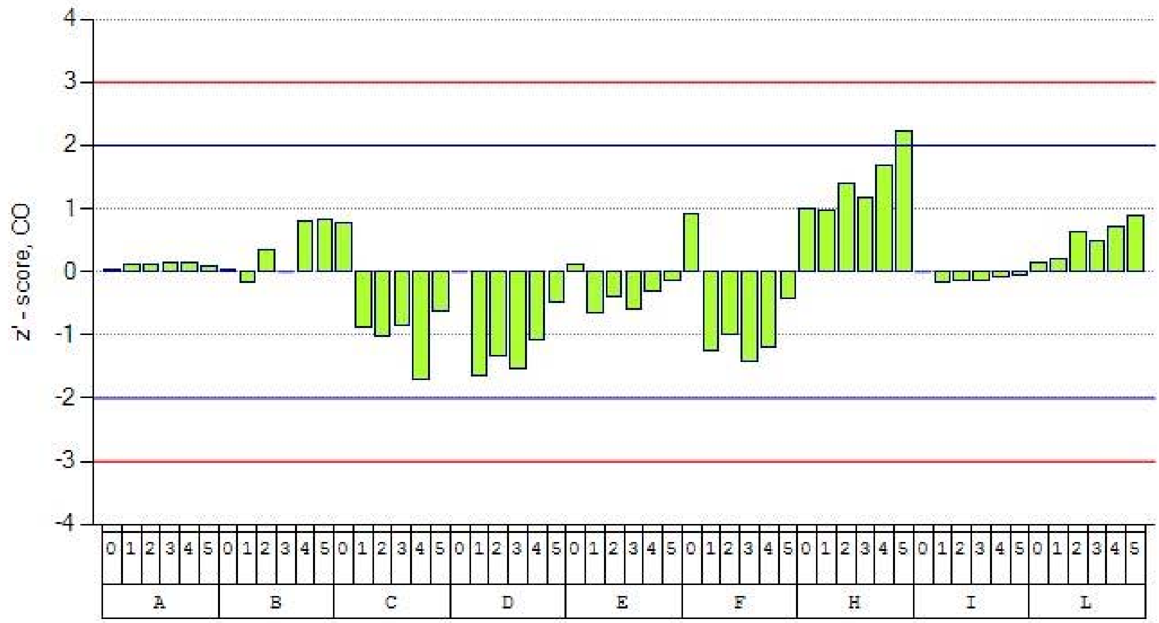

Figure 2: The z'-score evaluations of CO measurements
Scores are given for each participant and each tested concentration level (run). Run number order (with nominal concentration) is: 0 (0 µmol/mol), 1 (8 µmol/mol), 2 (4.5 µmol/mol), 3 (6 µmol/mol), 4 (3 µmol/mol), 5 (1 µmol/mol). The assessment criteria are presented as z'=±2 (blue line) and z'=±3 (red line). They represent the limits for the questionable and unsatisfactory results.

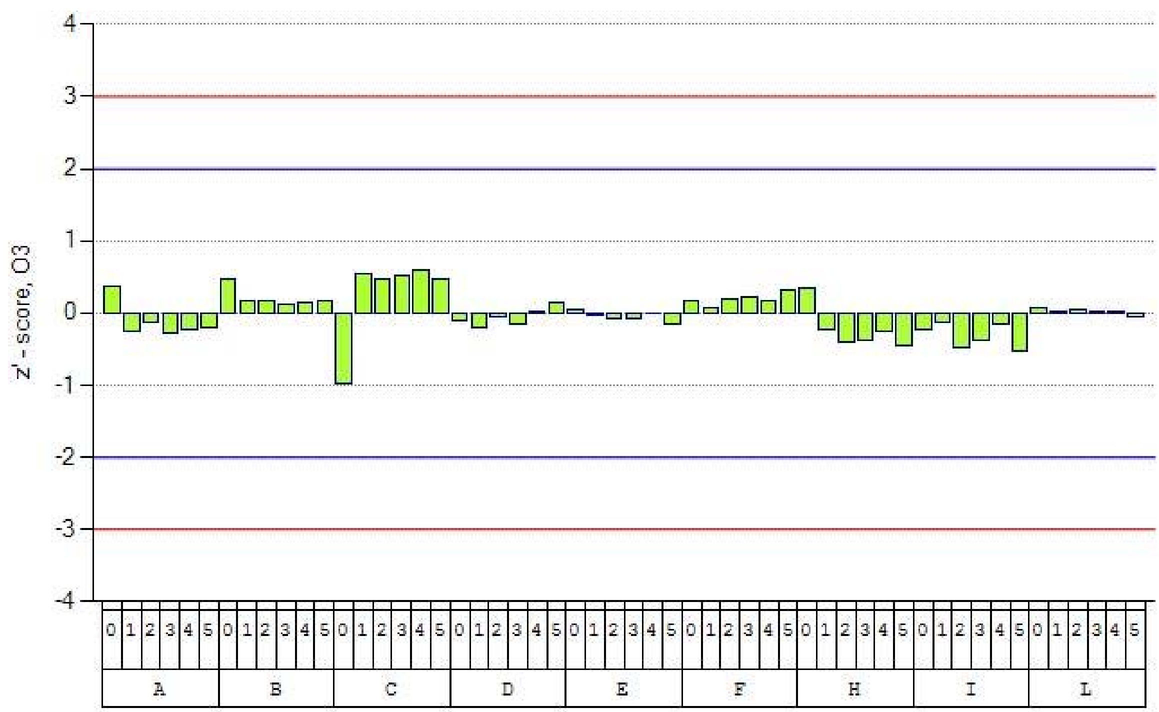

Figure 3: The z'-score evaluations of O_3 measurements
Scores are given for each participant and each concentration level (run). Run number order (with nominal concentration) is: 0 (0 nmol/mol), 1 (130 nmol/mol), 2 (25 nmol/mol), 3 (55 nmol/mol), 4 (95 nmol/mol), 5 (14 nmol/mol). The assessment criteria are presented as z'=±2 (blue line) and z'=±3 (red line). They represent the limits for the questionable and unsatisfactory results.

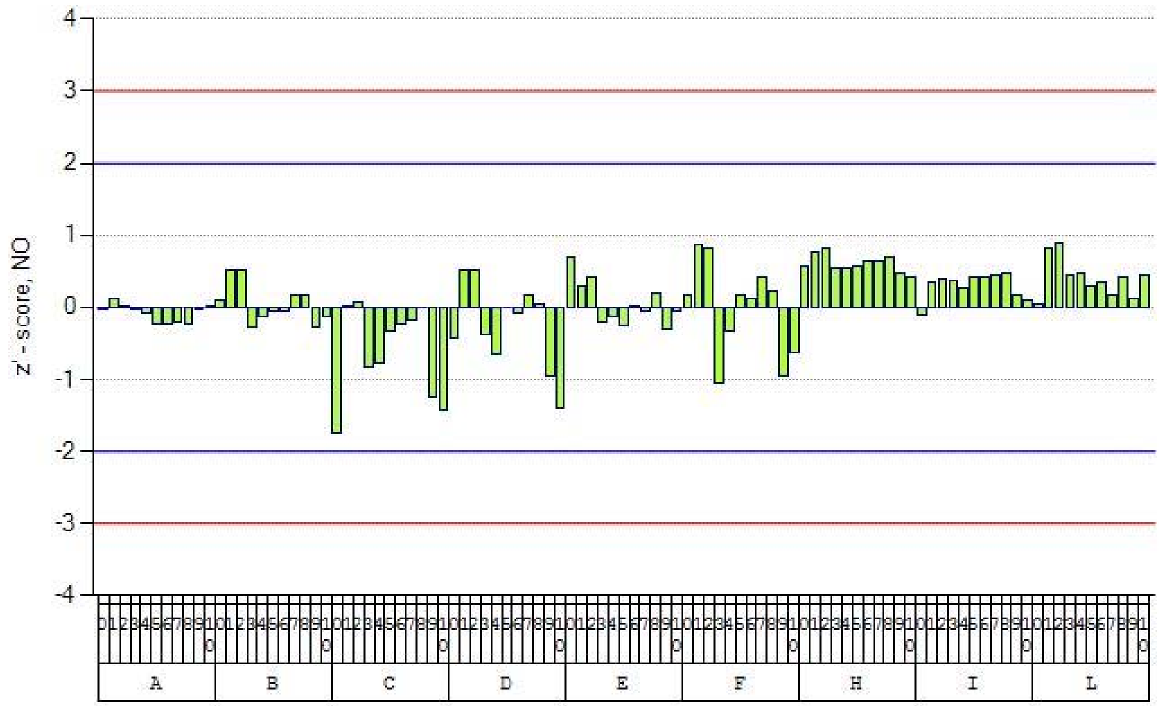

Figure 4: The z'-score evaluations of NO measurements
Scores are given for each participant and each tested concentration level (run). Run number order (with nominal concentration) is: 0 (0 nmol/mol), 1 (520 nmol/mol), 2 (390 nmol/mol), 3 (60 nmol/mol), 4 (35 nmol/mol), 5 (175 nmol/mol), 6 (120 nmol/mol), 7 (260 nmol/mol), 8 (165 nmol/mol), 9 (20 nmol/mol), 10 (6 nmol/mol). The assessment criteria are presented as z'=±2 (blue line) and z'=±3 (red line). They represent the limits for the questionable and unsatisfactory results.

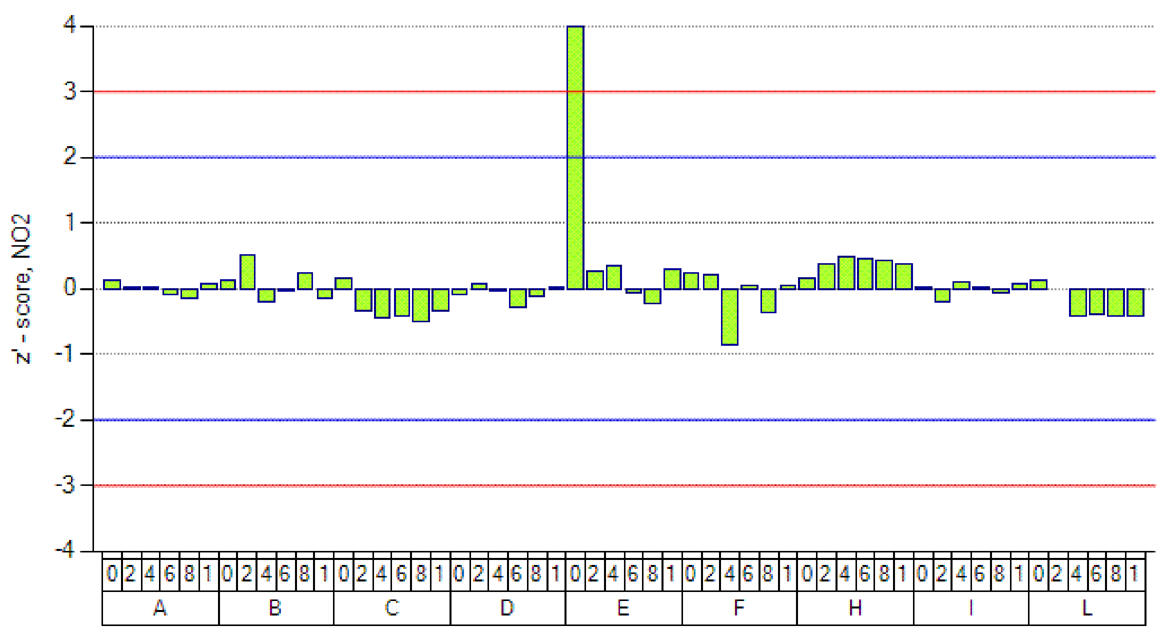

Figure 5: The z'-score evaluations of NO_2 measurements
Scores are given for each participant and each concentration level (run). Run number order (with nominal concentration) is: 0 (0 nmol/mol), 1 (130 nmol/mol), 2 (25 nmol/mol), 3 (55 nmol/mol), 4 (95 nmol/mol), 5 (14 nmol/mol). The assessment criteria are presented as z'=±2 (blue line) and z'=±3 (red line). They represent the limits for the questionable and unsatisfactory results.

2.2 E_n - number

The normalised deviations [13] (E_n) were calculated according to:

$$E_n = \frac{x_i - X}{\sqrt{U_{x_i}^2 + U_X^2}}$$ **Equation 2**

where 'X' is the assigned/reference value with an expanded uncertainty 'U_X' and 'x_i' is the participant's average value with an expanded uncertainty 'U_{Xi}'. Satisfactory results are the ones for which $|E_n| \leq 1$.

In Figure 6 to Figure 10 the bias of each participant (x_i-X) are plotted and error bars are used to show the value of denominator of equation $2\left(\sqrt{U_{x_i}^2 + U_X^2}\right)$. These plots represent also the E_n-number evaluations where, considering the E_n criteria ($|E_n| \leq 1$), all results with error bars touching or crossing x-axis are satisfactory. Reported standard uncertainties (Annex B) that are bigger than "standard deviation for proficiency assessments" (σ_p, Table 4) are considered not fit-for-purpose and are denoted with "*" in the x-axis of each figure.

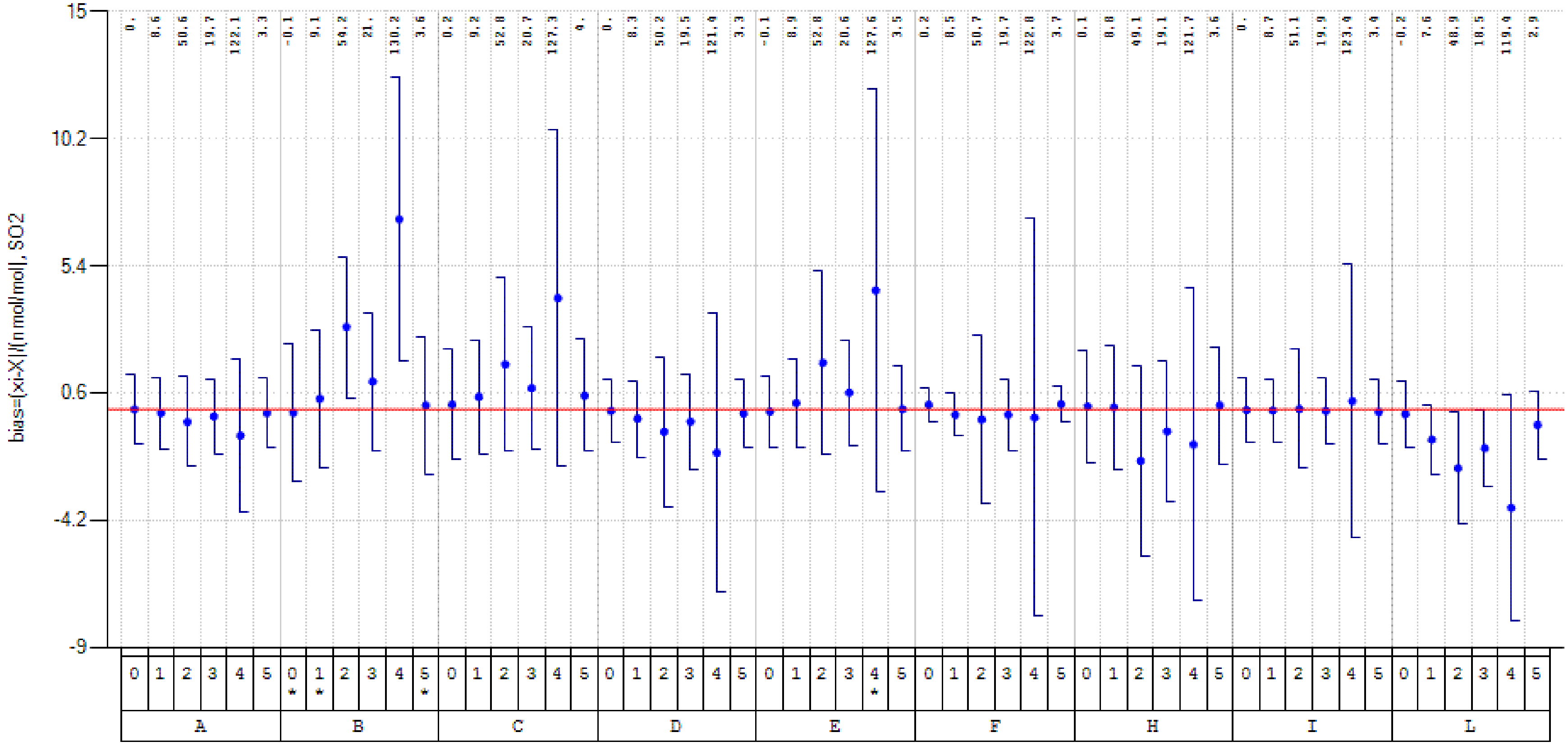

Figure 6: Bias of participant's SO_2 measurement results
Expanded uncertainty of bias for each run is presented as error bar. The results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 5) together with the participants rounded run average (nmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger than σ_p.

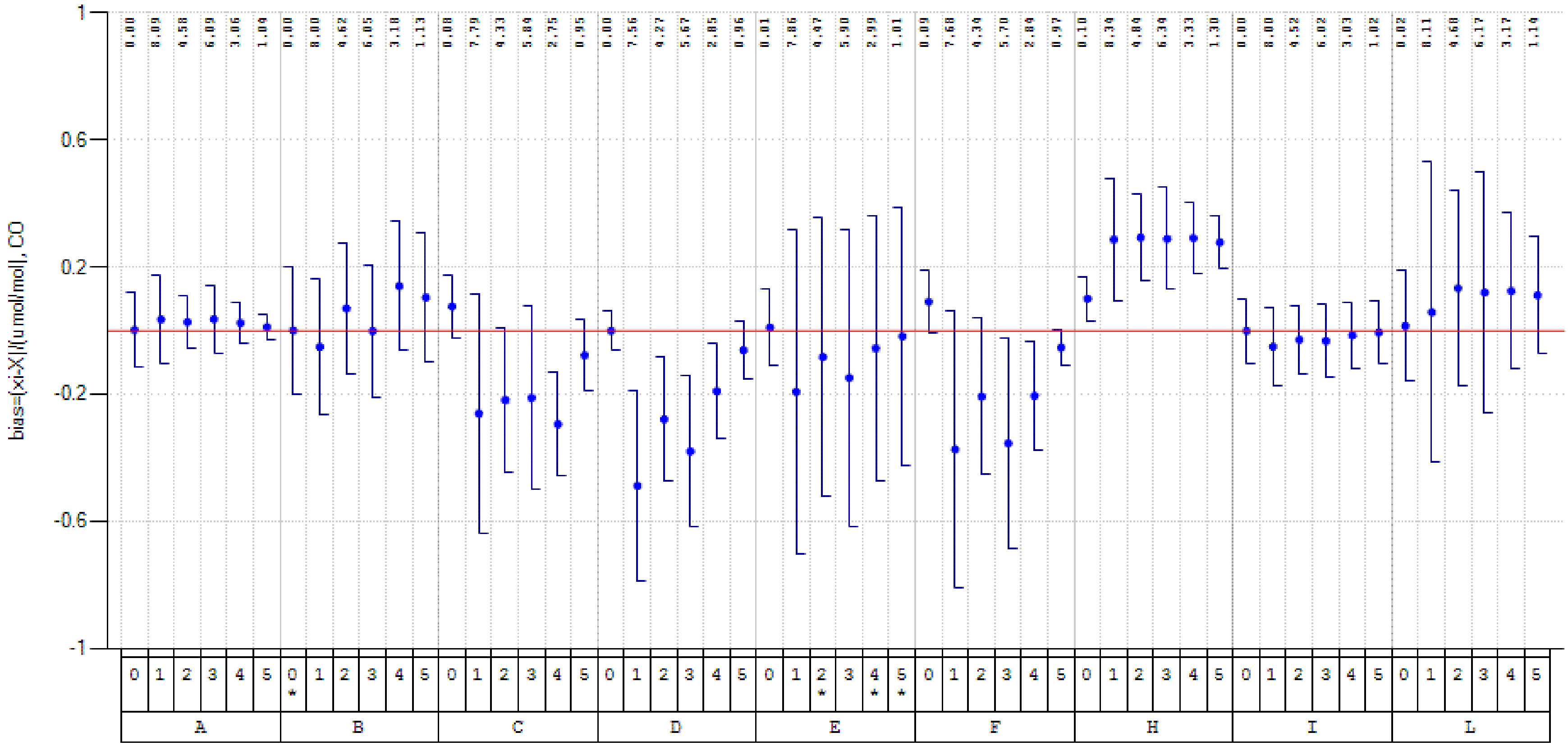

Figure 7: Bias of participant's CO measurement results
Expanded uncertainty of bias for each run is presented as error bar. Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 5) together with the participants rounded run average (µmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger than σ_p.

