Validation of low cost sensors for the monitoring of NO_2 and O_3 in ambient air

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JRC, European Commission Ispra (VA), Italy
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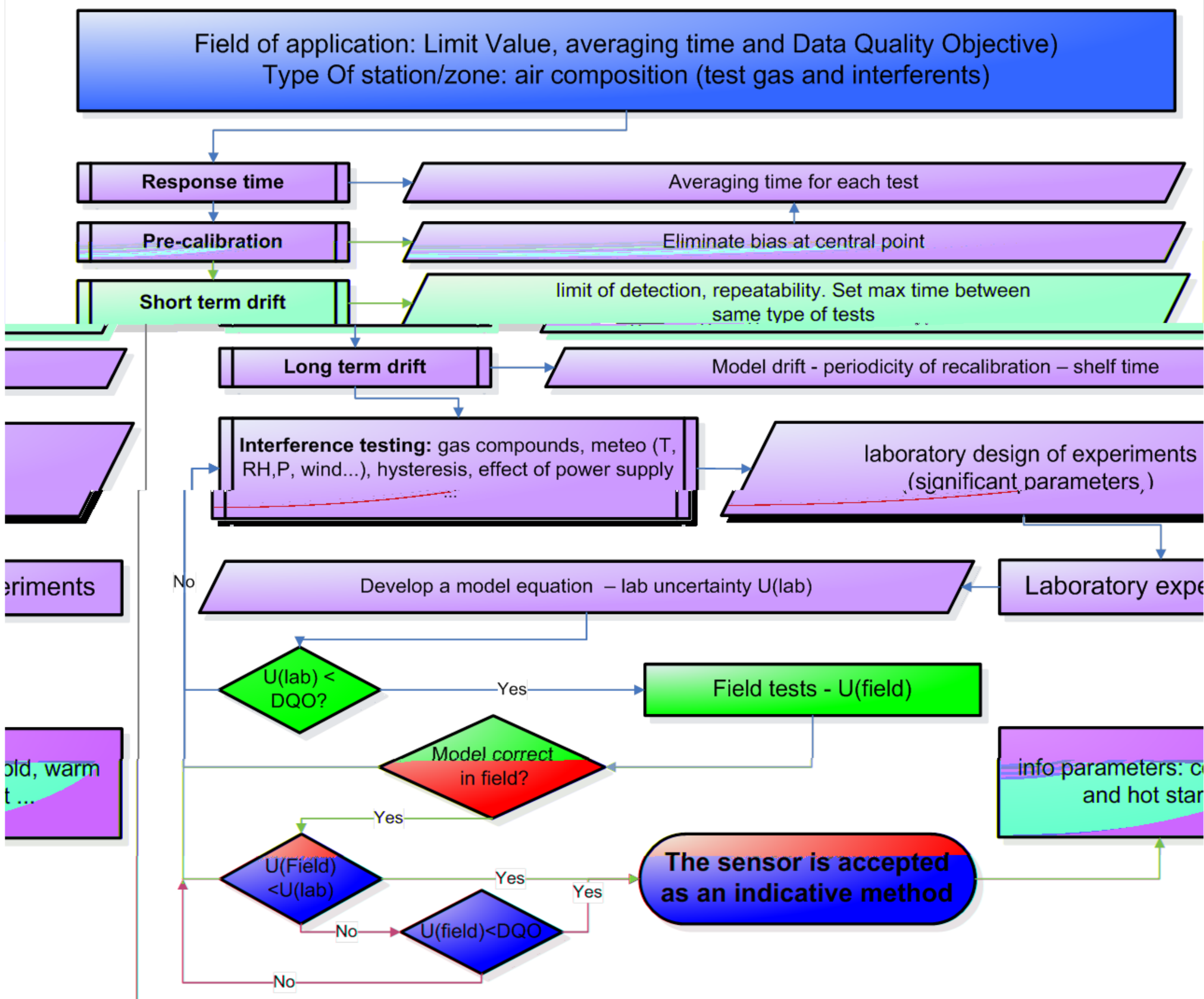
Data Quality Objectives (DQO) of the European Air Quality Directive

Uncertainty for	O_3	NO_2 / NO / NOx
fixed measurements	15 %	15 %
indicative measurements	**30 %**	**25 %**

