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EC Harmonization Programme for Air Quality Measurements:

The evaluation of the Interlaboratory comparison Exercise for SO_2, CO, O_3, NO and NO_2 14.- 17. June 2010

Maurizio Barbiere, Claudio A. Belis, Matej Kapus Dukarić, Friedrich Lagler and Federico Karagulian

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Contact information
Address: via Fermi, 2749 T.P. 442, 21027 Ispra (VA), Italy
E-mail: maurizio.barbiere@jrc.ec.europa.eu
Tel.: +39 0332 789350
Fax: +39 0332 789931

http://ies.jrc.ec.europa.eu/
http://www.jrc.ec.europa.eu/

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WHO COLLABORATING CENTRE FOR AIR QUALITY
MANAGEMENT AND AIR POLLUTION CONTROL

at the

FEDERAL ENVIRONMENTAL AGENCY

Executive Summary

From the 14th to the 17th of June 2010 9 Laboratories of AQUILA (Network of European Air Quality Reference Laboratories) met at an interlaboratory 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, 85% of the results reported by AQUILA laboratories were good both in terms of measured values and reported uncertainties. Another 12% of the results had good measured values, but the reported uncertainties were either too high (8%) or too small (4%).
The comparability of results among AQUILA participants at the highest generated concentration levels, excluding outliers, is acceptable for NO, CO and O_3 measurements while NO_2 and SO_2 measurements showed less satisfactory results.

Contents

List of tables

List of figures

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	Intercomparison 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 standardised 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 interlaboratory 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 14th to the 17th of June 2010 in Ispra (IT) in joint cooperation of EC/ JRC/IES/ERLAP and WHO CC.

Since 1990 ERLAP organises 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 intercomparison 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.

2. Communication and time schedule

The IE was announced in November 2009 to the members of the AQUILA network and the WHO CC representative. Registration was opened on January 2010 and the list of 9 participating laboratories was distributed in March 2010.
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, 14th June 2010, 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 8:30.

3. 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: Finland, Austria, Ireland, Bulgaria, United Kingdom, Netherland, Hungary and Spain.

Country	Laboratory	Code
Finland	Finnish Meteorological Institute	A
Austria	Umweltbundesamt	B
Ireland	Environmental Protection Agency	C
European Commission	European Reference Laboratory for Air Pollution	D
Austria	Oberösterreichische Landesregierung	E
Bulgaria	Executive Environmental Agency	F
United Kingdom	National Physics Laboratory	G
Netherland	National Institute for Public Health and the Environment	H
Hungary	Hungarian Meteorological Service	I
Spain	Instituto de salud CARLOS III	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 interlaboratory comparison exercise included those used in the calculation of the assigned values. As a whole, the instrumentation belongs to three different manufacturers with the exception of SO_2 where four brands are present. 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. This information is disclosed with the only purpose of making it possible to track the performance of the different models and type approvals and to evaluate their influence on the quality of the measurements. Nevertheless, the above-mentioned evaluation is beyond the scope of the present report.

Gas	Lab Code	Instrument
SO_2	A	Thermo Inc., 1997, TEI 43CTL
	B	Thermo Environmental Instruments, 1999, TEI 43 C
	C	Teledyne API 100A
	D	Thermo Electrom Corporation, 2009, 43i
	E	Horiba APSA 360
	F	Horiba APSA 370
	G	Teledyne API 100A
	H	Thermo Electron, 2009, 43i-TLE
	I	Thermo Electrom Corporation 43C
	L	Thermo Enviromental 43i
NO_X	A	Horiba, 2003, APNA-360
	B	Horiba, 2000, APNA 360 CE
	C	Teledyne-API M200A
	D	Thermo Electrom Corporation, 2010, 42i
	E	Horiba APNA 370
	F	Horiba APNA 370
	G	
	H	Teledyne-API 200E, 2005
	I	Thermo Electrom Corporation 42i
	L	Thermo Environmental 42i
CO	A	Horiba, 2008, APMA-370
	B	Horiba, 1997, APMA 360 CE
	C	Teledyne API M300
	D	Thermo Electronic Corporation, 2000, 48C
	E	Horiba APNA 370
	F	Horiba APMA 370
	G	Teledyne API 300A
	H	Thermo Electron, 2009, 48i-TLE
	I	Thermo Electronic Corporation 48C
	L	Thermo Environmental 48C
O_3	A	Thermo Inc., 1999, TEI 49 CPS
	B	Thermo Environmental Instruments, 1999, TEI 49C
	C	Teledyne API M400
	D	Thermo Electronic Corporation, 1996, 49C
	E	Thermo Electron 49i
	F	Horiba APOA 370
	G	Teledyne API 400A
	H	Thermo Electron, 2005, 49i
	I	Thermo Electronic Corporation 49C
	L	Thermo Environmental 49C

Table 2: The list of instruments used by participants

4. 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 (h)	run	installation	calibration	ZA (ppb)	NO (ppb)	NO_2 (ppb)	O_3 (ppb)	CO (ppm)	SO_2 (ppb)
14-Jun	12:00	5	/	X							
15-Jun	8:00	3	/		X						
15-Jun	11:00	1	NO-NO2 - O3 run 0			0					
15-Jun	12:00	2	NO-NO2 run 1				480				
15-Jun	14:00	2	NO-NO2 run 2				350	130			
15-Jun	16:00	2	O3 run 1						130		
15-Jun	18:00	2	NO-NO2 run 3				60				
15-Jun	20:00	2	NO-NO2 run 4				35	25			
15-Jun	22:00	2	O3 run 2						25		
16-Jun	0:00	2	NO-NO2 run 5				160				
16-Jun	2:00	2	NO-NO2 run 6				105	55			
16-Jun	4:00	2	O3 run 3						55		
16-Jun	6:00	2	NO-NO2 run 7				240				
16-Jun	8:00	2	NO-NO2 run 8				145	95			
16-Jun	10:00	2	O3 run 4						95		
16-Jun	12:00	2	NO-NO2 run 9				20				
16-Jun	14:00	2	NO-NO2 run 10				6	14			
16-Jun	16:00	2	O3 run 5						14		
16-Jun	< 18:00	2	calibration		X						
16-Jun	20:00	1	CO-SO2 run 0			0					
16-Jun	21:00	2:30	CO-SO2 run 1							9	8
16-Jun	23:30	2	CO-SO2 run 2							4.5	50
17-Jun	1:30	2	CO-SO2 run 3							6	20
17-Jun	3:30	2	CO-SO2 run 4							3	135
17-Jun	5:30	2	CO-SO2 run 5							1	3
17-Jun	7:30	1				0					
17-Jun	8:30	END									

Table 3: The sequence program of generated test gases

5. 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.

5.1 z' - score

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

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

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:

	$\sigma_p = a \cdot c + b$	
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.

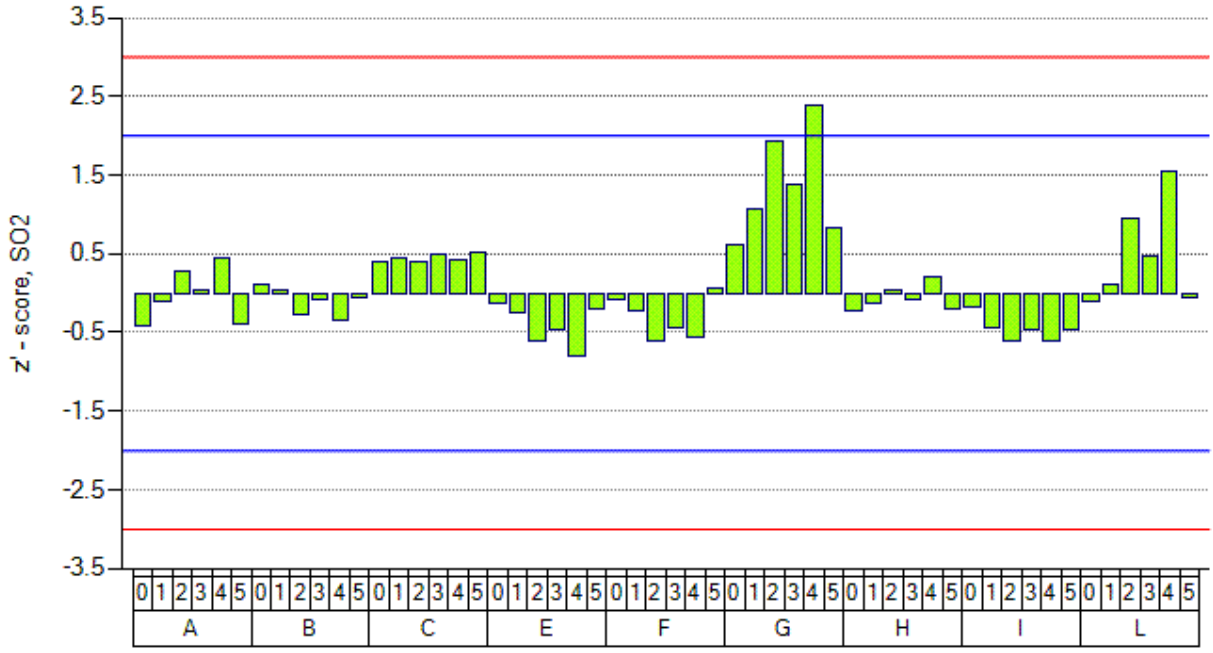

Figure 1: The z'-score evaluations of SO_2 measurements
Scores are given for each participant and each tested concentration level (run). Run number order (with nominal concentration) is: 0 (0 nmol/mol), 1 (8 nmol/mol), 2 (50 nmol/mol), 3 (20 nmol/mol), 4 (135 nmol/mol), 5 (3 nmol/mol). The assessment criteria are presented as z'=±2 (blue line) and z'=±3 (red line). They represent the limits for the questionable and unsatisfactory results.

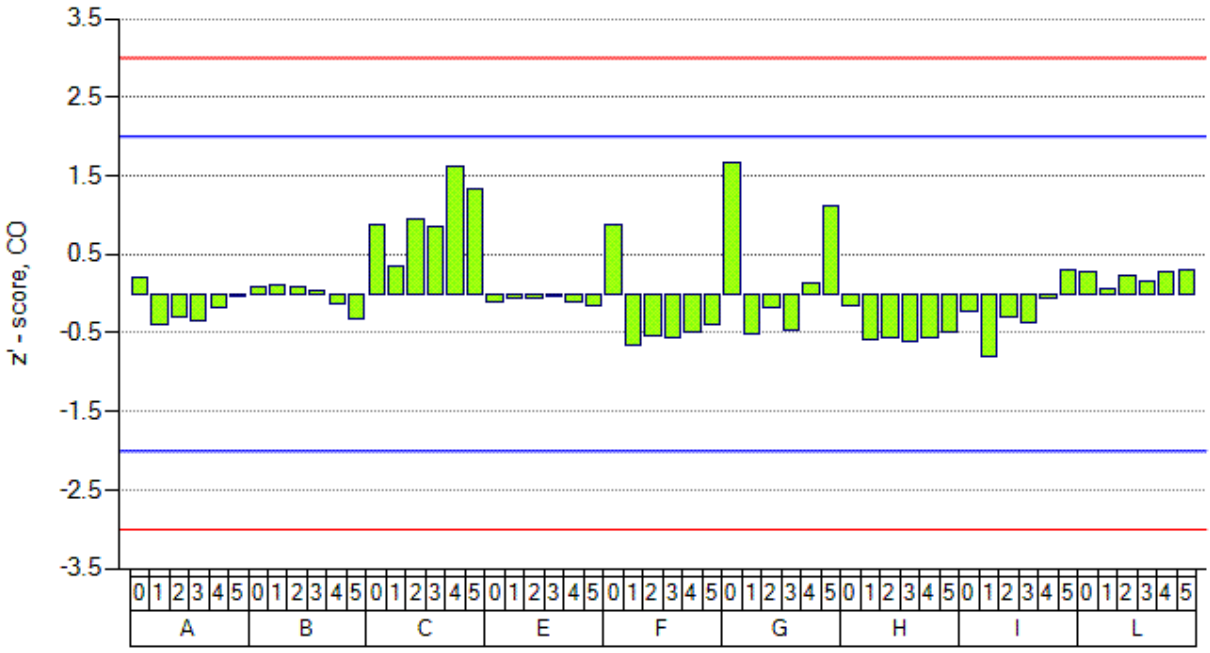

Figure 2: The z'-score evaluations of CO measurements
Scores are given for each participant and each tested concentration level (run). Run number order (with nominal concentration) is: 0 (0 µmol/mol), 1 (9 µmol/mol), 2 (4.5 µmol/mol), 3 (6 µmol/mol), 4 (3 µmol/mol), 5 (1 µmol/mol). The assessment criteria are presented as z'=±2 (blue line) and z'=±3 (red line). They represent the limits for the questionable and unsatisfactory results.

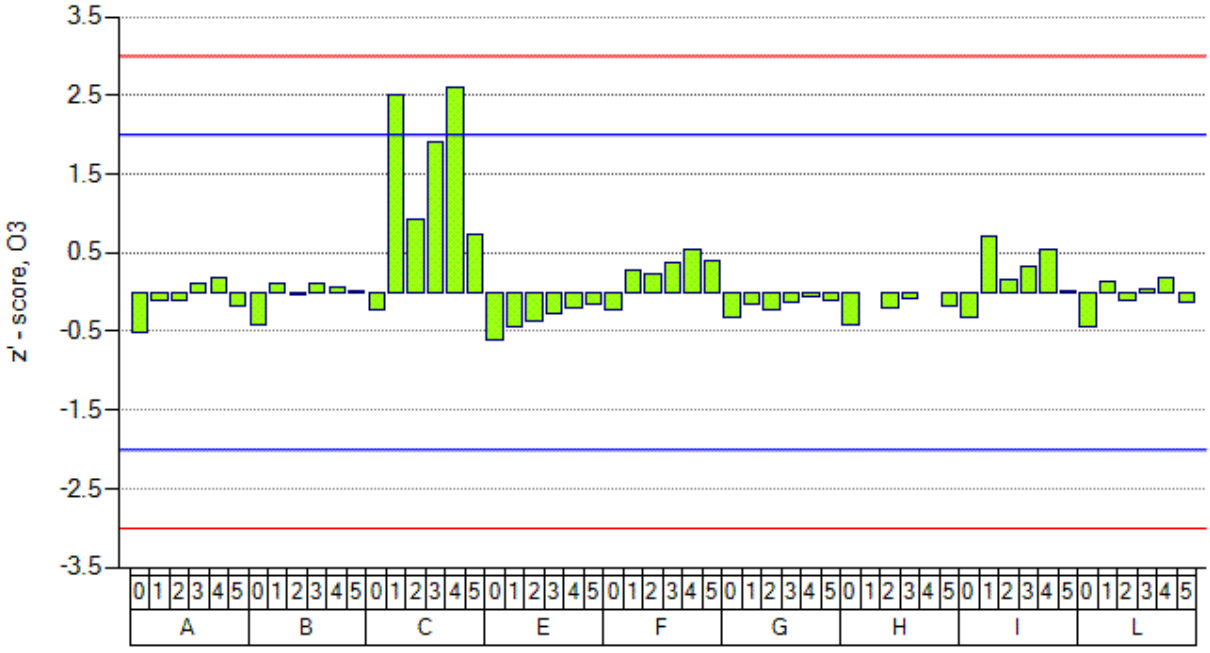

Figure 3: The z'-score evaluations of O_3 measurements
Scores are given for each participant and each concentration level (run). Run number order (with nominal concentration) is: 0 (0 nmol/mol), 1 (130 nmol/mol), 2 (25 nmol/mol), 3 (55 nmol/mol), 4 (95 nmol/mol), 5 (14 nmol/mol). The assessment criteria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

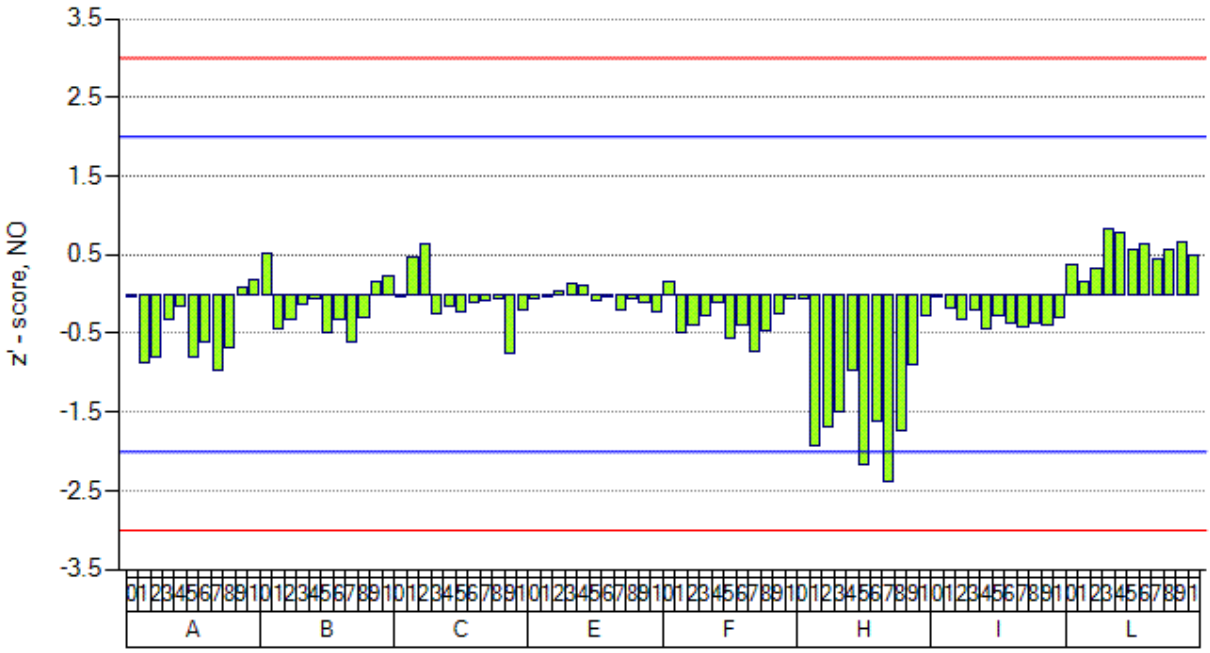

Figure 4: The z'-score evaluations of NO measurements
Scores are given for each participant and each tested concentration level (run). Run number order (with nominal concentration) is: 0 (0 nmol/mol), 1 (480 nmol/mol), 2 (350 nmol/mol), 3 (60 nmol/mol), 4 (35 nmol/mol) , 5 (160 nmol/mol) , 6 (105 nmol/mol) , 7 (240 nmol/mol) , 8 (145 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.

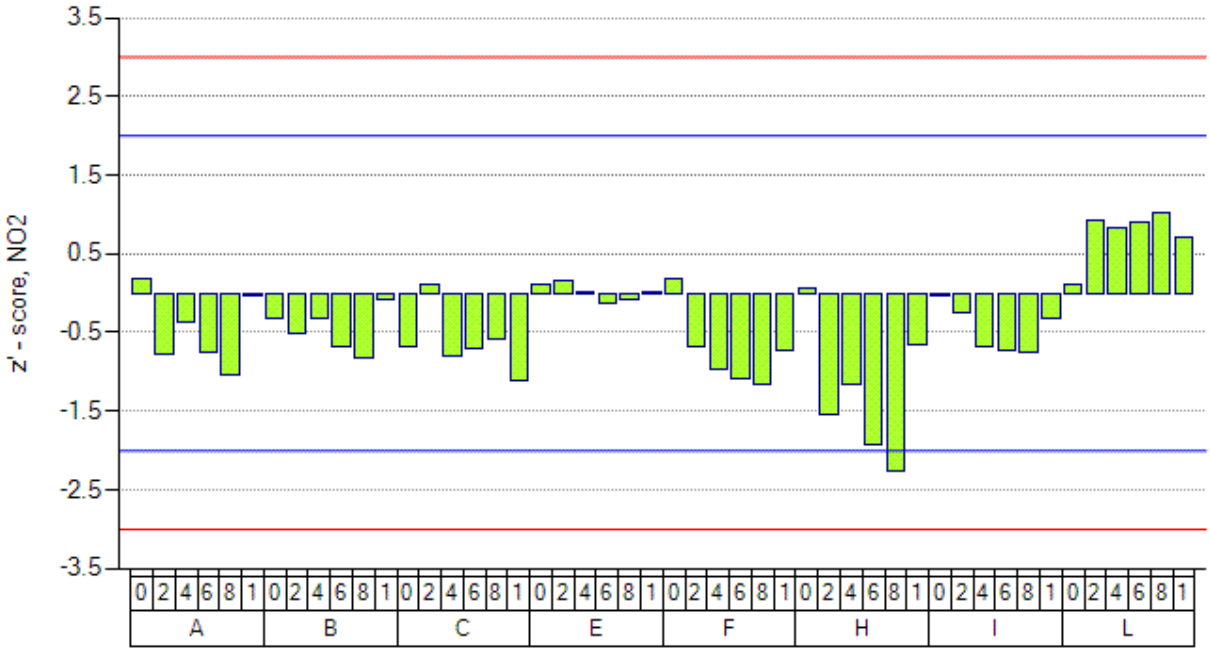

Figure 5: The z'-score evaluations of NO_2 measurements
Scores are given for each participant and each concentration level (run). Run number order (with nominal concentration) is: 0 (0 nmol/mol), 1 (130 nmol/mol), 2 (25 nmol/mol), 3 (55 nmol/mol), 4 (95 nmol/mol), 5 (14 nmol/mol). The assessment criteria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

5.2 E_n - number

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

$$E_n = \frac{x_i - X}{\sqrt{U_{x_i}^2 + U_X^2}} \qquad (2)$$

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.