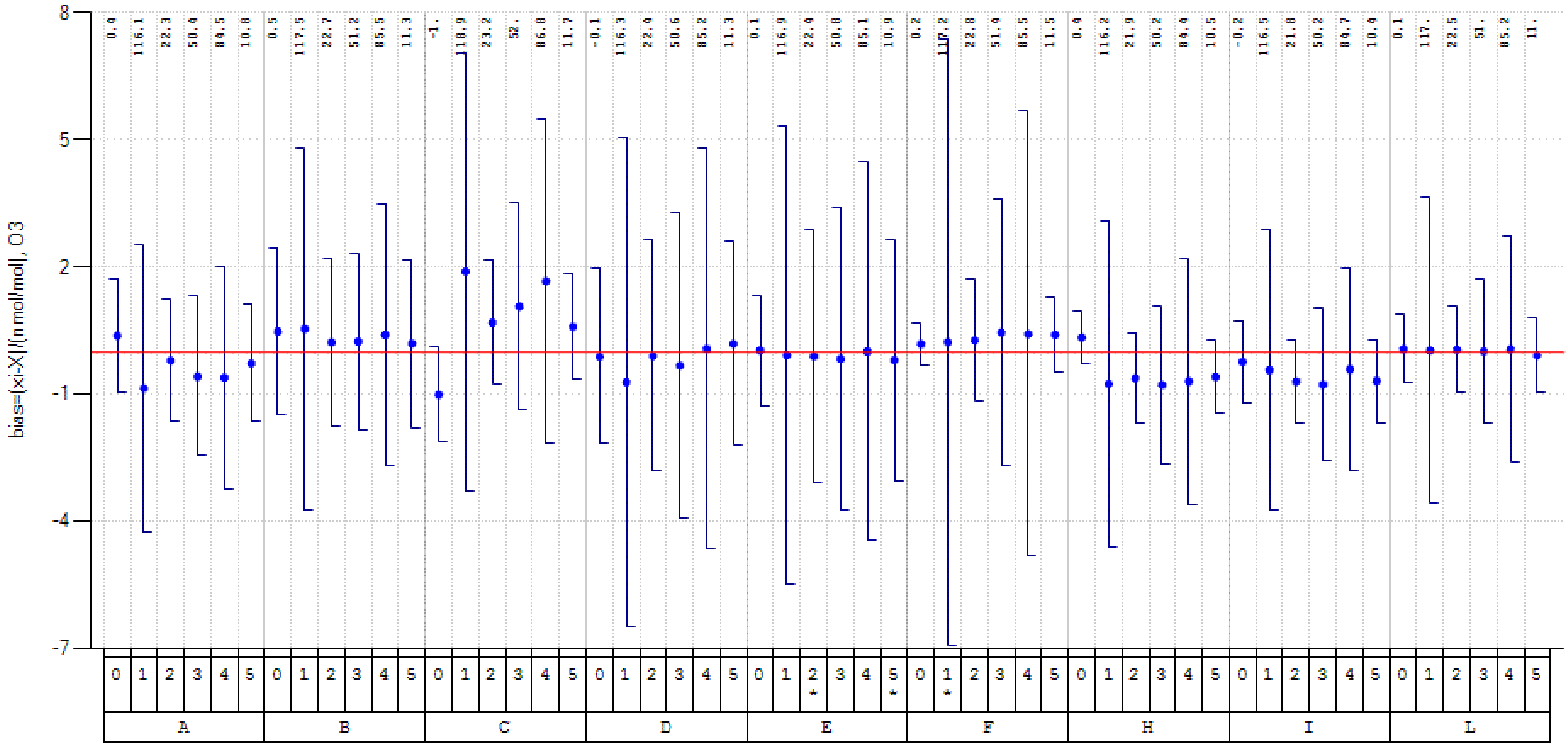

Figure 8: Bias of participant's O_3 measurement results
Expanded uncertainty of bias for each run is presented as error bar. Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 5) together with the participants rounded run average (nmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger than σ_p.

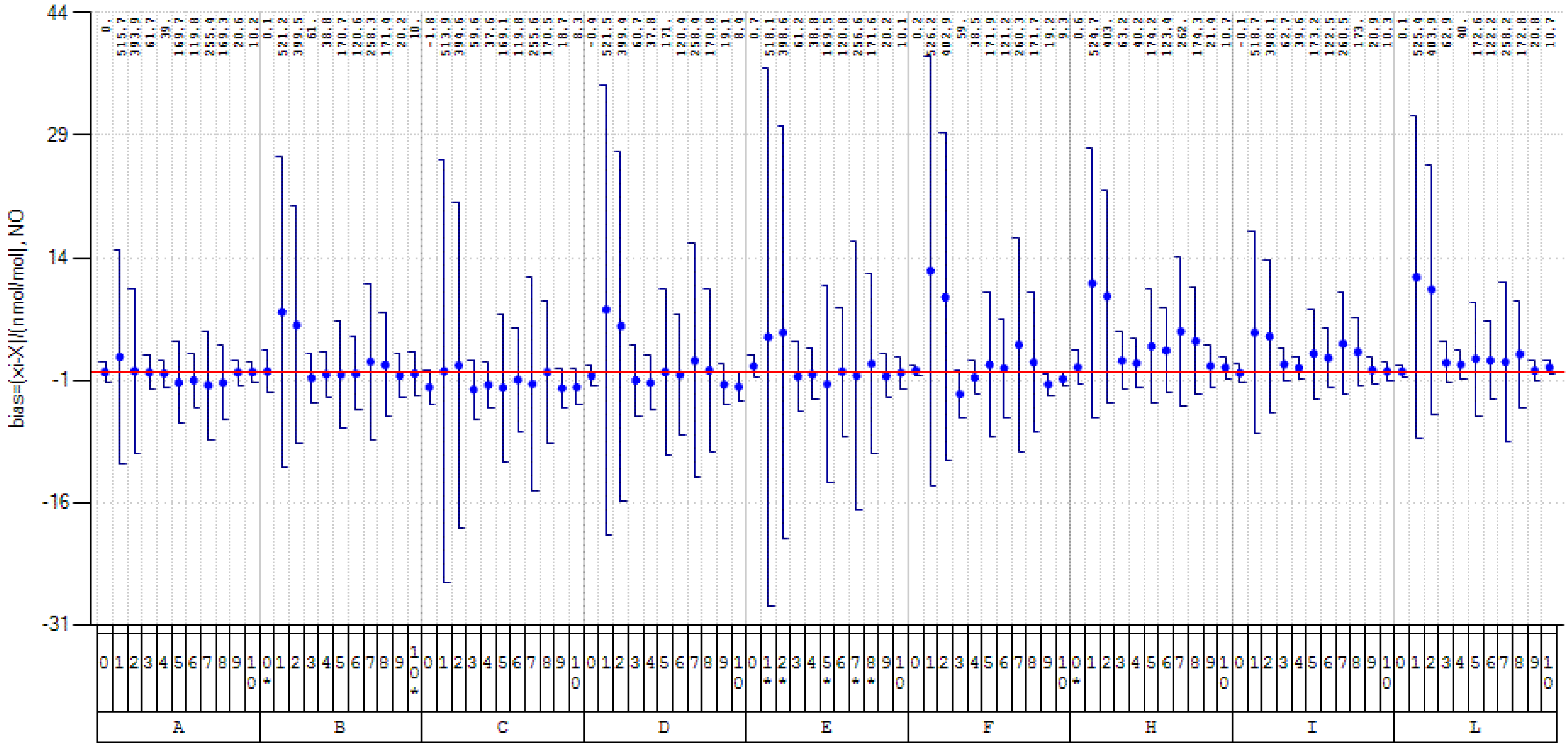

Figure 9: Bias of participant's NO measurement results
Expanded uncertainty of bias for each run is presented as error bar. Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 10) together with the participants rounded run average (nmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger than s_p.

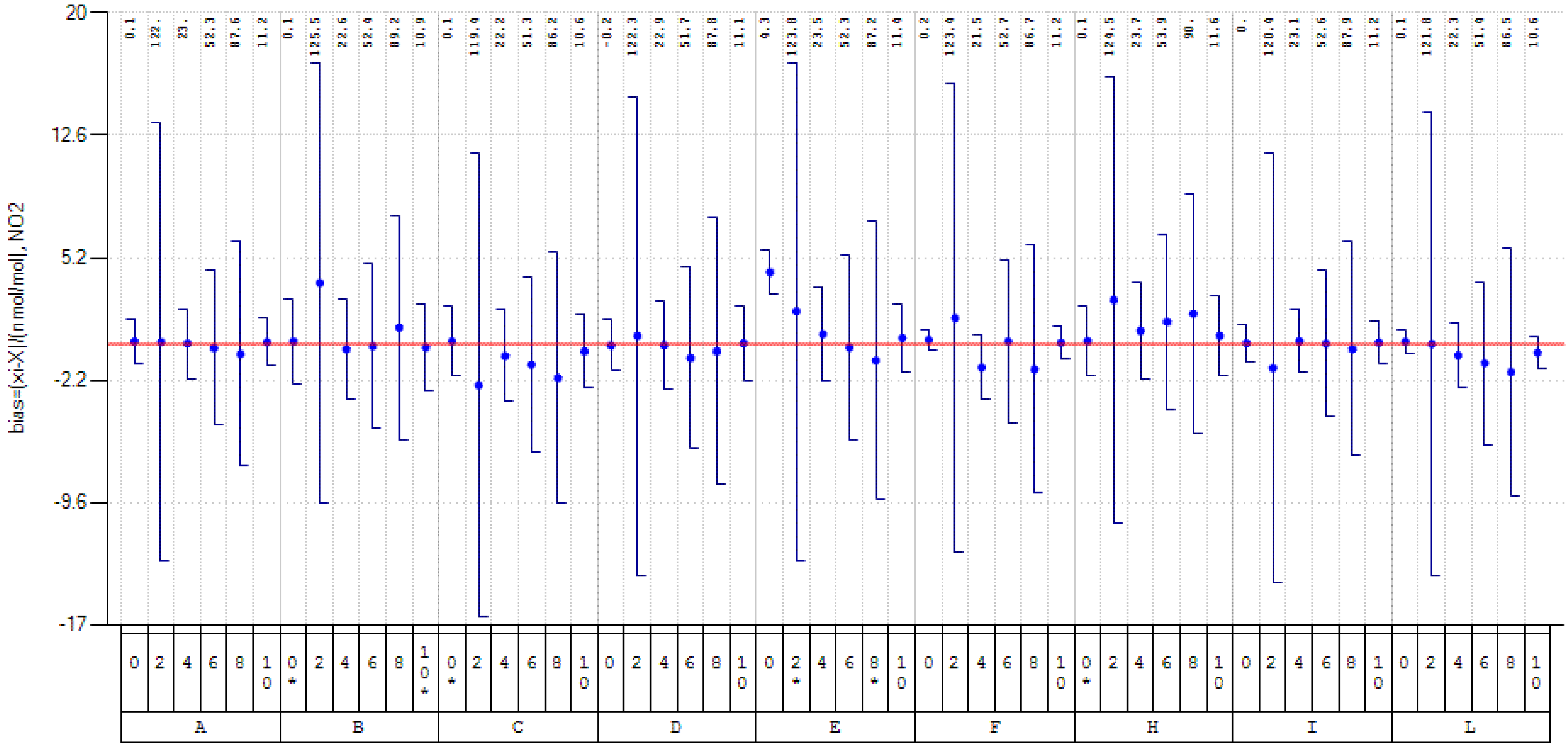

Figure 10: Bias of participant's NO_2 measurement results
Expanded uncertainty of bias is presented as error bar for NO_2 run numbers 0, 2, 4, 6, 8 and 10 (see Table 3). Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number together with the participants rounded run average (nmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger than σ_p.

3. Performance characteristics of individual laboratories

Individual participants' bias was evaluated and are presented in chapter 2 (Figure 6-Figure 10). Since the results of NO_2 runs 1, 3, 5, 7 and 9 was not treated in proficiency evaluation the bias of these runs is presented in Figure 11.

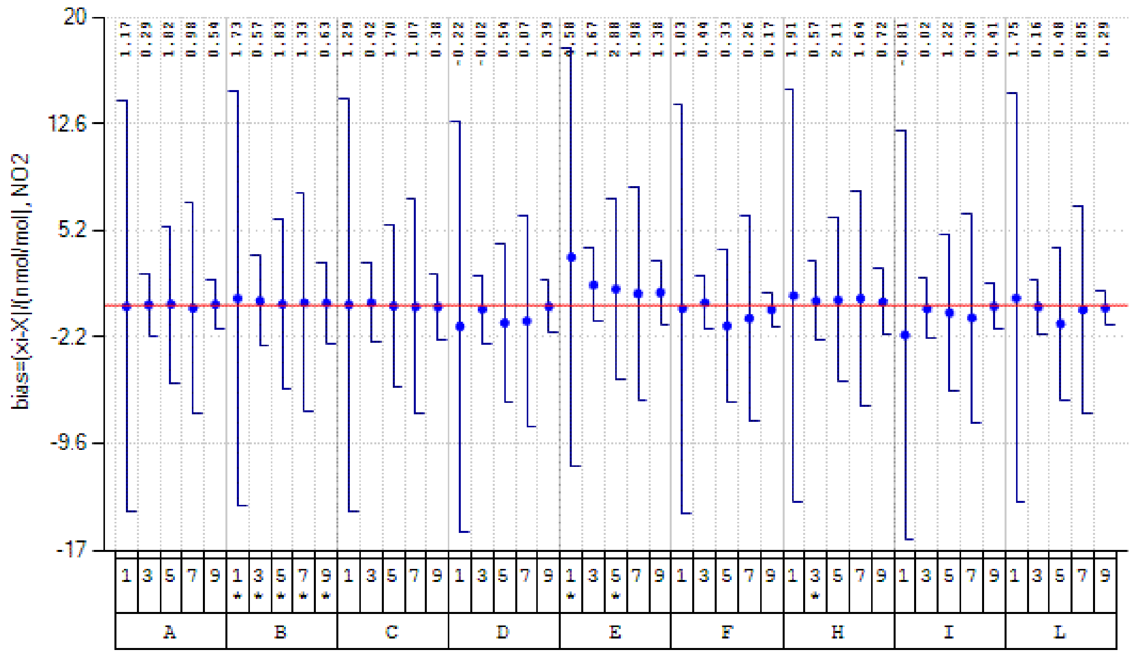

Figure 11: Bias of participant's NO_2 measurements for run numbers 1, 3, 5, 7 and 9
At these test gas mixtures the concentration levels of NO_2 were zero and the concentration levels of NO were not zero (see Table 3). In that perspective the figure shows the effect of NO concentration on NO_2 measurements. For each evaluation the run number together with the participants rounded run average (nmol/mol) is given.

3.1 The efficiency of NO2-to-NO converters of NOX analyzers

Since NO and NO_2 test gases were produced by gas phase titration it is possible to evaluate the efficiency of NO_2-to-NO converter of each participant's NO_X analyser. The evaluation takes each participant's NO and NO_2 measurements before and after oxidation by O_3. The converter efficiency (α) is calculated using Equation 3 [4]:

$$\alpha = \frac{[NO2]_i - [NO2]_{i-1}}{[NO]_{i-1} - [NO]_i} \cdot 100\% \qquad \textbf{Equation 3}$$

The O_3 measurements of each participant can also be compared to either NO or NO_2 change by calculating Δ^{NO} or Δ^{NO2} using Equation 4 and Equation 5 respectively:

$$\Delta^{NO} = [O3]_{i+1} - ([NO]_{i-1} - [NO]_i) \qquad \textbf{Equation 4}$$

$$\Delta^{NO2} = [O3]_{i+1} - ([NO2]_i - [NO2]_{i-1}) \qquad \textbf{Equation 5}$$

Ideal value for α is 100% while for Δ^{NO} and Δ^{NO2} it is 0 nmol/mol.

IE code	NO_2 nmol/mol	α %	Δ^{NO} nmol/mol	Δ^{NO2} nmol/mol
A	14	101.6		
A	95	100.6	-1.6	-2.1
A	55	101.1	0.4	-0.1
A	25	99.8	-0.5	-0.4
A	130	99.2	-5.7	-4.7
B	14	99.7		
B	95	101.2	-1.3	-2.4
B	55	100.9	1.1	0.6
B	25	99.4	0.5	0.6
B	130	101.8	-4.1	-6.3
C	14	98.7		
C	95	100.1	1.7	1.7
C	55	100.7	2.8	2.4
C	25	99.1	1.2	1.4
C	130	98.9	-0.5	0.8
D	14	99.6		
D	95	100.1	-2.5	-2.5
D	55	101.2	0.1	-0.5
D	25	99.9	-0.5	-0.5
D	130	100.4	-5.8	-6.3
E	14	99.6		
E	95	100.3	0.1	-0.1
E	55	101.4	2.1	1.3
E	25	97.7	0	0.5
E	130	99.8	-2.6	-2.4

IE code	NO_2 nmol/mol	α %	Δ^{NO} nmol/mol	Δ^{NO2} nmol/mol
F	14	111.7		
F	95	97.6	-3	-0.9
F	55	103.4	0.8	-0.9
F	25	102.5	2.2	1.7
F	130	99.3	-6.1	-5.2
G	14	101.1		
G	95	100.7	-1.4	-2
G	55	101.2	0.7	0.2
G	25	100.4	-0.1	-0.2
G	130	100.5	-3.1	-3.7
H	14	101.3		
H	95	100.9	-3.2	-4
H	55	102	-0.6	-1.6
H	25	101	-1.1	-1.3
H	130	100.8	-5.4	-6.4
I	14	100.9		
I	95	100.2	-2.8	-2.9
I	55	101.2	-0.6	-1.2
I	25	100.3	-1.3	-1.3
I	130	100.6	-4	-4.7
L	14	101.5		
L	95	100.2	-0.3	-0.5
L	55	101	0.6	0.1
L	25	96.7	-0.3	0.4
L	130	98.8	-4.6	-3.1

Table 5: The efficiency of NO_2-to-NO converters.

The evaluation of Equation 4 and Equation **5** cannot be made at the lowest NO_2 level (14 ppb) because, due to the low concentration of NO, O_3 and NO_2 are not detectable with the necessary accuracy. The evaluation of equations 3, 4 and 5 for each participant at different concentration levels are given in Table 5.