Evaluation Validation Protocol



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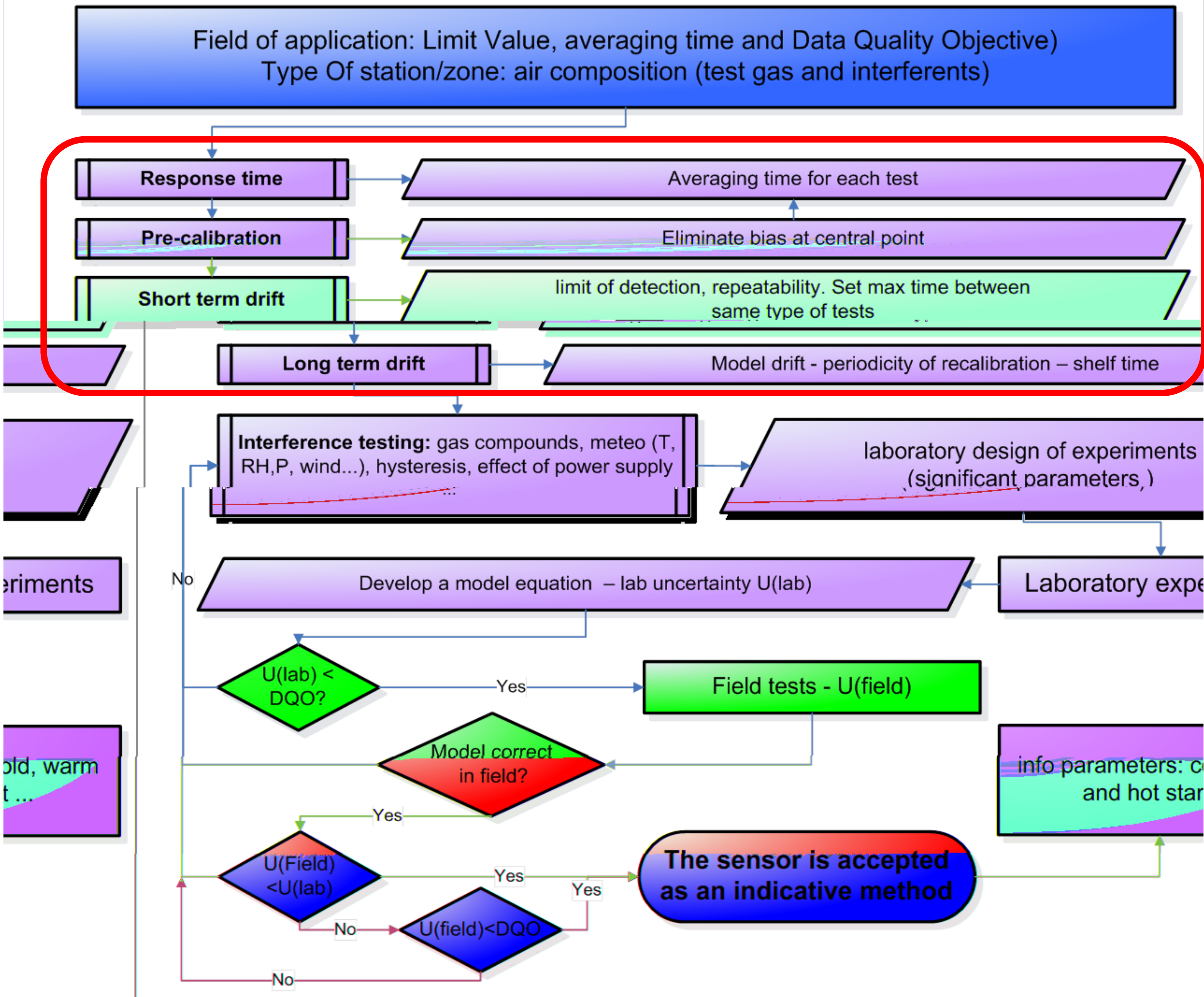
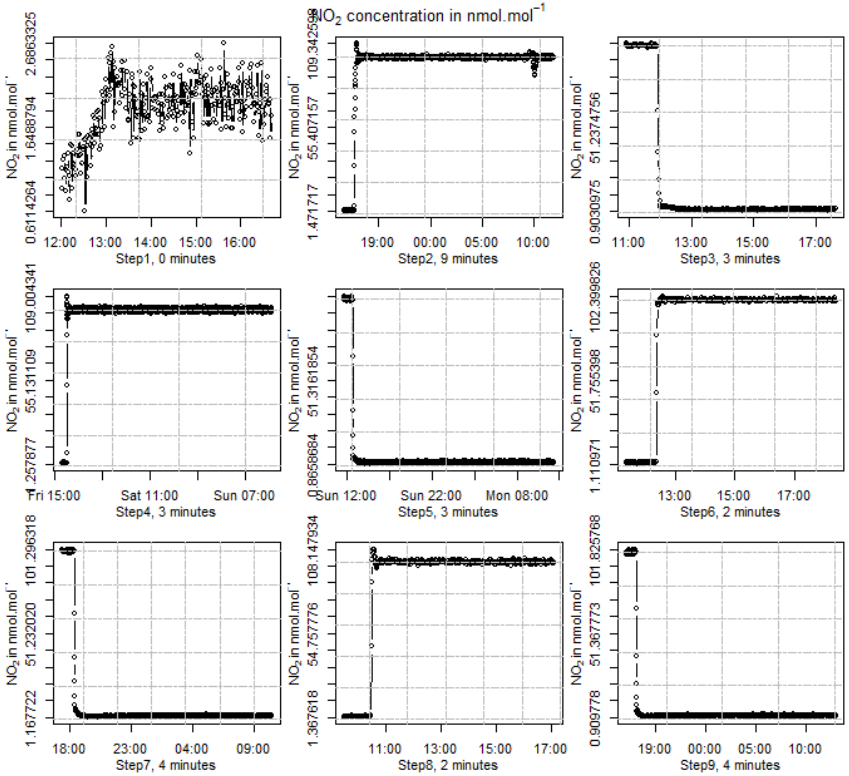
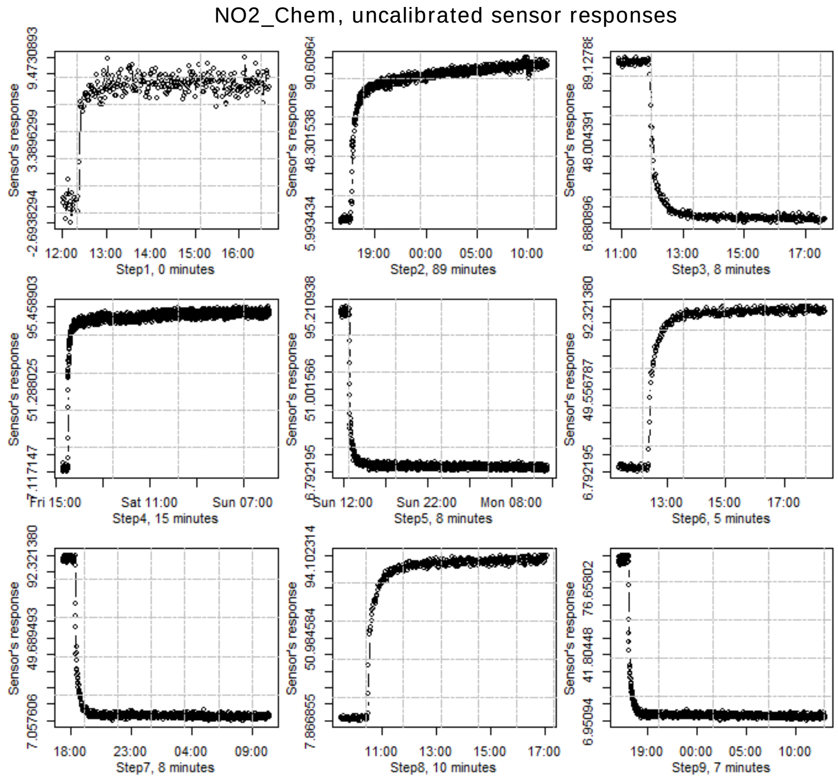