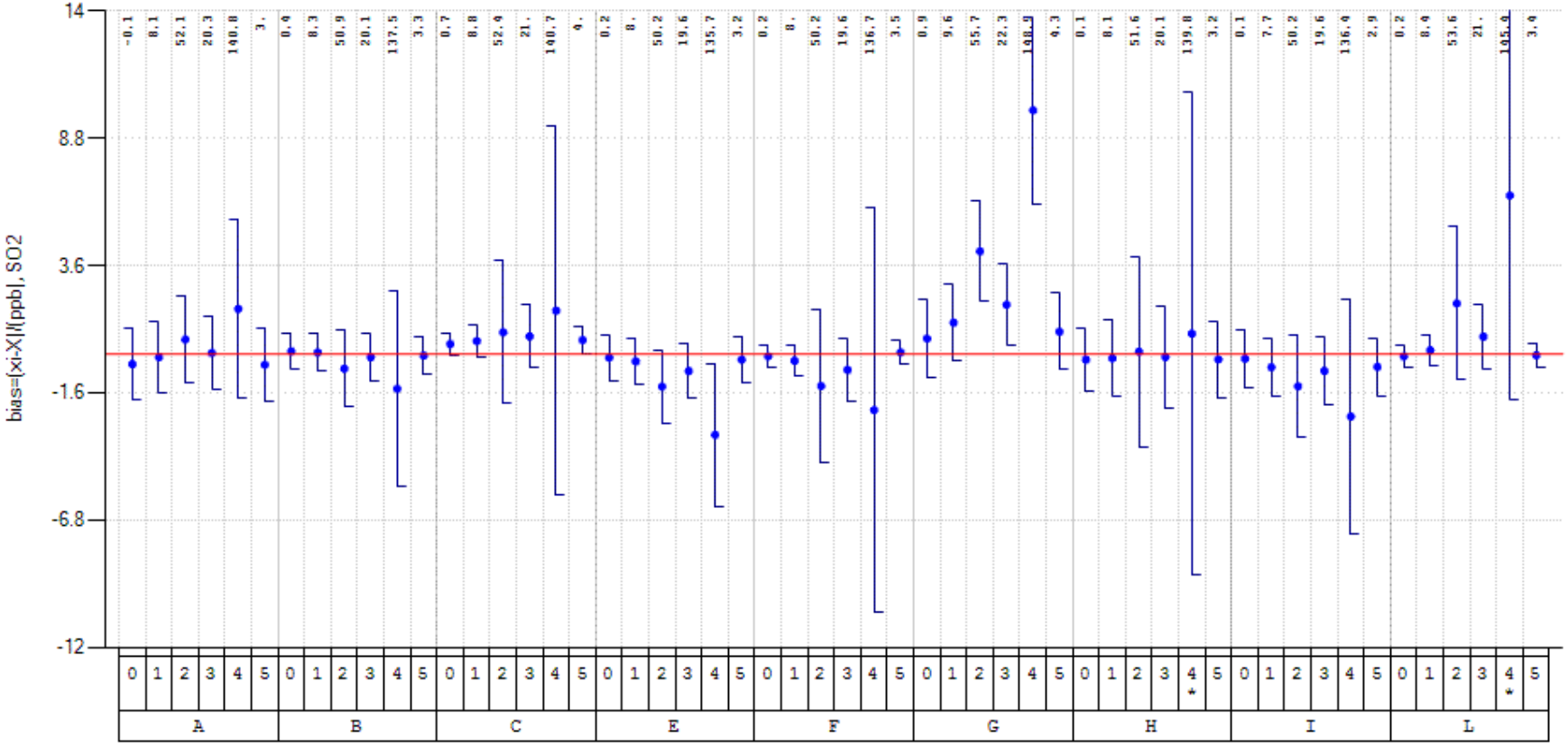

Figure 6: Bias of participant's SO_2 measurement results
Expanded uncertainty of bias for each run is presented as error bar. The results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 5) together with the participants rounded run average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

- 11 -

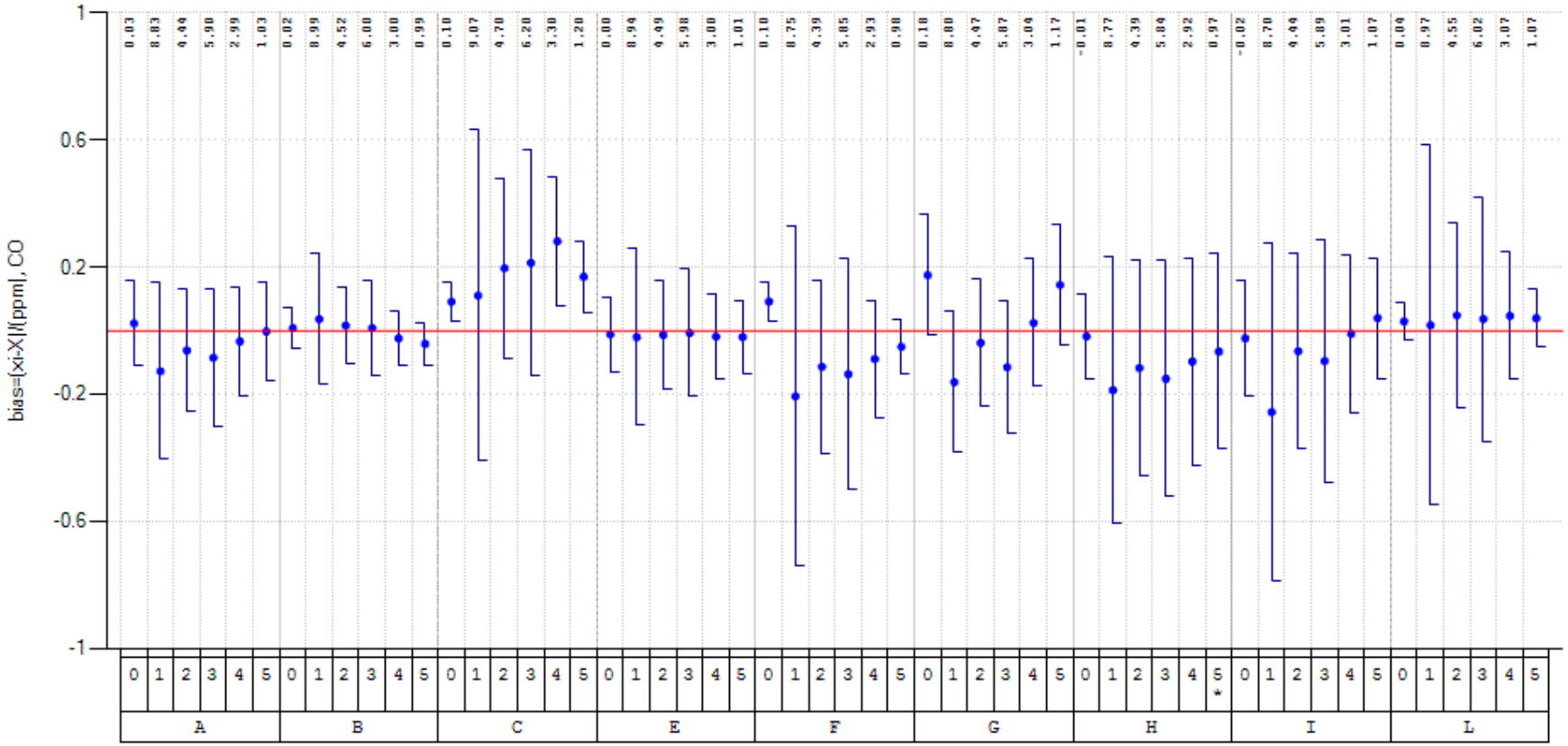

Figure 7: Bias of participant's CO measurement results
Expanded uncertainty of bias for each run is presented as error bar. Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 5) together with the participants rounded run average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

- 12 -

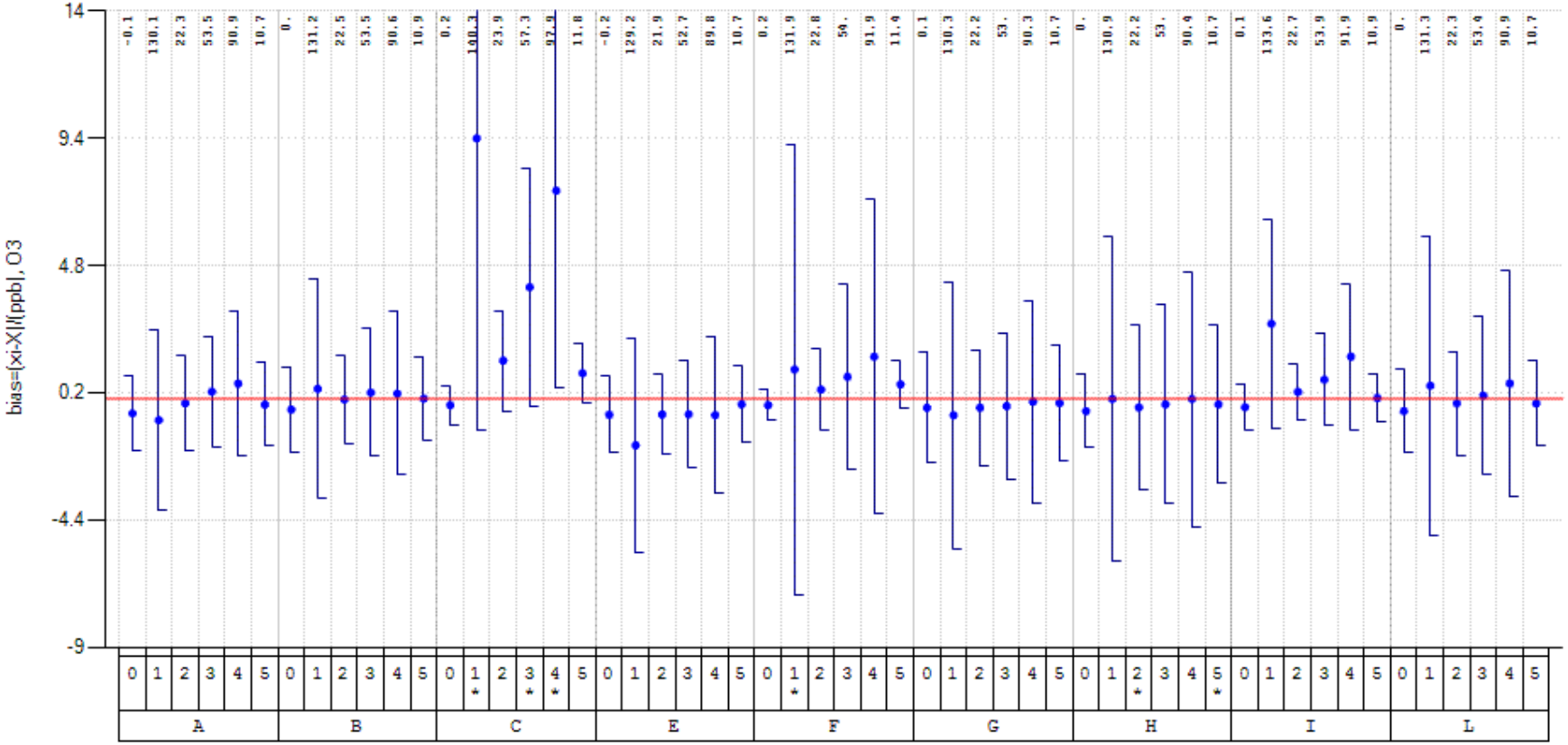

Figure 8: Bias of participant's O_3 measurement results
Expanded uncertainty of bias for each run is presented as error bar. Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 5) together with the participants rounded run average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

- 13 -

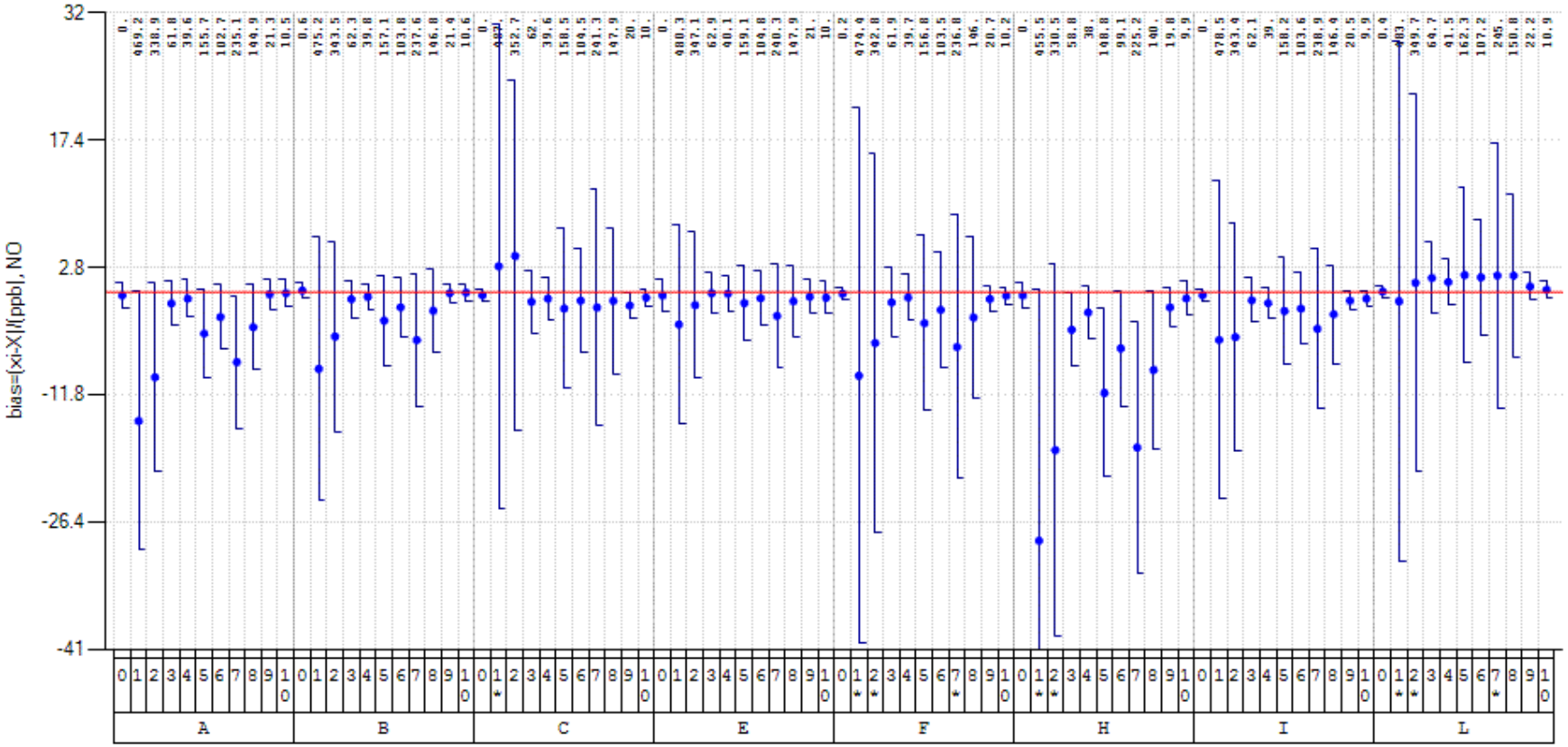

Figure 9: Bias of participant's NO measurement results
Expanded uncertainty of bias for each run is presented as error bar. Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 10) together with the participants rounded run average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

- 14 -

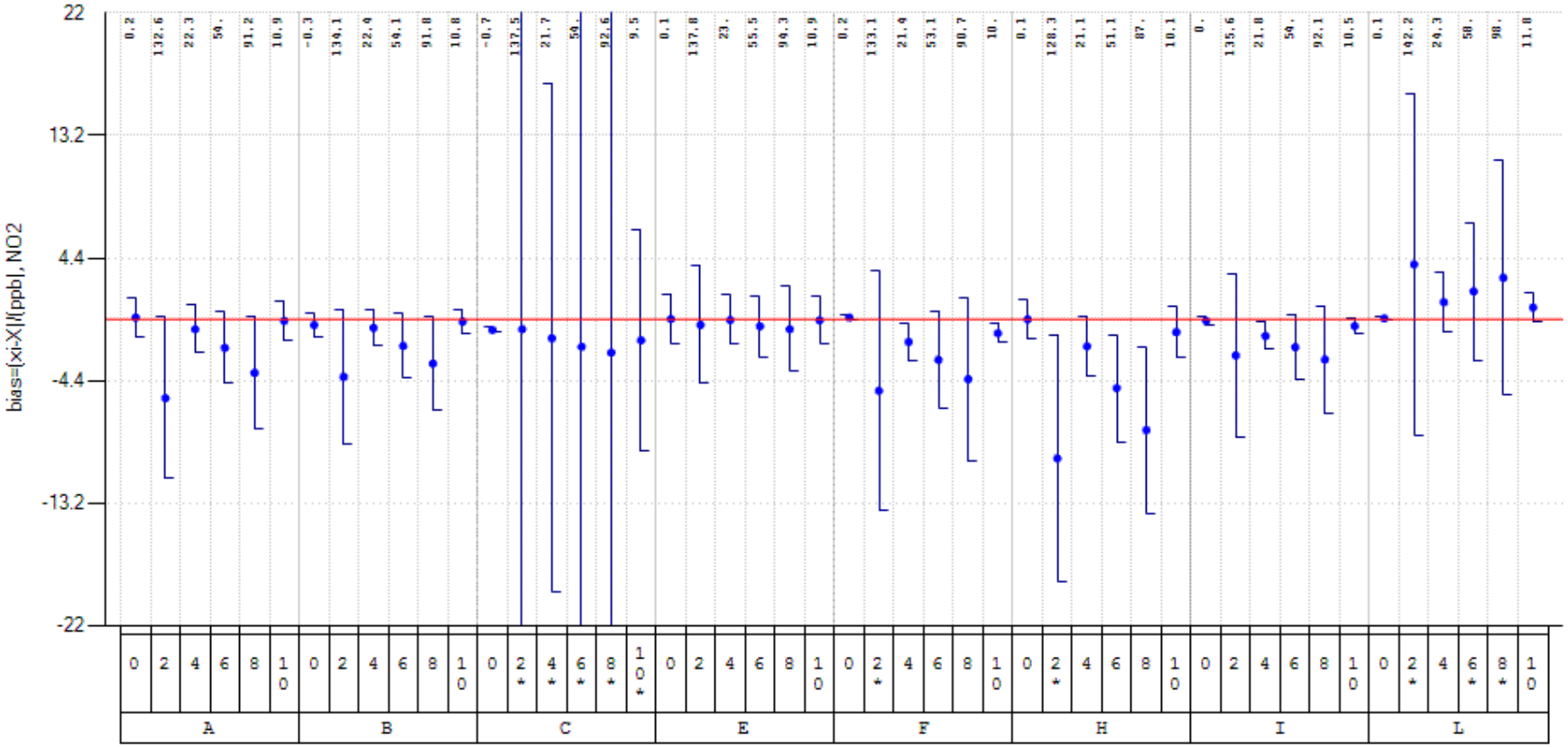

Figure 10: Bias of participant's NO_2 measurement results
Expanded uncertainty of bias is presented as error bar for NO_2 run numbers 0, 2, 4, 6, 8 and 10 (see Table 3). Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number together with the participants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

- 15 -

6. Performance characteristics of individual laboratories

Individual participants' bias was evaluated and are presented in chapter 5 (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.

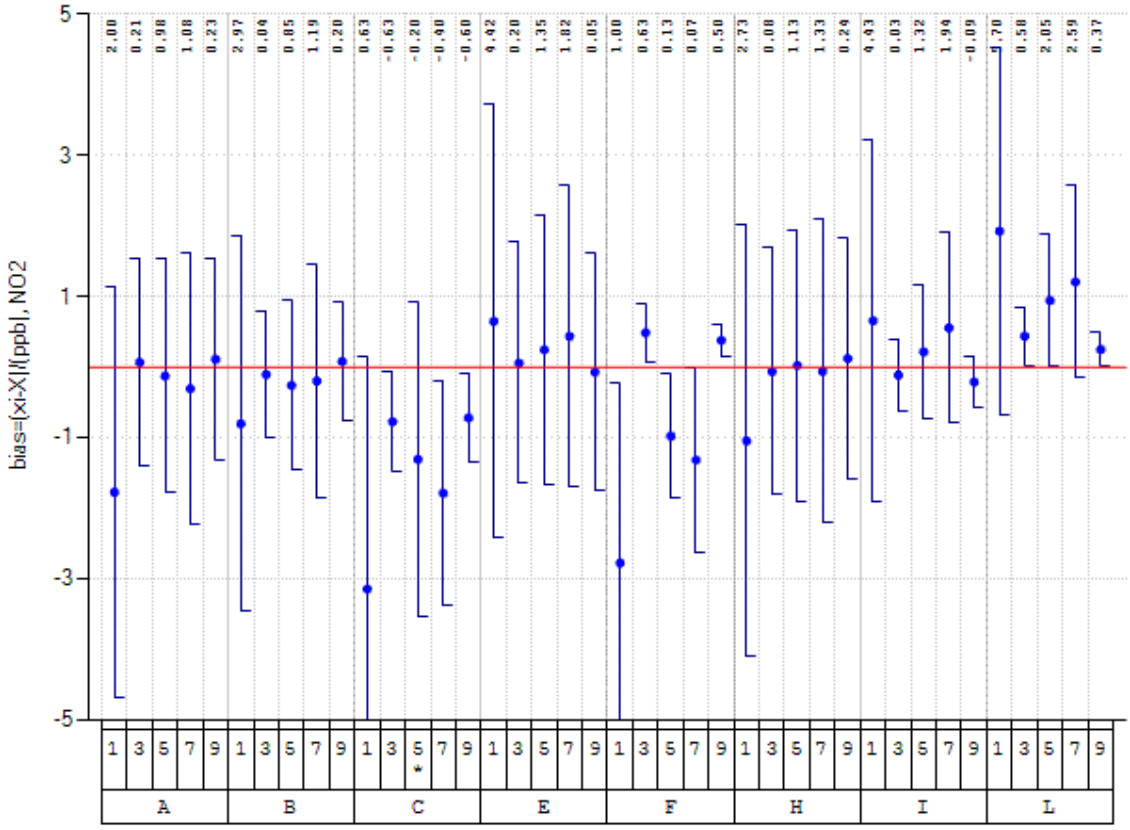

Figure 11: Bias of participant's NO_2 measurements for run numbers 1, 3, 5, 7 and 9
At these test gas mixtures the concentration levels of NO_2 were zero and the concentration levels of NO were not zero (see Table 3). In that perspective the figure shows the effect of NO concentration on NO_2 measurements.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

6.1 The efficiency of NO_2-to-NO converters of NO_X 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]:

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

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 5 respectively:

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

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

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

The evaluation of equation 4 and 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.