4. Discussion

For a general assessment of the quality of each result a decision diagram was developed (

Figure 12) that results in seven categories (1 to 7). The general comments for each category are:

1: measurement result is completely satisfactory

2: measurement result is satisfactory (z′-score satisfactory and En-number ok) but the reported uncertainty is too high

3: measured value is satisfactory (z′-score satisfactory) but the reported uncertainty is underestimated (En-number not ok)

4: measurement result is questionable (z′-score questionable) but due to a high reported uncertainty can be considered valid (En-number ok)

5: measurement result is questionable (z′-score questionable and En-number not ok)

6: measurement result is unsatisfactory (z′-score unsatisfactory) but due to a high reported uncertainty can be considered valid (En-number ok)

7: measurement result is unsatisfactory (z′-score unsatisfactory and En-number not ok)

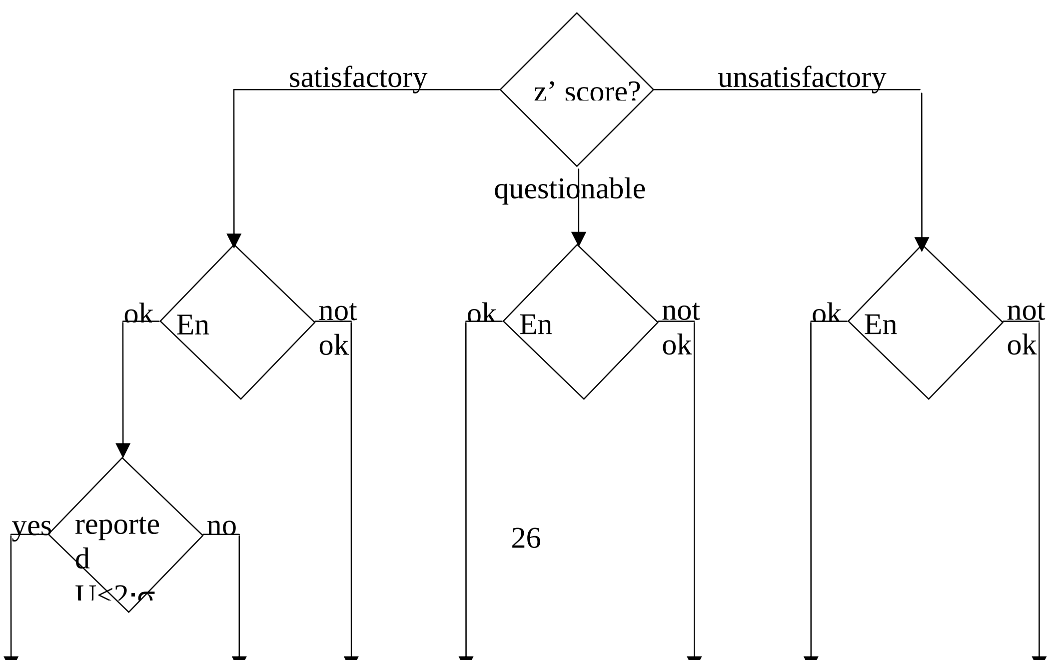

Figure 12: The decision diagram for general assessment of proficiency results.

The results of the IE were assigned to categories according to the diagram given in

Figure 12 and are presented in Table 6.

	run number	Ref. conc. level	IE code								
			A	B	C	D	E	F	H	I	L
CO (µmol/mol)	0	-0.001	1	2	1	1	1	1	3	1	1
	1	8.050	1	1	1	3	1	1	3	1	1
	2	4.549	1	1	1	3	2	1	3	1	1
	3	6.050	1	1	1	3	1	3	3	1	1
	4	3.039	1	1	3	3	2	3	3	1	1
	5	1.025	1	1	1	1	2	1	5	1	1
NO (nmol/mol)	0	0.0	1	2	1	1	1	1	2	1	1
	1	513.8	1	1	1	1	2	1	1	1	1
	2	393.8	1	1	1	1	2	1	1	1	1
	3	61.7	1	1	1	1	1	1	1	1	1
	4	39.1	1	1	1	1	1	1	1	1	1
	5	171.0	1	1	1	1	2	1	1	1	1
	6	120.8	1	1	1	1	1	1	1	1	1
	7	257.0	1	1	1	1	2	1	1	1	1
	8	170.5	1	1	1	1	2	1	1	1	1
	9	20.7	1	1	1	1	1	3	1	1	1
	10	10.2	1	2	1	1	1	3	1	1	1
NO2 (nmol/mol	0	-0.05	1	2	2	1	7	1	2	1	1
	2	121.847	1	1	1	1	2	1	1	1	1
	4	22.947	1	1	1	1	1	1	1	1	1
	6	52.537	1	1	1	1	1	1	1	1	1
	8	88.21	1	1	1	1	2	1	1	1	1
	10	11.08	1	2	1	1	1	1	1	1	1
O3 (nmol/mol)	0	0.0	1	1	1	1	1	1	1	1	1
	1	117.0	1	1	1	1	1	2	1	1	1
	2	22.5	1	1	1	1	2	1	1	1	1
	3	51.0	1	1	1	1	1	1	1	1	1
	4	85.1	1	1	1	1	1	1	1	1	1
	5	11.1	1	1	1	1	2	1	1	1	1
SO2 (nmol/mol	0	0.0	1	2	1	1	1	1	1	1	1
	1	8.7	1	2	1	1	1	1	1	1	1
	2	51.1	1	3	1	1	1	1	1	1	3
	3	19.9	1	1	1	1	1	1	1	1	1
	4	123.1	1	3	1	1	2	1	1	1	1
	5	3.5	1	2	1	1	1	1	1	1	1

Table 6: The general assessment of proficiency results.

5. 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 (σ_p) 86% of the results reported (Table 7) by AQUILA laboratories fall into category '1' and are good both in terms of measured values and evaluated uncertainties. Among the remaining results the majority presented good measured values, but the evaluated uncertainties were either too high, category '2' (7.9%), or too small, category '3' (5.4%) and there is a value in category '5' and one in category '7'.

	Categories %						
IE	1	2	3	4	5	6	7
Apr-08	68.4	18.1	7.3	1.0	1.0	2.6	1.6
Oct-08 (I)	37.9	40.8	14.2	0.6	3.6	1.0	1.9
Oct-08 (II)	34.3	38.9	23.7	1.0	2.0	0.0	0.0
Sep-09	60.8	29.9	3.1	4.1	1.0	1.0	0.0
Oct-09	85.0	5.7	7.5	0.4	1.4	0.0	0.0
Jun-10	84.6	8.1	4.4	0.7	2.3	0.0	0.0
Sep-11	86.0	7.9	5.4	0.0	0.3	0.0	0.3
Oct-11 (I)	78.5	12.5	7.6	0.0	1.3	0.0	0.0

Table 7: Flags summary

As in previous IEs, 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 IEs [20], [21], [22], [23], [24], [25] are 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 the present IE a high share of '1' results can be observed confirming the trend of the most recent IEs.

In this exercise there was only one unsatisfactory results in the z'-score evaluations (Table 8) for laboratory E at the zero level of NO2. Laboratory H obtained 1 questionable result for CO.

Inter-comparison	Site	Questionable	Unsatisfactory	Satisfactory
June-05	Ispra (IT)	2.3%	2.3%	95.5%
June-07	Ispra (IT)	1.9%	0.3%	97.8%
October-07	Essen (DE)	4.6%	2.2%	93.2%
April-08	Ispra (IT)	2.1%	4.1%	93.8%
October 2008_1	Ispra (IT)	4.2%	2.9%	92.9%
October 2008_2	Ispra (IT)	3.0%	0.0%	97.0%
September-09	Langen (DE)	4.7%	0.9%	94.3%
October-09	Ispra (IT)	1.8%	0.0%	98.2%
June-10	Ispra (IT)	3.0%	0.0%	97.0%
September-11	Ispra (IT)	0.3%	0.3%	99.7%
October-11	Ispra (IT)	1.3%	0.0%	98.7%

Table 8: Z'-score summary

Comparability of results among AQUILA participants at the highest concentration level, excluding outliers, is acceptable for all pollutants. CO measurements at concentration of 3μmol/mol showed less satisfactory results.
The relative reproducibility limits, at the highest studied concentration levels, are 7.3% for CO, 8.6% for O_3 and 2.9% for NO, 10.3% for NO_2 and 10.5% for SO_2 all within the objective derived from criteria imposed by the European Commission (σ_p).
During this IE the performance of all NRL has been quite good. Only two outliers have been identified at zero level for NO and NO_2 (Table 51).

6. References

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Annex A. Assigned values

The assigned values of tested concentration levels (run) were derived from ERLAPs 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].
ERLAP's SO_2, CO and NO analysers were calibrated according to the methodology described in the ISO 6143 [6]. Reference gas mixtures were produced from the primary reference materials (produced and certified by NMi Van Swinden Laboratorium) by dynamic dilution method using mass flow controllers [8]. All flows were measured with a certified molbloc/molbox1 system. For O_3 measurements, the analyzers 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_2 channel of NO_X analyser the GPT test was performed to establish the efficiency of NO_2-converter.
ERLAP's measurement results were validated by comparison to the group statistics (x* and s*) for every parameter and concentration level of the IE. These statistics are calculated from participants, applying the robust method described in the Annex C of the ISO 13528 [13]. The validation is taking into account ERLAP's measurement result (X) and its standard uncertainty (u_X) as given in expression 6 [13]:

$$\frac{\left|x^* - X\right|}{\sqrt{\frac{\left(1{,}25 \cdot s^*\right)^2}{p} + u_X^2}} < 2$$

Equation 6

Where 'x*' and 's*' represent robust average and robust standard deviation respectively and 'p' is the number of participants.
In Table 9 all inputs for expression 6 are given and all ERLAP's measurement results are confirmed to be valid.

As a group evaluation robust average (x*) and robust standard deviation (s*) were calculated (applying the procedure described in Annex C of ISO 13528) for each run, and are presented in the following table.

run	unit	X	uX'	x*	s*	p	val.
NO _0	nmol/mol	0.01	0.3	0.042	0.258	10	OK
NO _1	nmol/mol	513.79	5.38	519.901	5.252	10	OK
NO _2	nmol/mol	393.75	4.13	398.775	4.307	10	OK
NO _3	nmol/mol	61.72	0.73	61.396	1.482	10	OK
NO _4	nmol/mol	39.117	0.52	38.948	0.97	10	OK
NO _5	nmol/mol	170.973	2.11	171.267	1.862	10	OK
NO _6	nmol/mol	120.763	1.31	121.028	1.109	10	OK
NO _7	nmol/mol	256.983	2.73	258.202	2.462	10	OK
NO _8	nmol/mol	170.537	1.83	171.536	1.501	10	OK
NO _9	nmol/mol	20.657	0.51	20.319	0.789	10	OK
NO _10	nmol/mol	10.153	0.32	10.002	0.599	10	OK
NO2 _0	nmol/mol	-0.05	0.3	0.086	0.105	10	OK
NO2 _1	nmol/mol	1.233	7.09	1.282	0.794	10	OK
NO2 _2	nmol/mol	121.847	6.38	122.484	2.089	10	OK
NO2 _3	nmol/mol	0.243	0.92	0.349	0.293	10	OK
NO2 _4	nmol/mol	22.947	0.81	22.821	0.66	10	OK
NO2 _5	nmol/mol	1.737	2.65	1.522	0.742	10	OK
NO2 _6	nmol/mol	52.537	2.13	52.306	0.47	10	OK
NO2 _7	nmol/mol	1.15	3.59	0.963	0.699	10	OK
NO2 _8	nmol/mol	88.21	3.1	87.662	1.23	10	OK
NO2 _9	nmol/mol	0.463	0.58	0.472	0.204	10	OK
NO2 _10	nmol/mol	11.08	0.4	11.104	0.279	10	OK

run	unit	X	uX'	x*	s*	p	val.
CO _0	µmol/mol	-0.001	0.006	0.009	0.011	10	OK
CO _1	µmol/mol	8.0503	0.036	7.961	0.207	10	OK
CO _2	µmol/mol	4.5493	0.021	4.517	0.187	10	OK
CO _3	µmol/mol	6.0503	0.028	5.99	0.21	10	OK
CO _4	µmol/mol	3.0393	0.014	3.021	0.2	10	OK
CO _5	µmol/mol	1.0247	0.007	1.038	0.083	10	OK
O3 _0	nmol/mol	0.01	0.26	0.089	0.322	10	OK
O3 _1	nmol/mol	116.953	0.87	116.84	0.649	10	OK
O3 _2	nmol/mol	22.47	0.27	22.426	0.362	10	OK
O3 _3	nmol/mol	50.95	0.41	50.842	0.583	10	OK
O3 _4	nmol/mol	85.087	0.64	85.102	0.542	10	OK
O3 _5	nmol/mol	11.067	0.29	11.029	0.419	10	OK
SO2 _0	nmol/mol	0.03	0.32	0.027	0.139	10	OK
SO2 _1	nmol/mol	8.697	0.33	8.688	0.36	10	OK
SO2 _2	nmol/mol	51.067	0.45	51.075	1.768	10	OK
SO2 _3	nmol/mol	19.927	0.36	19.86	0.814	10	OK
SO2 _4	nmol/mol	123.063	0.8	123.195	2.338	10	OK
SO2 _5	nmol/mol	3.45	0.33	3.463	0.221	10	OK

Table 9: The validation of assigned values (X)
by comparison to the robust averages (x*) with taking into account the standard uncertainties of assigned values (uX'), and robust standard deviations (s*) as denoted by Equation 6.

The homogeneity of test gas was evaluated from measurements at the beginning and end of the distribution line. From the relative differences between beginning and end measurements, average and standard deviation were calculated, and the uncertainty of test gas due to lack of homogeneity was calculated as the sum of squares of these average and standard deviation. The upper and lower limits of bias due to homogeneity was evaluated to be smaller than 0.5% which constitutes the relative standard uncertainty of 0,3% of each concentration level. The standard uncertainties of assigned/reference values ($u_{X'}$) were calculated with Equation 7 and used in the proficiency evaluations of chapter 2.

$$u_{X'}^2 = u_X^2 + \left(X \cdot u_{homogeneity}\right)^2$$ **Equation 7**

Annex B. The results of the IE

In this annex are reported participant's results, presented both in tables and graphs. For each run, participants were asked to report 3 results representing 30 minutes measurement each (x_{ij}). 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_i) and standard deviation (s_i) of each participant are presented.
The assigned value is indicated on the graphs with the red line and the individual laboratories expanded uncertainties (Ux_i) are indicated with error bars.

Reported values for SO_2

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	0.03	-0.10	0.21	-0.03	-0.06	0.20	0.03	0.14	0.00	-0.15
u(xi) (nmol/mol)	0.58	1.30	1.00	0.50	0.60	0.00	0.32	1.00	0.50	0.54
U(xi) (nmol/mol)	1.16	2.50	2.00	1.00	1.20	0.01	0.64	2.00	1.00	1.08

Table 10: Reported values for SO_2 run 0.

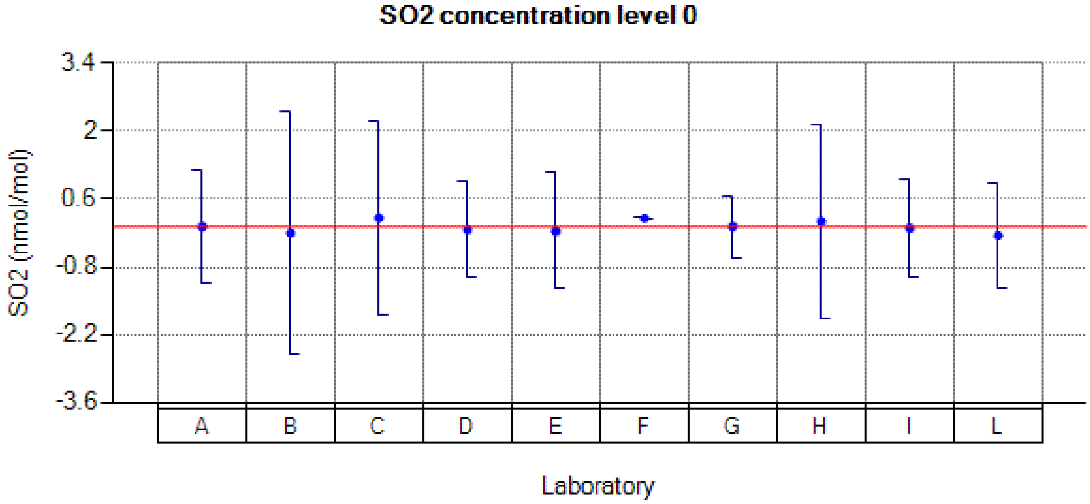

Figure 13: Reported values for SO_2 run 0.

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	8.49	9.00	9.24	8.35	8.92	8.45	8.65	8.75	8.65	7.54
xi,2 (nmol/mol)	8.61	9.20	9.16	8.34	8.95	8.49	8.70	8.80	8.62	7.48
xi,3 (nmol/mol)	8.59	9.10	9.07	8.33	8.95	8.52	8.74	8.75	8.69	7.62
Xi (nmol/mol)	8.56	9.10	9.15	8.34	8.94	8.48	8.69	8.76	8.65	7.54
Si (nmol/mol)	0.06	0.10	0.08	0.01	0.01	0.03	0.04	0.02	0.03	0.07
u(xi) (nmol/mol)	0.58	1.30	1.02	0.64	0.36	0.24	0.33	1.13	0.50	0.55
U(xi) (nmol/mol)	1.17	2.50	2.04	1.28	1.53	0.48	0.66	2.26	1.00	1.11

Table 11: Reported values for SO_2 run 1.

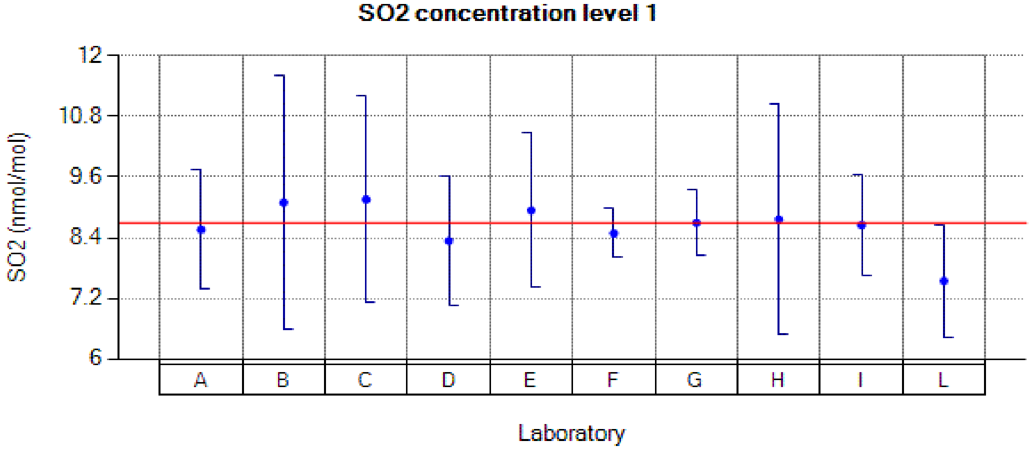

Figure 14: Reported values for SO_2 run 1.

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	50.61	54.10	52.39	50.04	52.73	50.60	51.06	49.02	51.00	48.87
xi,2 (nmol/mol)	50.57	54.30	53.08	50.25	52.83	50.70	51.06	49.14	51.09	48.68
xi,3 (nmol/mol)	50.58	54.10	52.82	50.38	52.90	50.75	51.08	49.21	51.15	49.01
Xi (nmol/mol)	50.58	54.16	52.76	50.22	52.82	50.68	51.06	49.12	51.08	48.85
Si (nmol/mol)	0.02	0.11	0.34	0.17	0.08	0.07	0.01	0.09	0.07	0.16
u(xi) (nmol/mol)	0.72	1.30	1.56	1.33	0.78	1.51	0.45	1.74	1.03	0.95
U(xi) (nmol/mol)	1.44	2.50	3.13	2.66	3.35	3.01	0.90	3.47	2.06	1.90

Table 12: Reported values for SO_2 run 2.