Metrological parameters

1 – Response Time



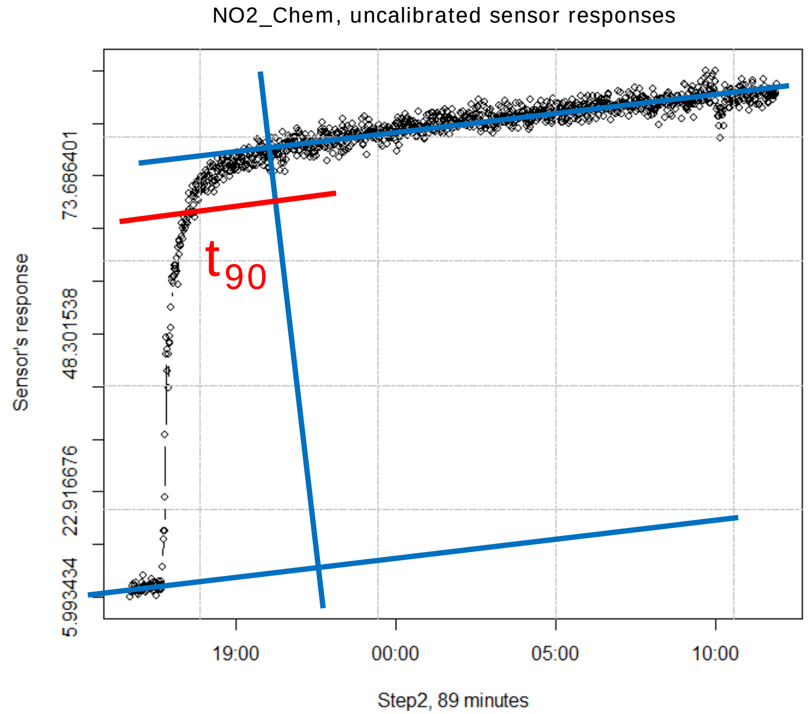


Metrological parameters

1 – Response Time

t_{90}: time needed by the sensor to reach 90 % of the final stable value

t0-90 or t90-0	Step 2	Step 3	Step 4	Step 5	Step 6	Step 7	Step 8	Step 9
	Rise	Fall	Rise	Fall	Rise	Fall	Rise	Fall
NO2, chemilumi-nescence	9	3	3	3	2	4	2	4
NO2_Chem	80	5	12	5	3	4	8	7