IE	NO_2	α	Δ^{NO}	Δ^{NO2}
code	nmol/mol	%	nmol/mol	nmol/mol
F	14	89.9		
F	95	99.9	1.2	1.3
F	55	99.3	0.7	1.1
F	25	93.5	0.6	2.1
F	130	100.3	0.3	-0.2
C	14	101.0		
C	95	99.6	4.5	4.9
C	55	100.5	3.3	3
C	25	99.6	1.5	1.6
C	130	102.0	6	3.4
D	14	99.6		
D	95	99.4	-3.7	-3.2
D	55	100.0	-1.6	-1.6
D	25	100.5	-0.3	-0.4
D	130	99.3	-4.5	-3.6
A	14	98.9		
A	95	99.9	0.8	0.9
A	55	99.9	0.5	0.5
A	25	99.6	0.1	0.2
A	130	100.1	-0.3	-0.5
I	14	99.3		
I	95	97.5	-0.6	1.7
I	55	96.4	-0.7	1.3
I	25	94.5	-0.3	0.9
I	130	97.1	-1.5	2.4
L	14	101.8		
L	95	101.4	-3.2	-4.5
L	55	101.4	-1.8	-2.6
L	25	101.9	-0.9	-1.3
L	130	102.4	-2	-5.1
E	14	98.9		
E	95	100	-2.6	-2.7
E	55	99.6	-1.7	-1.5
E	25	99.8	-0.9	-0.8
E	130	100.2	-4	-4.2
H	14	99.8		
H	95	100.6	5.2	4.7
H	55	100.3	3.3	3.1
H	25	101.1	1.4	1.2
H	130	100.4	5.8	5.3
B	14	98.2		
B	95	99.8	-0.2	-0.1
B	55	99.8	0.1	0.2
B	25	99.4	0	0.1
B	130	99.6	-0.5	0.1

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

The uncertainty in the evaluation of the converter efficiency decreases as NO_2 concentrations increase. The average standard uncertainty of the converter efficiency was calculated by estimating the standard deviation of repeated measurements of quantities in equation 3 at different NO_2 levels. It was found to be approximately 1%, at 130 nmol/mol of NO_2, and 2%, at 14 nmol/mol of NO_2.

7. Discussion

For a general assessment of the quality of each result a decision diagram was developed (Figure 12) that categorises results in seven categories (a1 to a7). The general comments for each category are:

- a1: measurement result is completely satisfactory
- a2: measurement result is satisfactory (z'-score satisfactory and En-number ok) but the reported uncertainty is too high
- a3: measured value is satisfactory (z'-score satisfactory) but the reported uncertainty is underestimated (En-number not ok)
- a4: measurement result is questionable (z'-score questionable) but due to a high reported uncertainty can be considered valid (En-number ok)
- a5: measurement result is questionable (z'-score questionable and En-number not ok)
- a6: measurement result is unsatisfactory (z'-score unsatisfactory) but due to a high reported uncertainty can be considered valid (En-number ok)
- a7: measurement result is unsatisfactory (z'-score unsatisfactory and En-number not ok)

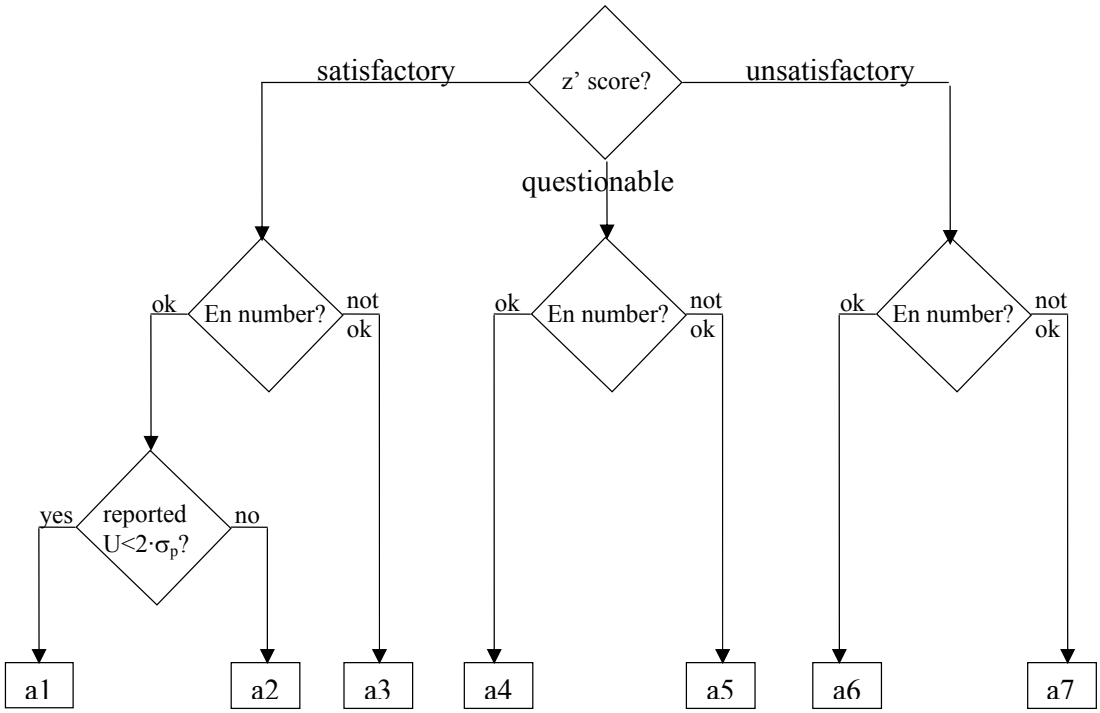

Figure 12: The decision diagram for general assessment of proficiency results.

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	conc. level	IE code								
			A	B	C	E	F	G	H	I	L
CO (µmol/mol)	0	0.014	a1	a1	a3	a1	a3	a1	a1	a1	a1
	5	1.003	a1	a1	a3	a1	a1	a1	a2	a1	a1
	4	1.976	a1	a1	a3	a1	a1	a1	a1	a1	a1
	3	4.272	a1	a1	a1	a1	a1	a1	a1	a1	a1
	2	5.959	a1	a1	a1	a1	a1	a1	a1	a1	a1
	1	8.547	a1	a1	a1	a1	a1	a1	a1	a1	a1
NO (nmol/mol)	0	0.3	a1	a1	a1	a1	a1	ND	a1	a1	a1
	10	3.4	a1	a1	a1	a1	a1	ND	a1	a1	a1
	9	17.1	a1	a1	a3	a1	a1	ND	a1	a1	a1
	8	31.8	a1	a1	a1	a1	a1	ND	a1	a1	a1
	7	52.5	a3	a1	a1	a1	a2	ND	a5	a1	a2
	6	94.9	a1	a1	a1	a1	a1	ND	a1	a1	a1
	5	154.5	a1	a1	a1	a1	a1	ND	a5	a1	a1
	4	154.0	a1	a1	a1	a1	a1	ND	a1	a1	a1
	3	253.8	a1	a1	a1	a1	a1	ND	a1	a1	a1
	2	383.2	a1	a1	a1	a1	a2	ND	a2	a1	a2
	1	502.0	a1	a1	a2	a1	a2	ND	a4	a1	a2
NO_2 (nmol/mol)	0	-0.2	a1	a1	a3	a1	a1	ND	a1	a1	a1
	10	13.5	a1	a1	a2	a1	a3	ND	a1	a1	a1
	8	20.6	a1	a1	a2	a1	a1	ND	a5	a1	a2
	6	59.9	a1	a1	a2	a1	a1	ND	a5	a1	a2
	4	101.3	a1	a1	a2	a1	a3	ND	a1	a3	a1
	2	121.9	a1	a1	a2	a1	a2	ND	a5	a1	a2
O_3 (nmol/mol)	0	0.4	a1	a1	a1	a1	a1	a1	a1	a1	a1
	5	13.9	a1	a1	a1	a1	a1	a1	a2	a1	a1
	4	20.8	a1	a1	a5	a1	a1	a1	a1	a1	a1
	3	59.2	a1	a1	a2	a1	a1	a1	a1	a1	a1
	2	98.7	a1	a1	a1	a1	a1	a1	a2	a1	a1
	1	117.0	a1	a1	a4	a1	a2	a1	a1	a1	a1
SO_2 (nmol/mol)	0	0.1	a1	a1	a1	a1	a1	a1	a1	a1	a1
	5	3.0	a1	a1	a1	a1	a1	a1	a1	a1	a1
	4	7.4	a1	a1	a1	a3	a1	a5	a2	a1	a2
	3	18.8	a1	a1	a1	a1	a1	a3	a1	a1	a1
	2	47.9	a1	a1	a1	a1	a1	a3	a1	a1	a1
	1	134.9	a1	a1	a1	a1	a1	a1	a1	a1	a1

Table 6: The general assessment of proficiency results. ND refers to Not Delivered results.

7.1 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) 85% of the results reported by AQUILA laboratories fall into 'a1' category 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 'a2' (8%), or too small, category '3' (4%). 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 'a1' results can be observed confirming the trend of the most recent IEs. This conclusion could be considered as an improvement in the ability of NRLs to estimate their uncertainty (not too high, not too small) but may also reflect the effect of the new (more tolerant) criteria for uncertainty at zero level implemented in 2009 for the first time.
In this exercise there were no unsatisfactory results in the z'-score evaluations. Laboratory H obtained 3 questionable results for NO_2 and NO each. According to the protocol in force, participation to the next IE is required in order to demonstrate remediation measures. Laboratory C showed two questionable results for O_3 while Laboratory G presented one questionable result for SO_2. These performances are considered as a warning and no action is required.

Comparability of results among AQUILA participants at the highest concentration level, excluding outliers, is acceptable for NO, CO and O_3 measurements while NO_2 and SO_2 measurements showed less satisfactory results.
The relative reproducibility limits, at the highest studied concentration levels, are 4.6% for CO, 7.7% for O_3 and 7.0% for NO, all within the objective derived from criteria imposed by the European Commission (σ_p). This is not the case for NO_2 and SO_2 where the relative reproducibility limits, 10.9% and 9.6% respectively, are beyond the relevant targets of 9.1% and 9.3%. The poor reproducibility of these two measurement methods in this IE requires further investigation to identify the causes. In particular, SO_2 measurements presented inadequate comparability among participants in two of the latest IEs (2008, 2009) and the highest number of outliers (5). Also NO_2 presented poor performance in three of the more recent intercomparisons (2007, 2008, and 2009) but the number of outliers was lower than those for SO_2 analyses (3).

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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 volumeter. 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 composition evaluation 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]:

$$\frac{\left|x^* - X\right|}{\sqrt{\frac{\left(1{,}25 \cdot s^*\right)^2}{p} + u_{X'}^2}} < 2 \qquad (6)$$

Where 'x*' and 's*' represent robust average and robust standard deviation respectively and 'p' is the number of participants.

In *Table 7* all inputs for expression 6 are given and all ERLAP's measurement results are confirmed to be valid.

run	unit	X	uX'	x*	s*	p	val.
NO_0	nmol/mol	0.37	0.32	0.04	0.07	9	OK
NO_1	nmol/mol	484.00	4.94	477.81	7.29	9	OK
NO_2	nmol/mol	348.60	3.59	344.67	6.18	9	OK
NO_3	nmol/mol	63.08	0.78	62.23	0.64	9	OK
NO_4	nmol/mol	40.31	0.58	39.72	0.67	9	OK
NO_5	nmol/mol	160.39	1.72	158.04	2.35	9	OK
NO_6	nmol/mol	105.51	1.19	104.00	1.56	9	OK
NO_7	nmol/mol	243.06	2.54	238.96	4.12	9	OK
NO_8	nmol/mol	148.94	1.61	146.95	1.95	9	OK
NO_9	nmol/mol	21.51	0.43	20.92	0.76	9	OK
NO_10	nmol/mol	10.63	0.36	10.29	0.42	9	OK
NO2_0	nmol/mol	0.05	0.06	0.04	0.16	9	OK
NO2_1	nmol/mol	3.77	0.06	3.07	1.91	9	OK
NO2_2	nmol/mol	138.22	1.96	135.59	3.95	9	OK
NO2_3	nmol/mol	0.14	0.01	0.15	0.17	9	OK
NO2_4	nmol/mol	23.01	0.44	22.27	0.98	9	OK
NO2_5	nmol/mol	1.10	0.02	1.05	0.43	9	OK
NO2_6	nmol/mol	55.98	0.86	54.31	1.53	9	OK
NO2_7	nmol/mol	1.38	0.02	1.29	0.83	9	OK
NO2_8	nmol/mol	94.98	1.41	92.43	2.37	9	OK
NO2_9	nmol/mol	0.12	0.01	0.17	0.23	9	OK
NO2_10	nmol/mol	10.96	0.44	10.64	0.56	9	OK

run	unit	X	uX'	x*	s*	p	val.
CO_0	µmol/mol	0.008	0.030	0.03	0.05	10	OK
CO_1	µmol/mol	8.956	0.048	8.88	0.14	10	OK
CO_2	µmol/mol	4.503	0.033	4.48	0.07	10	OK
CO_3	µmol/mol	5.986	0.044	5.94	0.09	10	OK
CO_4	µmol/mol	3.018	0.031	3.01	0.05	10	OK
CO_5	µmol/mol	1.030	0.030	1.04	0.06	10	OK
O3_0	nmol/mol	0.43	0.28	0.06	0.17	10	OK
O3_1	nmol/mol	130.87	0.97	131.17	1.13	10	OK
O3_2	nmol/mol	22.50	0.29	22.44	0.35	10	OK
O3_3	nmol/mol	53.24	0.43	53.44	0.57	10	OK
O3_4	nmol/mol	90.38	0.68	90.85	0.79	10	OK
O3_5	nmol/mol	10.88	0.27	10.83	0.17	10	OK
SO2_0	nmol/mol	0.29	0.22	0.22	0.20	10	OK
SO2_1	nmol/mol	8.27	0.22	8.24	0.35	10	OK
SO2_2	nmol/mol	51.54	0.41	51.70	1.56	10	OK
SO2_3	nmol/mol	20.25	0.28	20.28	0.72	10	OK
SO2_4	nmol/mol	138.96	0.87	139.54	3.56	10	OK
SO2_5	nmol/mol	3.40	0.22	3.33	0.31	10	OK

Table 7: The validation of assigned values (X)
by comparison to the robust averages (x*) with taking into the account the standard uncertainties of assigned values (uX'), and robust standard deviations (s*) as denoted by expression 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 5.

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

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. 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 tables. 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)	-0.12	0.40	0.70	0.29	0.15	0.20	0.92	0.06	0.10	0.19
u(xi) (nmol/mol)	0.70	0.30	0.01	0.22	0.41	0.00	0.75	0.60	0.54	0.01
U(xi) (nmol/mol)	1.40	0.60	0.01	0.44	0.82	0.01	1.50	1.20	1.08	0.02

Table 8: Reported values for SO_2 run 0.

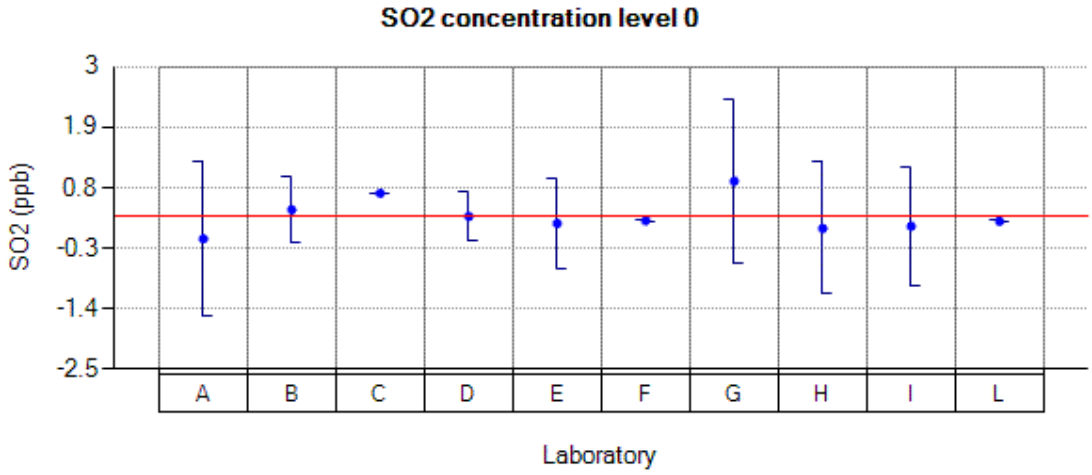

Figure 13: Reported values for SO_2 run 0.

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	8.18	8.28	8.70	8.27	7.96	8.00	9.52	8.06	7.70	8.48
xi,2 (nmol/mol)	8.16	8.45	8.80	8.27	7.97	8.00	9.54	8.09	7.72	8.43
xi,3 (nmol/mol)	8.09	8.27	8.90	8.27	7.97	8.00	9.60	8.14	7.78	8.36
Xi (nmol/mol)	8.14	8.33	8.80	8.27	7.96	8.00	9.55	8.09	7.73	8.42
Si (nmol/mol)	0.04	0.10	0.10	0.00	0.00	0.00	0.04	0.04	0.04	0.06
u(xi) (nmol/mol)	0.70	0.30	0.27	0.22	0.42	0.24	0.75	0.36	0.55	0.24
U(xi) (nmol/mol)	1.40	0.60	0.53	0.44	0.84	0.47	1.50	1.50	1.11	0.48

Table 9: Reported values for SO_2 run 1.

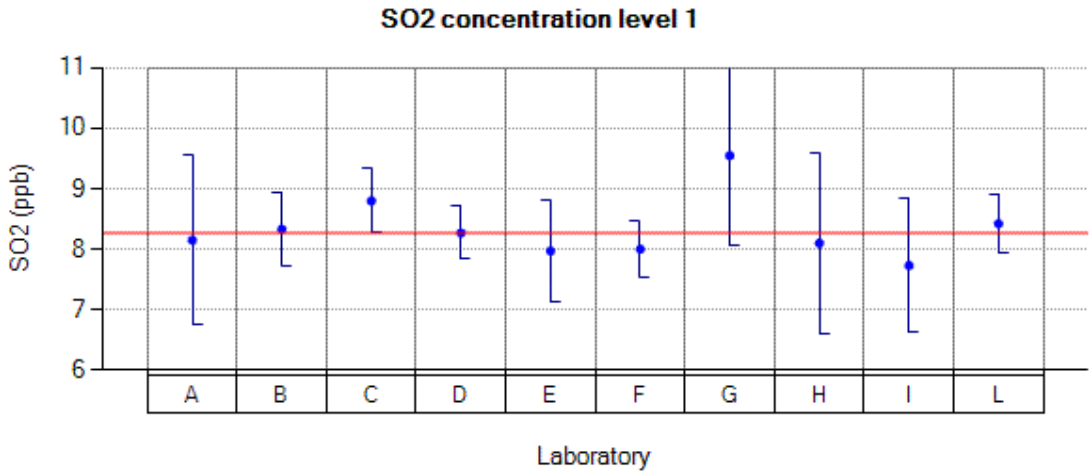

Figure 14: Reported values for SO_2 run 1.

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	52.12	50.96	52.30	51.38	50.19	50.10	55.64	51.59	49.90	53.44
xi,2 (nmol/mol)	52.09	50.86	52.40	51.57	50.18	50.30	55.75	51.69	50.36	53.65
xi,3 (nmol/mol)	52.17	51.01	52.60	51.66	50.27	50.30	55.78	51.64	50.39	53.72
Xi (nmol/mol)	52.12	50.94	52.43	51.53	50.21	50.23	55.72	51.64	50.21	53.60
Si (nmol/mol)	0.04	0.07	0.15	0.14	0.04	0.11	0.07	0.05	0.27	0.14
u(xi) (nmol/mol)	0.80	0.66	1.40	0.38	0.62	1.51	0.95	0.90	0.96	1.51
U(xi) (nmol/mol)	1.60	1.32	2.79	0.76	1.24	3.01	1.90	3.80	1.93	3.02

Table 10: Reported values for SO_2 run 2.

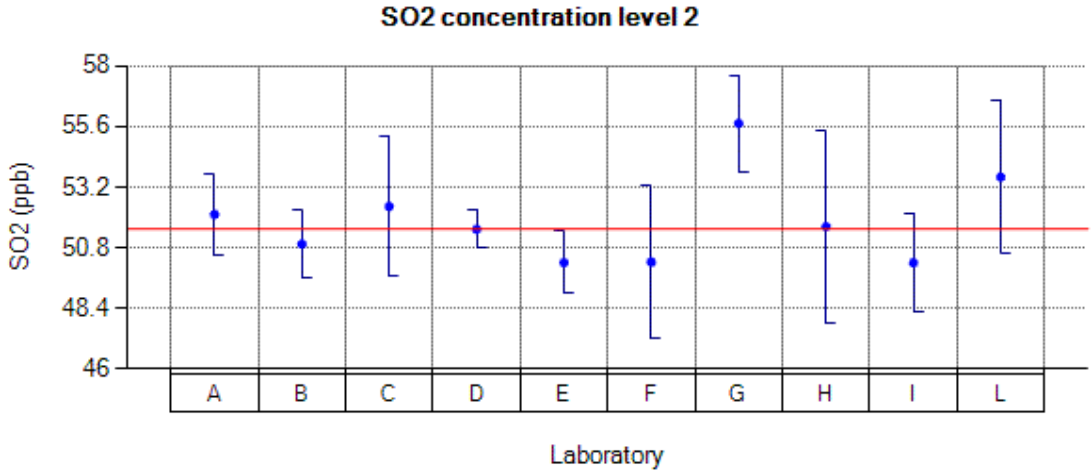

Figure 15: Reported values for SO_2 run 2.