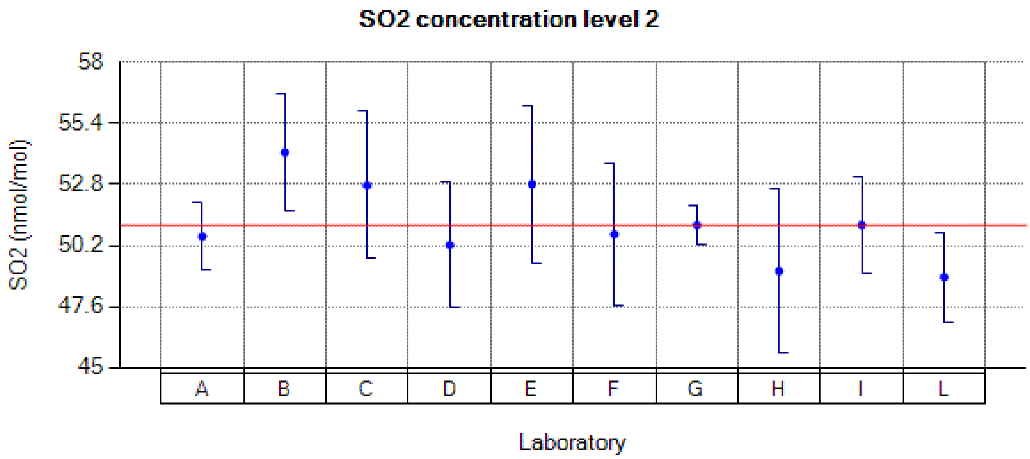

Figure 15: Reported values for SO_2 run 2.

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	19.63	21.00	20.75	19.48	20.57	19.60	19.96	19.15	19.88	18.49
xi,2 (nmol/mol)	19.75	21.10	20.75	19.43	20.60	19.75	19.91	19.11	19.81	18.39
xi,3 (nmol/mol)	19.61	20.80	20.66	19.47	20.50	19.80	19.91	19.04	19.92	18.49
Xi (nmol/mol)	19.66	20.96	20.72	19.46	20.55	19.71	19.92	19.10	19.87	18.45
Si (nmol/mol)	0.07	0.15	0.05	0.02	0.05	0.10	0.02	0.05	0.05	0.05
u(xi) (nmol/mol)	0.60	1.30	1.11	0.82	0.43	0.58	0.36	1.29	0.50	0.61
U(xi) (nmol/mol)	1.21	2.50	2.21	1.64	1.86	1.16	0.71	2.57	1.00	1.23

Table 13: Reported values for SO_2 run 3.

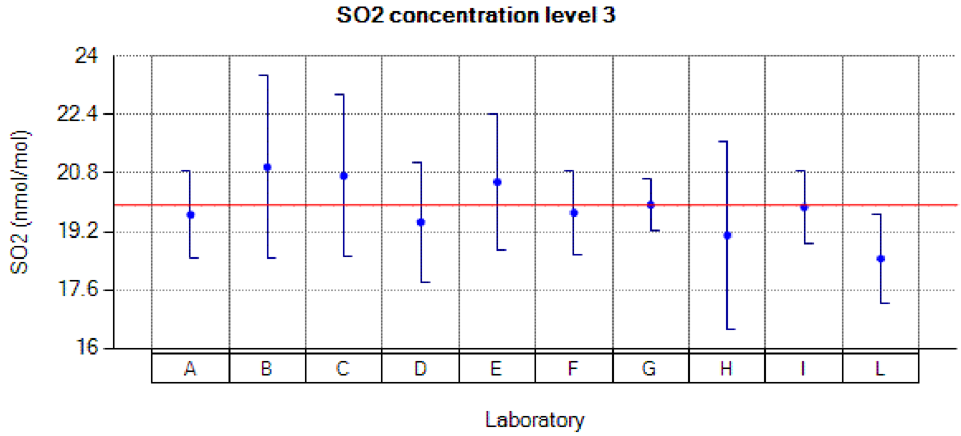

Figure 16: Reported values for SO_2 run 3.

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	121.85	130.60	127.18	121.32	127.56	122.15	122.96	121.64	123.29	119.39
xi,2 (nmol/mol)	122.09	130.40	127.12	121.48	127.47	122.85	122.94	121.70	123.28	119.13
xi,3 (nmol/mol)	122.28	129.70	127.48	121.50	127.62	123.25	123.29	121.87	123.58	119.54
Xi (nmol/mol)	122.07	130.23	127.26	121.43	127.55	122.75	123.06	121.73	123.38	119.35
Si (nmol/mol)	0.21	0.47	0.19	0.09	0.07	0.55	0.19	0.11	0.17	0.20
u(xi) (nmol/mol)	1.18	2.50	3.07	2.50	1.73	3.66	0.80	2.83	2.45	1.97
U(xi) (nmol/mol)	2.37	5.10	6.14	5.01	7.43	7.32	1.60	5.65	4.90	3.95

Table 14: Reported values for SO_2 run 4.

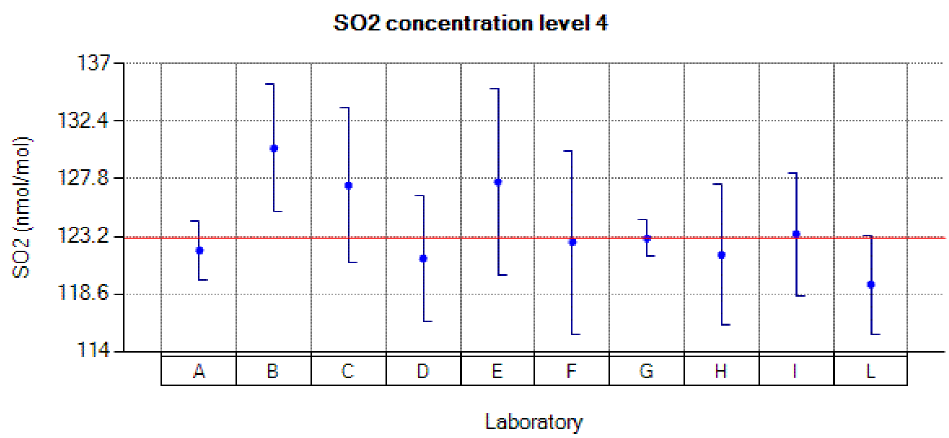

Figure 17: Reported values for SO_2 run 4.

values	laboratories									
	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	3.36	3.70	4.09	3.31	3.49	3.35	3.51	3.65	3.39	2.82
xi,2 (nmol/mol)	3.36	3.60	3.92	3.28	3.47	3.65	3.44	3.58	3.34	2.83
xi,3 (nmol/mol)	3.22	3.50	3.89	3.28	3.43	3.95	3.40	3.57	3.32	2.94
Xi (nmol/mol)	3.31	3.60	3.96	3.29	3.46	3.65	3.45	3.60	3.35	2.86
Si (nmol/mol)	0.08	0.10	0.10	0.01	0.03	0.30	0.05	0.04	0.03	0.06
u(xi) (nmol/mol)	0.58	1.30	1.00	0.55	0.34	0.10	0.33	1.05	0.50	0.54
U(xi) (nmol/mol)	1.16	2.50	2.01	1.11	1.46	0.20	0.65	2.11	1.00	1.09

Table 15: Reported values for SO_2 run 5.

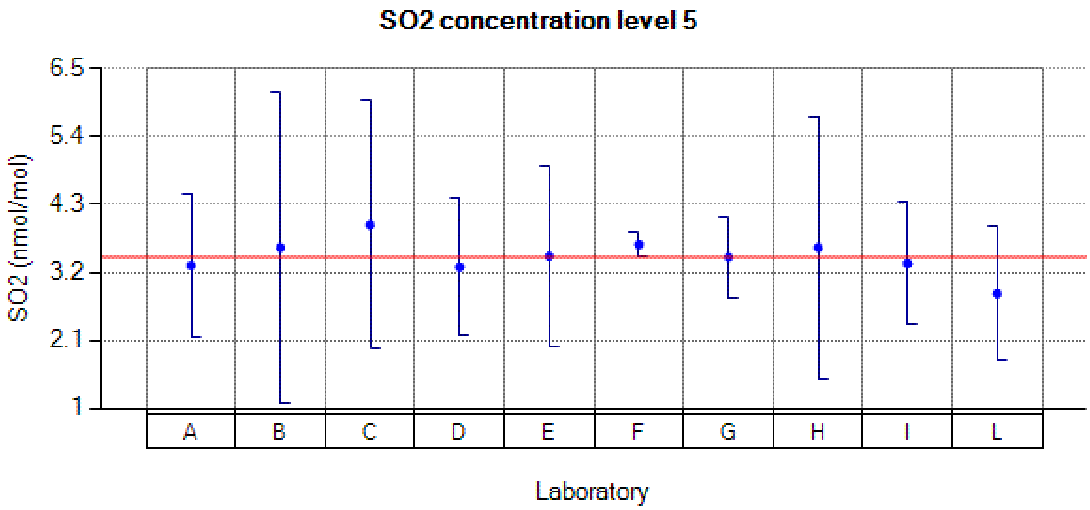

Figure 18: Reported values for SO_2 run 5.

Reported values for CO

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (µmol/mol)	0.002	0.000	0.075	-0.001	0.010	0.090	-0.001	0.100	-0.001	0.015
u(xi) (µmol/mol)	0.058	0.100	0.050	0.030	0.060	0.005	0.006	0.034	0.050	0.087
U(xi) (µmol/mol)	0.117	0.200	0.100	0.060	0.120	0.100	0.012	0.068	0.100	0.174

Table 16: Reported values for CO run 0.

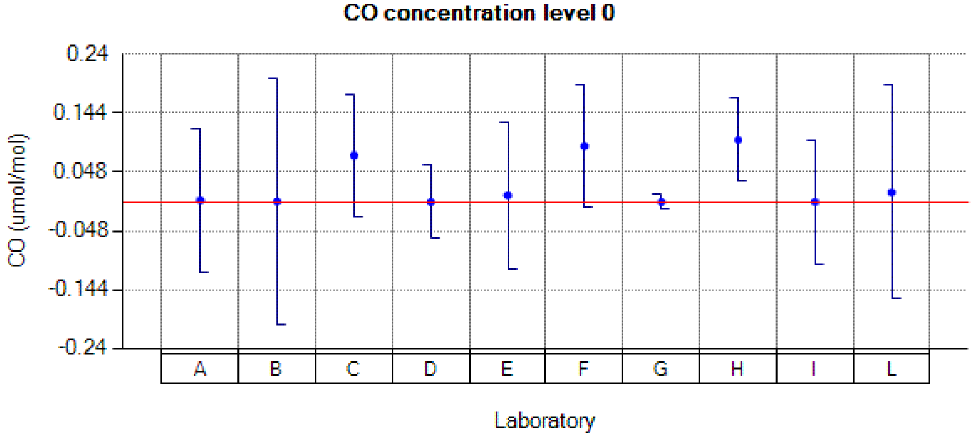

Figure 19: Reported values for CO run 0.

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (µmol/mol)	8.080	8.000	7.794	7.566	7.853	7.551	8.050	8.332	7.999	8.102
xi,2 (µmol/mol)	8.090	8.000	7.794	7.562	7.858	7.659	8.052	8.339	8.001	8.111
xi,3 (µmol/mol)	8.092	8.000	7.784	7.560	7.865	7.825	8.049	8.342	8.003	8.115
Xi (µmol/mol)	8.087	8.000	7.791	7.563	7.859	7.678	8.050	8.338	8.001	8.109
Si (µmol/mol)	0.006	0.000	0.006	0.003	0.006	0.138	0.002	0.005	0.002	0.007
u(xi) (µmol/mol)	0.058	0.100	0.185	0.145	0.117	0.214	0.036	0.089	0.050	0.233
U(xi) (µmol/mol)	0.117	0.200	0.369	0.290	0.505	0.428	0.072	0.178	0.100	0.467

Table 17: Reported values for CO run 1.

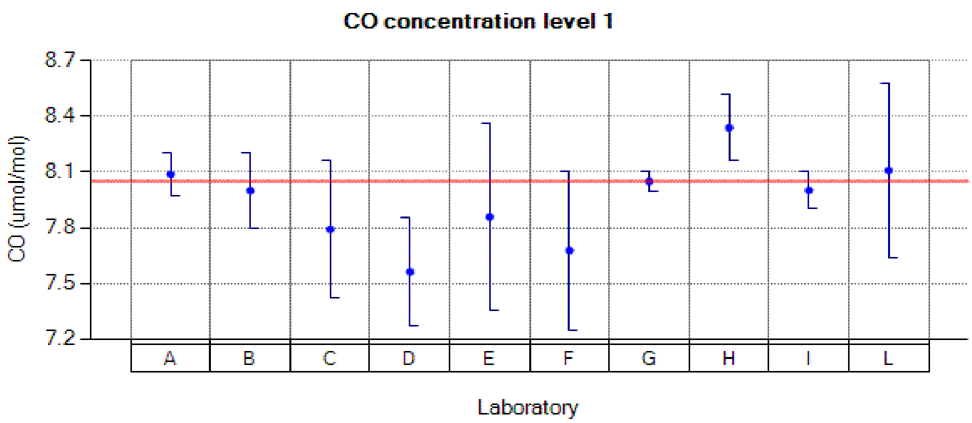

Figure 20: Reported values for CO run 1.

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (µmol/mol)	4.578	4.620	4.345	4.275	4.464	4.285	4.550	4.841	4.522	4.675
xi,2 (µmol/mol)	4.578	4.620	4.335	4.270	4.468	4.358	4.550	4.842	4.521	4.688
xi,3 (µmol/mol)	4.574	4.620	4.315	4.270	4.470	4.386	4.548	4.845	4.522	4.685
Xi (µmol/mol)	4.577	4.620	4.332	4.272	4.467	4.343	4.549	4.843	4.522	4.683
Si (µmol/mol)	0.002	0.000	0.015	0.003	0.003	0.052	0.001	0.002	0.001	0.007
u(xi) (µmol/mol)	0.036	0.100	0.111	0.095	0.102	0.121	0.021	0.066	0.050	0.151
U(xi) (µmol/mol)	0.072	0.200	0.221	0.190	0.437	0.242	0.041	0.131	0.100	0.303

Table 18: Reported values for CO run 2.

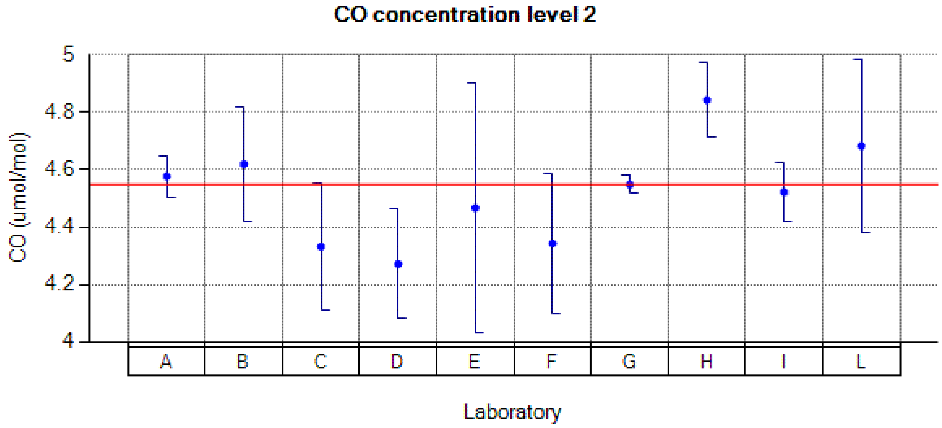

Figure 21: Reported values for CO run 2.

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (µmol/mol)	6.085	6.050	5.837	5.670	5.900	5.625	6.048	6.338	6.017	6.172
xi,2 (µmol/mol)	6.088	6.050	5.837	5.672	5.903	5.685	6.048	6.341	6.020	6.169
xi,3 (µmol/mol)	6.092	6.050	5.847	5.671	5.905	5.780	6.055	6.341	6.021	6.171
Xi (µmol/mol)	6.088	6.050	5.840	5.671	5.903	5.697	6.050	6.340	6.019	6.171
Si (µmol/mol)	0.004	0.000	0.006	0.001	0.003	0.078	0.004	0.002	0.002	0.002
u(xi) (µmol/mol)	0.045	0.100	0.142	0.116	0.107	0.163	0.028	0.076	0.050	0.186
U(xi) (µmol/mol)	0.091	0.200	0.285	0.232	0.463	0.326	0.055	0.151	0.100	0.373

Table 19: Reported values for CO run 3.

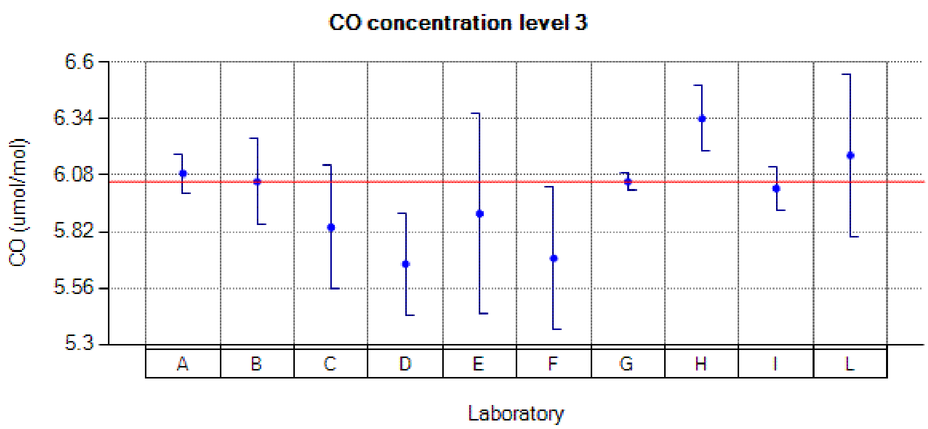

Figure 22: Reported values for CO run 3.

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (µmol/mol)	3.062	3.180	2.753	2.849	2.984	2.796	3.041	3.333	3.024	3.163
xi,2 (µmol/mol)	3.062	3.180	2.743	2.850	2.985	2.805	3.040	3.329	3.025	3.163
xi,3 (µmol/mol)	3.067	3.180	2.743	2.850	2.986	2.903	3.037	3.332	3.027	3.169
Xi (µmol/mol)	3.064	3.180	2.746	2.850	2.985	2.835	3.039	3.331	3.025	3.165
Si (µmol/mol)	0.003	0.000	0.006	0.001	0.001	0.059	0.002	0.002	0.002	0.003
u(xi) (µmol/mol)	0.027	0.100	0.080	0.073	0.097	0.084	0.014	0.056	0.050	0.121
U(xi) (µmol/mol)	0.055	0.200	0.160	0.147	0.417	0.168	0.028	0.111	0.100	0.243

Table 20: Reported values for CO run 4.

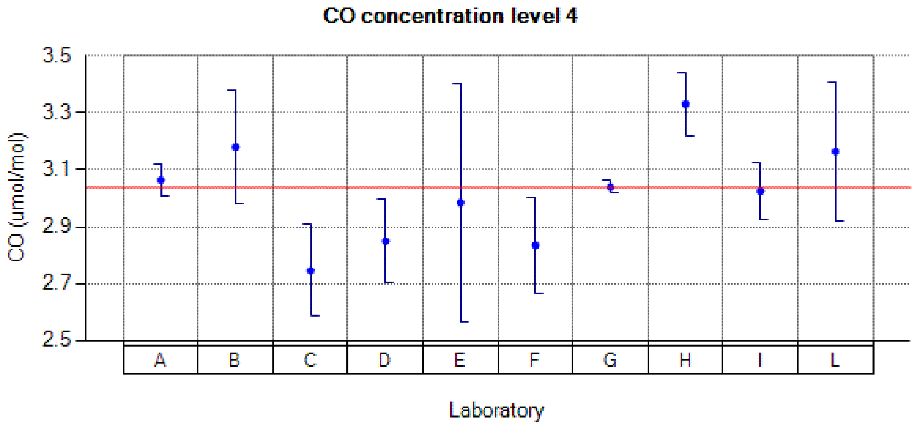

Figure 23: Reported values for CO run 4.