Required time: ¼ of 1h

NO2_Chem: 5 min (average) < required time

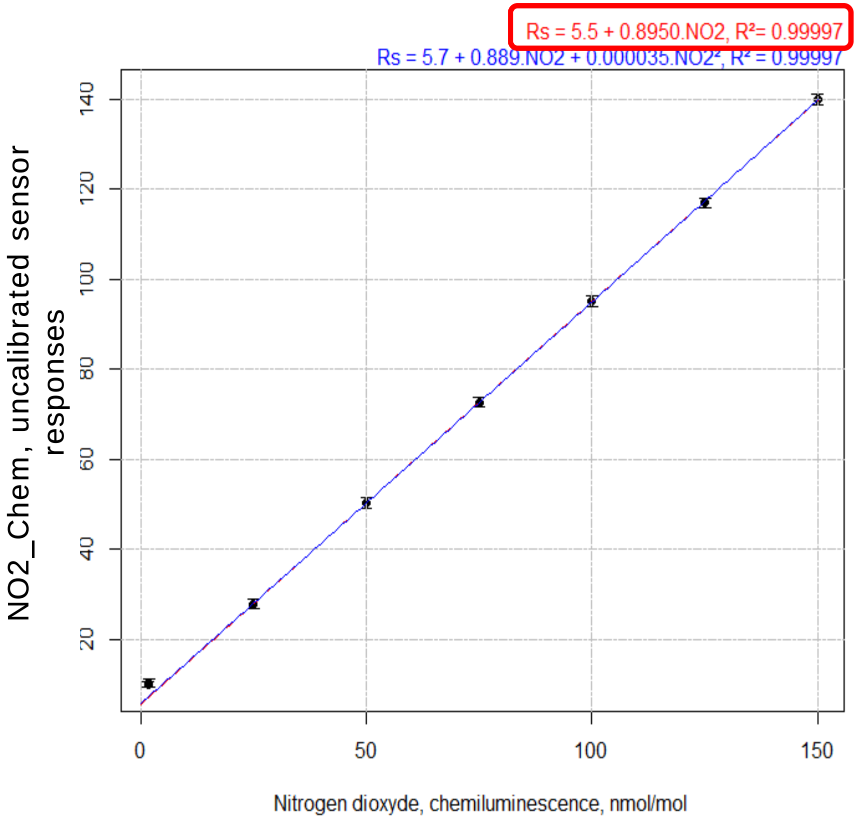
Metrological parameters

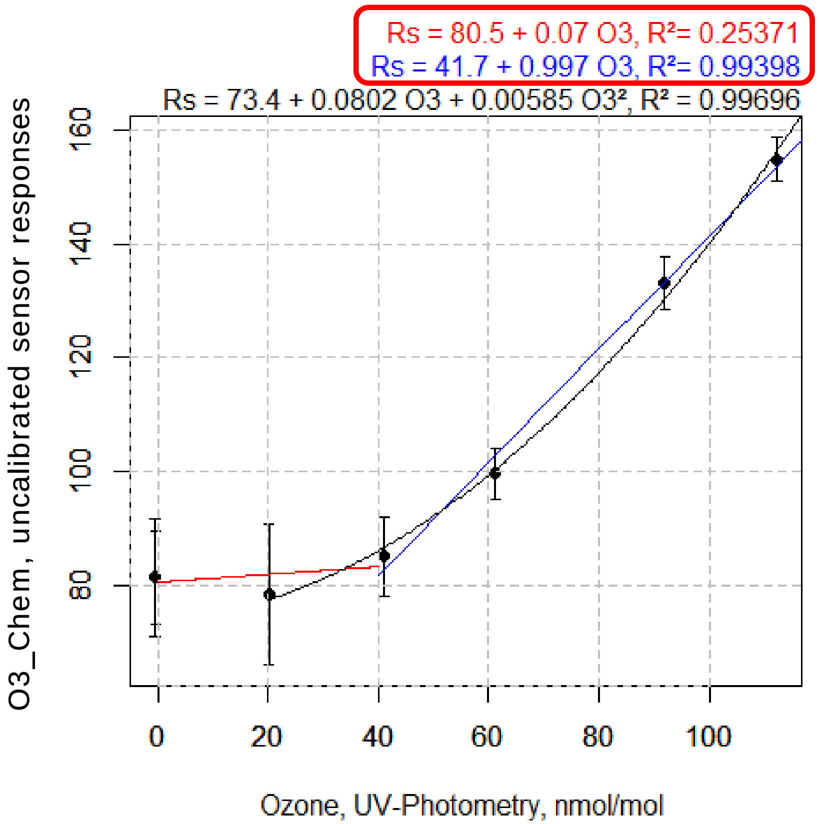
1 – Response Time: O_3

		Rise Time (n=4)	Fall Time (n=4)	Average Time	Response time per type
Chamber – UV analyser (**substracted**)		3 ‘	5 ‘	4 ‘	**3’**
MOx	Res_1	33 '	66 '	50 '	**Rise: 33’** **Fall: 47’** **Ave: 40’**
	Res_2	0.3 '	10 '	5 '	
	Res_3	57'	54'	56'	
	Res_4	8 '	13 '	10 '	
	Res_5	20 ‘	25 ‘	23 ‘	
	Res_6	> 116 ‘	> 177 ‘	> 146 ‘	
	Res_7	19 '	27'	23'	
	Res_8	6.5 '	13 '	10 '	
Elec	Chem_1	1.5 '	0.5 '	1 '	**Rise: 1’** **Fall: 1,7’** **Ave: 1,3’**
	Chem_2	0.8 '	1.8 '	1.3 '	
	Chem_3	2.3 '	0.8 '	1.5 '	
	Chem_4	2.6 '	0.8 '	1.7 '	

Metrological parameters

2 – Pre-calibration





Metrological parameters

2 – Pre-calibration

	NO_2	Fitting equation
Elect	Chem_1	Linear Linear
	Chem_2 *	Linear
	Chem_3	Linear Linear
	Chem_4 *	Not Linear
	Chem_5	Linear
Mox	Res_1	Linear Linear
	Res_2	Parabolic