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	20.23	20.07	20.90	20.25	19.55	19.50	22.21	20.11	19.66	21.00
xi,2 (nmol/mol)	20.25	20.13	21.10	20.25	19.59	19.60	22.39	20.15	19.52	20.96
xi,3 (nmol/mol)	20.40	20.15	20.90	20.25	19.55	19.70	22.26	20.14	19.51	20.93
Xi (nmol/mol)	20.29	20.12	20.97	20.25	19.56	19.60	22.29	20.13	19.56	20.96
Si (nmol/mol)	0.09	0.04	0.12	0.00	0.02	0.10	0.09	0.02	0.08	0.04
u(xi) (nmol/mol)	0.70	0.40	0.57	0.27	0.47	0.58	0.80	0.46	0.62	0.59
U(xi) (nmol/mol)	1.40	0.80	1.15	0.54	0.94	1.16	1.60	2.00	1.25	1.18

Table 11: Reported values for SO_2 run 3.

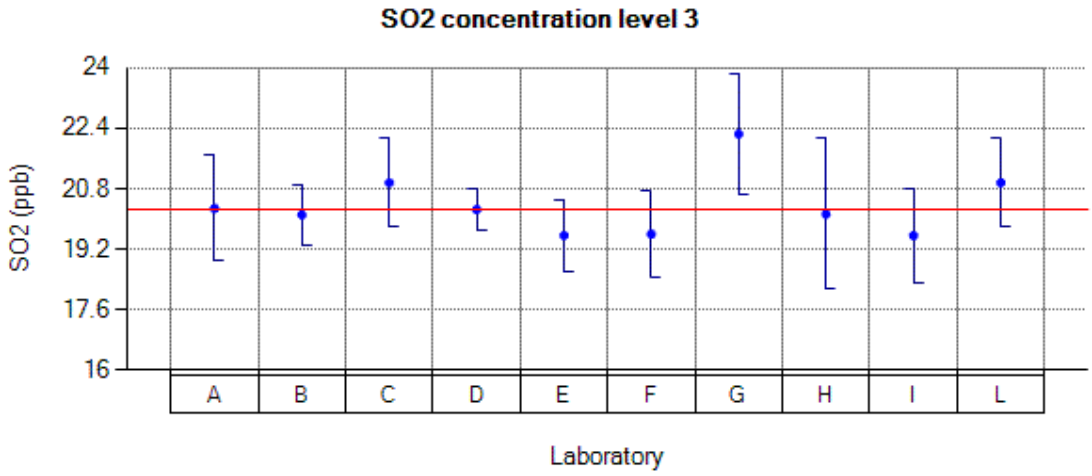

Figure 16: Reported values for SO_2 run 3.

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	140.69	137.70	140.80	138.96	135.56	136.70	148.92	139.93	137.05	145.31
xi,2 (nmol/mol)	140.91	137.54	140.60	138.96	135.65	136.70	148.96	139.77	136.26	145.48
xi,3 (nmol/mol)	140.81	137.38	140.80	138.96	135.76	136.60	148.81	139.68	135.93	145.49
Xi (nmol/mol)	140.80	137.54	140.73	138.96	135.65	136.66	148.89	139.79	136.41	145.42
Si (nmol/mol)	0.11	0.16	0.11	0.00	0.10	0.05	0.07	0.12	0.57	0.10
u(xi) (nmol/mol)	1.60	1.79	3.65	0.77	1.16	4.03	1.70	2.20	2.23	4.09
U(xi) (nmol/mol)	3.20	3.58	7.30	1.54	2.32	8.06	3.40	9.70	4.47	8.18

Table 12: Reported values for SO_2 run 4.

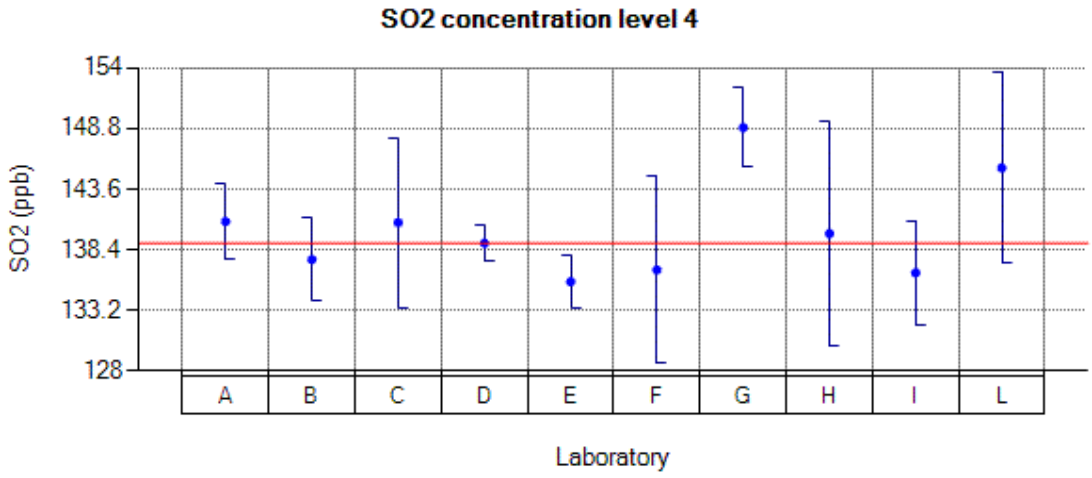

Figure 17: Reported values for SO_2 run 4.

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	3.07	3.33	4.00	3.46	3.18	3.50	4.24	3.19	2.82	3.44
xi,2 (nmol/mol)	2.91	3.39	3.90	3.37	3.19	3.50	4.36	3.17	3.04	3.30
xi,3 (nmol/mol)	2.89	3.29	4.00	3.37	3.13	3.40	4.32	3.17	2.77	3.32
Xi (nmol/mol)	2.95	3.33	3.96	3.40	3.16	3.46	4.30	3.17	2.87	3.35
Si (nmol/mol)	0.09	0.05	0.05	0.05	0.03	0.05	0.06	0.01	0.14	0.07
u(xi) (nmol/mol)	0.70	0.30	0.18	0.22	0.42	0.10	0.75	0.34	0.54	0.10
U(xi) (nmol/mol)	1.40	0.60	0.35	0.44	0.84	0.21	1.50	1.50	1.09	0.20

Table 13: Reported values for SO_2 run 5.

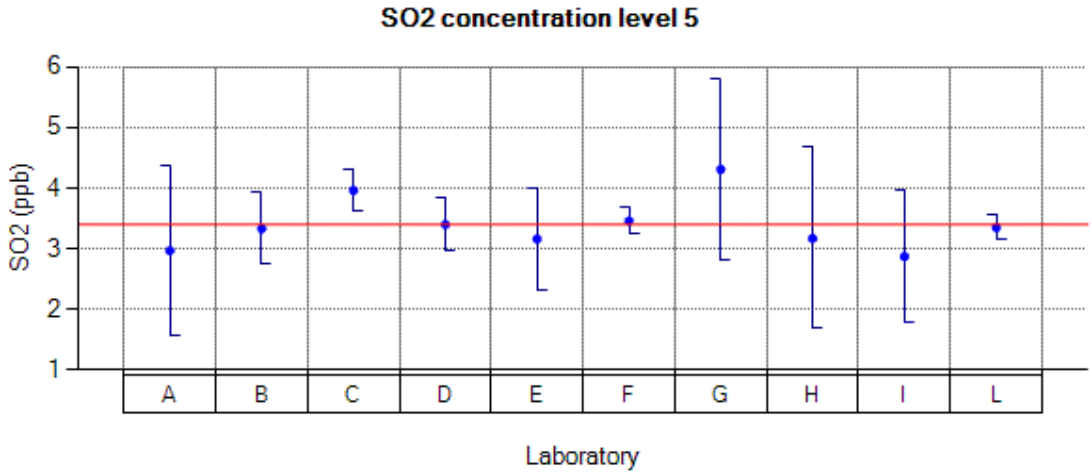

Figure 18: Reported values for SO_2 run 5.

Reported values for CO

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	0.032	0.017	0.100	0.008	-0.003	0.100	0.183	-0.009	-0.015	0.038
u(xi) (nmol/mol)	0.060	0.010	0.001	0.030	0.050	0.003	0.090	0.059	0.080	0.001
U(xi) (nmol/mol)	0.120	0.020	0.001	0.060	0.100	0.006	0.180	0.120	0.170	0.002

Table 14: Reported values for CO run 0.

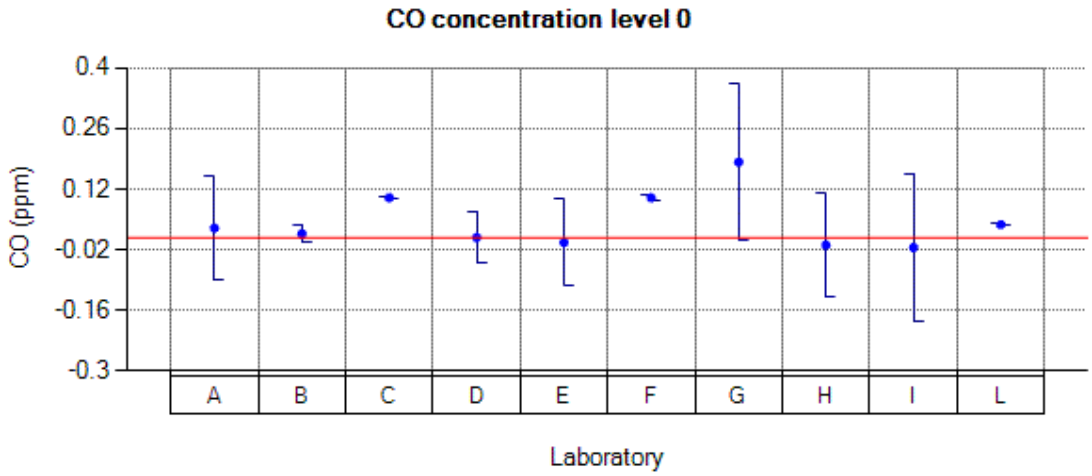

Figure 19: Reported values for CO run 0.

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	8.831	8.989	9.000	8.957	8.930	8.750	8.789	-	8.700	8.976
xi,2 (nmol/mol)	8.829	8.991	9.100	8.947	8.940	8.750	8.790	8.770	8.702	8.979
xi,3 (nmol/mol)	8.826	9.000	9.100	8.964	8.940	8.750	8.806	-	8.702	8.967
Xi (nmol/mol)	8.829	8.993	9.067	8.956	8.937	8.750	8.795	8.770	8.701	8.974
Si (nmol/mol)	0.003	0.006	0.058	0.009	0.006	0.000	0.010	-	0.001	0.006
u(xi) (nmol/mol)	0.130	0.090	0.255	0.040	0.130	0.263	0.100	0.210	0.260	0.279
U(xi) (nmol/mol)	0.260	0.180	0.511	0.080	0.260	0.525	0.200	0.410	0.520	0.558

Table 15: Reported values for CO run 1.

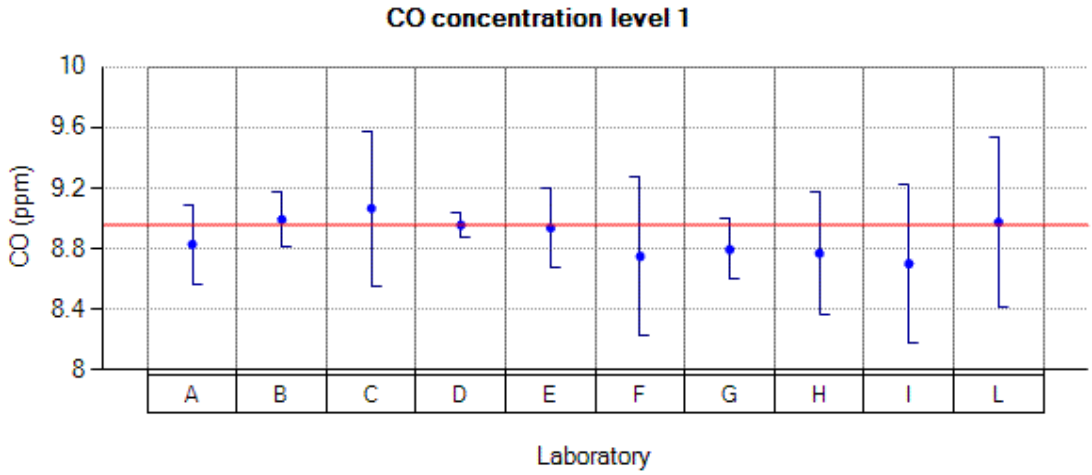

Figure 20: Reported values for CO run 1.

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	4.440	4.523	4.700	4.493	4.490	4.390	4.460	-	4.414	4.548
xi,2 (nmol/mol)	4.442	4.520	4.700	4.508	4.490	4.390	4.483	4.386	4.444	4.551
xi,3 (nmol/mol)	4.441	4.517	4.700	4.507	4.490	4.390	4.453	-	4.460	4.554
Xi (nmol/mol)	4.441	4.520	4.700	4.503	4.490	4.390	4.465	4.386	4.439	4.551
Si (nmol/mol)	0.001	0.003	0.000	0.008	0.000	0.000	0.016	-	0.023	0.003
u(xi) (nmol/mol)	0.090	0.050	0.138	0.030	0.080	0.132	0.095	0.190	0.150	0.141
U(xi) (nmol/mol)	0.180	0.100	0.276	0.060	0.160	0.263	0.190	0.330	0.300	0.282

Table 16: Reported values for CO run 2.

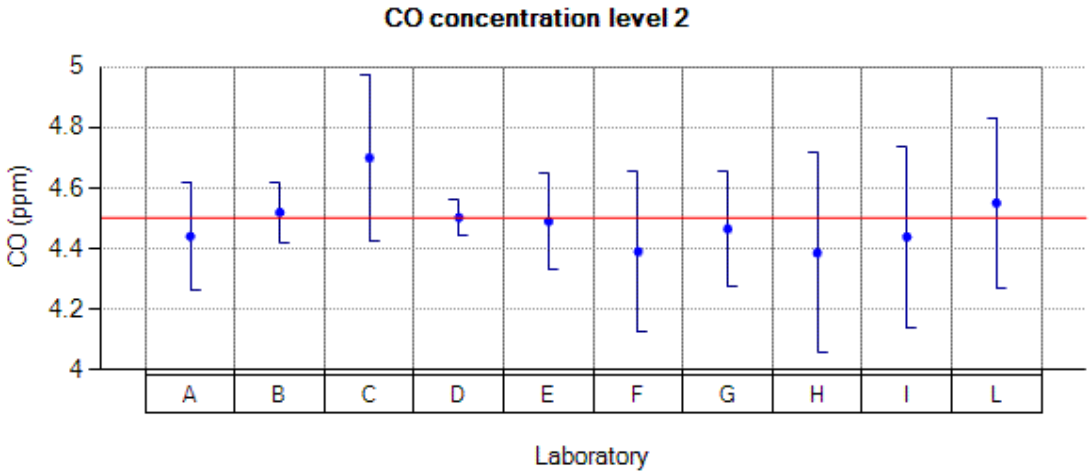

Figure 21: Reported values for CO run 2.

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	5.899	5.997	6.200	5.989	5.980	5.850	5.866	-	5.893	6.026
xi,2 (nmol/mol)	5.901	5.996	6.200	5.993	5.980	5.850	5.858	5.836	5.890	6.024
xi,3 (nmol/mol)	5.905	5.991	6.200	5.977	5.980	5.850	5.892	-	5.893	6.022
Xi (nmol/mol)	5.902	5.995	6.200	5.986	5.980	5.850	5.872	5.836	5.892	6.024
Si (nmol/mol)	0.003	0.003	0.000	0.008	0.000	0.000	0.018	-	0.002	0.002
u(xi) (nmol/mol)	0.100	0.060	0.171	0.040	0.090	0.176	0.095	0.180	0.180	0.187
U(xi) (nmol/mol)	0.200	0.120	0.343	0.080	0.180	0.351	0.190	0.360	0.370	0.374

Table 17: Reported values for CO run 3.

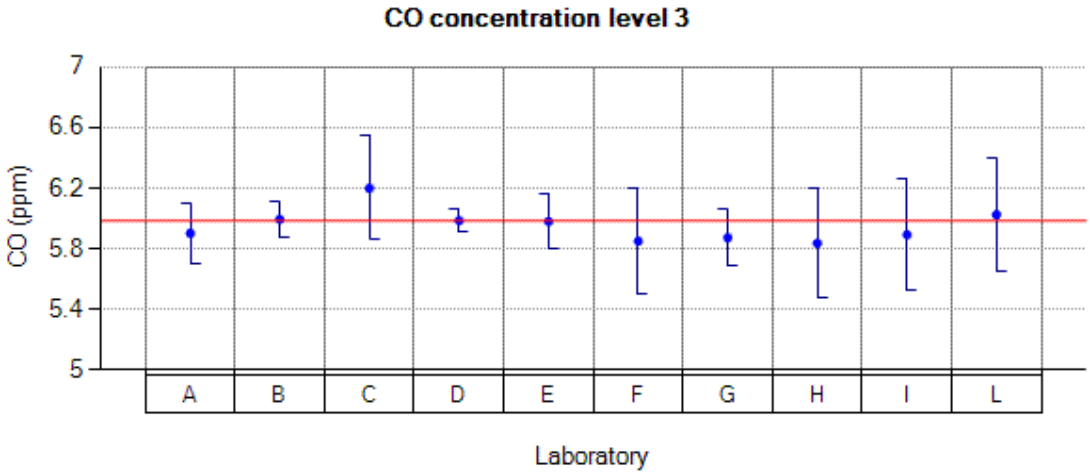

Figure 22: Reported values for CO run 3.

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	2.985	2.997	3.300	3.024	3.000	2.930	3.046	-	3.008	3.066
xi,2 (nmol/mol)	2.985	2.993	3.300	3.009	3.000	2.930	3.041	2.922	3.005	3.064
xi,3 (nmol/mol)	2.986	2.996	3.300	3.021	3.000	2.930	3.042	-	3.013	3.065
Xi (nmol/mol)	2.985	2.995	3.300	3.018	3.000	2.930	3.043	2.922	3.009	3.065
Si (nmol/mol)	0.001	0.002	0.000	0.008	0.000	0.000	0.003	-	0.004	0.001
u(xi) (nmol/mol)	0.080	0.030	0.095	0.030	0.060	0.086	0.095	0.160	0.120	0.095
U(xi) (nmol/mol)	0.160	0.060	0.191	0.060	0.120	0.173	0.190	0.320	0.240	0.190

Table 18: Reported values for CO run 4.

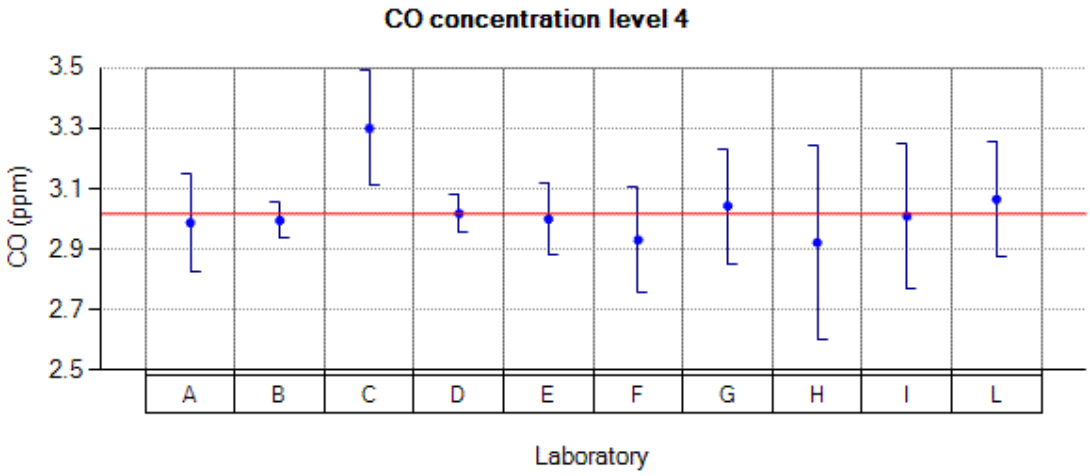

Figure 23: Reported values for CO run 4.

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	1.028	0.981	1.200	1.020	1.010	0.980	1.188	-	1.070	1.067
xi,2 (nmol/mol)	1.027	0.989	1.200	1.031	1.010	0.980	1.162	0.965	1.070	1.071
xi,3 (nmol/mol)	1.028	0.996	1.200	1.038	1.010	0.980	1.171	-	1.071	1.071
Xi (nmol/mol)	1.028	0.989	1.200	1.030	1.010	0.980	1.174	0.965	1.070	1.070
Si (nmol/mol)	0.001	0.008	0.000	0.009	0.000	0.000	0.013	-	0.001	0.002
u(xi) (nmol/mol)	0.070	0.020	0.048	0.030	0.050	0.029	0.090	0.150	0.090	0.033
U(xi) (nmol/mol)	0.140	0.030	0.096	0.060	0.100	0.059	0.180	0.300	0.180	0.066

Table 19: Reported values for CO run 5.

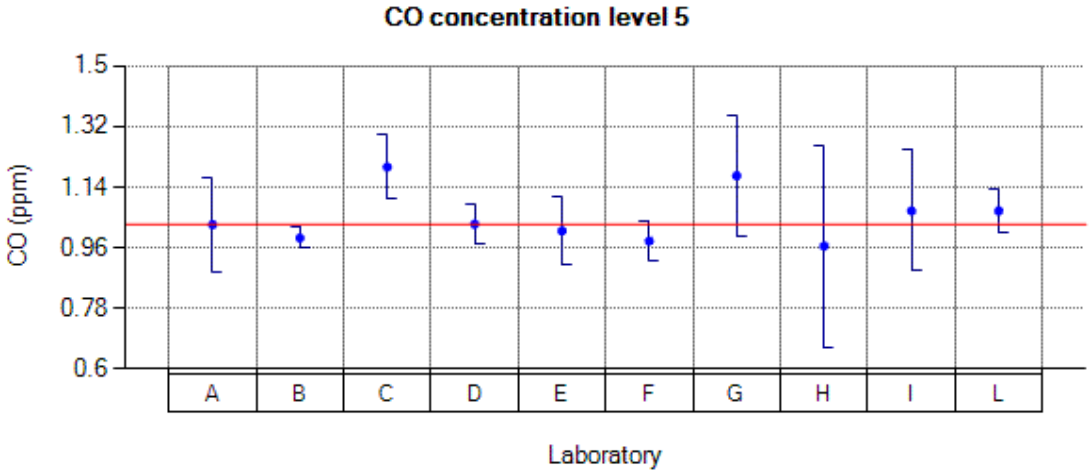

Figure 24: Reported values for CO run 5.