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (µmol/mol)	1.036	1.130	0.945	0.963	1.006	0.965	1.025	1.303	1.020	1.137
xi,2 (µmol/mol)	1.035	1.130	0.955	0.964	1.007	0.975	1.025	1.302	1.020	1.135
xi,3 (µmol/mol)	1.041	1.130	0.945	0.964	1.007	0.980	1.024	1.304	1.020	1.138
Xi (µmol/mol)	1.037	1.130	0.948	0.964	1.007	0.973	1.025	1.303	1.020	1.137
Si (µmol/mol)	0.003	0.000	0.006	0.001	0.001	0.008	0.001	0.001	0.000	0.002
u(xi) (µmol/mol)	0.019	0.100	0.054	0.045	0.094	0.027	0.007	0.042	0.050	0.092
U(xi) (µmol/mol)	0.038	0.200	0.109	0.089	0.403	0.054	0.014	0.084	0.100	0.185

Table 21: Reported values for CO run 5.

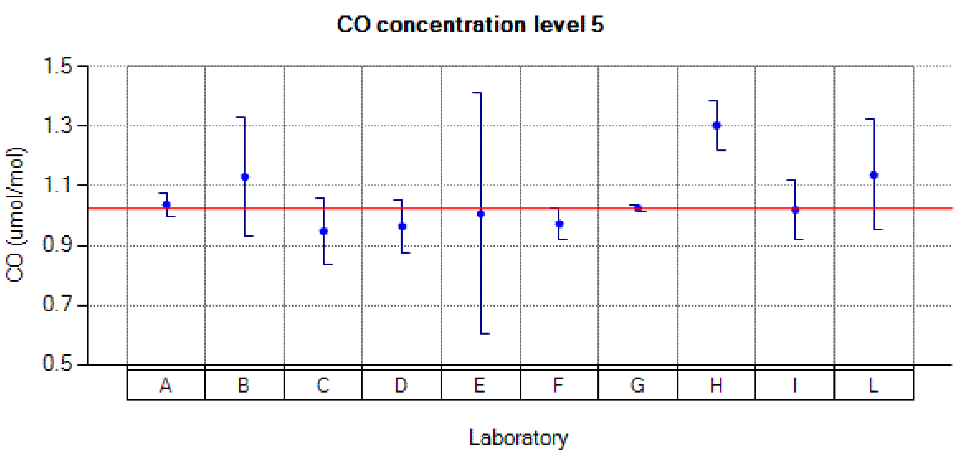

Figure 24: Reported values for CO run 5.

Reported values for O_3

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	0.40	0.50	-1.00	-0.10	0.05	0.20	0.01	0.36	-0.22	0.08
u(xi) (nmol/mol)	0.62	0.90	0.50	1.00	0.60	0.01	0.26	0.18	0.40	0.31
U(xi) (nmol/mol)	1.24	1.90	1.00	2.00	1.20	0.02	0.51	0.36	0.80	0.62

Table 22: Reported values for O_3 run 0.

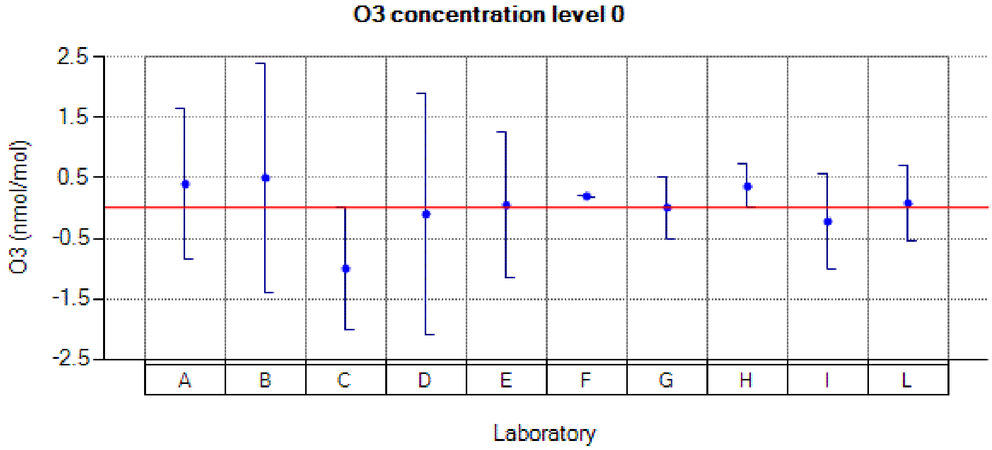

Figure 25: Reported values for O3 run 0.

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	116.13	117.50	118.73	116.12	116.88	117.07	116.94	116.30	116.58	116.91
xi,2 (nmol/mol)	116.18	117.60	119.06	116.41	116.97	117.15	117.06	116.33	116.69	117.07
xi,3 (nmol/mol)	115.98	117.40	118.77	116.21	116.78	117.35	116.86	115.99	116.31	116.98
Xi (nmol/mol)	116.09	117.50	118.85	116.24	116.87	117.19	116.95	116.20	116.52	116.98
Si (nmol/mol)	0.10	0.10	0.18	0.14	0.09	0.14	0.10	0.18	0.19	0.08
u(xi) (nmol/mol)	1.45	1.90	2.43	2.74	1.19	3.46	0.87	1.71	1.40	1.57
U(xi) (nmol/mol)	2.91	3.90	4.86	5.49	5.12	6.92	1.74	3.43	2.80	3.15

Table 23: Reported values for O_3 run 1

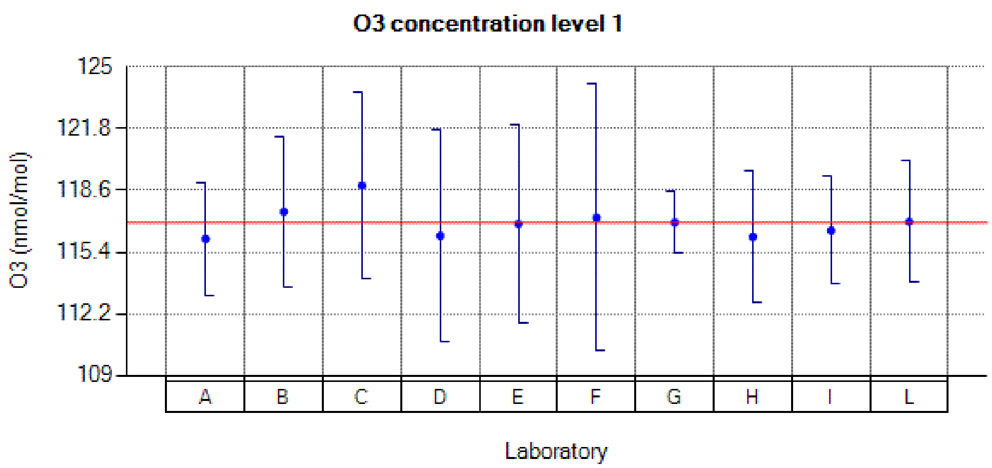

Figure 26: Reported values for O_3 run 1.

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	22.28	22.70	23.23	22.36	22.37	22.65	22.43	21.83	21.78	22.51
xi,2 (nmol/mol)	22.26	22.70	23.10	22.39	22.33	22.75	22.47	21.84	21.72	22.55
xi,3 (nmol/mol)	22.26	22.70	23.15	22.39	22.41	22.85	22.51	21.90	21.83	22.52
Xi (nmol/mol)	22.26	22.70	23.16	22.38	22.37	22.75	22.47	21.85	21.77	22.52
Si (nmol/mol)	0.01	0.00	0.06	0.01	0.04	0.10	0.04	0.03	0.05	0.02
u(xi) (nmol/mol)	0.67	0.90	0.68	1.34	0.68	0.67	0.27	0.46	0.40	0.43
U(xi) (nmol/mol)	1.35	1.90	1.36	2.67	2.93	1.34	0.54	0.93	0.80	0.88

Table 24: Reported values for O_3 run 2.

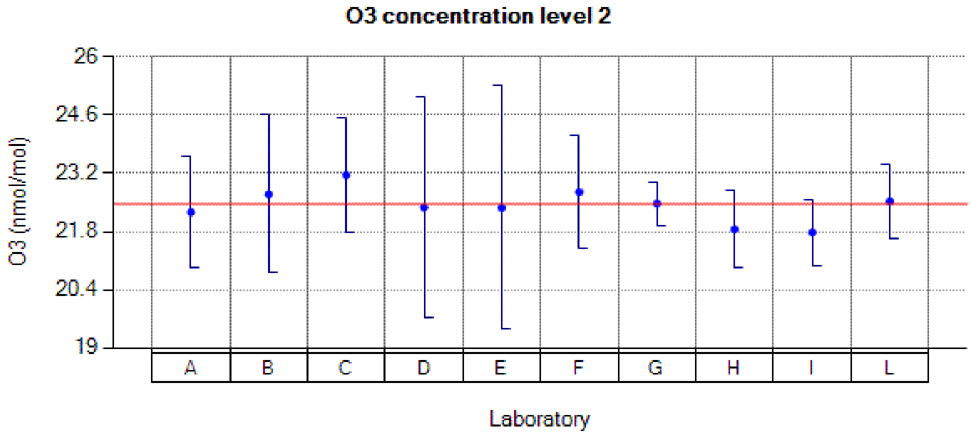

Figure 27: Reported values for O_3 run 2.

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	50.35	51.10	51.97	50.56	50.63	51.05	50.88	50.12	50.06	50.91
xi,2 (nmol/mol)	50.39	51.30	52.05	50.62	50.83	51.45	50.96	50.15	50.32	51.00
xi,3 (nmol/mol)	50.41	51.20	52.08	50.71	50.90	51.76	51.01	50.26	50.20	50.99
Xi (nmol/mol)	50.38	51.20	52.03	50.63	50.78	51.42	50.95	50.17	50.19	50.96
Si (nmol/mol)	0.03	0.10	0.05	0.07	0.14	0.35	0.06	0.07	0.13	0.04
u(xi) (nmol/mol)	0.85	0.90	1.15	1.76	0.81	1.51	0.41	0.84	0.80	0.74
U(xi) (nmol/mol)	1.70	1.90	2.31	3.52	3.47	3.02	0.81	1.68	1.60	1.49

Table 25: Reported values for O_3 run 3.

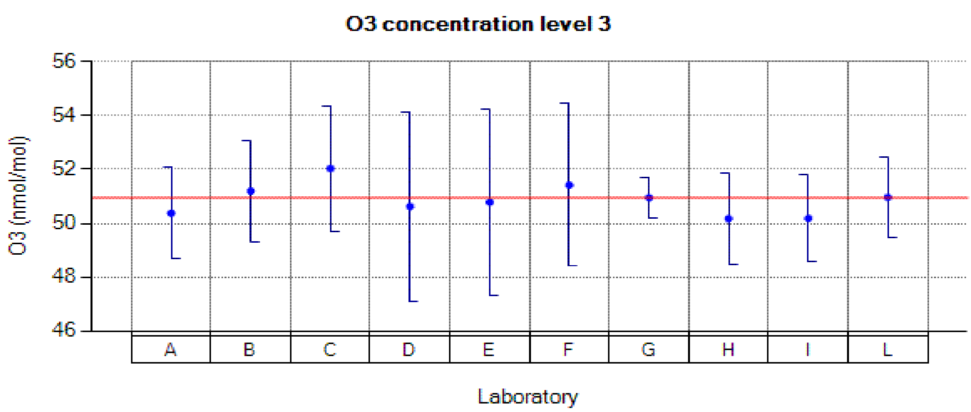

Figure 28: Reported values for O_3 run 3.

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	84.36	85.40	86.76	84.89	84.97	85.35	85.02	84.31	84.59	85.05
xi,2 (nmol/mol)	84.56	85.60	86.93	85.30	85.14	85.50	85.14	84.35	84.67	85.20
xi,3 (nmol/mol)	84.56	85.50	86.60	85.32	85.18	85.72	85.10	84.53	84.77	85.22
Xi (nmol/mol)	84.49	85.50	86.76	85.17	85.09	85.52	85.08	84.39	84.67	85.15
Si (nmol/mol)	0.11	0.10	0.16	0.24	0.11	0.18	0.06	0.11	0.09	0.09
u(xi) (nmol/mol)	1.14	1.40	1.81	2.28	1.00	2.54	0.64	1.29	1.00	1.17
U(xi) (nmol/mol)	2.29	2.80	3.61	4.56	4.28	5.08	1.28	2.59	2.00	2.34

Table 26: Reported values for O_3 run 4.

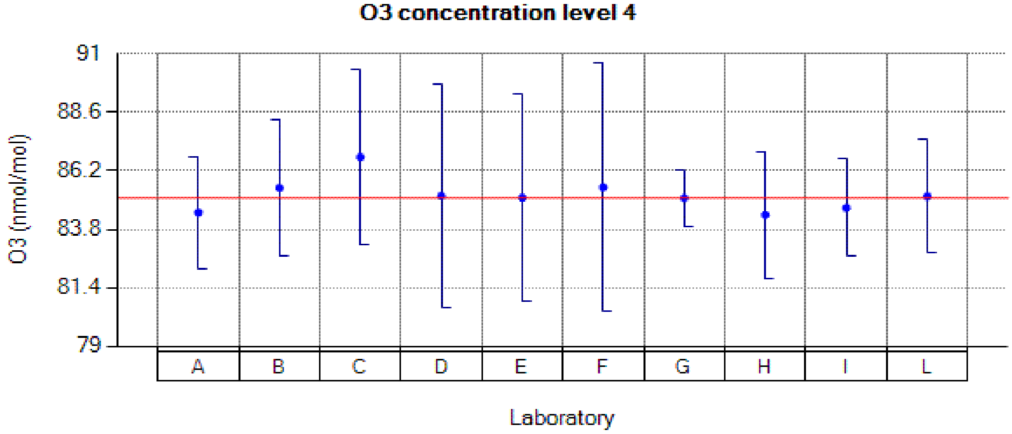

Figure 29: Reported values for O_3 run 4.

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	10.79	11.30	11.67	11.09	10.86	11.25	11.01	10.44	10.34	10.90
xi,2 (nmol/mol)	10.77	11.30	11.59	11.25	10.88	11.40	11.05	10.51	10.39	11.02
xi,3 (nmol/mol)	10.83	11.20	11.75	11.44	10.89	11.80	11.14	10.51	10.43	11.04
Xi (nmol/mol)	10.79	11.26	11.67	11.26	10.87	11.48	11.06	10.48	10.38	10.98
Si (nmol/mol)	0.03	0.05	0.08	0.17	0.01	0.28	0.06	0.04	0.04	0.07
u(xi) (nmol/mol)	0.63	0.90	0.55	1.17	0.65	0.33	0.29	0.31	0.40	0.34
U(xi) (nmol/mol)	1.26	1.90	1.10	2.34	2.78	0.66	0.57	0.63	0.80	0.69

Table 27: Reported values for O_3 run 5.

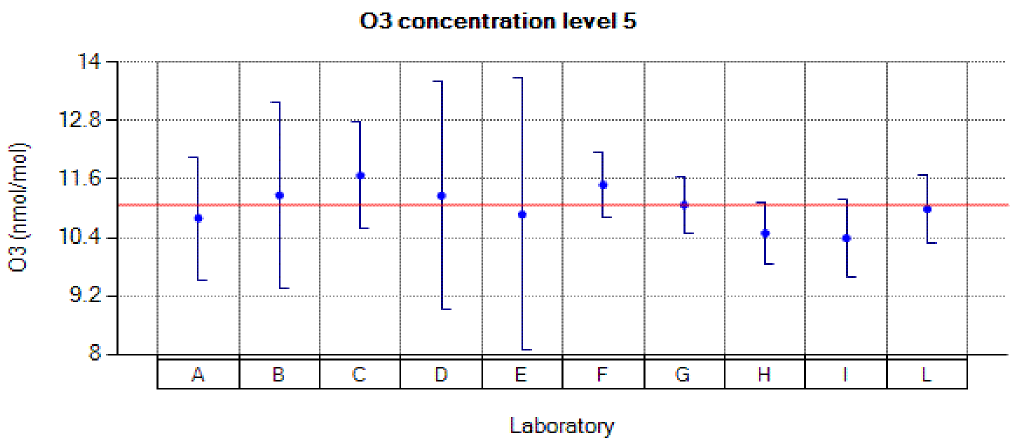

Figure 30: Reported values for O_3 run 5.

Reported values for NO

values	laboratories									
	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	0.00	0.10	-1.83	-0.43	0.73	0.20	0.01	0.61	-0.09	0.06
u(xi) (nmol/mol)	0.58	1.30	1.00	0.50	0.60	0.02	0.30	1.01	0.50	0.17
U(xi) (nmol/mol)	1.16	2.60	2.00	1.00	1.20	0.04	0.59	2.01	1.00	0.35

Table 28: Reported values for NO run 0.

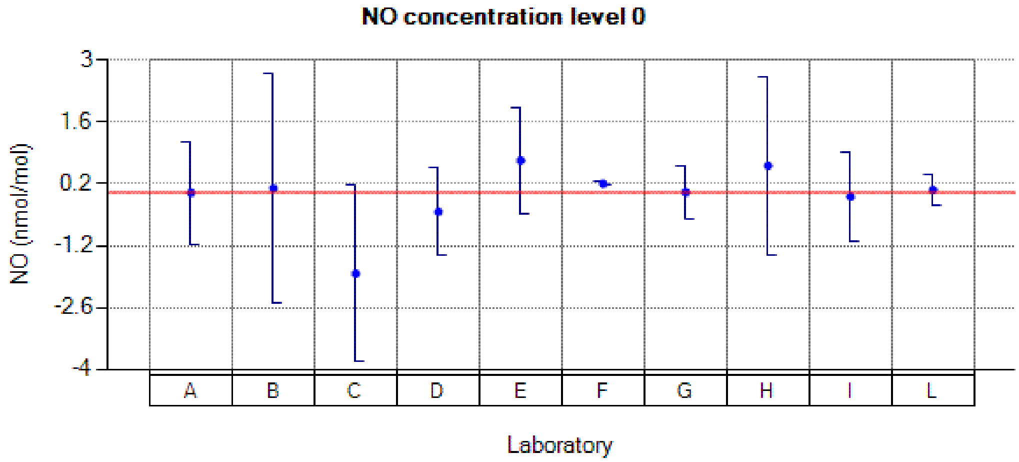

Figure 31: Reported values for NO run 0.

values	laboratories									
	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	515.09	519.20	512.52	521.04	517.29	525.37	513.42	524.42	517.80	525.00
xi,2 (nmol/mol)	516.22	521.20	513.14	521.65	517.65	526.79	513.82	524.66	518.56	525.40
xi,3 (nmol/mol)	515.67	523.10	516.06	521.69	519.30	526.38	514.13	524.97	519.58	525.90
Xi (nmol/mol)	515.66	521.16	513.90	521.46	518.08	526.18	513.79	524.68	518.64	525.43
Si (nmol/mol)	0.56	1.95	1.89	0.36	1.07	0.73	0.35	0.27	0.89	0.45
u(xi) (nmol/mol)	3.71	7.80	11.76	12.67	7.24	11.99	5.38	6.25	2.95	8.33
U(xi) (nmol/mol)	7.43	15.60	23.52	25.35	31.17	23.98	10.77	12.49	5.90	16.65

Table 29: Reported values for NO run 1.