	O_3	Fitting equation
MOx	Res_1	Not linear
	Res_2	Not linear
	Res_3	Not Linear and limited in range
	Res_4	Not linear
	Res_5	-
	Res_6	-
	Res_7	-
	Res_8	Slightly parabolic
Elec	Chem_1	Slightly parabolic
	Chem_2	Out of work
	Chem_3	Linear
	Chem_4	Strongly parabolic
	Chem_5 *	Strongly parabolic

* theses are not O_3/NO_2 sensor but were tested in agreement with the manufacturer

Metrological parameters

3 – Repeatability

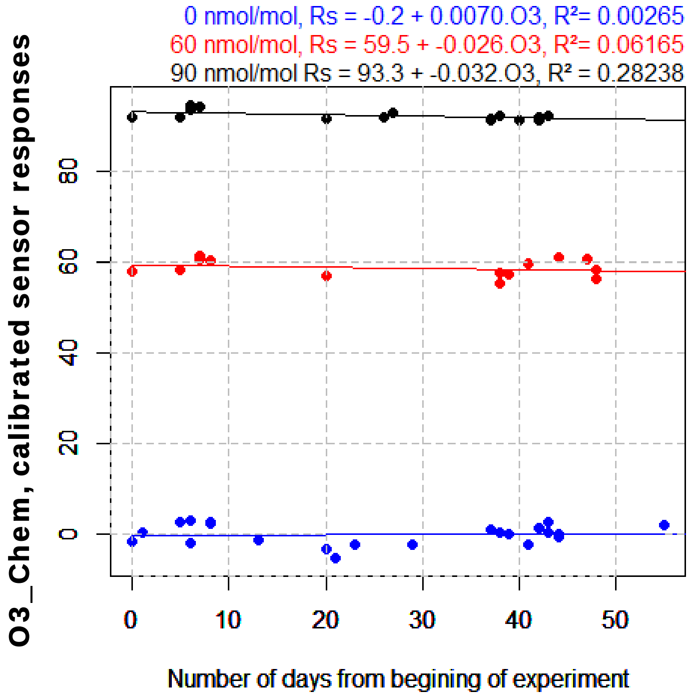
4 – Short term Drift

NO_2	Repeatability (nmol/mol)	Short term Drift (nmol/mol)
Chem_1	3.59	3.96
	5.18	5.47
Chem_2 *	3.60	4.31
Chem_3	0.78	1.43
	1.68	1.07
Chem_4 *	2.53	2.08
Chem_5	2.70	1.60
Res_1	4.67	24.29
	5.49	25.51
Res_2	8.31	14.56

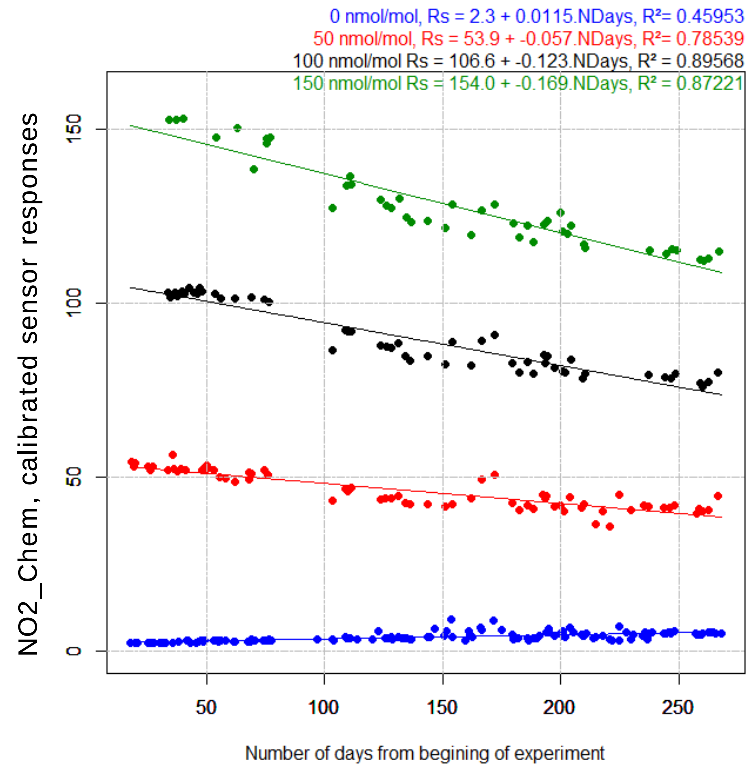
O_3	Repeatability (nmol/mol)	Short term Drift (nmol/mol)
Res_1	3.9	3.42
Res_2	28.1	-
Res_3	13.7	12.40
Res_4	-	2.37
Res_5	-	-
Res_6	-	-
Res_7	-	2.33
Res_8	2.6	2.57
Chem_1	1.3	1.32
Chem_2	Out of work	-
Chem_3	0.9	2.08
Chem_4	1.2	2.67