Reported values for O_3

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	-0.07	0.04	0.20	0.43	-0.15	0.20	0.07	-0.02	0.12	-0.02
u(xi) (nmol/mol)	0.60	0.71	0.22	0.28	0.63	0.01	0.95	0.58	0.31	0.70
U(xi) (nmol/mol)	1.20	1.42	0.43	0.56	1.26	0.02	1.90	1.20	0.63	1.40

Table 20: Reported values for O_3 run 0.

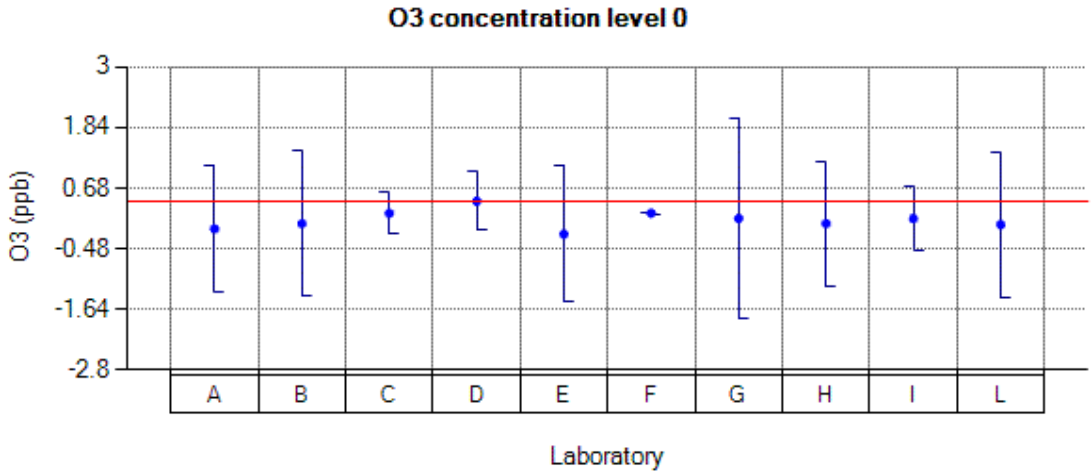

Figure 25: Reported values for O3 run 0.

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	129.77	130.90	139.30	130.67	128.80	131.40	130.01	130.66	133.00	131.09
xi,2 (nmol/mol)	130.53	131.31	140.60	130.94	129.25	132.10	130.38	130.91	133.82	131.36
xi,3 (nmol/mol)	130.98	131.49	140.90	131.00	129.52	132.30	130.43	131.00	133.92	131.57
Xi (nmol/mol)	130.42	131.23	140.26	130.87	129.19	131.93	130.27	130.85	133.58	131.34
Si (nmol/mol)	0.61	0.30	0.85	0.17	0.36	0.47	0.23	0.17	0.50	0.24
u(xi) (nmol/mol)	1.30	1.73	5.20	0.89	1.66	4.00	2.20	1.30	1.61	2.52
U(xi) (nmol/mol)	2.60	3.46	10.38	1.78	3.32	7.90	4.40	5.50	3.22	5.04

Table 21: Reported values for O_3 run 1

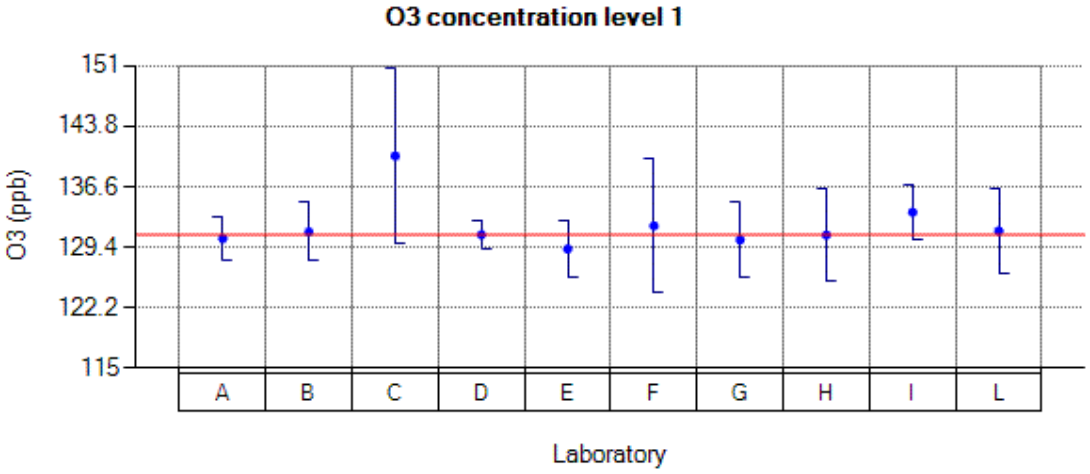

Figure 26: Reported values for O_3 run 1.

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	22.33	22.52	23.80	22.45	21.96	22.80	22.17	22.15	22.74	22.31
xi,2 (nmol/mol)	22.43	22.45	24.00	22.53	21.93	22.80	22.11	22.18	22.85	22.36
xi,3 (nmol/mol)	22.30	22.44	23.80	22.51	21.91	22.90	22.15	22.22	22.62	22.32
Xi (nmol/mol)	22.35	22.47	23.86	22.49	21.93	22.83	22.14	22.18	22.73	22.33
Si (nmol/mol)	0.05	0.04	0.11	0.04	0.02	0.05	0.03	0.03	0.11	0.02
u(xi) (nmol/mol)	0.80	0.75	0.86	0.28	0.67	0.70	1.00	0.68	0.41	0.89
U(xi) (nmol/mol)	1.60	1.50	1.72	0.56	1.34	1.37	2.00	2.90	0.82	1.78

Table 22: Reported values for O_3 run 2.

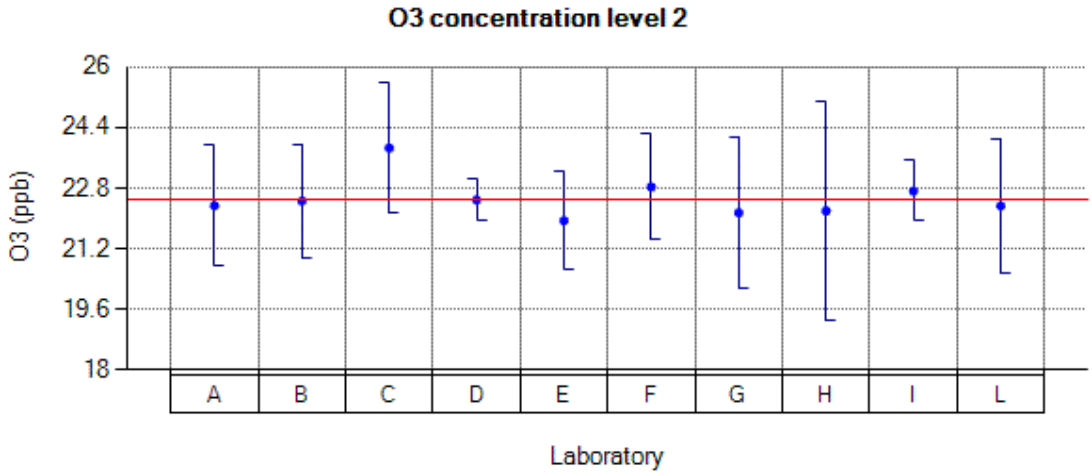

Figure 27: Reported values for O_3 run 2.

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	53.25	53.32	57.00	53.15	52.65	53.90	52.87	52.96	53.80	53.23
xi,2 (nmol/mol)	53.56	53.52	57.30	53.28	52.72	54.10	53.02	53.08	53.90	53.41
xi,3 (nmol/mol)	53.55	53.55	57.50	53.29	52.66	54.10	53.02	53.08	54.08	53.41
Xi (nmol/mol)	53.45	53.46	57.26	53.24	52.67	54.03	52.97	53.04	53.92	53.35
Si (nmol/mol)	0.17	0.12	0.25	0.07	0.03	0.11	0.08	0.06	0.14	0.10
u(xi) (nmol/mol)	0.90	1.07	2.10	0.40	0.88	1.60	1.25	0.81	0.71	1.35
U(xi) (nmol/mol)	1.80	2.14	4.20	0.80	1.76	3.24	2.50	3.50	1.42	2.70

Table 23: Reported values for O_3 run 3.

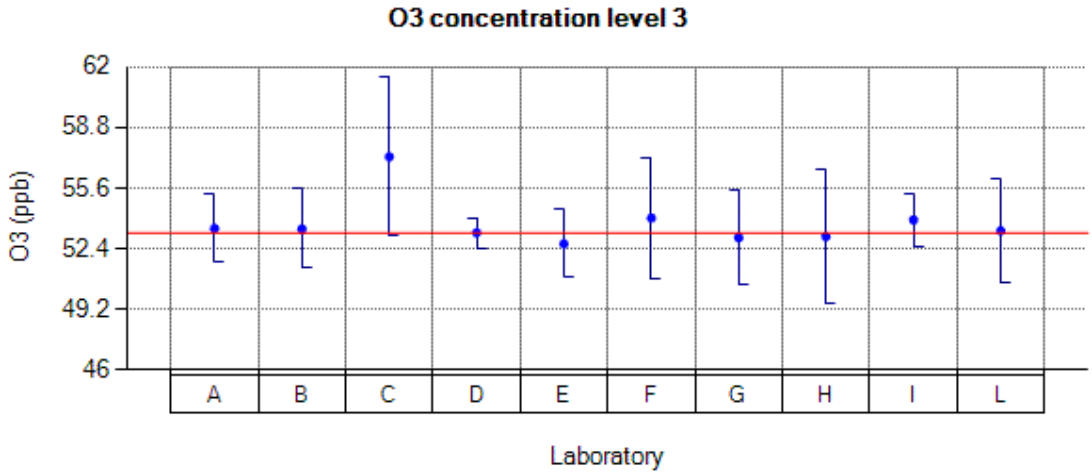

Figure 28: Reported values for O_3 run 3.

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	90.85	90.50	97.60	90.29	89.77	91.70	90.09	90.18	91.76	90.84
xi,2 (nmol/mol)	90.93	90.59	98.00	90.42	89.80	92.00	90.27	90.43	91.84	90.96
xi,3 (nmol/mol)	90.99	90.63	98.10	90.44	89.80	92.00	90.35	90.50	92.10	91.00
Xi (nmol/mol)	90.92	90.57	97.90	90.38	89.79	91.90	90.23	90.37	91.90	90.93
Si (nmol/mol)	0.07	0.06	0.26	0.08	0.01	0.17	0.13	0.16	0.17	0.08
u(xi) (nmol/mol)	1.10	1.31	3.51	0.62	1.23	2.76	1.70	1.00	1.12	1.91
U(xi) (nmol/mol)	2.20	2.62	7.02	1.24	2.46	5.52	3.40	4.40	2.26	3.82

Table 24: Reported values for O_3 run 4.

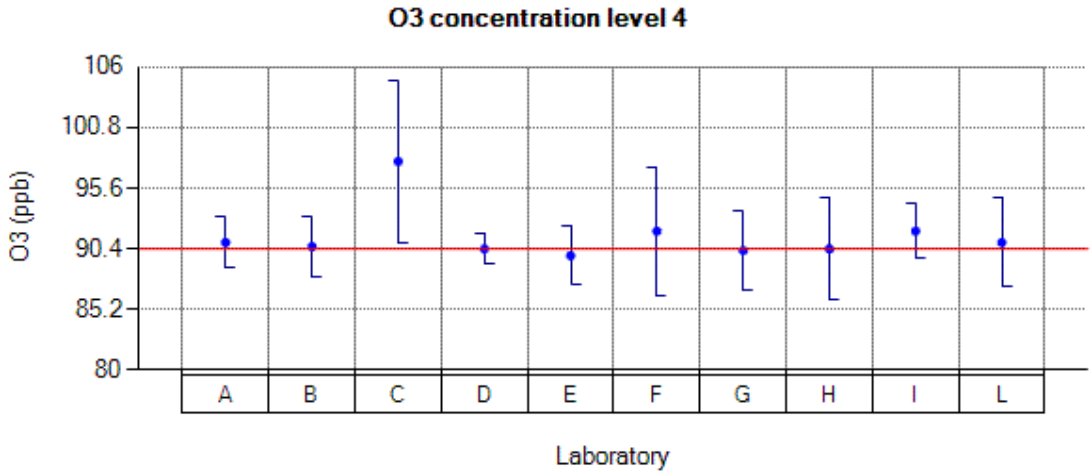

Figure 29: Reported values for O_3 run 4.

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi,1 (nmol/mol)	10.66	11.00	11.70	10.88	10.65	11.40	10.74	10.63	11.11	10.69
xi,2 (nmol/mol)	10.76	10.79	11.80	10.83	10.69	11.40	10.81	10.71	10.88	10.69
xi,3 (nmol/mol)	10.51	10.88	11.90	10.94	10.71	11.40	10.71	10.71	10.74	10.74
Xi (nmol/mol)	10.64	10.89	11.80	10.88	10.68	11.40	10.75	10.68	10.91	10.70
Si (nmol/mol)	0.12	0.10	0.10	0.05	0.03	0.00	0.05	0.04	0.18	0.02
u(xi) (nmol/mol)	0.70	0.71	0.48	0.27	0.64	0.34	1.00	0.64	0.34	0.71
U(xi) (nmol/mol)	1.40	1.42	0.96	0.54	1.28	0.68	2.00	2.80	0.68	1.42

Table 25: Reported values for O_3 run 5.

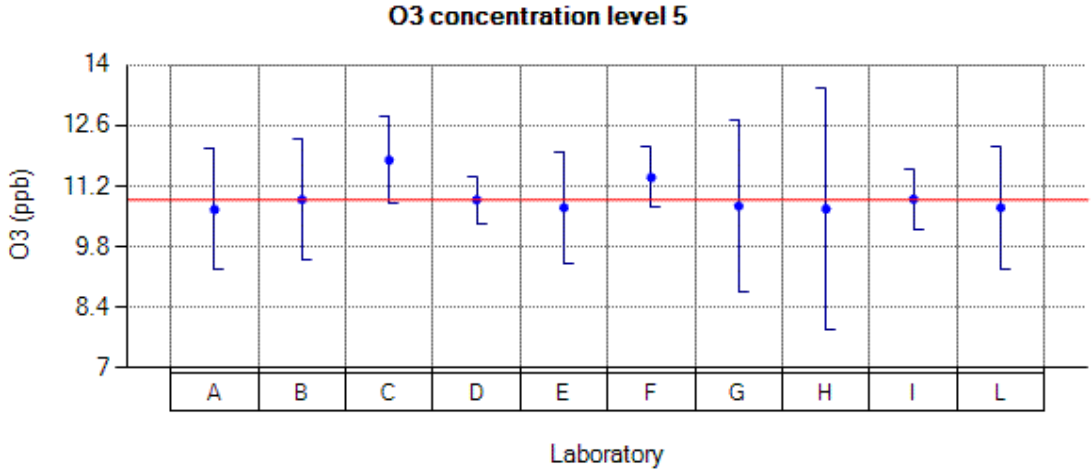

Figure 30: Reported values for O_3 run 5.

Reported values for NO

	laboratories								
values	A	B	C	D	E	F	H	I	L
xi,1 (nmol/mol)	0.03	0.56	0.00	0.37	-0.03	0.20	-0.02	0.01	0.42
u(xi) (nmol/mol)	0.70	0.30	-0.05	0.32	0.87	0.02	0.70	0.14	0.01
U(xi) (nmol/mol)	1.40	0.60	-0.10	0.65	1.74	0.04	1.40	0.29	0.02

Table 26: Reported values for NO run 0.

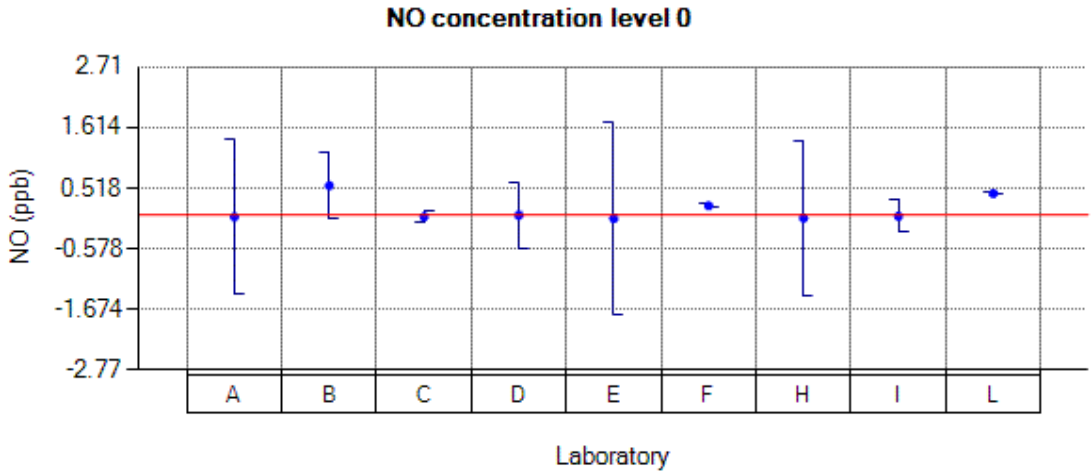

Figure 31: Reported values for NO run 0.

	laboratories								
values	A	B	C	D	E	F	H	I	L
xi,1 (nmol/mol)	468.57	474.45	487.70	483.22	479.57	473.40	455.43	477.91	482.39
xi,2 (nmol/mol)	469.40	475.28	484.30	484.09	480.44	474.50	455.96	478.45	483.08
xi,3 (nmol/mol)	469.69	475.91	488.90	484.69	480.85	475.40	455.16	479.24	483.42
Xi (nmol/mol)	469.22	475.21	486.96	484.00	480.28	474.43	455.51	478.53	482.96
Si (nmol/mol)	0.58	0.73	2.38	0.73	0.65	1.00	0.40	0.66	0.52
u(xi) (nmol/mol)	5.50	5.70	12.95	4.72	2.85	14.50	6.30	7.61	14.06
U(xi) (nmol/mol)	11.00	11.40	25.90	9.45	5.70	29.00	27.00	15.23	28.12

Table 27: Reported values for NO run 1.

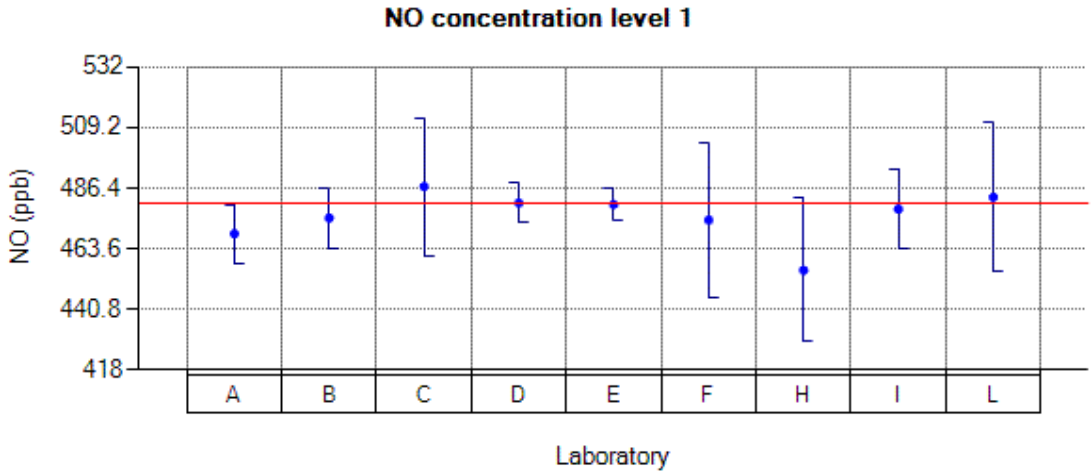

Figure 32: Reported values for NO run 1.

	laboratories								
values	A	B	C	D	E	F	H	I	L
xi,1 (nmol/mol)	339.03	343.58	350.60	348.77	347.09	343.00	329.79	343.65	349.66
xi,2 (nmol/mol)	338.65	343.55	353.60	348.42	347.10	342.80	331.11	343.25	349.75
xi,3 (nmol/mol)	338.86	343.39	354.00	348.60	347.15	342.50	330.58	343.41	349.56
Xi (nmol/mol)	338.85	343.50	352.73	348.59	347.11	342.76	330.49	343.43	349.65
Si (nmol/mol)	0.15	0.10	1.85	0.17	0.03	0.25	0.66	0.20	0.09
u(xi) (nmol/mol)	4.00	4.12	9.35	3.43	2.11	10.29	4.60	5.46	10.18
U(xi) (nmol/mol)	8.00	8.24	18.71	6.87	4.22	20.58	20.00	10.92	20.36

Table 28: Reported values for NO run 2.