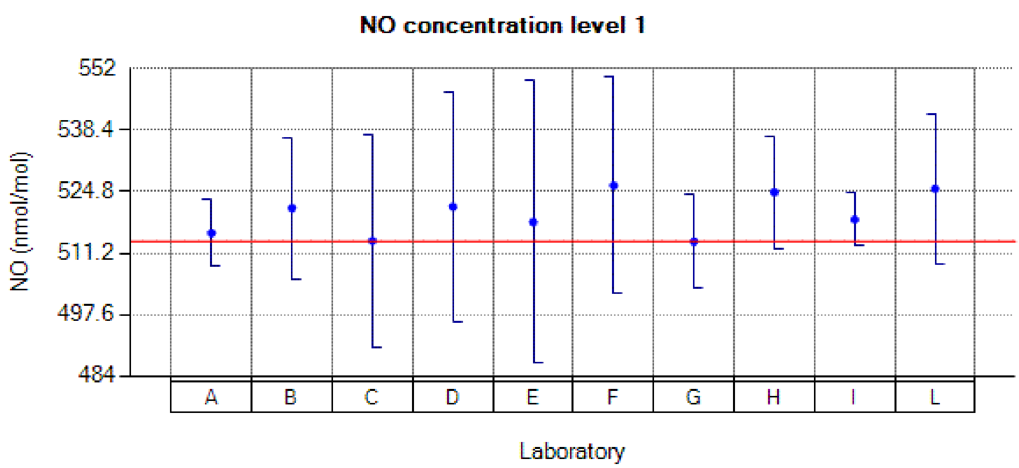

Figure 32: Reported values for NO run 1.

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	393.88	399.90	394.46	399.52	398.04	402.79	393.90	402.93	398.09	403.80
xi,2 (nmol/mol)	393.72	399.30	394.62	399.41	398.76	402.16	393.58	402.96	397.85	404.00
xi,3 (nmol/mol)	394.03	399.40	394.64	399.37	399.01	403.85	393.77	403.24	398.45	403.82
Xi (nmol/mol)	393.87	399.53	394.57	399.43	398.60	402.93	393.75	403.04	398.13	403.87
Si (nmol/mol)	0.15	0.32	0.09	0.07	0.50	0.85	0.16	0.17	0.30	0.11
u(xi) (nmol/mol)	2.86	6.00	9.05	9.87	5.55	9.15	4.13	5.03	2.21	6.40
U(xi) (nmol/mol)	5.73	12.00	18.11	19.73	23.88	18.30	8.26	10.06	4.42	12.81

Table 30: Reported values for NO run 2.

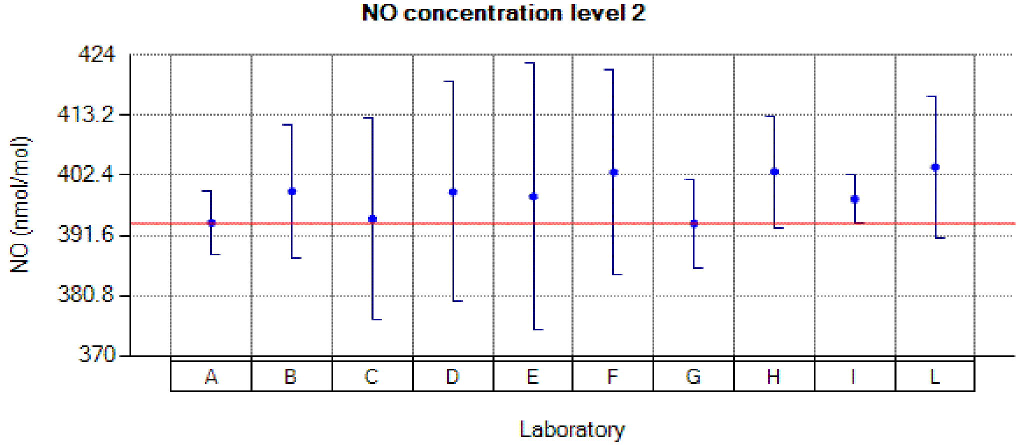

Figure 33: Reported values for NO run 2.

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	61.68	61.00	59.29	60.73	61.06	58.18	61.64	63.05	62.60	62.74
xi,2 (nmol/mol)	61.72	61.00	59.42	60.70	61.24	59.21	61.72	63.22	62.73	62.80
xi,3 (nmol/mol)	61.66	61.10	60.01	60.76	61.34	59.65	61.80	63.18	62.64	63.12
Xi (nmol/mol)	61.68	61.03	59.57	60.73	61.21	59.01	61.72	63.15	62.65	62.88
Si (nmol/mol)	0.03	0.05	0.38	0.03	0.14	0.75	0.08	0.08	0.06	0.20
u(xi) (nmol/mol)	0.73	1.30	1.69	2.08	0.94	1.30	0.73	1.63	0.63	1.01
U(xi) (nmol/mol)	1.46	2.60	3.37	4.15	4.07	2.60	1.46	3.26	1.26	2.01

Table 31: Reported values for NO run 3.

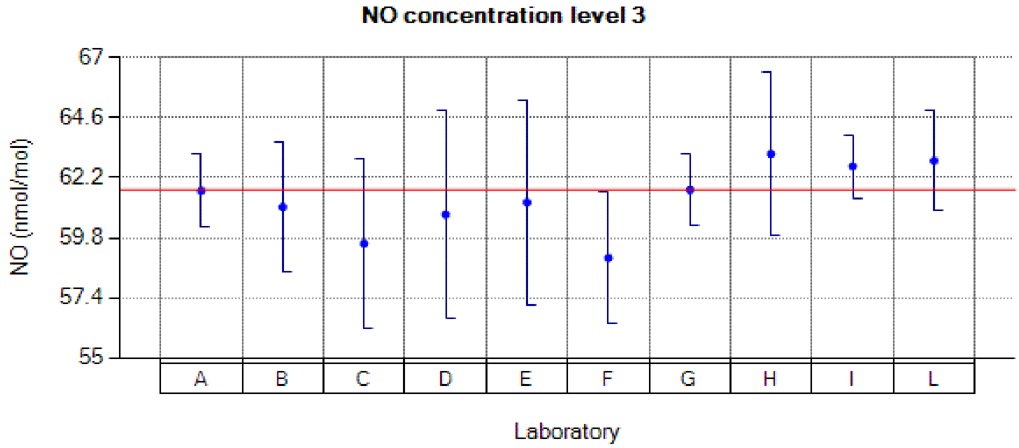

Figure 34: Reported values for NO run 3.

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	38.95	38.80	37.62	37.69	38.84	38.10	39.05	40.13	39.58	40.11
xi,2 (nmol/mol)	38.91	38.80	37.42	37.91	38.90	38.32	39.13	40.17	39.58	39.99
xi,3 (nmol/mol)	39.02	38.90	37.68	37.85	38.76	38.96	39.17	40.35	39.72	40.01
Xi (nmol/mol)	38.96	38.83	37.57	37.81	38.83	38.46	39.11	40.21	39.62	40.03
Si (nmol/mol)	0.05	0.05	0.13	0.11	0.07	0.44	0.06	0.11	0.08	0.06
u(xi) (nmol/mol)	0.64	1.30	1.32	1.55	0.68	0.86	0.52	1.40	0.50	0.65
U(xi) (nmol/mol)	1.29	2.60	2.63	3.10	2.91	1.72	1.05	2.80	1.00	1.30

Table 32: Reported values for NO run 4.

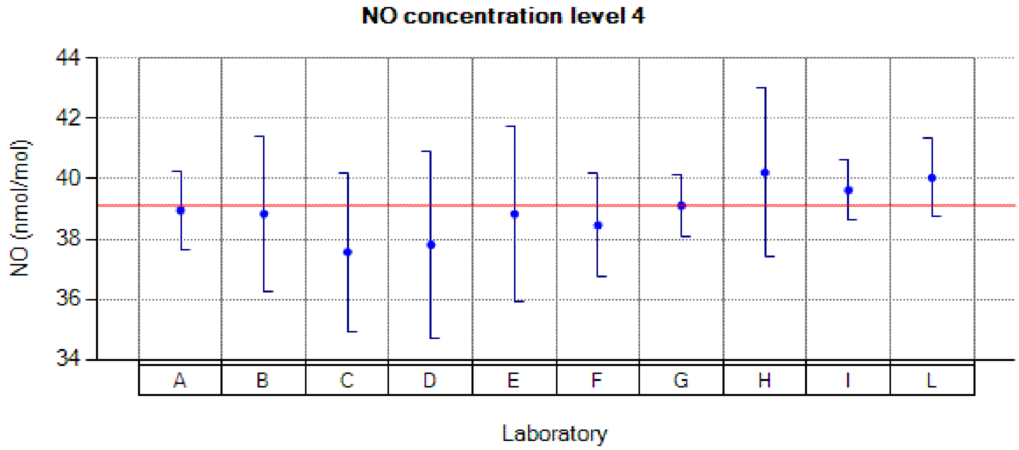

Figure 35: Reported values for NO run 4.

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	168.01	169.00	167.49	169.26	167.43	171.09	169.33	172.36	171.54	170.99
xi,2 (nmol/mol)	170.46	171.30	169.74	171.69	170.30	172.25	171.64	175.00	173.90	173.31
xi,3 (nmol/mol)	170.67	171.70	169.98	171.99	170.87	172.36	171.95	175.08	174.28	173.51
Xi (nmol/mol)	169.71	170.66	169.07	170.98	169.53	171.90	170.97	174.14	173.24	172.60
Si (nmol/mol)	1.47	1.45	1.37	1.49	1.84	0.70	1.43	1.54	1.48	1.40
u(xi) (nmol/mol)	1.35	2.60	3.98	4.61	2.62	3.87	2.11	2.74	1.77	2.75
U(xi) (nmol/mol)	2.70	5.10	7.97	9.22	11.26	7.74	4.23	5.48	3.54	5.51

Table 33: Reported values for NO run 5.

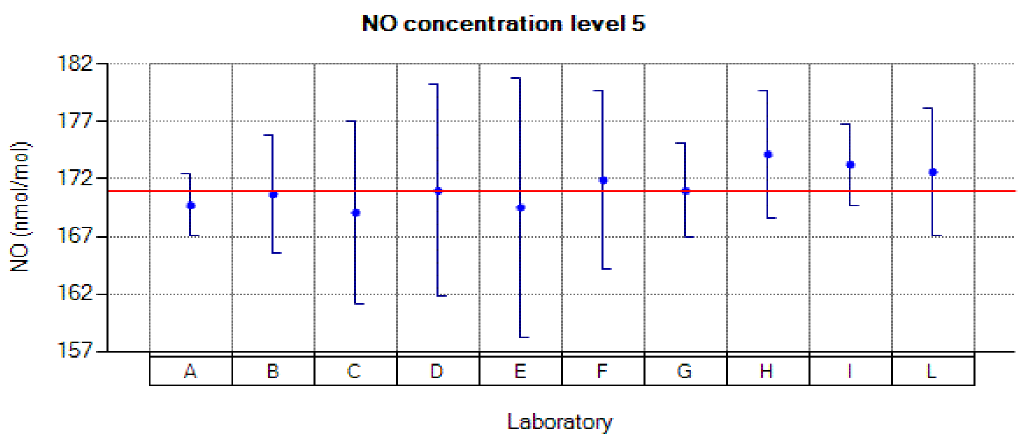

Figure 36: Reported values for NO run 5.

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	119.84	120.70	119.96	120.49	120.86	120.93	120.93	123.51	122.53	122.31
xi,2 (nmol/mol)	119.83	120.50	119.52	120.44	120.70	121.15	120.72	123.41	122.50	122.34
xi,3 (nmol/mol)	119.64	120.50	120.01	120.35	120.83	121.63	120.64	123.32	122.46	121.95
Xi (nmol/mol)	119.77	120.56	119.83	120.42	120.79	121.23	120.76	123.41	122.49	122.20
Si (nmol/mol)	0.11	0.11	0.27	0.07	0.08	0.35	0.15	0.09	0.03	0.21
u(xi) (nmol/mol)	1.03	1.80	2.91	3.45	1.73	2.70	1.31	2.23	1.23	1.94
U(xi) (nmol/mol)	2.07	3.60	5.82	6.90	7.43	5.40	2.62	4.47	2.46	3.89

Table 34: Reported values for NO run 6.

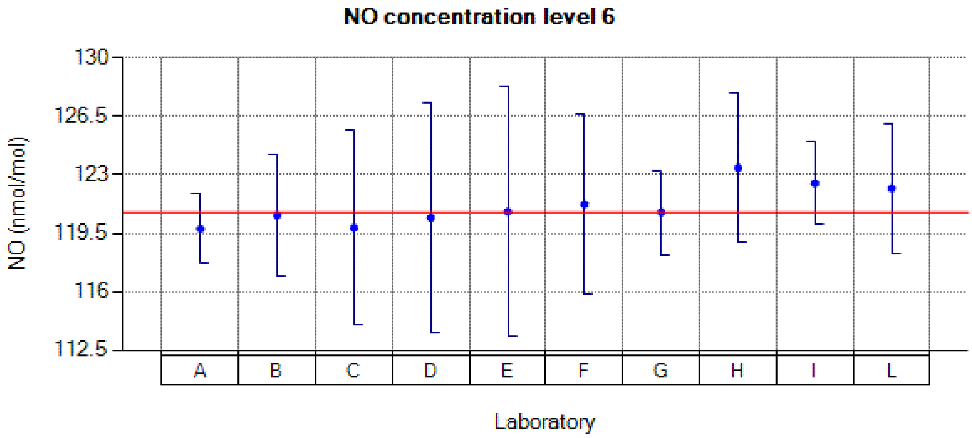

Figure 37: Reported values for NO run 6.

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	254.82	257.80	255.01	257.84	255.71	259.96	256.77	261.37	260.05	257.49
xi,2 (nmol/mol)	255.47	258.50	255.56	258.76	256.91	260.15	257.08	262.16	260.55	258.41
xi,3 (nmol/mol)	255.87	258.50	256.07	258.56	257.03	260.80	257.10	262.39	260.80	258.80
Xi (nmol/mol)	255.38	258.26	255.54	258.38	256.55	260.30	256.98	261.97	260.46	258.23
Si (nmol/mol)	0.53	0.40	0.53	0.48	0.73	0.44	0.18	0.53	0.38	0.67
u(xi) (nmol/mol)	1.91	3.90	5.91	6.62	3.62	5.90	2.73	3.60	1.49	4.10
U(xi) (nmol/mol)	3.82	7.80	11.83	13.24	15.56	11.80	5.45	7.24	2.98	8.21

Table 35: Reported values for NO run 7.

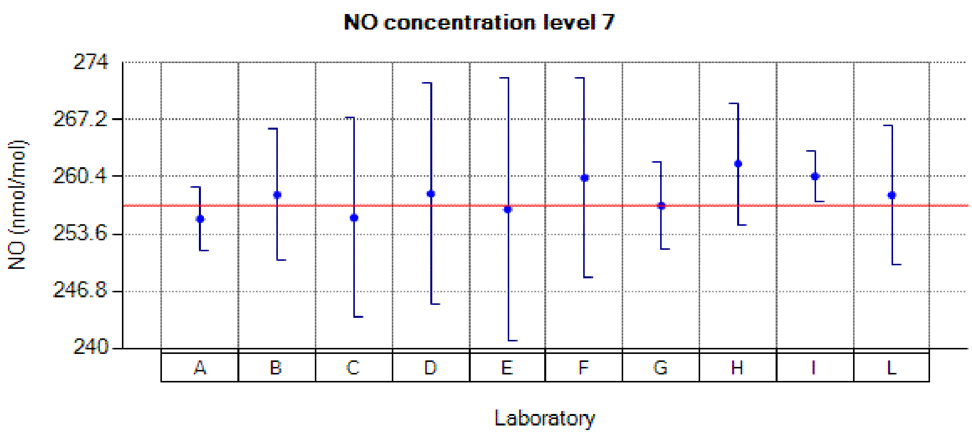

Figure 38: Reported values for NO run 7.

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	169.51	171.80	170.94	171.15	171.94	171.16	170.87	174.62	173.41	173.00
xi,2 (nmol/mol)	168.95	171.40	170.29	170.51	171.44	171.92	170.25	174.14	172.72	172.68
xi,3 (nmol/mol)	169.29	171.10	170.35	170.60	171.37	172.15	170.49	174.26	172.88	172.60
Xi (nmol/mol)	169.25	171.43	170.52	170.75	171.58	171.74	170.53	174.34	173.00	172.76
Si (nmol/mol)	0.28	0.35	0.35	0.34	0.31	0.51	0.31	0.25	0.36	0.21
u(xi) (nmol/mol)	1.34	2.60	4.02	4.61	2.43	3.86	1.83	2.74	1.02	2.74
U(xi) (nmol/mol)	2.68	5.10	8.03	9.21	10.44	7.72	3.66	5.49	2.04	5.48

Table 36: Reported values for NO run 8.

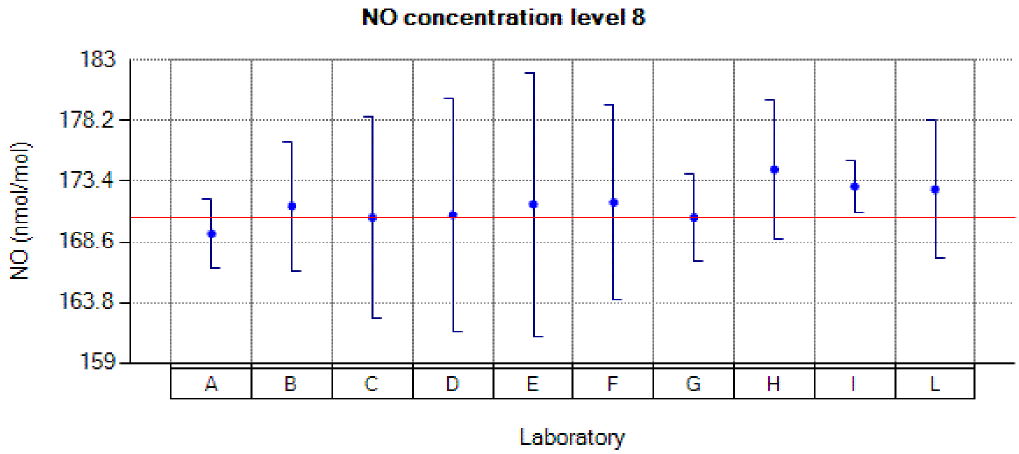

Figure 39: Reported values for NO run 8.

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	20.02	19.60	18.19	18.55	19.56	19.10	19.99	20.70	20.22	20.12
xi,2 (nmol/mol)	20.83	20.50	18.92	19.36	20.49	19.15	20.94	21.61	21.21	21.21
xi,3 (nmol/mol)	21.04	20.60	19.00	19.51	20.53	19.25	21.04	21.89	21.31	21.20
Xi (nmol/mol)	20.63	20.23	18.70	19.14	20.19	19.16	20.65	21.40	20.91	20.84
Si (nmol/mol)	0.53	0.55	0.44	0.51	0.54	0.07	0.58	0.62	0.60	0.62
u(xi) (nmol/mol)	0.60	1.30	1.09	1.12	0.58	0.43	0.51	1.21	0.64	0.36
U(xi) (nmol/mol)	1.20	2.60	2.17	2.24	2.52	0.86	1.02	2.43	1.28	0.73

Table 37: Reported values for NO run 9.