Metrological parameters

5 – Long term Drift

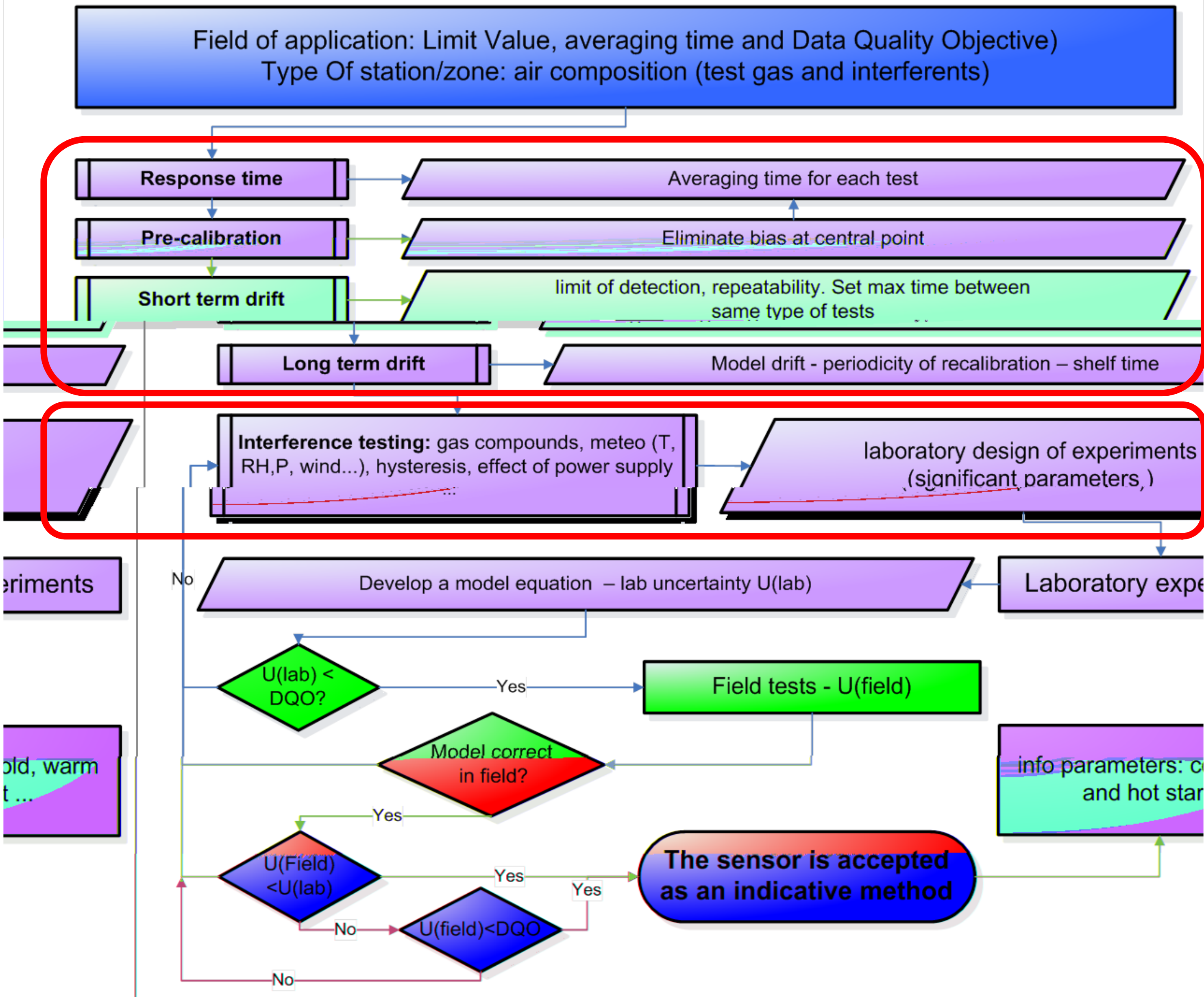


D_{ls} = 1.7 ± 1.9 nmol/mol



D_{ls} = f([NO2].[Ndays])

Evaluation Validation Protocol



Interfering effect

1 – Gaseous compounds

NO_2	O3	NO	CO	CO2	NH3
Chem_1	80.3 %	-6.4 %	-34.8 %	-31.9 %	-26.8 %
	81.2 %	-5.9 %	-36.8 %	5.3 %	-24.1 %
Chem_2 *	71.2 %	-10.0 %	-10.7 %	-4.6 %	-18.9 %
Chem_3	69.3 %	-10.0 %	-27.6 %	7.5 %	-17.3 %
	63.9 %	-9.7 %	-22.7 %	5.2 %	-14.2 %
Chem_4 *	79.3 %	-	-34.9 %	2.5 %	-36.4 %
Chem_5	38.8 %	-1.8 %	-7.8 %	8.3 %	-6.3 %
Res_1	-	-	-	-	-
	-	-	-	-	-
Res_2	63.9 %	-25.3 %	-44.2 %	12.9 %	-88.7 %

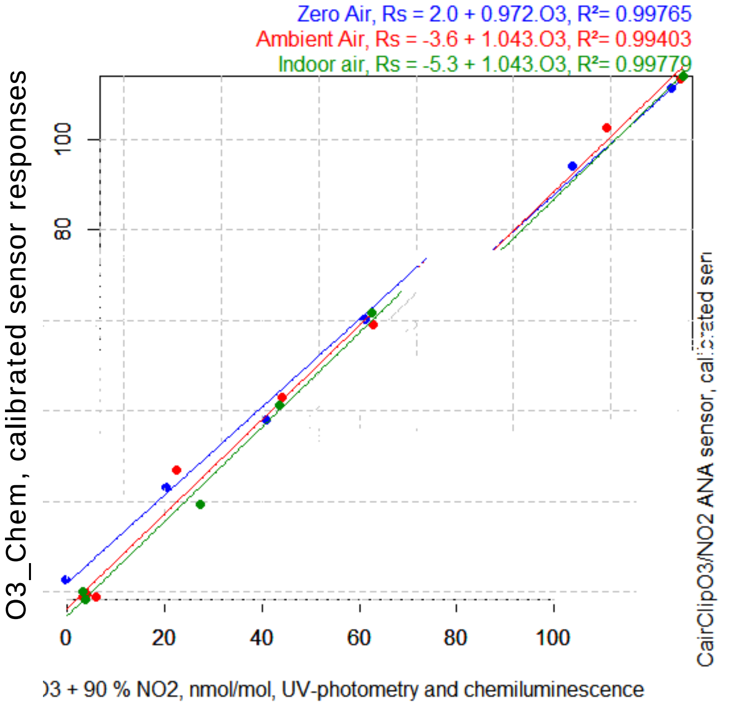
O_3	NO2	NO	CO	CO2	NH3
Res_1	14.1 %	-5.3 %	9.8 %	-6.2 %	6.0 %
Res_2	-3.3 %	-	3.6 %	-0.1 %	-0.3 %
Res_3	14.5 %	-10 %	13.4 %	5.0 %	18 %
Res_4	12.6 %	-1.6 %	-8.9 %	1.0 %	3.5 %
Res_5	-	-	-	-	-
Res_6	-	-	-	-	-
Res_7	-	-	-	-	-
Res_8	1.2 %	-0.8 %	0.1 %	-0.2 %	-1.9 %
Chem_1	89.3 %	1.3 %	-0.9 %	0.2 %	1.2 %
Chem_2	-	-	-	-	-
Chem_3	33.7 %	-7.7 %	-1.2 %	-0.4 %	0.1 %
Chem_4	107.7 %	-1.5 %	-2.4 %	0.4 %	2.3 %