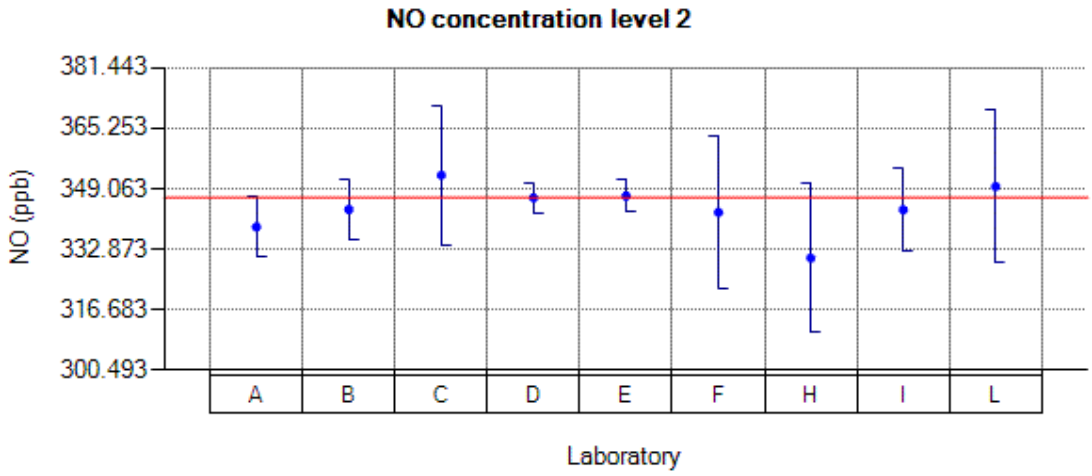

Figure 33: Reported values for NO run 2.

	laboratories								
values	A	B	C	D	E	F	H	I	L
xi,1 (nmol/mol)	61.75	62.26	62.10	62.94	62.90	61.70	58.79	62.09	64.70
xi,2 (nmol/mol)	61.73	62.24	61.90	63.14	62.91	61.90	58.81	62.12	64.72
xi,3 (nmol/mol)	61.79	62.32	61.90	63.13	62.98	62.10	58.65	62.16	64.66
Xi (nmol/mol)	61.75	62.27	61.96	63.07	62.93	61.90	58.75	62.12	64.69
Si (nmol/mol)	0.03	0.04	0.11	0.11	0.04	0.20	0.08	0.03	0.03
u(xi) (nmol/mol)	1.00	0.75	1.62	0.76	0.89	1.83	0.91	0.99	1.88
U(xi) (nmol/mol)	2.00	1.50	3.23	1.52	1.78	3.66	3.90	1.99	3.76

Table 29: Reported values for NO run 3.

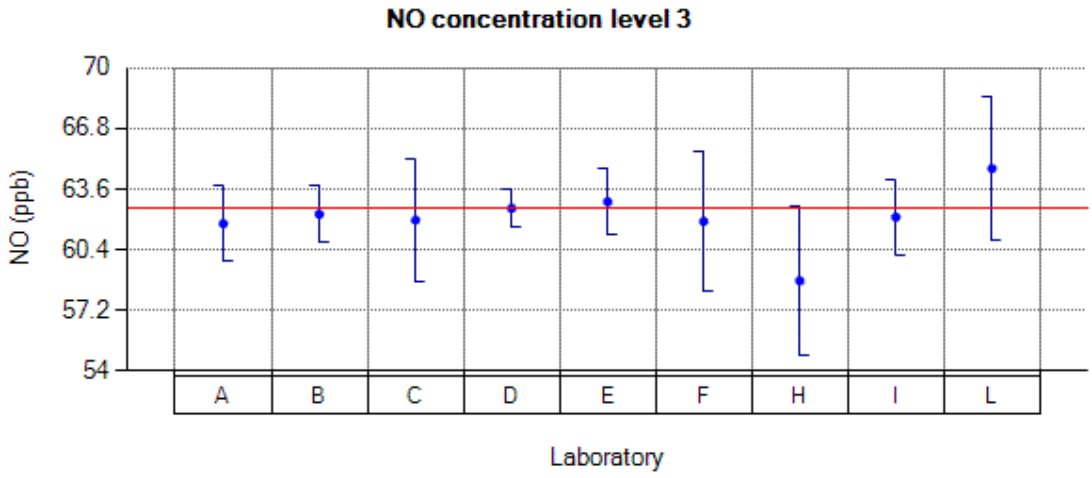

Figure 34: Reported values for NO run 3.

	laboratories								
values	A	B	C	D	E	F	H	I	L
xi,1 (nmol/mol)	39.58	39.75	39.60	40.30	40.20	39.60	38.15	39.03	41.50
xi,2 (nmol/mol)	39.52	39.76	39.70	40.31	40.14	39.70	37.92	39.05	41.48
xi,3 (nmol/mol)	39.58	39.81	39.40	40.32	40.02	39.80	37.87	39.05	41.43
Xi (nmol/mol)	39.56	39.77	39.56	40.31	40.12	39.70	37.98	39.04	41.47
Si (nmol/mol)	0.03	0.03	0.15	0.01	0.09	0.10	0.14	0.01	0.03
u(xi) (nmol/mol)	0.90	0.48	1.05	0.56	0.86	1.17	0.66	0.64	1.21
U(xi) (nmol/mol)	1.80	0.96	2.10	1.13	1.72	2.34	2.80	1.28	2.42

Table 30: Reported values for NO run 4.

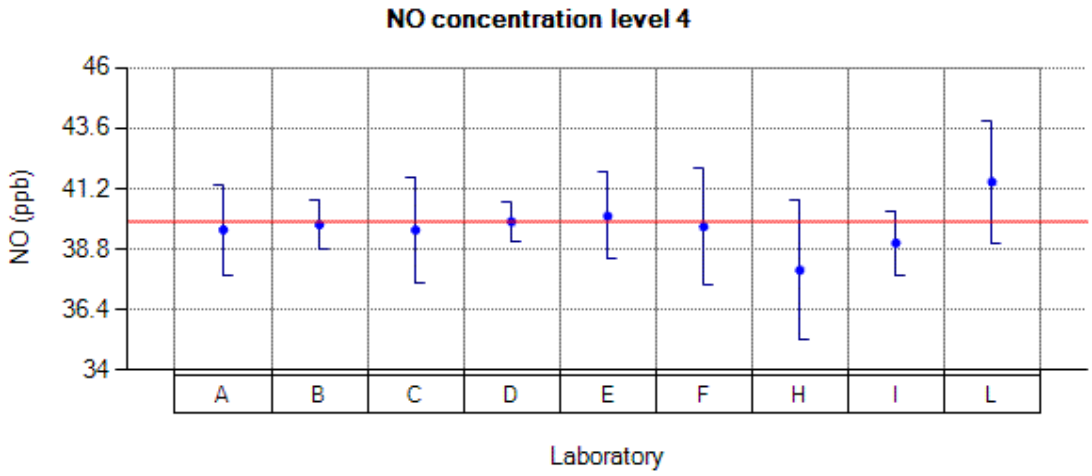

Figure 35: Reported values for NO run 4.

	laboratories								
values	A	B	C	D	E	F	H	I	L
xi,1 (nmol/mol)	155.45	156.86	157.70	160.18	159.01	156.60	148.58	158.12	162.11
xi,2 (nmol/mol)	155.73	157.18	158.70	160.47	159.20	156.90	149.11	158.20	162.43
xi,3 (nmol/mol)	155.76	157.34	159.10	160.53	159.18	157.00	148.80	158.37	162.49
Xi (nmol/mol)	155.64	157.12	158.50	160.39	159.13	156.83	148.83	158.23	162.34
Si (nmol/mol)	0.17	0.24	0.72	0.18	0.10	0.20	0.26	0.12	0.20
u(xi) (nmol/mol)	1.90	1.89	4.23	1.66	1.21	4.71	2.10	2.52	4.73
U(xi) (nmol/mol)	3.80	3.77	8.47	3.31	2.42	9.41	9.00	5.04	9.46

Table 31: Reported values for NO run 5.

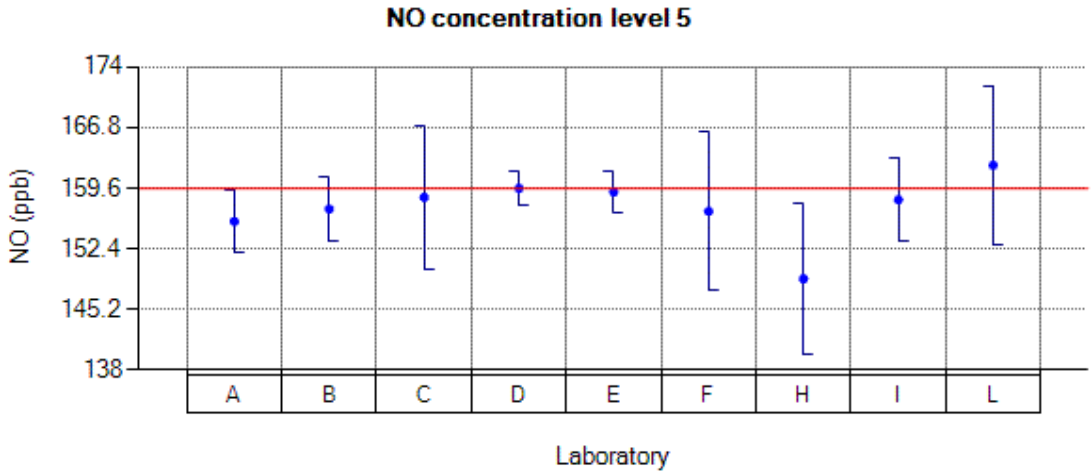

Figure 36: Reported values for NO run 5.

	laboratories								
values	A	B	C	D	E	F	H	I	L
xi,1 (nmol/mol)	102.73	103.89	104.60	105.56	104.91	103.60	99.12	103.66	107.32
xi,2 (nmol/mol)	102.68	103.73	104.40	105.49	104.67	103.30	99.31	103.65	107.14
xi,3 (nmol/mol)	102.55	103.71	104.60	105.47	104.79	103.50	98.75	103.48	107.14
Xi (nmol/mol)	102.65	103.77	104.53	105.50	104.79	103.46	99.06	103.59	107.20
Si (nmol/mol)	0.09	0.09	0.11	0.04	0.12	0.15	0.28	0.10	0.10
u(xi) (nmol/mol)	1.40	1.25	2.75	1.14	1.02	3.11	1.40	1.65	3.12
U(xi) (nmol/mol)	2.80	2.50	5.49	2.29	2.02	6.21	6.20	3.31	6.24

Table 32: Reported values for NO run 6.

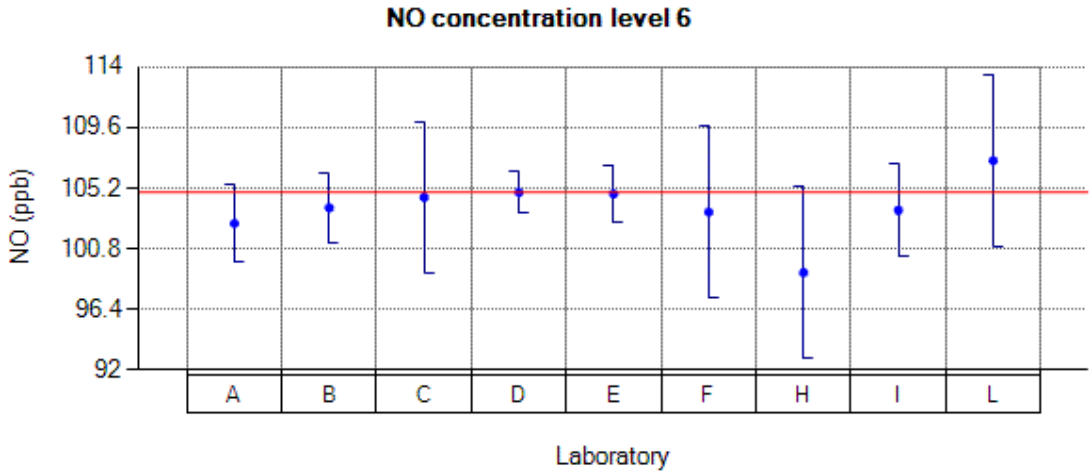

Figure 37: Reported values for NO run 6.

	laboratories								
values	A	B	C	D	E	F	H	I	L
xi,1 (nmol/mol)	234.95	237.19	240.90	242.93	240.25	236.50	225.17	238.68	244.53
xi,2 (nmol/mol)	235.07	237.68	241.50	243.15	240.45	236.80	225.29	238.91	244.95
xi,3 (nmol/mol)	235.05	237.88	241.50	243.11	240.29	237.00	225.27	238.98	245.40
Xi (nmol/mol)	235.02	237.58	241.30	243.06	240.33	236.76	225.24	238.85	244.96
Si (nmol/mol)	0.06	0.35	0.34	0.11	0.10	0.25	0.06	0.15	0.43
u(xi) (nmol/mol)	2.80	2.85	6.29	2.44	1.57	7.10	3.10	3.80	7.13
U(xi) (nmol/mol)	5.60	5.70	12.59	4.87	3.14	14.20	13.50	7.60	14.26

Table 33: Reported values for NO run 7.

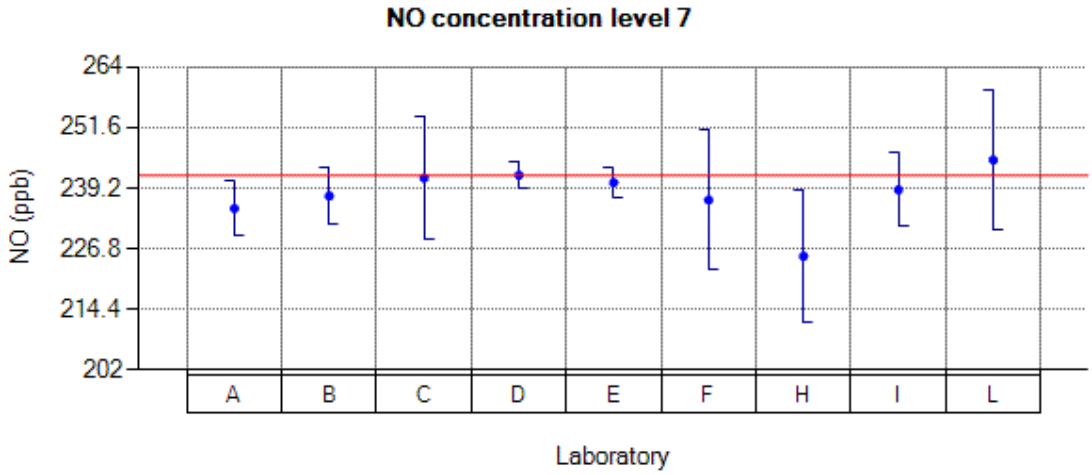

Figure 38: Reported values for NO run 7.

	laboratories								
values	A	B	C	D	E	F	H	I	L
xi,1 (nmol/mol)	145.10	147.01	147.40	149.21	148.02	146.20	140.37	146.44	151.00
xi,2 (nmol/mol)	144.91	146.79	148.10	148.88	147.94	146.10	140.15	146.50	150.77
xi,3 (nmol/mol)	144.77	146.63	148.30	148.74	147.75	145.80	139.56	146.24	150.76
Xi (nmol/mol)	144.92	146.81	147.93	148.94	147.90	146.03	140.02	146.39	150.84
Si (nmol/mol)	0.16	0.19	0.47	0.24	0.13	0.20	0.41	0.13	0.13
u(xi) (nmol/mol)	1.80	1.76	3.87	1.55	1.19	4.38	2.00	2.33	4.39
U(xi) (nmol/mol)	3.60	3.52	7.74	3.10	2.38	8.76	8.50	4.67	8.78

Table 34: Reported values for NO run 8.

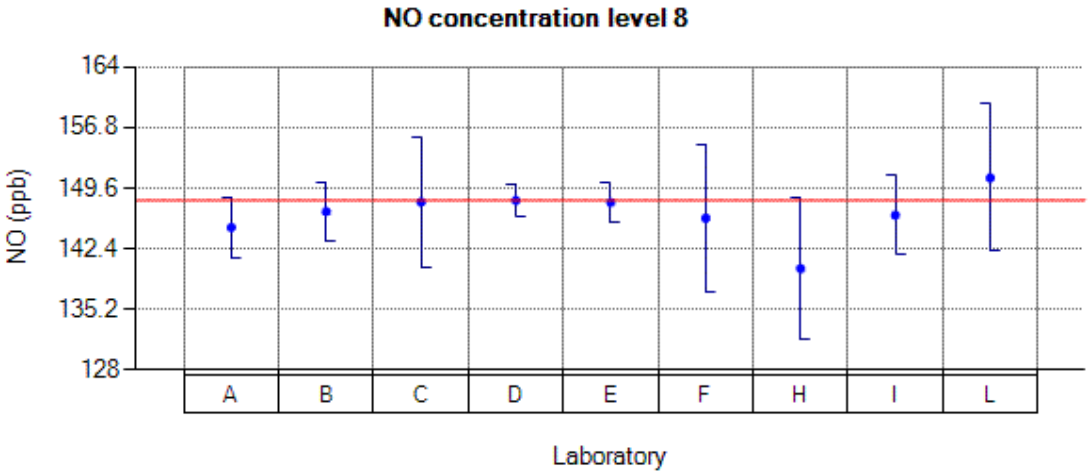

Figure 39: Reported values for NO run 8.

	laboratories								
values	A	B	C	D	E	F	H	I	L
xi,1 (nmol/mol)	21.19	21.43	19.80	21.45	20.94	20.80	19.55	20.42	22.12
xi,2 (nmol/mol)	21.27	21.41	20.20	21.52	21.07	20.60	19.88	20.46	22.15
xi,3 (nmol/mol)	21.30	21.30	19.90	21.57	20.89	20.80	19.82	20.72	22.17
Xi (nmol/mol)	21.25	21.38	19.96	21.51	20.96	20.73	19.75	20.53	22.14
Si (nmol/mol)	0.05	0.07	0.20	0.06	0.09	0.11	0.17	0.16	0.02
u(xi) (nmol/mol)	0.80	0.30	0.57	0.42	0.86	0.62	0.48	0.36	0.64
U(xi) (nmol/mol)	1.60	0.60	1.13	0.85	1.72	1.24	2.10	0.71	1.28

Table 35: Reported values for NO run 9.

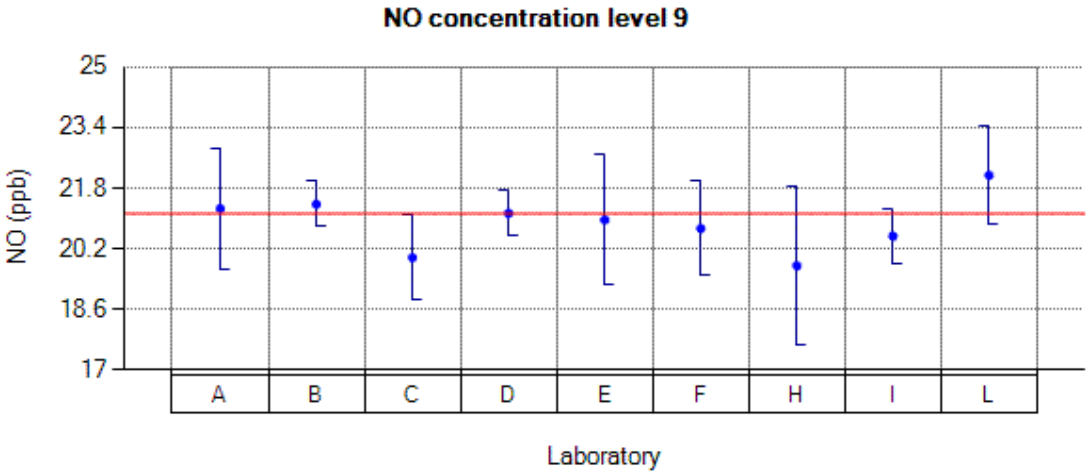

Figure 40: Reported values for NO run 9.

	laboratories								
values	A	B	C	D	E	F	H	I	L
xi,1 (nmol/mol)	10.53	10.77	9.80	10.68	10.12	10.40	10.05	9.90	10.93
xi,2 (nmol/mol)	10.51	10.49	10.00	10.61	9.94	10.20	10.04	9.88	10.90
xi,3 (nmol/mol)	10.52	10.46	10.20	10.59	9.90	10.00	9.63	9.88	10.85
Xi (nmol/mol)	10.52	10.57	10.00	10.62	9.98	10.20	9.90	9.88	10.89
Si (nmol/mol)	0.01	0.17	0.20	0.04	0.11	0.20	0.24	0.01	0.04
u(xi) (nmol/mol)	0.70	0.30	0.29	0.36	0.85	0.30	0.42	0.22	0.32
U(xi) (nmol/mol)	1.40	0.60	0.59	0.72	1.70	0.60	1.80	0.43	0.64

Table 36: Reported values for NO run 10.

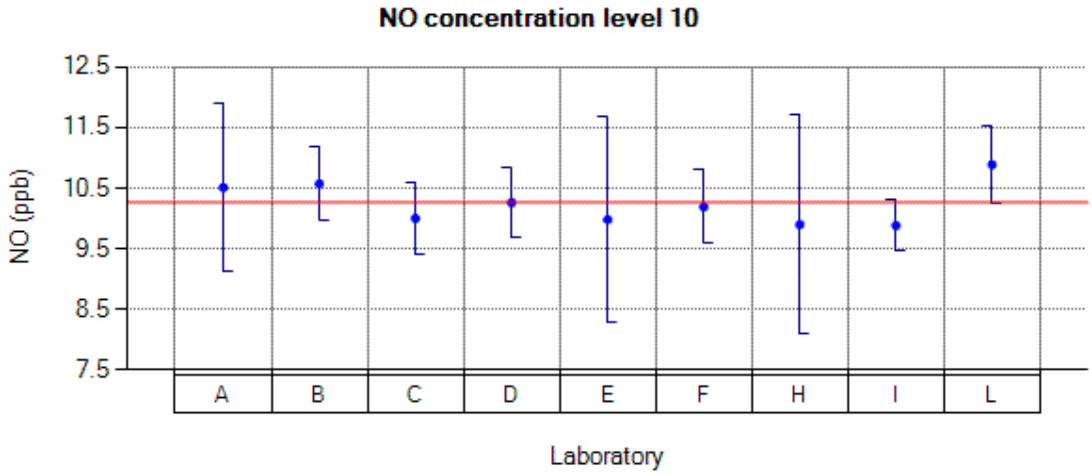

Figure 41: Reported values for NO run 10.