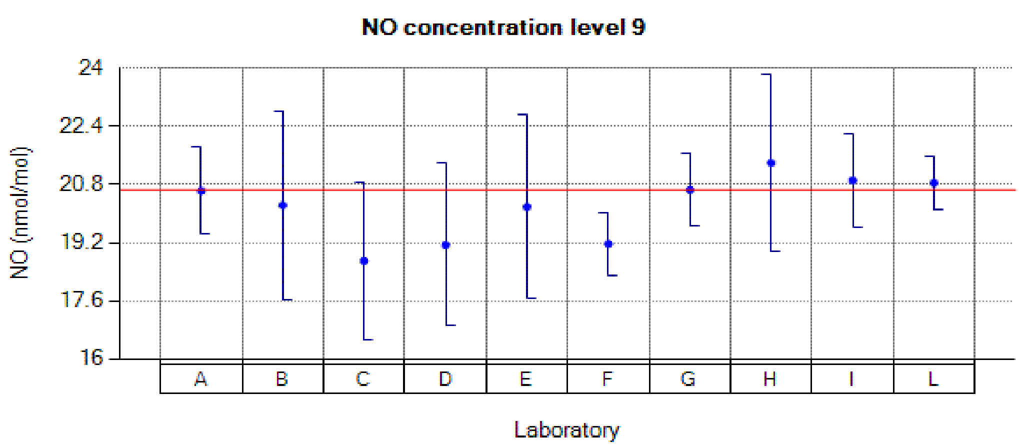

Figure 40: Reported values for NO run 9.

values	laboratories									
	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	10.24	10.10	8.32	8.45	10.15	9.25	10.20	10.79	10.32	10.90
xi,2 (nmol/mol)	10.14	9.90	8.43	8.36	10.12	9.30	10.15	10.68	10.29	10.55
xi,3 (nmol/mol)	10.11	9.90	8.21	8.31	10.01	9.45	10.11	10.61	10.19	10.71
Xi (nmol/mol)	10.16	9.96	8.32	8.37	10.09	9.33	10.15	10.69	10.26	10.72
Si (nmol/mol)	0.06	0.11	0.11	0.07	0.07	0.10	0.04	0.09	0.06	0.17
u(xi) (nmol/mol)	0.58	1.30	1.02	0.87	0.43	0.21	0.32	1.11	0.50	0.22
U(xi) (nmol/mol)	1.17	2.60	2.04	1.74	1.85	0.42	0.64	1.21	1.00	0.46

Table 38: Reported values for NO run 10.

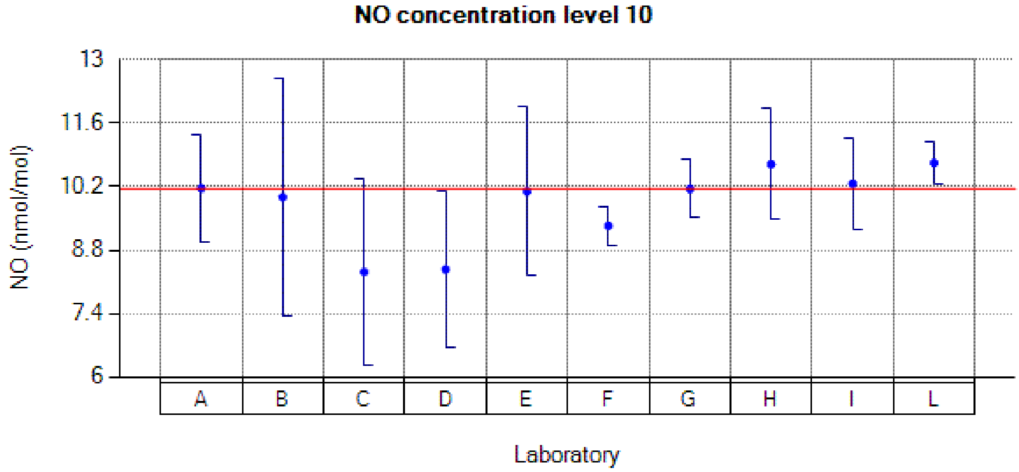

Figure 41: Reported values for NO run 10.

Reported values for NO_2

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	0.10	0.10	0.11	-0.15	4.27	0.20	-0.05	0.12	-0.02	0.08
u(xi) (nmol/mol)	0.58	1.30	1.00	0.71	0.60	0.02	0.30	1.00	0.50	0.17
U(xi) (nmol/mol)	1.16	2.50	2.00	1.42	1.20	0.04	0.60	2.00	1.00	0.35

Table 39: Reported values for NO_2 run 0.

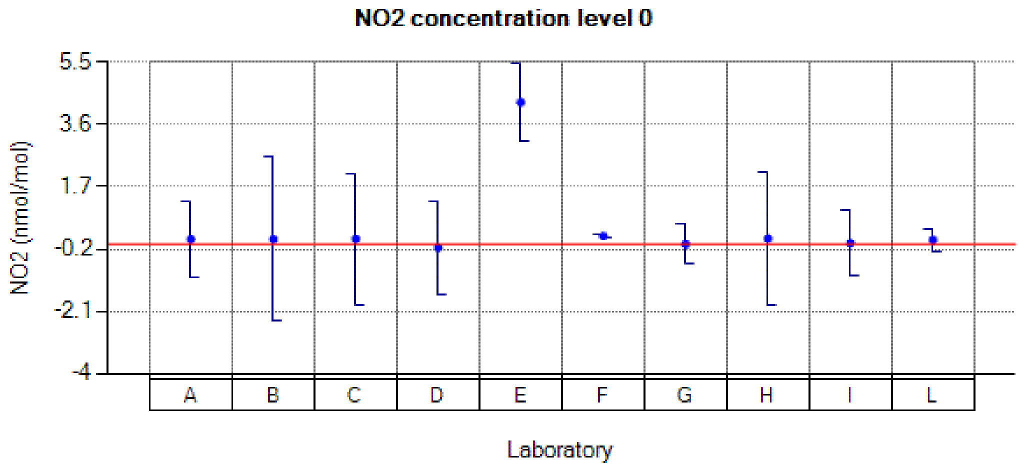

Figure 42: Reported values for NO_2 run 0.

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	122.26	125.80	119.60	122.40	124.45	123.05	122.19	124.73	120.64	122.20
xi,2 (nmol/mol)	121.68	125.50	119.18	122.29	123.57	123.15	121.99	124.41	120.40	121.65
xi,3 (nmol/mol)	121.95	125.30	119.28	122.31	123.45	124.00	121.36	124.34	120.10	121.68
Xi (nmol/mol)	121.96	125.53	119.35	122.33	123.82	123.40	121.84	124.49	120.38	121.84
Si (nmol/mol)	0.29	0.25	0.21	0.05	0.54	0.52	0.43	0.20	0.27	0.30
u(xi) (nmol/mol)	1.77	1.90	2.90	3.40	1.85	3.08	6.38	2.24	1.24	2.92
U(xi) (nmol/mol)	3.55	3.80	5.80	6.80	7.94	6.15	12.76	4.49	2.48	5.84

Table 40: Reported values for NO_2 run 2.

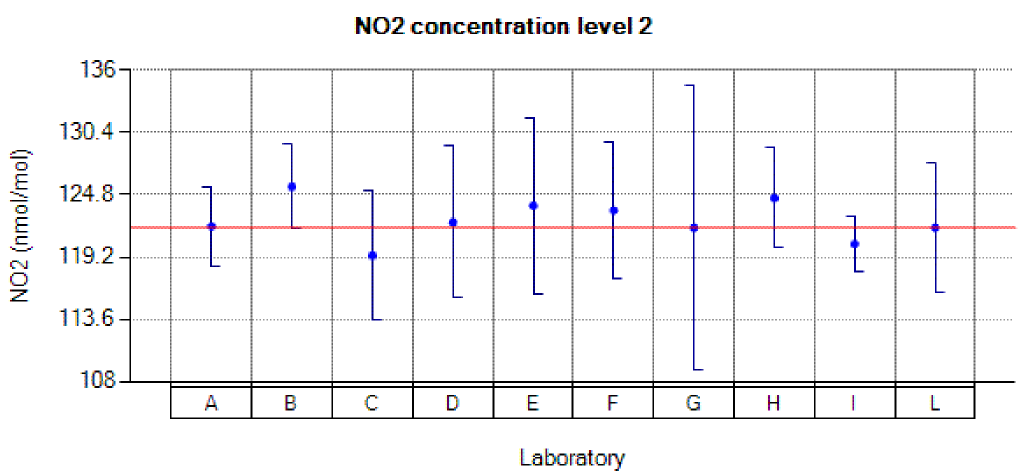

Figure 43: Reported values for NO_2 run 2.

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	23.04	22.70	22.31	23.00	23.57	21.19	23.02	23.84	23.19	22.15
xi,2 (nmol/mol)	22.95	22.60	22.45	22.71	23.48	21.38	22.97	23.78	23.13	22.38
xi,3 (nmol/mol)	22.93	22.60	21.89	22.86	23.58	21.95	22.85	23.61	23.04	22.28
Xi (nmol/mol)	22.97	22.63	22.21	22.85	23.54	21.50	22.94	23.74	23.12	22.27
Si (nmol/mol)	0.05	0.05	0.29	0.14	0.05	0.39	0.08	0.11	0.07	0.11
u(xi) (nmol/mol)	0.66	1.30	1.12	1.04	0.53	0.52	0.81	1.24	0.50	0.55
U(xi) (nmol/mol)	1.32	2.50	2.24	2.08	2.27	1.04	1.63	2.47	1.00	1.11

Table 41: Reported values for NO_2 run 4.

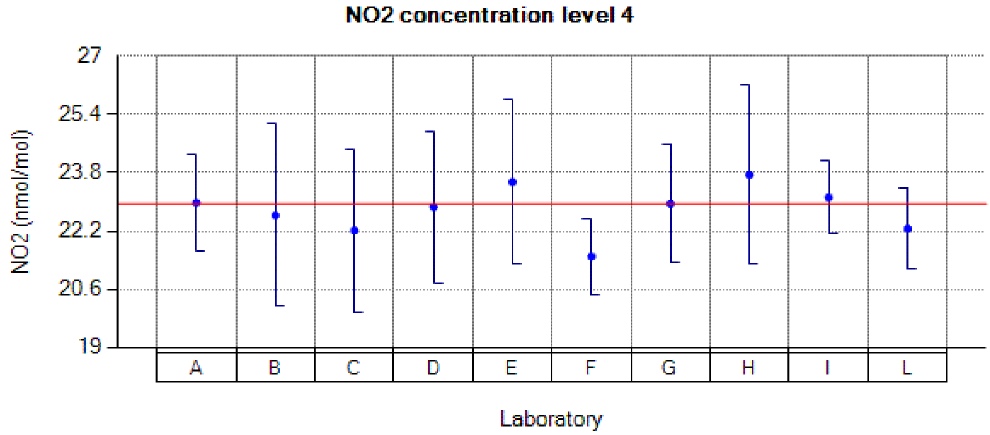

Figure 44: Reported values for NO_2 run 4.

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	52.22	52.30	51.38	51.64	52.28	52.25	52.37	53.75	52.56	51.21
xi,2 (nmol/mol)	52.23	52.40	51.31	51.62	52.31	52.77	52.58	53.89	52.50	51.50
xi,3 (nmol/mol)	52.43	52.50	51.18	51.82	52.37	53.05	52.66	53.93	52.62	51.44
Xi (nmol/mol)	52.29	52.40	51.29	51.69	52.32	52.69	52.53	53.85	52.56	51.38
Si (nmol/mol)	0.11	0.10	0.10	0.11	0.04	0.40	0.15	0.09	0.06	0.15
u(xi) (nmol/mol)	0.94	1.30	1.54	1.73	0.85	1.25	2.13	1.54	0.50	1.23
U(xi) (nmol/mol)	1.88	2.50	3.08	3.45	3.65	2.50	4.26	3.08	1.00	2.47

Table 42: Reported values for NO_2 run 6.

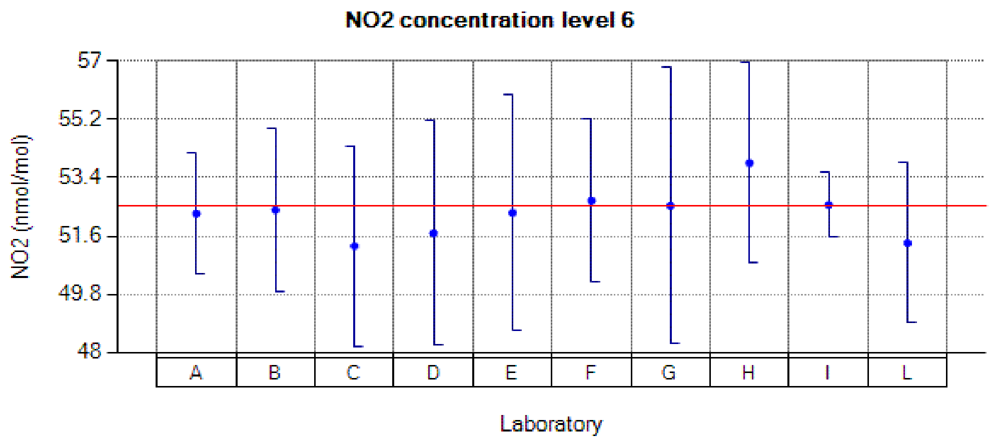

Figure 45: Reported values for NO_2 run 6.

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	87.34	89.00	85.99	87.77	87.09	86.17	88.02	89.91	87.66	86.00
xi,2 (nmol/mol)	87.83	89.60	86.26	87.83	87.40	86.75	88.60	90.23	88.21	87.10
xi,3 (nmol/mol)	87.65	89.00	86.22	87.67	87.15	87.05	88.01	89.99	87.82	86.44
Xi (nmol/mol)	87.60	89.20	86.15	87.75	87.21	86.65	88.21	90.04	87.89	86.51
Si (nmol/mol)	0.24	0.34	0.14	0.08	0.16	0.44	0.33	0.16	0.28	0.55
u(xi) (nmol/mol)	1.33	1.30	2.20	2.58	1.31	2.10	3.10	1.90	0.93	2.07
U(xi) (nmol/mol)	2.67	2.70	4.41	5.16	5.65	4.20	6.19	3.80	1.86	4.14

Table 43: Reported values for NO_2 run 8.

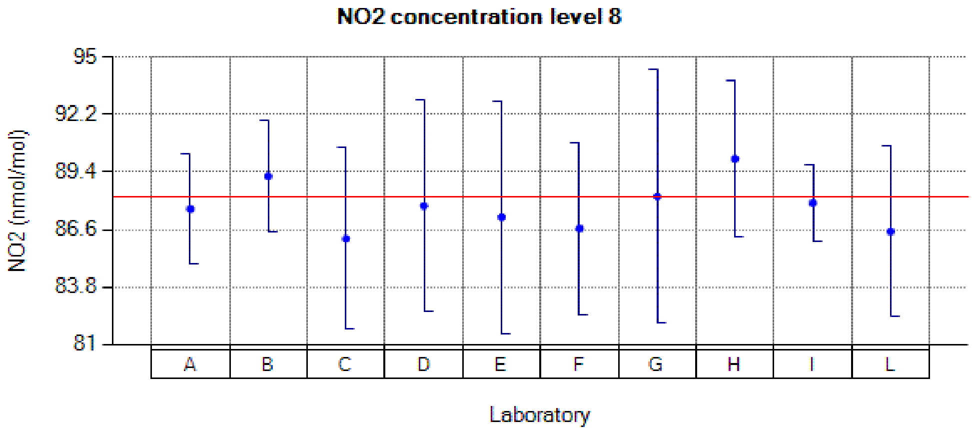

Figure 46: Reported values for NO_2 run 8.

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	11.09	10.90	10.35	11.06	11.52	11.05	11.08	11.50	11.14	10.61
xi,2 (nmol/mol)	11.19	10.90	10.92	11.17	11.45	11.15	11.08	11.60	11.13	10.50
xi,3 (nmol/mol)	11.26	10.80	10.62	11.11	11.36	11.26	11.08	11.61	11.20	10.58
Xi (nmol/mol)	11.18	10.86	10.63	11.11	11.44	11.15	11.08	11.57	11.15	10.56
Si (nmol/mol)	0.08	0.05	0.28	0.05	0.08	0.10	0.00	0.06	0.03	0.05
u(xi) (nmol/mol)	0.60	1.30	1.03	1.05	0.44	0.27	0.40	1.12	0.50	0.29
U(xi) (nmol/mol)	1.21	2.50	2.06	2.11	1.87	0.54	0.79	2.23	1.00	0.58

Table 44: Reported values for NO_2 run 10.

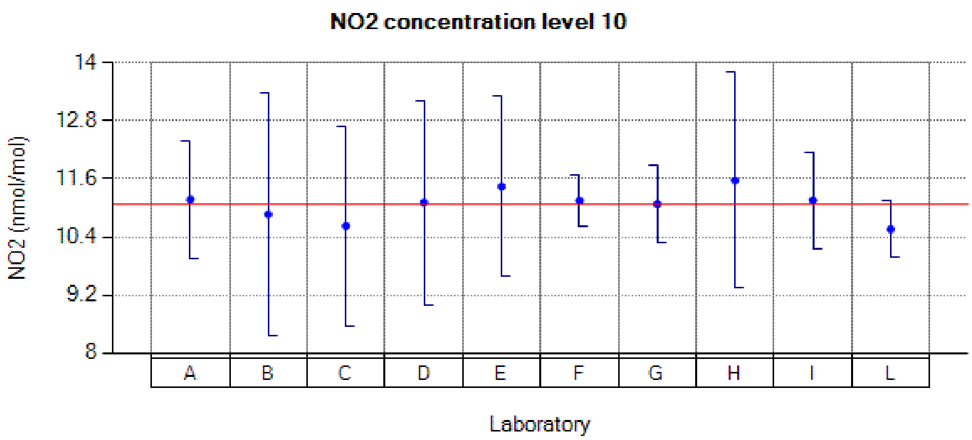

Figure 47: Reported values for NO_2 run 10.

Annex C. The precision of standardized measurement methods

For the main purpose of monitoring trends between different IEs undertaken by ERLAP the precision of standardized SO_2, CO, O_3 and NO_X measurement methods [2], [3], [4] and [5] as implemented by NRLs was evaluated. Applied methodology is described in ISO 5725-1, -2 and -6 [14], [15] and [16]. The precision experiment has involved a total of nine laboratories, the actual number of labs (p_j) varying from run to run (Table 45). Six concentration levels (for run 0 is requested only one value so repeatability cannot be evaluated) were tested for O_3, CO, SO_2 and NO_2, and eleven for NO. Outlier tests were performed and results are reported in Annex D.

The repeatability standard deviation (s_r) was calculated in accordance with ISO 5725-2 as the square root of average within laboratory variance. The repeatability limit (r) is calculated using Equation 8 [16]. It represents the biggest difference between two test results found on an identical test gas by one laboratory using the same apparatus within the shortest feasible time interval, that should not been exceeded on average more than once in 20 cases in the normal and correct operation of method.

$$r = t_{95\%,\nu} \cdot \sqrt{2} \cdot s_r \qquad \textbf{Equation 8}$$

The reproducibility standard deviation (s_R) was calculated in accordance with ISO 5725-2 as the square root of sum of repeatability and between laboratory variance. The reproducibility limit (R) is calculated using Equation 9 [16]. It represents the biggest difference between two measurements on an identical test gas reported by two laboratories, which should not occur on average more than once in 20 cases in the normal and correct operation of method.

$$R = t_{95\%,\nu} \cdot \sqrt{2} \cdot s_R \qquad \textbf{Equation 9}$$

The repeatability standard deviation was evaluated with (p_j*(3-1)) degrees of freedom (ν) and reproducibility standard deviation with (p_j-1) degrees of freedom. The critical range student factors ($t_{\alpha,\nu}$) are reported in Table 45.

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	2.228
NO	1,2,3,4,5,6,7,8,9,10	10	2.086	2.228
NO_2	1,2,3,4,5,6,7,8,9,10	10	2.086	2.228
O_3	1,2,3,4,5	10	2.086	2.228
SO_2	1,2,3,4,5	10	2.086	2.228

Table 45: Critical values of t used in the repeatability (r) and reproducibility (R) evaluation.

The repeatability (r) and reproducibility (R) limits of measurement methods are presented from Table 46 to Table 50 and from Figure 48 to Figure 52. It is also reported the reproducibility from common criteria (R (from σ_p))' calculated by substituting s_R in Equation 9 with a 'standard deviation for proficiency assessment' (Table 4). Comparison between R and R (from σ_p) serves to indicate that σ_p is realistic ([13] 6.3.1) or from the other point of view, that the general methodology implemented by NRLs is appropriate for σ_p.

SO_2 data (nmol/mol) without outliers			
group average	repeatability limit : r	reproducibility limit : R	reproducibility limit (relative)
0.0		0.9	
3.0	0.2	0.9	
7.4	0.4	2.8	
19.0	0.3	4.0	
48.1	0.3	5.8	
135.4	0.6	14.2	10.5%

Table 46: The R and r of SO_2 standard measurement method.