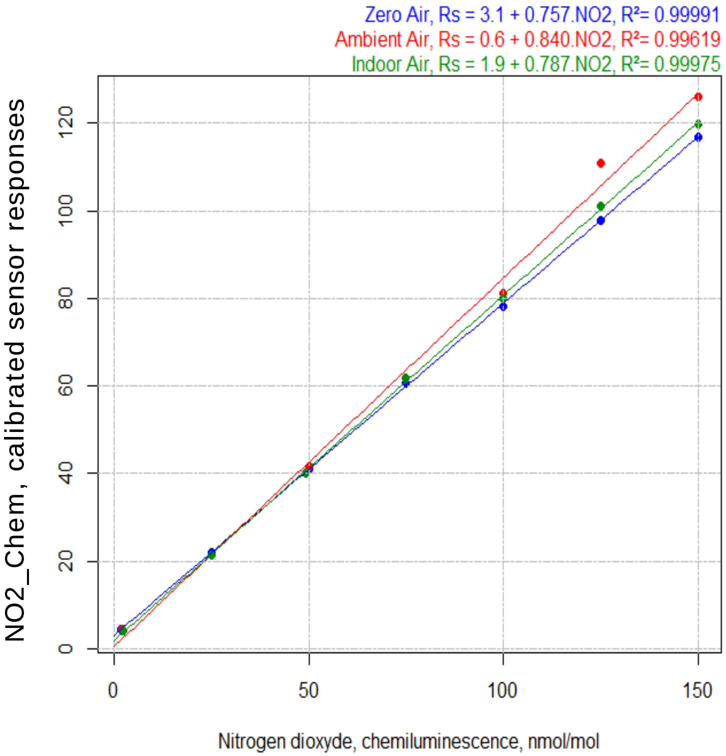
Main interferent gas: O_3

Main interferent gas: NO_2

Interfering effect

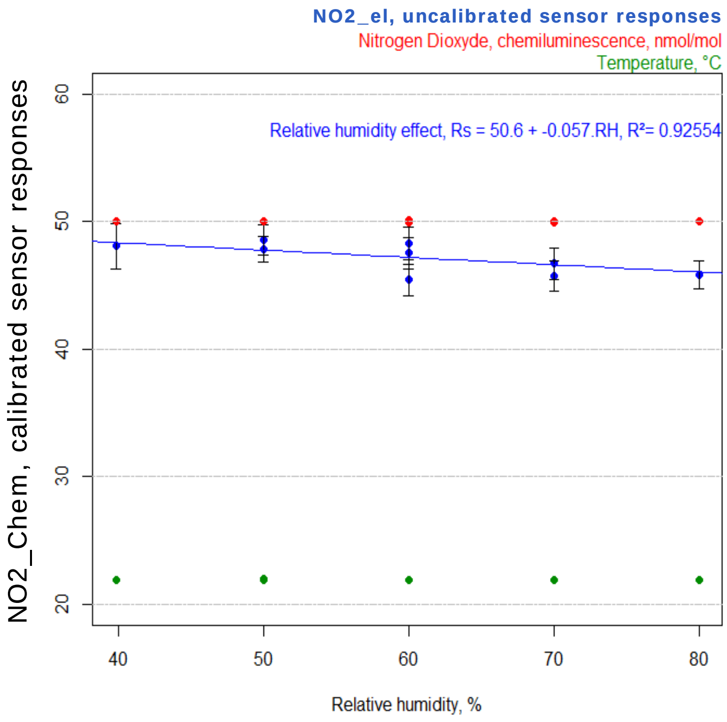
2 – Air Matrix

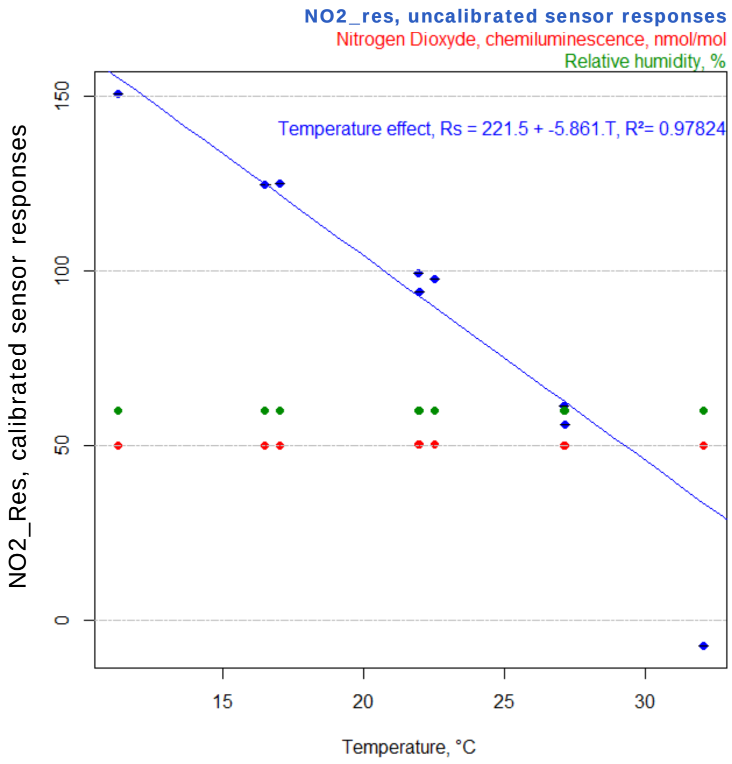




Interfering effect

3 – Meteorological effect:
Relative Humidity / Temperature

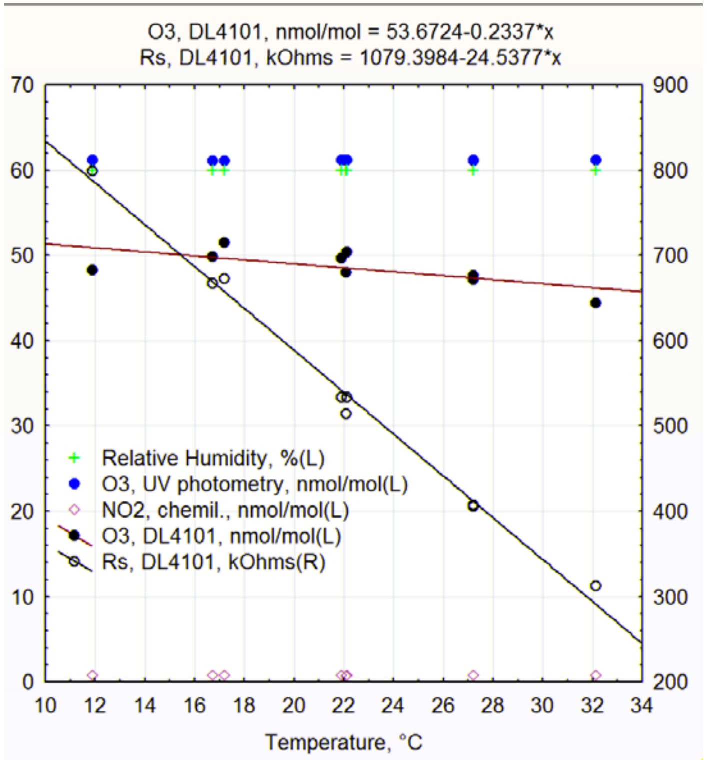




Interfering effect

3 – Meteorological effect: Relative humidity / Temperature

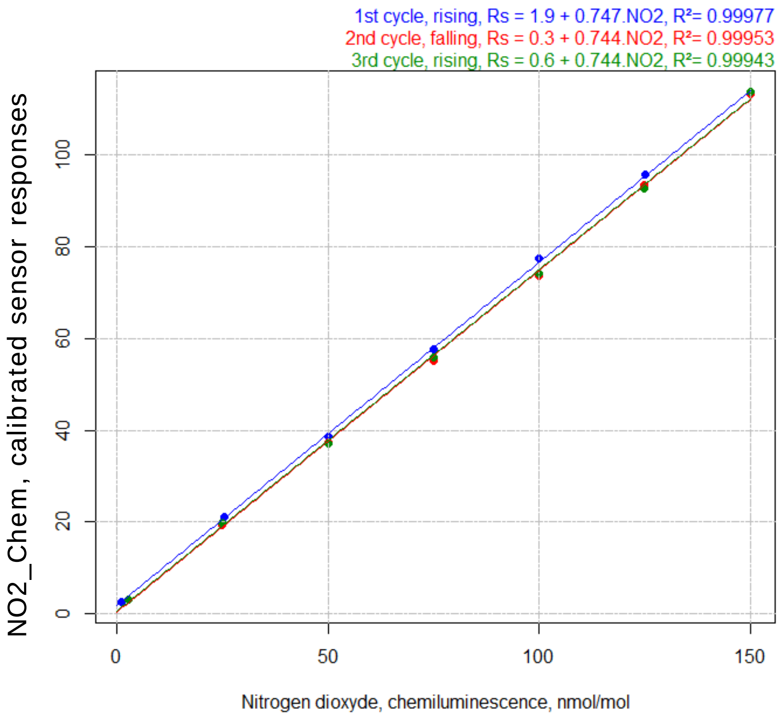
NO_2	Relative Humidity (nmol/mol)	Temperature (nmol/mol)
Chem_1	6.47	8.32
	3.30	4.21
Chem_2 *	6.07	6.07
Chem_3	0.26	1.17
	0.46	0.79
Chem_4 *	0.54	3.35
Chem_5	0.30	0.10
Res_1	3.04	43.65
	1.88	50.32
Res_2	3.96	6.50