Reported values for NO_2

	laboratories								
values	A	B	C	D	E	F	H	I	L
xi,1 (nmol/mol)	0.17	-0.34	-0.70	0.05	0.09	0.20	0.07	-0.04	0.13
u(xi) (nmol/mol)	0.70	0.40	0.00	0.09	0.88	0.02	0.70	0.14	0.01
U(xi) (nmol/mol)	1.40	0.80	-0.01	0.17	1.76	0.04	1.40	0.29	0.02

Table 37: Reported values for NO_2 run 0.

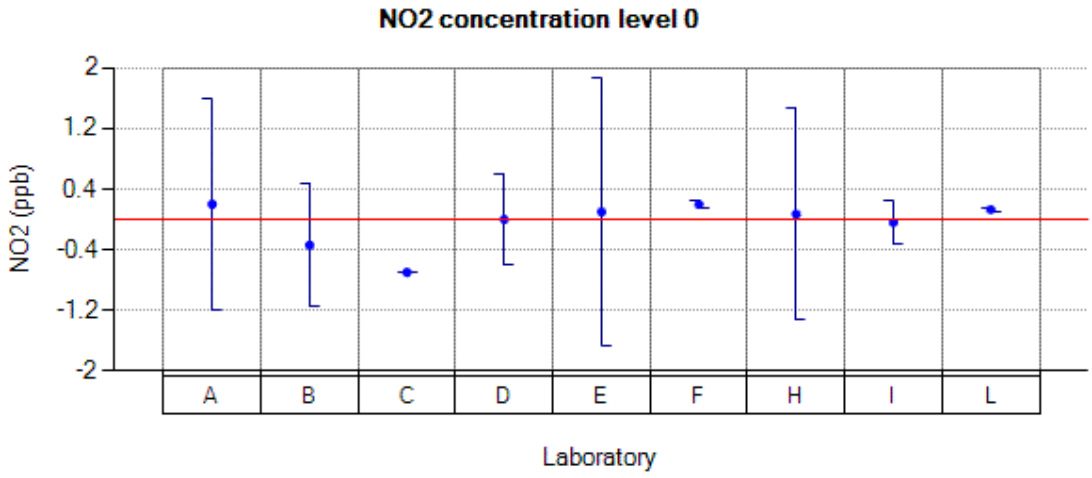

Figure 42: Reported values for NO_2 run 0.

	laboratories								
values	A	B	C	D	E	F	H	I	L
xi,1 (nmol/mol)	2.07	3.09	1.00	3.97	4.49	1.00	3.00	4.42	5.91
xi,2 (nmol/mol)	1.96	2.86	0.30	3.73	4.39	1.00	2.86	4.30	5.64
xi,3 (nmol/mol)	1.92	2.97	0.60	3.61	4.35	1.00	2.33	4.57	5.56
Xi (nmol/mol)	1.98	2.97	0.63	3.77	4.41	1.00	2.73	4.43	5.70
Si (nmol/mol)	0.07	0.11	0.35	0.18	0.07	0.00	0.35	0.13	0.18
u(xi) (nmol/mol)	0.70	0.40	1.06	1.27	0.86	0.03	0.40	0.16	0.26
U(xi) (nmol/mol)	1.40	0.80	2.11	2.54	1.72	0.06	1.70	0.33	0.52

Table 38: Reported values for NO_2 run 1.

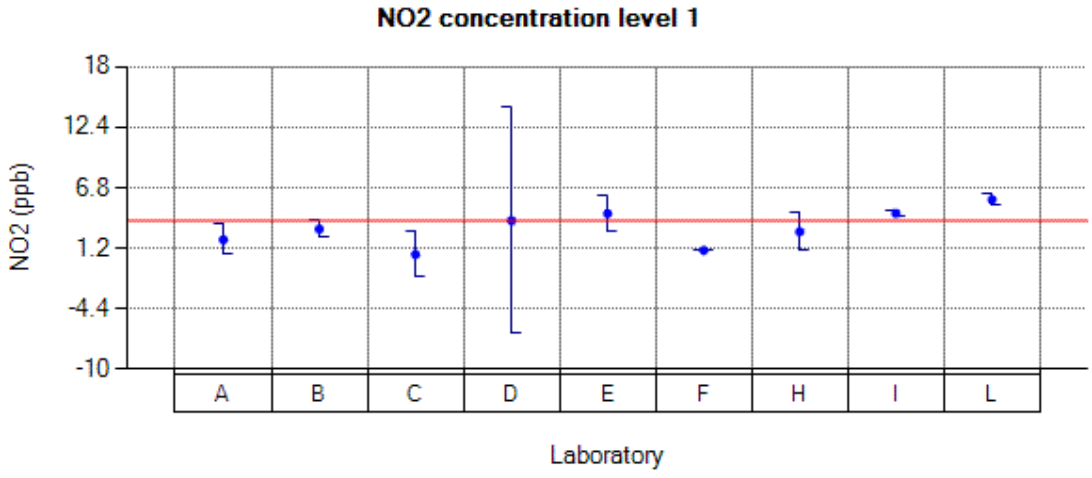

Figure 43: Reported values for NO_2 run 1.

	laboratories								
values	A	B	C	D	E	F	H	I	L
xi,1 (nmol/mol)	132.59	134.27	137.30	138.40	137.78	133.30	127.92	135.72	141.98
xi,2 (nmol/mol)	132.50	134.07	138.00	138.00	137.70	132.90	128.21	135.55	142.27
xi,3 (nmol/mol)	132.62	133.95	137.30	138.25	138.02	133.10	128.65	135.65	142.30
Xi (nmol/mol)	132.57	134.09	137.53	138.21	137.83	133.10	128.26	135.64	142.18
Si (nmol/mol)	0.06	0.16	0.40	0.20	0.16	0.20	0.36	0.08	0.17
u(xi) (nmol/mol)	2.30	1.61	57.97	1.71	1.16	3.93	1.90	2.32	5.87
U(xi) (nmol/mol)	4.60	3.22	115.94	3.42	2.32	7.85	8.10	4.65	11.74

Table 39: Reported values for NO_2 run 2.

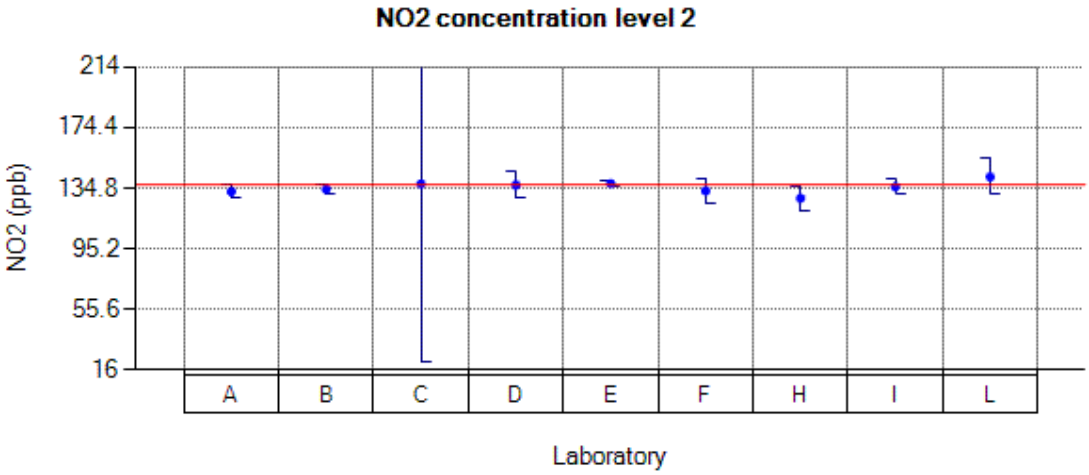

Figure 44: Reported values for NO_2 run 2.

	laboratories								
values	A	B	C	D	E	F	H	I	L
xi,1 (nmol/mol)	0.16	0.09	-0.80	0.20	0.36	0.60	0.14	0.12	0.53
xi,2 (nmol/mol)	0.21	0.07	-0.50	0.09	0.11	0.70	0.09	0.00	0.56
xi,3 (nmol/mol)	0.24	-0.03	-0.60	0.13	0.12	0.60	0.01	-0.04	0.65
Xi (nmol/mol)	0.20	0.04	-0.63	0.14	0.19	0.63	0.08	0.02	0.58
Si (nmol/mol)	0.04	0.06	0.15	0.05	0.14	0.05	0.06	0.08	0.06
u(xi) (nmol/mol)	0.70	0.40	-0.29	0.20	0.83	0.02	0.40	0.14	0.04
U(xi) (nmol/mol)	1.40	0.80	-0.59	0.41	1.66	0.04	1.70	0.29	0.08

Table 40: Reported values for NO_2 run 3.

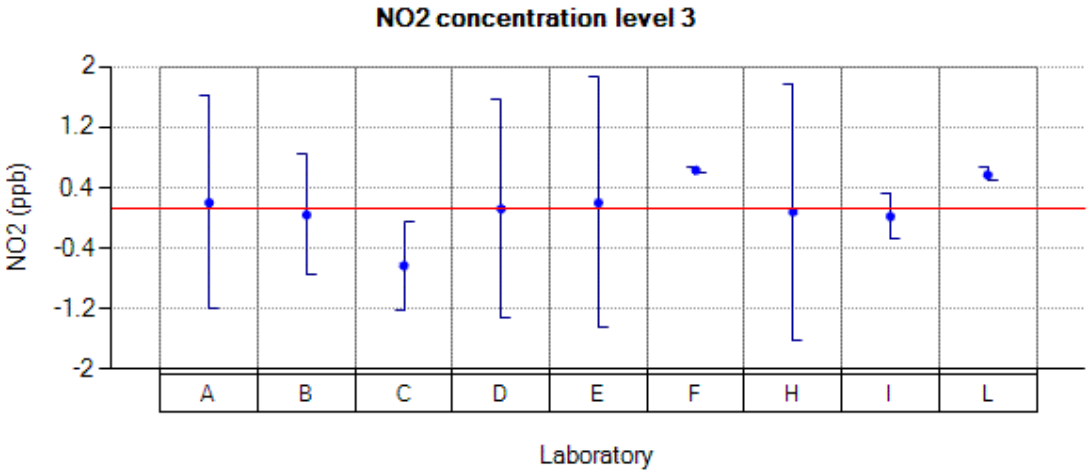

Figure 45: Reported values for NO_2 run 3.

	laboratories								
values	A	B	C	D	E	F	H	I	L
xi,1 (nmol/mol)	22.30	22.36	21.70	22.99	22.94	21.40	21.16	21.87	24.13
xi,2 (nmol/mol)	22.35	22.42	21.60	22.99	22.94	21.40	20.97	21.79	24.27
xi,3 (nmol/mol)	22.37	22.44	21.70	23.04	23.01	21.40	21.12	21.82	24.35
Xi (nmol/mol)	22.34	22.40	21.66	23.00	22.96	21.40	21.08	21.82	24.25
Si (nmol/mol)	0.03	0.04	0.05	0.02	0.04	0.00	0.10	0.04	0.11
u(xi) (nmol/mol)	0.80	0.60	9.11	0.26	0.84	0.63	0.50	0.40	1.00
U(xi) (nmol/mol)	1.60	1.20	18.23	0.53	1.68	1.26	2.10	0.80	2.00

Table 41: Reported values for NO_2 run 4.

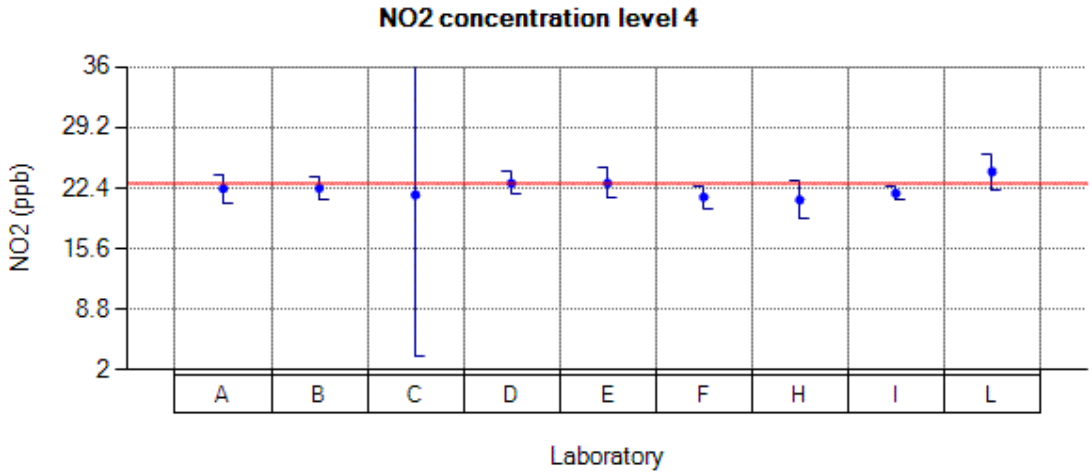

Figure 46: Reported values for NO_2 run 4.

	laboratories								
values	A	B	C	D	E	F	H	I	L
xi,1 (nmol/mol)	1.07	0.89	0.20	1.26	1.52	0.10	1.24	1.48	2.23
xi,2 (nmol/mol)	1.02	0.78	-0.20	1.04	1.28	0.20	0.93	1.38	1.81
xi,3 (nmol/mol)	0.86	0.88	-0.60	1.01	1.25	0.10	1.21	1.11	2.11
Xi (nmol/mol)	0.98	0.85	-0.20	1.10	1.35	0.13	1.12	1.32	2.05
Si (nmol/mol)	0.11	0.06	0.40	0.13	0.14	0.05	0.17	0.19	0.21
u(xi) (nmol/mol)	0.70	0.40	1.03	0.44	0.84	0.05	0.40	0.15	0.15
U(xi) (nmol/mol)	1.40	0.80	2.05	0.89	1.68	0.01	1.70	0.30	0.30

Table 42: Reported values for NO_2 run 5.

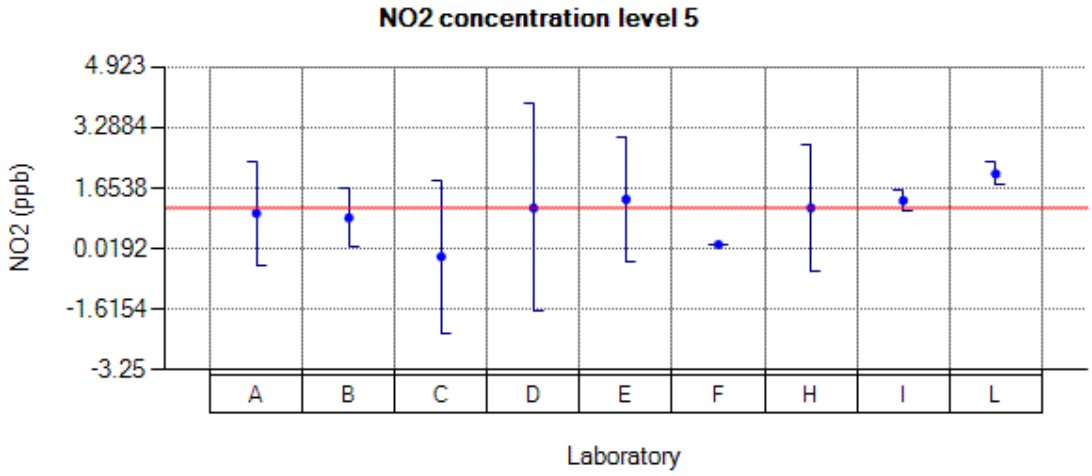

Figure 47: Reported values for NO_2 run 5.

	laboratories								
values	A	B	C	D	E	F	H	I	L
xi,1 (nmol/mol)	53.85	54.02	54.00	55.91	55.35	53.10	51.02	53.97	58.01
xi,2 (nmol/mol)	53.88	54.14	54.20	55.96	55.62	53.10	51.08	53.97	57.88
xi,3 (nmol/mol)	54.04	54.14	53.90	56.08	55.51	53.10	51.07	54.05	58.08
Xi (nmol/mol)	53.92	54.10	54.03	55.98	55.49	53.10	51.05	53.99	57.99
Si (nmol/mol)	0.10	0.06	0.15	0.08	0.13	0.00	0.03	0.04	0.10
u(xi) (nmol/mol)	1.10	1.00	22.70	0.65	0.88	1.60	0.83	0.93	2.39
U(xi) (nmol/mol)	2.20	1.90	45.40	1.30	1.76	3.19	3.60	1.87	4.78

Table 43: Reported values for NO_2 run 6.

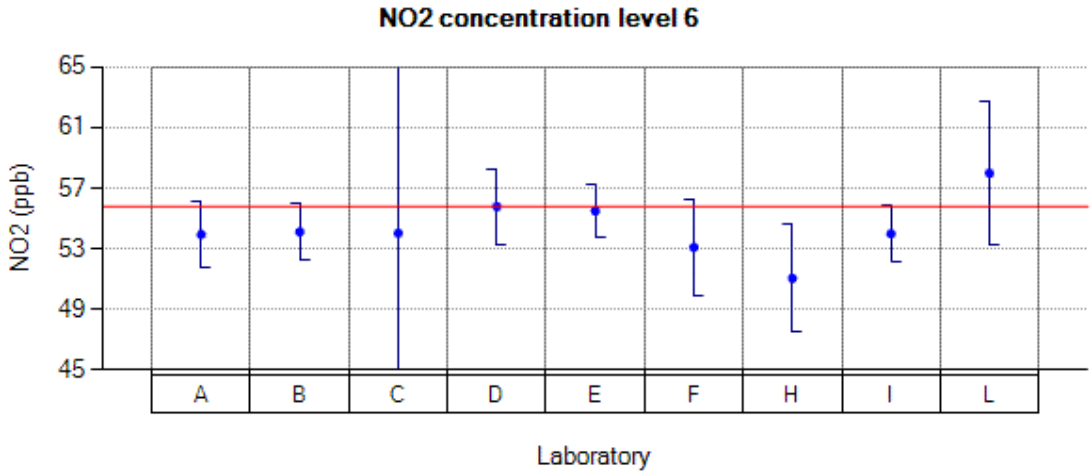

Figure 48: Reported values for NO_2 run 6.

	laboratories								
values	A	B	C	D	E	F	H	I	L
xi,1 (nmol/mol)	1.02	1.12	-0.20	1.43	1.80	0.10	1.30	2.01	2.83
xi,2 (nmol/mol)	0.97	1.13	-0.50	1.32	1.68	0.00	1.21	2.08	2.59
xi,3 (nmol/mol)	1.23	1.32	-0.50	1.40	1.96	0.10	1.47	1.74	2.35
Xi (nmol/mol)	1.07	1.19	-0.40	1.38	1.81	0.06	1.32	1.94	2.59
Si (nmol/mol)	0.13	0.11	0.17	0.05	0.14	0.05	0.13	0.18	0.24
u(xi) (nmol/mol)	0.70	0.50	-0.45	0.65	0.84	0.01	0.40	0.15	0.18
U(xi) (nmol/mol)	1.40	1.00	-0.91	1.31	1.68	0.01	1.70	0.30	0.36

Table 44: Reported values for NO_2 run 7.

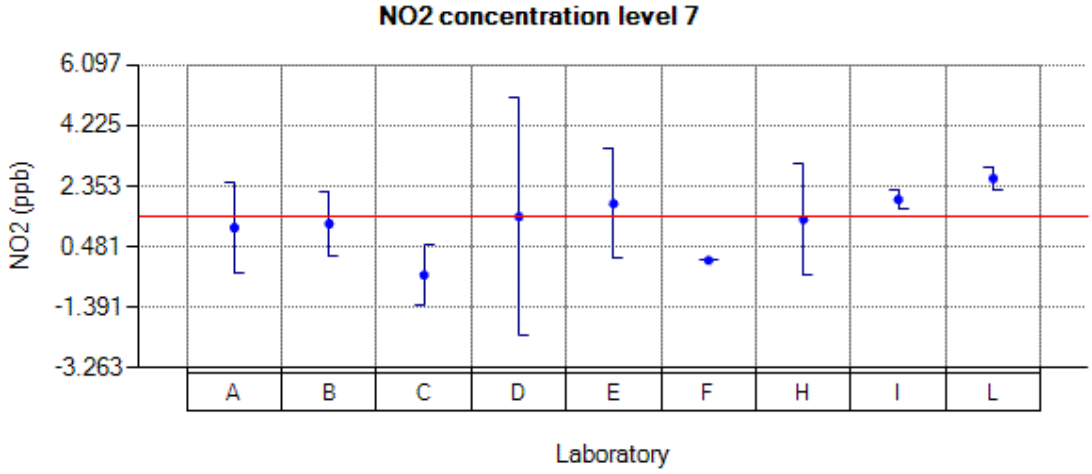

Figure 49: Reported values for NO_2 run 7.

	laboratories								
values	A	B	C	D	E	F	H	I	L
xi,1 (nmol/mol)	90.99	91.84	92.80	94.95	94.08	90.70	86.82	92.07	98.01
xi,2 (nmol/mol)	91.16	91.66	92.20	95.03	94.31	90.80	86.91	92.13	97.86
xi,3 (nmol/mol)	91.26	91.95	92.80	94.96	94.48	90.60	87.40	92.11	98.08
Xi (nmol/mol)	91.13	91.81	92.60	94.98	94.29	90.70	87.04	92.10	97.98
Si (nmol/mol)	0.13	0.14	0.34	0.04	0.20	0.10	0.31	0.03	0.11
u(xi) (nmol/mol)	1.70	1.30	38.92	1.05	1.08	2.72	1.30	1.58	4.04
U(xi) (nmol/mol)	3.40	2.60	77.85	2.09	2.16	5.44	5.60	3.16	8.08

Table 45: Reported values for NO_2 run 8.