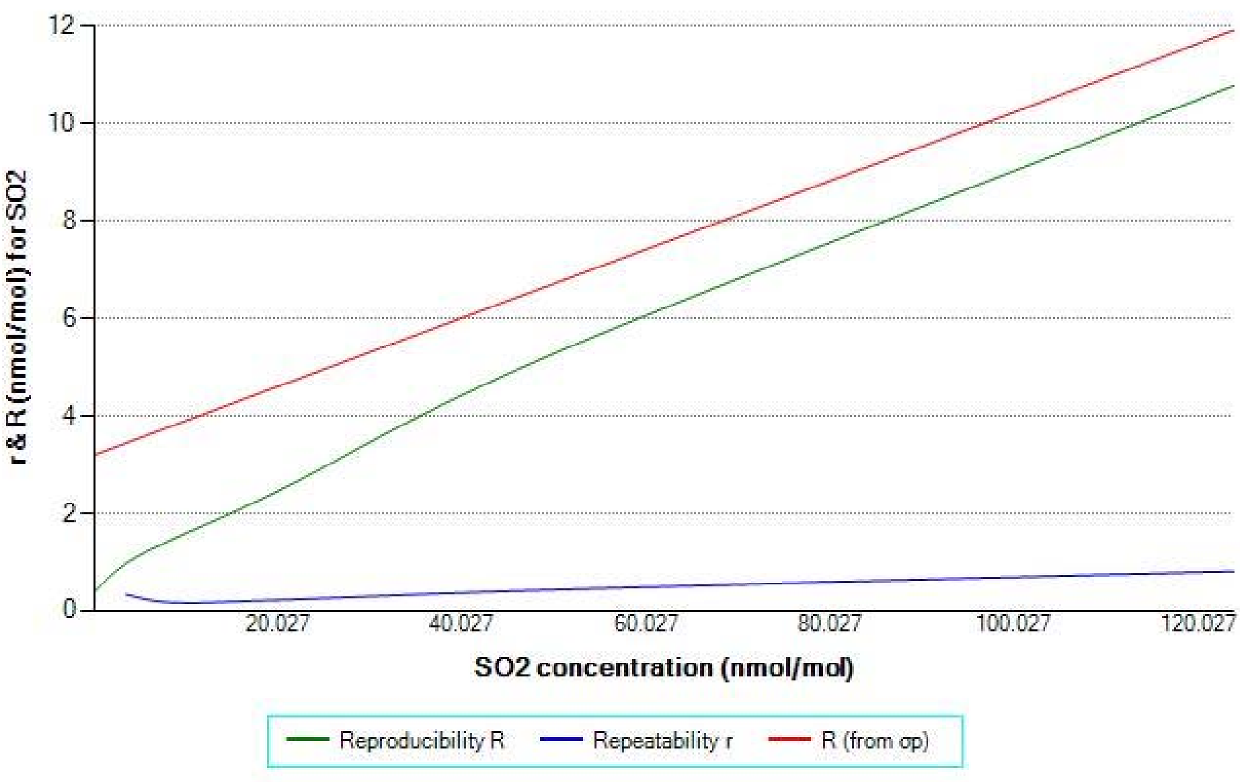

Figure 48: The R and r of SO_2 standard measurement method as a function of concentration.

CO data (µmol/mol) without outliers			
group average	repeatability limit : r	reproducibility limit : R	reproducibility limit (relative)
-0.001		0.086	
1.012	0.012	0.206	
2.004	0.015	0.329	
4.282	0.02	0.378	
5.940	0.012	0.448	
8.465	0.026	0.618	7.3%

Table 47: The R and r of CO standard measurement method.

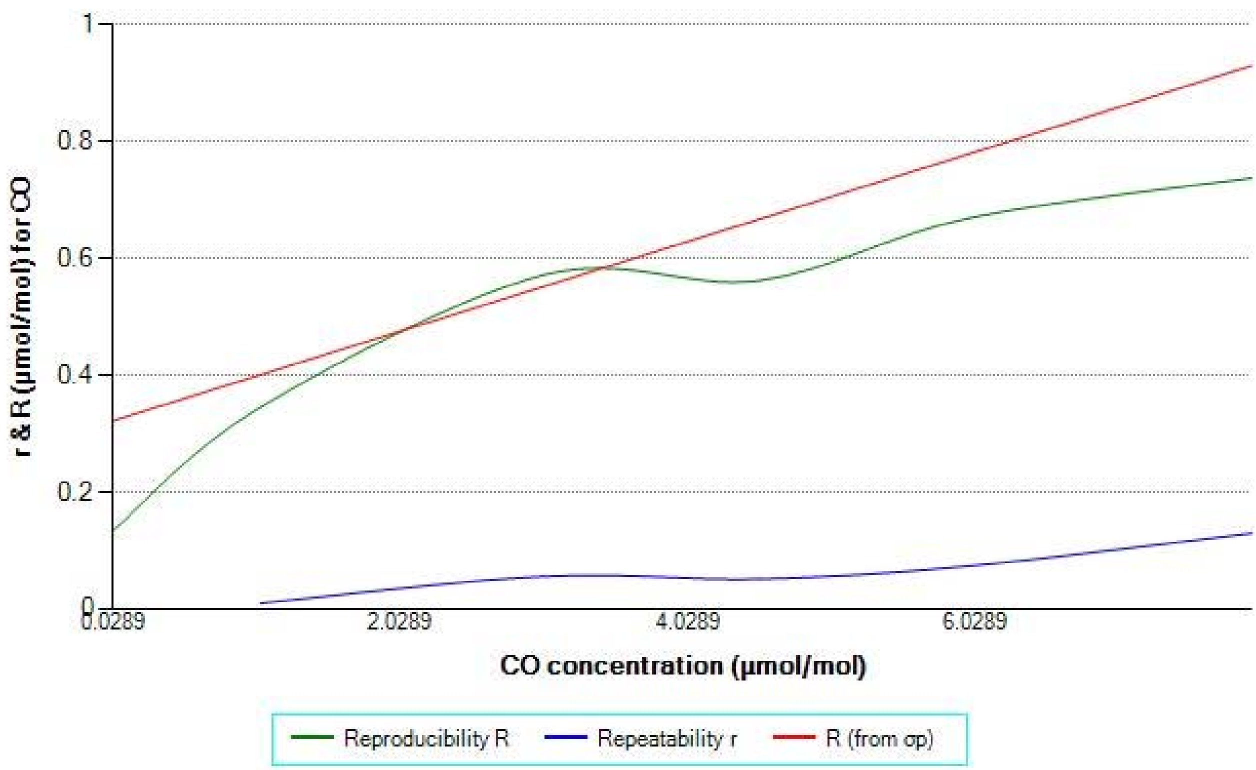

Figure 49: The R and r of CO standard measurement method as a function of concentration.

O_3 data (nmol/mol) without outliers			
group average	repeatability limit: r	reproducibility limit: R	reproducibility limit (relative)
0.0		1.2	
14.0	0.2	2.0	
21.1	0.1	3.0	
59.9	0.1	2.4	
101.0	1.4	8.8	
119.6	1.5	10.3	8.6%

Table 48: The R and r of O_3 standard measurement method.

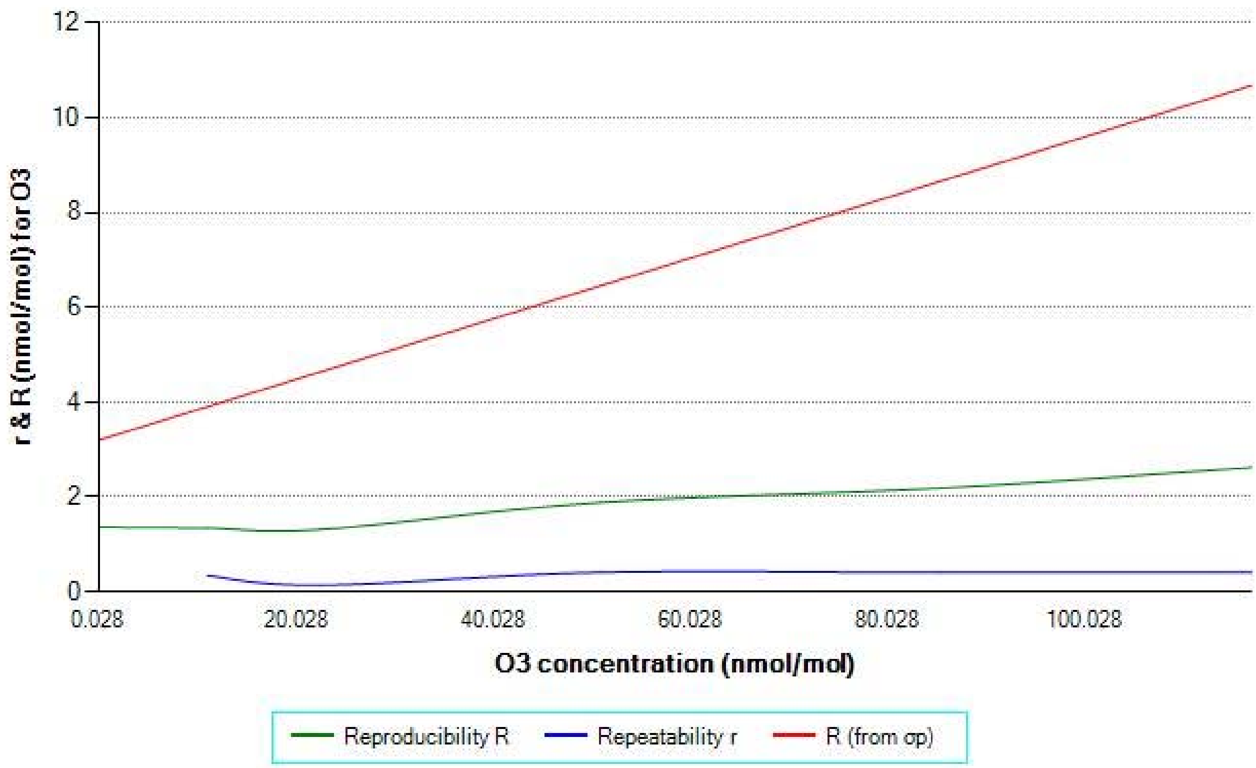

Figure 50: The R and r of O_3 standard measurement method as a function of concentration.

NO data (nmol/mol) without outliers			
group average	repeatability limit: r	reproducibility limit: R	reproducibility limit (relative)
-0.1		2.3	
9.8	0.3	2.8	
20.2	1.6	3.2	
38.9	0.5	2.8	
61.4	0.8	4.4	
121.2	0.5	3.8	
171.3	4.3	6.5	
171.6	1.0	4.8	
258.2	1.5	7.1	
398.8	1.1	12.2	
519.9	3.1	15.1	2.9%

Table 49: The R and r of NO standard measurement method.

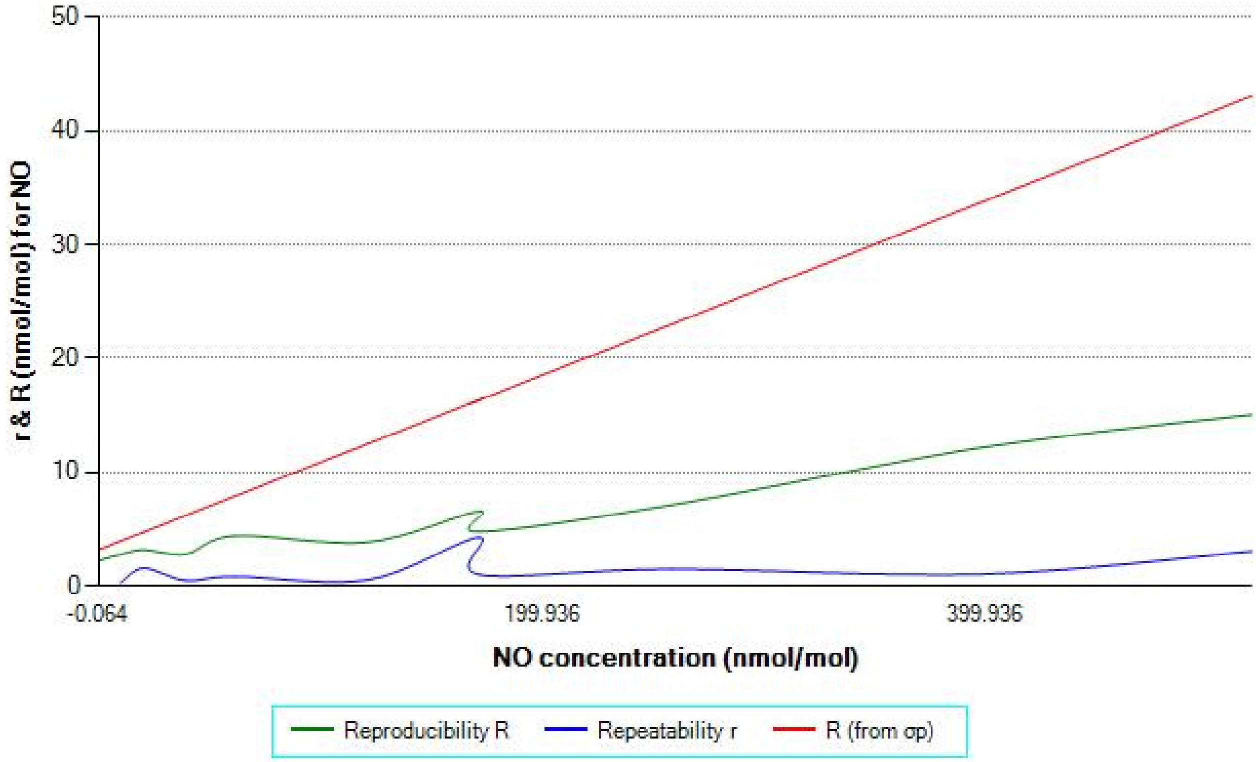

Figure 51: The R and r of NO standard measurement method as a function of concentration.

NO_2 data (nmol/mol) without outliers			
group average	repeatability limit: r	reproducibility limit: R	reproducibility limit (relative)
0.02		0.94	
13.41	0.22	2.13	
20.22	0.16	2.51	
58.96	0.29	6.36	
99.78	0.61	11.60	
119.43	0.87	12.25	10.26%

Table 50: The R and r of NO_2 standard measurement method.

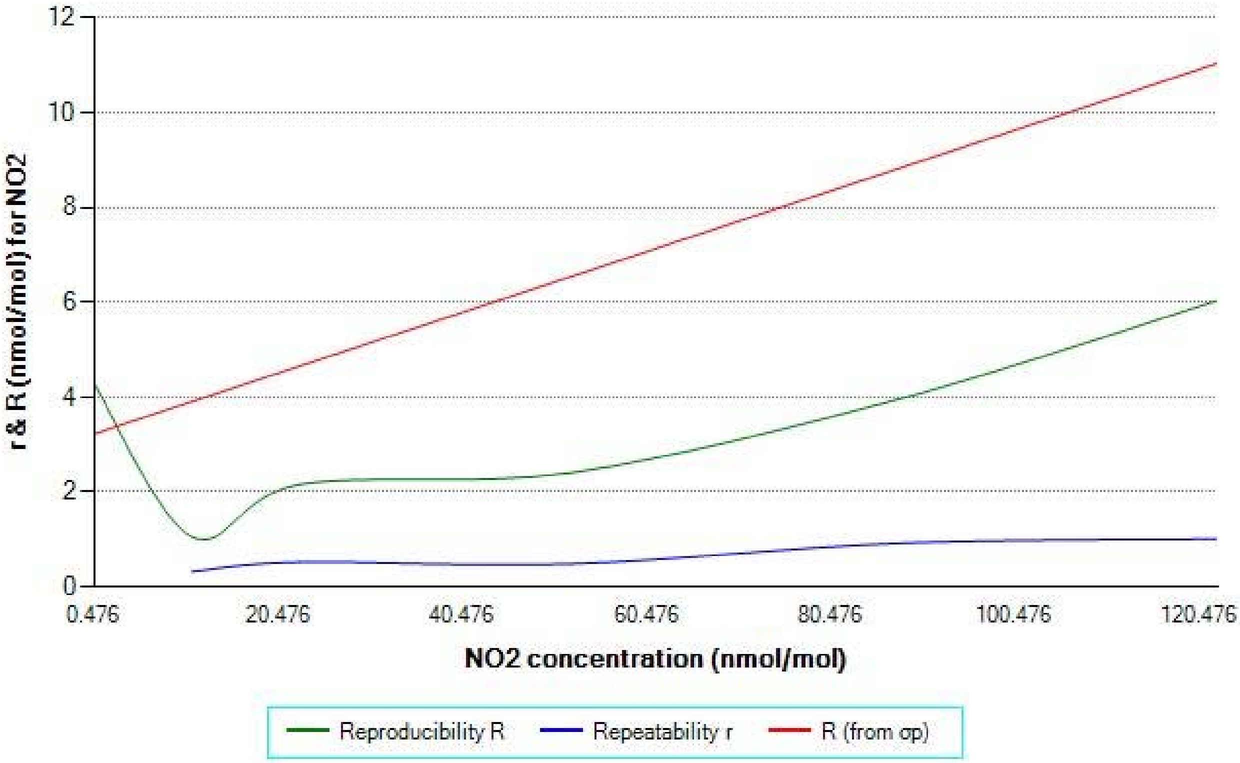

Figure 52: The R and r of NO_2 standard measurement method as a function of concentration.

Annex D. The 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 5725-2.
Laboratories showing some form of statistical inconsistency were requested to investigate the cause of discrepancies.
Laboratories were allowed to correct their results in case of identification of exceptional errors. Subsequently, data were considered definitive and "Grubb's one outlying observation test" was performed.
For runs where outliers were detected outliers were removed and "Grubb's one outlying observation test" was repeated until no more outliers were observed. Statistical outliers obtained at this stage are not considered as due to extraordinary errors but due to significant difference in participant's standard operating procedure.
During this IE the statistical outliers presented in the table below are related only to zero levels and for NO_2 laboratory E identified already the cause of the problem:

parameter	run	laboratory	measured value	failing test	confidence level
NO	0	C	-1.83	G1 minimum	1%, 5%
NO2	0	E	4.27	G1 maximum	1%, 5%

Table 51: "Genuine" statistical outliers according to Grubb's one outlying observation test.

The precision of standardized measurement methods reported in Annex C are calculated using the database without outliers.

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Abstract

From the 26th to the 29th of June 2012 in Ispra (IT), 9 Laboratories of AQUILA (Network of European Air Quality Reference Laboratories) met for a laboratory comparison exercise to evaluate their proficiency in the analysis of inorganic gaseous pollutants covered by European Directive about air quality (SO_2, CO, NO, NO_2 and O_3).

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

On the basis of criteria imposed by the European Commission, 86% of the results reported by AQUILA laboratories were good both in terms of measured values and reported uncertainties. Another 13% of the results had good measured values, but the reported uncertainties were either too high (7.9%) or too small (5.4%). One value fell in category 5 (0.3%) and one in 7 (0.3%).

Comparability of results among AQUILA participants at the highest concentration level, excluding outliers, is acceptable for all pollutants. Only CO measurement methods showed less satisfactory results at concentrations around 3μmol\mol.

As the Commission's in-house science service, the Joint Research Centre's mission is to provide EU policies with independent, evidence-based scientific and technical support throughout the whole policy cycle.

Working in close cooperation with policy Directorates-General, the JRC addresses key societal challenges while stimulating innovation through developing new standards, methods and tools, and sharing and transferring its know-how to the Member States and international community.

Key policy areas include: environment and climate change; energy and transport; agriculture and food security; health and consumer protection; information society and digital agenda; safety and security including nuclear; all supported through a cross-cutting and multi-disciplinary approach.

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