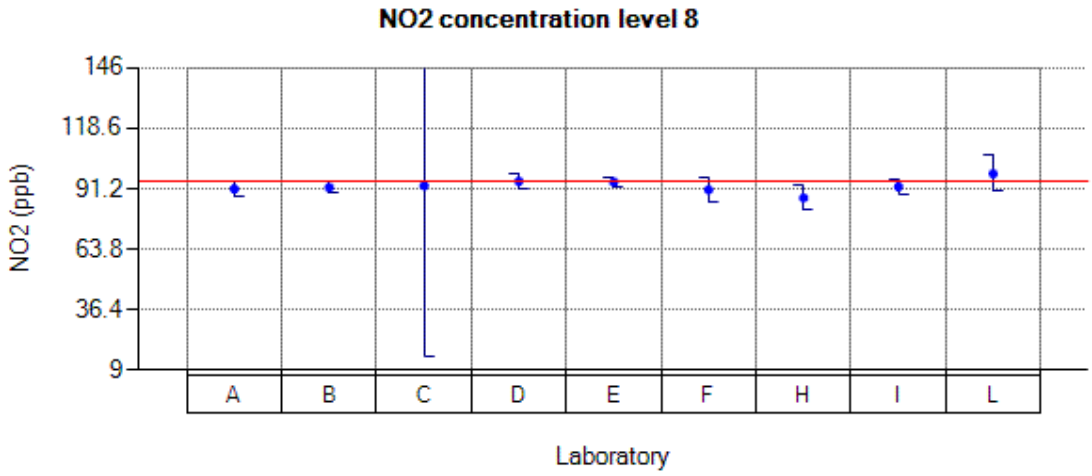

Figure 50: Reported values for NO_2 run 8.

	laboratories								
values	A	B	C	D	E	F	H	I	L
xi,1 (nmol/mol)	0.22	0.27	-0.60	0.18	0.11	0.50	0.32	-0.08	0.41
xi,2 (nmol/mol)	0.33	0.08	-0.50	0.10	0.05	0.50	0.14	-0.10	0.36
xi,3 (nmol/mol)	0.14	0.24	-0.70	0.07	0.00	0.50	0.25	-0.08	0.33
Xi (nmol/mol)	0.23	0.19	-0.60	0.11	0.05	0.50	0.23	-0.08	0.36
Si (nmol/mol)	0.09	0.10	0.10	0.05	0.05	0.00	0.09	0.01	0.04
u(xi) (nmol/mol)	0.70	0.40	-0.28	0.11	0.83	0.02	0.40	0.15	0.03
U(xi) (nmol/mol)	1.40	0.80	-0.57	0.23	1.66	0.03	1.70	0.29	0.06

Table 46: Reported values for NO_2 run 9.

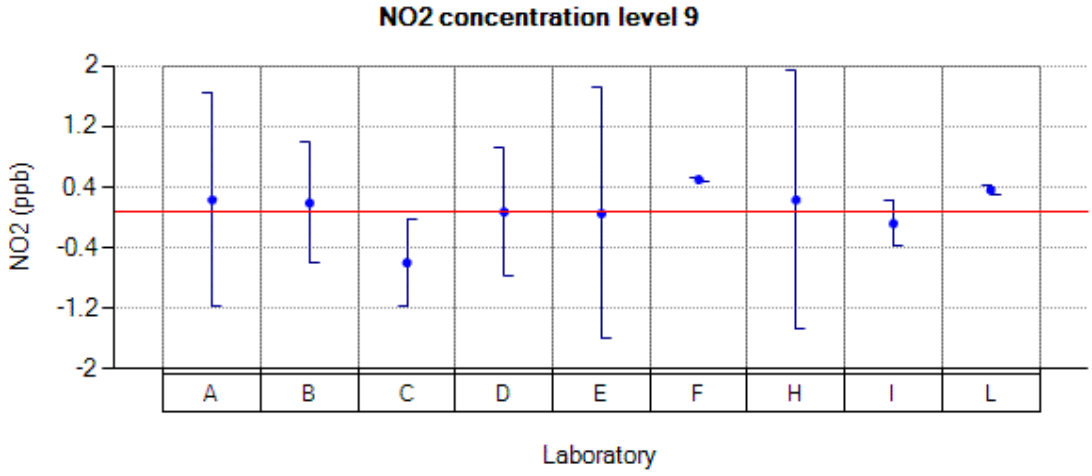

Figure 51: Reported values for NO_2 run 9.

	laboratories								
values	A	B	C	D	E	F	H	I	L
xi,1 (nmol/mol)	10.82	10.92	9.40	10.94	10.85	9.90	9.94	10.41	11.79
xi,2 (nmol/mol)	10.90	10.86	9.50	10.97	10.91	9.90	10.10	10.46	11.81
xi,3 (nmol/mol)	10.89	10.66	9.50	10.96	10.95	10.10	10.15	10.57	11.87
Xi (nmol/mol)	10.87	10.81	9.46	10.95	10.90	9.96	10.06	10.48	11.82
Si (nmol/mol)	0.04	0.13	0.05	0.01	0.05	0.11	0.11	0.08	0.04
u(xi) (nmol/mol)	0.70	0.40	3.97	0.12	0.83	0.30	0.40	0.23	0.49
U(xi) (nmol/mol)	1.40	0.80	7.93	0.25	1.66	0.59	1.80	0.46	0.98

Table 47: Reported values for NO_2 run 10.

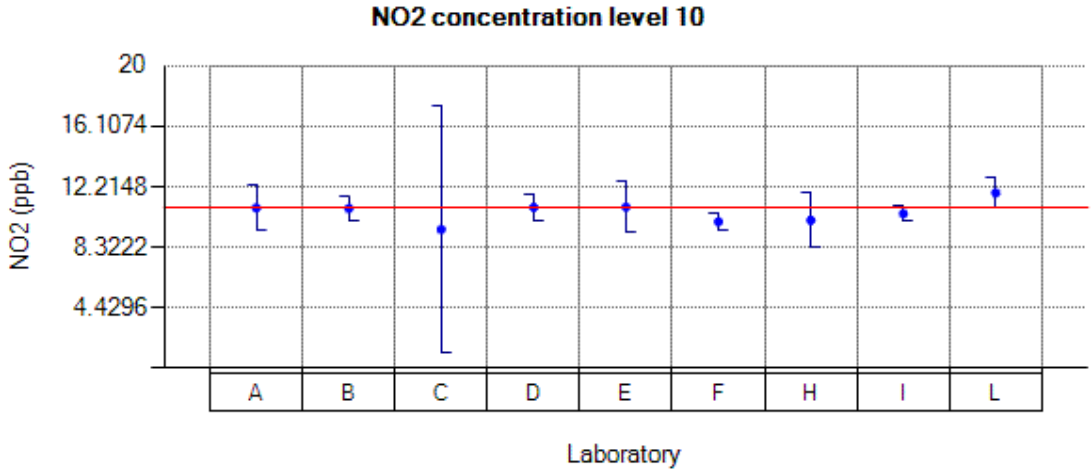

Figure 52: Reported values for NO_2 run 10.

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 eight laboratories, the actual number of labs (p_j) varying from run to run (Table 48). Six concentration levels 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.

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

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.

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

The repeatability standard deviation was evaluated with ($p_j \cdot (3\text{-}1)$) 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 48.

parameter	run	p_j	t critical value 95% for r	t critical value 95% for R
CO	1,2,3,4,5	9	2.101	2.306
NO	1,2,3,4,5,6,7,8,9,10	9	2.101	2.306
NO_2	1,2,3,4,5,6,7,8,9,10	9	2.101	2.306
O_3	1,2,3,4,5	10	2.086	2.262
SO_2	1,2,3,4,5	10	2.086	2.262

Table 48: 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 49 to Table 53 and from Figure 53 to Figure 57. 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)
0.3		1.0	
3.4	0.2	1.4	
8.3	0.2	1.7	
20.4	0.2	2.7	
51.9	0.4	5.6	
140.1	0.6	13.5	9.6%

Table 49: The R and r of SO_2 standard measurement method.

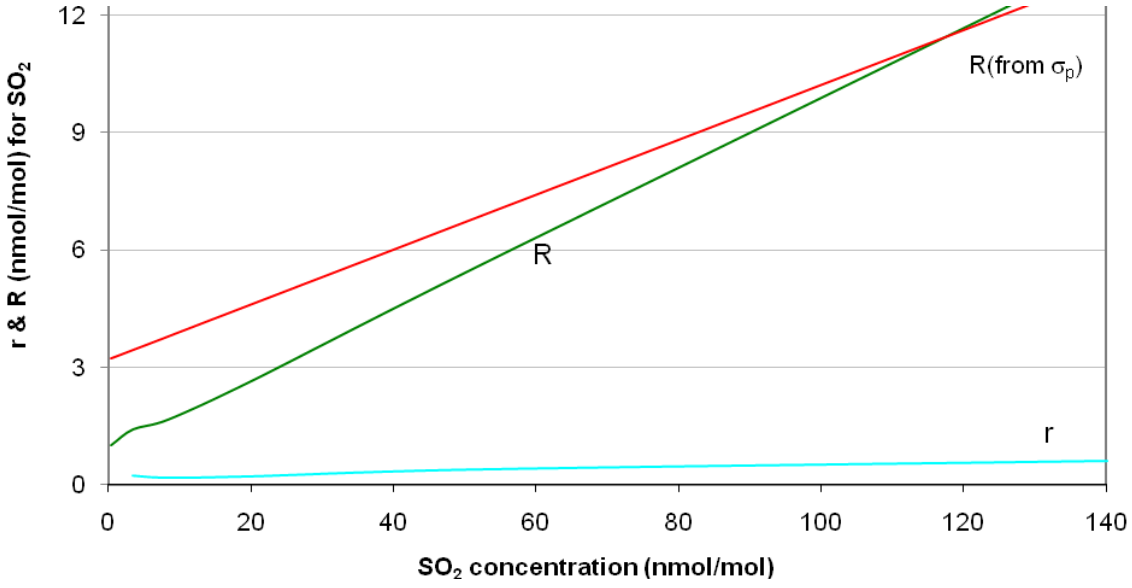

Figure 53: The R and r of SO_2 standard measurement method as a function of concentration.

CO data (µmol/mol) without outliers			
group average	repeatability limit : r	reproducibility limit : R	reproducibility limit (relative)
0.045		0.204	
1.061	0.018	0.255	
3.039	0.01	0.343	
4.500	0.03	0.292	
5.967	0.02	0.349	
8.889	0.06	0.409	4.6%

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

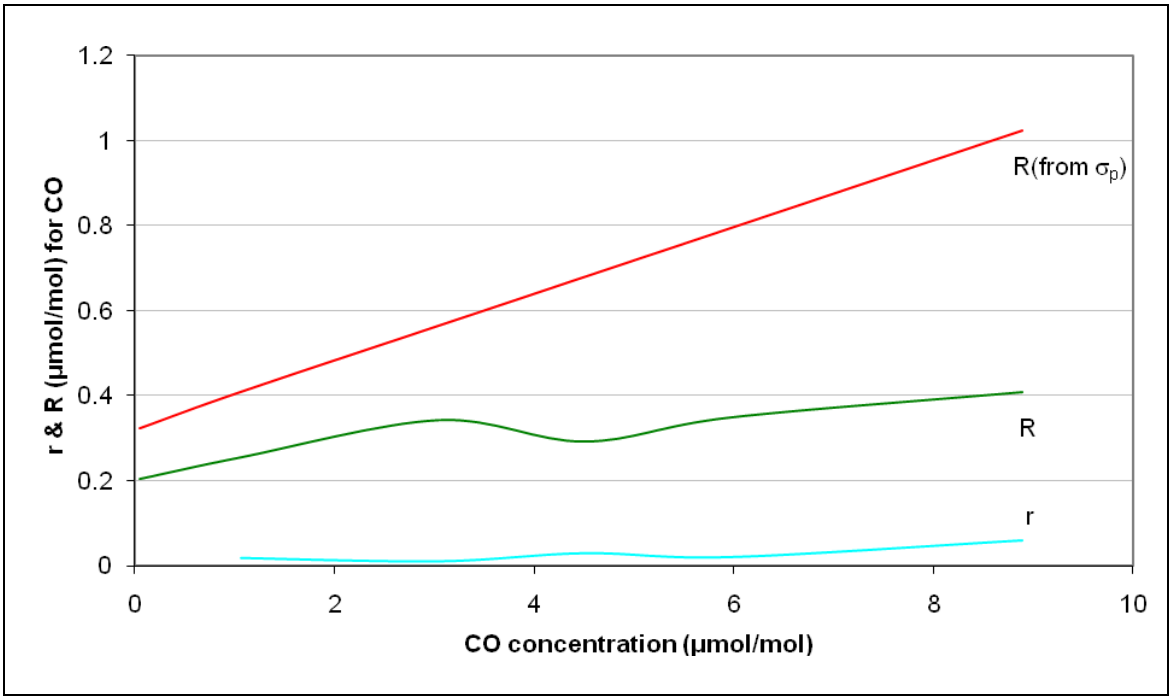

Figure 54: The R and r of CO standard measurement method as a function of concentration.

O_3 data (nmol/mol) without outliers			
group average	repeatability limit : r	reproducibility limit : R	reproducibility limit (relative)
0.1		0.6	
10.9	0.3	1.2	
22.5	0.2	1.7	
53.7	0.4	4.2	
91.5	0.4	7.5	
132.0	1.3	10.1	7.7%

Table 51: The R and r of O_3 standard measurement method.

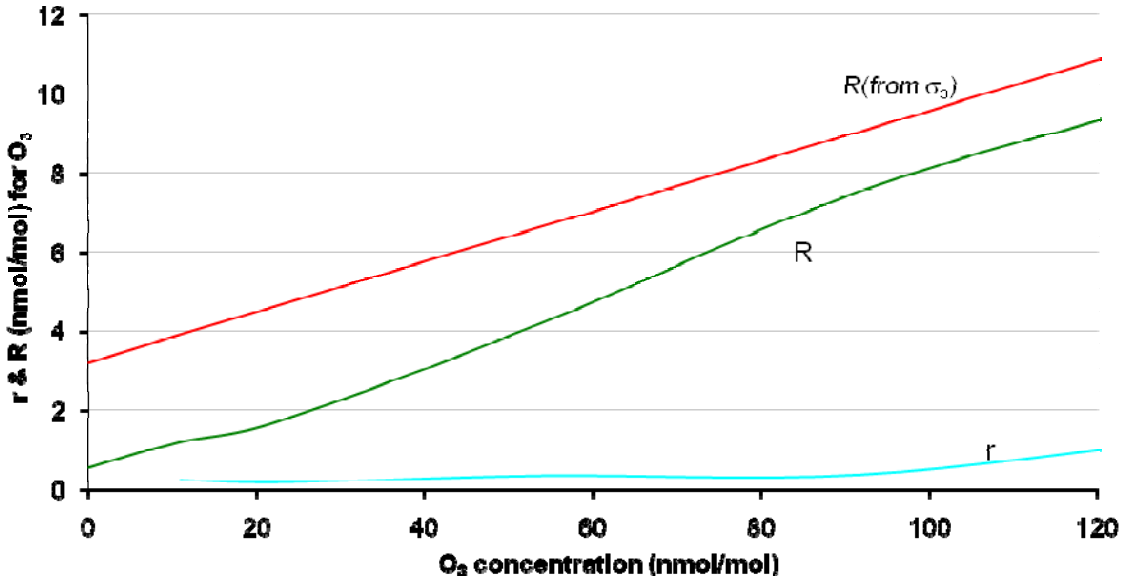

Figure 55: The R and r of O_3 standard measurement method as a function of concentration.

NO data (nmol/mol) without outliers			
group average	repeatability limit : r	reproducibility limit : R	reproducibility limit (relative)
0.2		0.7	
10.3	0.4	1.3	
20.9	0.4	2.5	
39.7	0.3	3.1	
62.2	0.3	5.1	
103.8	0.4	7.3	
146.6	0.8	9.9	
157.5	0.9	12.4	
238.1	0.7	18.8	
344.1	2.0	21.6	
476.4	3.0	31.2	7.0%

Table 52: The R and r of NO standard measurement method.

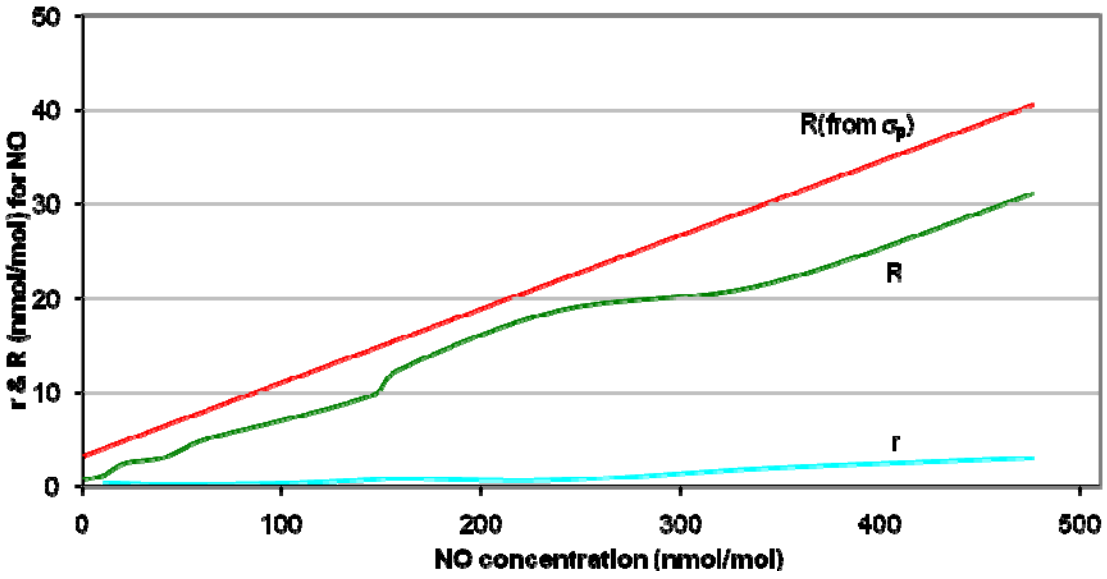

Figure 56: The R and r of NO standard measurement method as a function of concentration.

NO_2			
group average	repeatability limit : r	reproducibility limit : R	reproducibility limit (relative)
0.0		1.0	
13.4	0.2	2.3	
20.2	0.1	2.7	
58.8	0.3	6.9	
99.6	0.6	12.6	
119.1	0.8	13.0	10.90%

Table 53: The R and r of NO_2 standard measurement method.

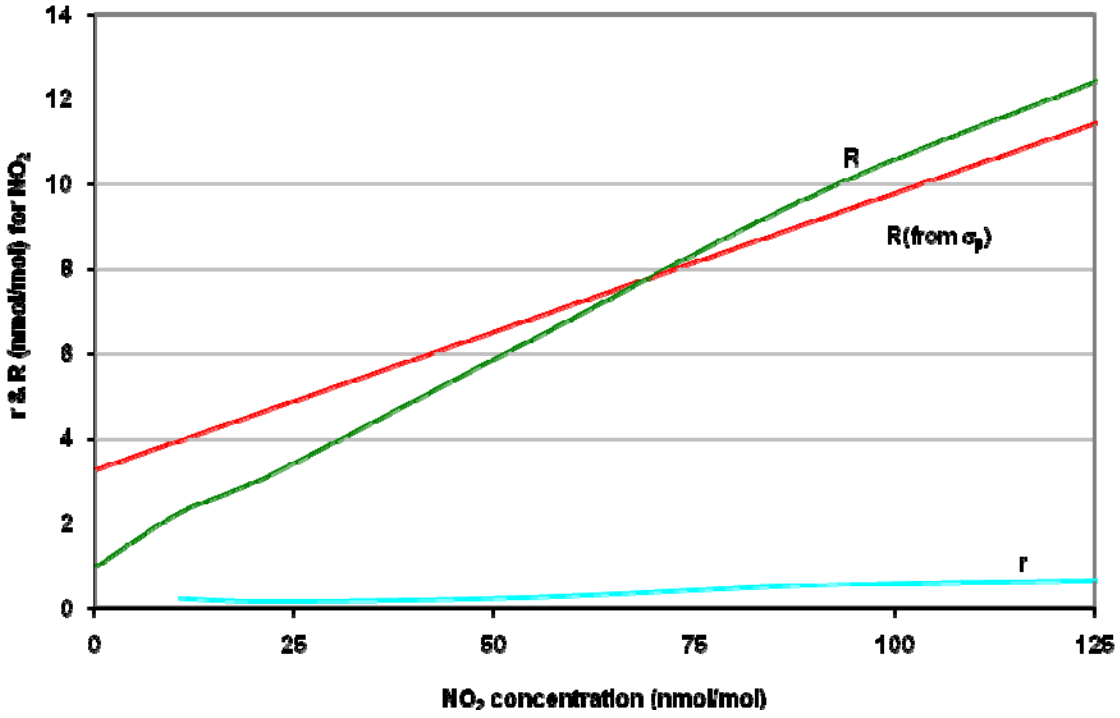

Figure 57: The R and r of NO_2 standard measurement method as a function of concentration.

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. Despite laboratories were allowed to correct their results in case of identification of exceptional errors none did so. 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.
These "genuine" statistical outliers are presented in the table below:

parameter	run	laboratory	measured value	failing test	confidence level
CO	4	C	3.3	G1 maximum	1%, 5%
O3	1	C	140.2	G1 maximum	1%, 5%
O3	3	C	57.2	G1 maximum	1%, 5%
O3	4	C	97.9	G1 maximum	1%, 5%

Table 54: "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.

European Commission

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Abstract

From the 14th to the 17th of June 2010 in Ispra (IT), 9 Laboratories of AQUILA (Network of European Air Quality Reference Laboratories) met at an interlaboratory 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, 85% of the results reported by AQUILA laboratories were good both in terms of measured values and reported uncertainties. Another 12% of the results had good measured values, but the reported uncertainties were either too high (8%) or too small (4%).

Comparability of results among AQUILA participants at the highest concentration level, excluding outliers, is acceptable in NO, CO and O_3 measurements while NO_2 and SO_2 measurement methods showed less satisfactory results.

The mission of the JRC is to provide customer-driven scientific and technical support for the conception, development, implementation and monitoring of EU policies. As a service of the European Commission, the JRC functions as a reference centre of science and technology for the Union. Close to the policy-making process, it serves the common interest of the Member States, while being independent of special interests, whether private or national.

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