Interfering effect

3 – Hysteresis in concentration

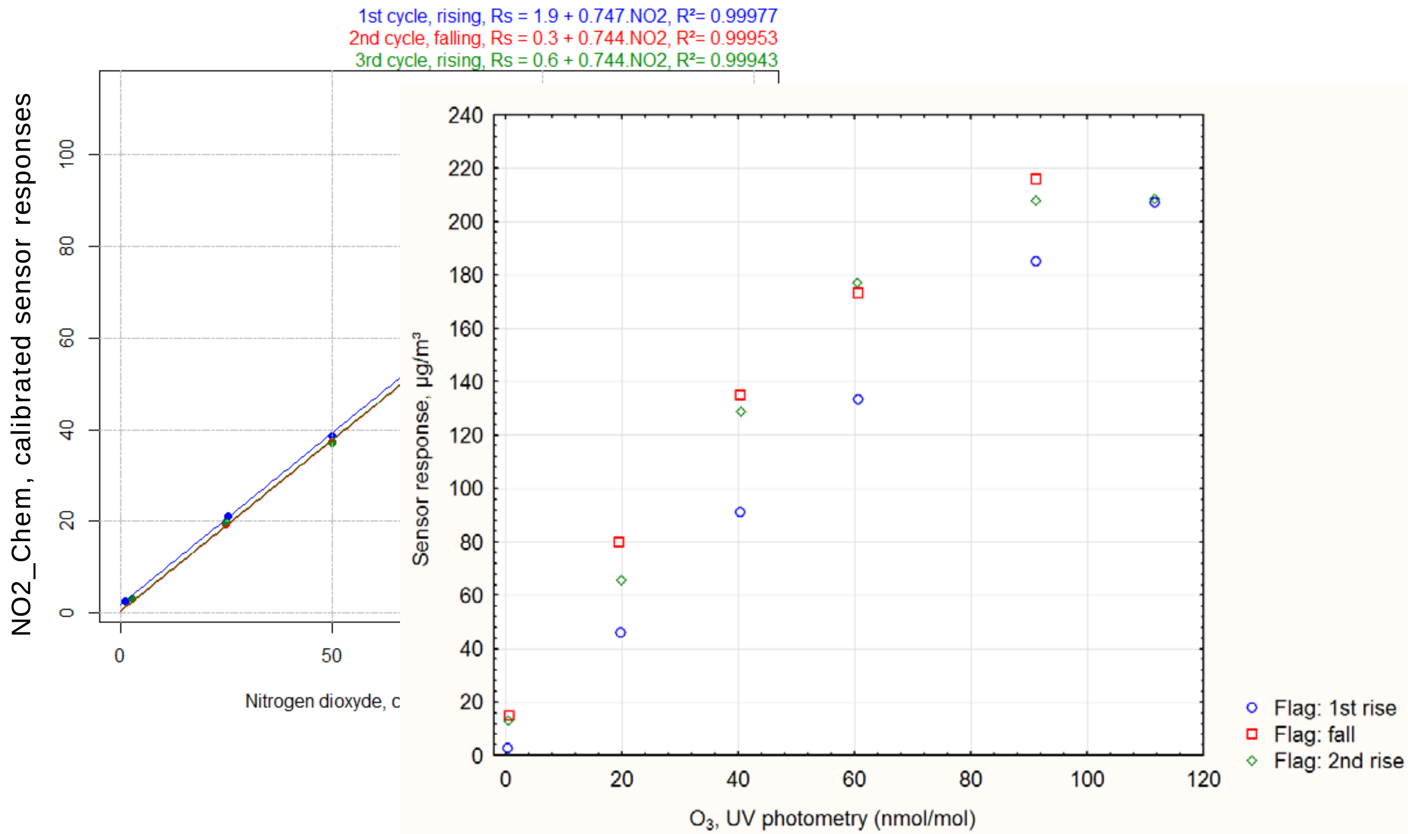
NO_2	Hysteresis (nmol/mol)
Chem_1	< 3.0 < 10.0
Chem_2 *	< 3.0
Chem_3	< 1.5 < 1.0
Chem_4 *	< 2.5
Chem_5	< 1.5
Res_1	< 50.0 < 15.0
Res_2	< 22.0



Interfering effect

3 – Hysteresis in concentration

NO_2	Hysteresis (nmol/mol)
Chem_1	< 3.0
	< 10.0
Chem_2 *	< 3.0
Chem_3	< 1.5
	< 1.0
Chem_4 *	< 2.5
Chem_5	< 1.5
Res_1	< 50.0
	< 15.0
Res_2	< 22.0



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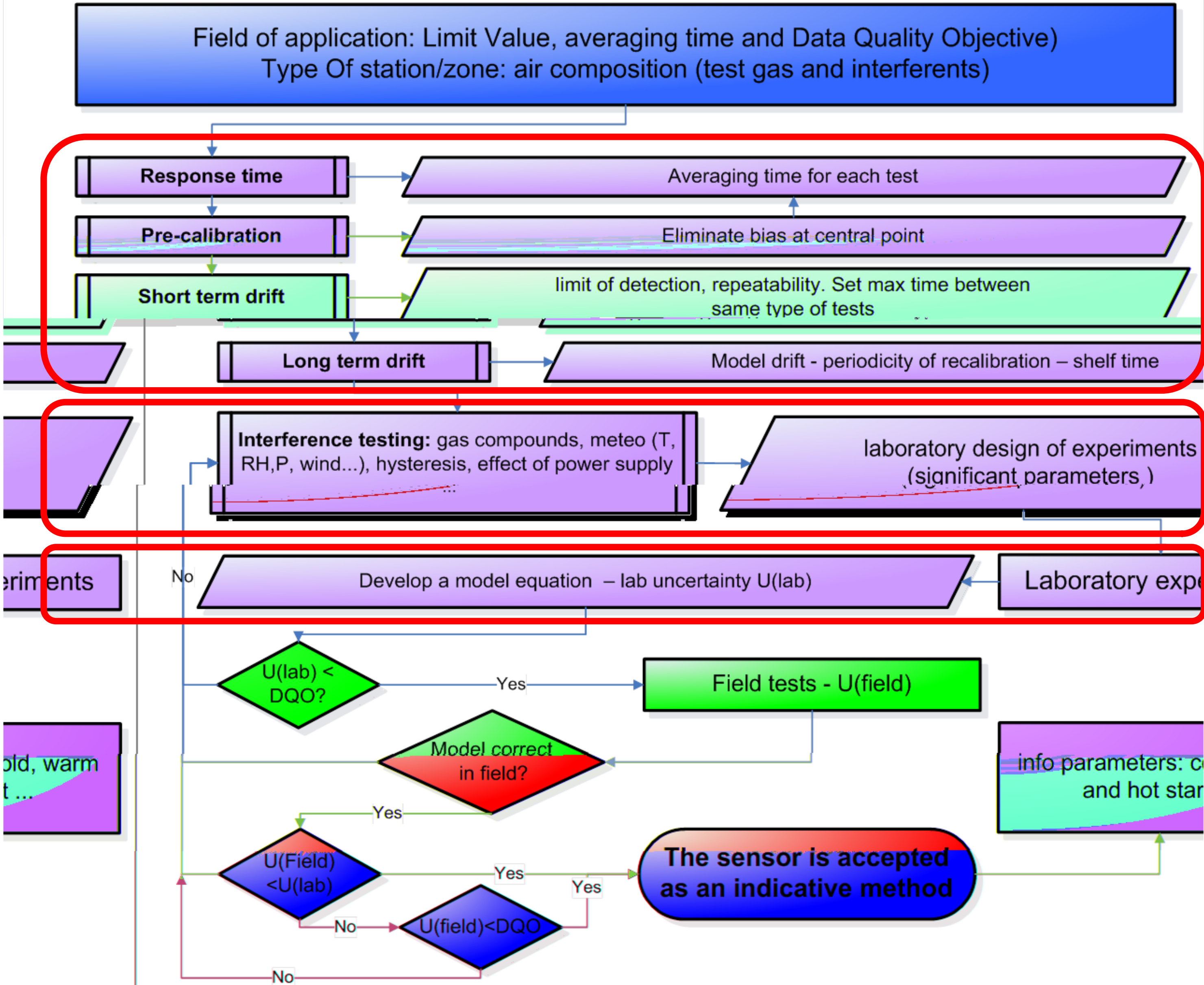


Design of Experiment

O_3 sensors: 6 O_3 levels x 2 NO_2 levels x 3 Temp. x 3 Rel. Hum.

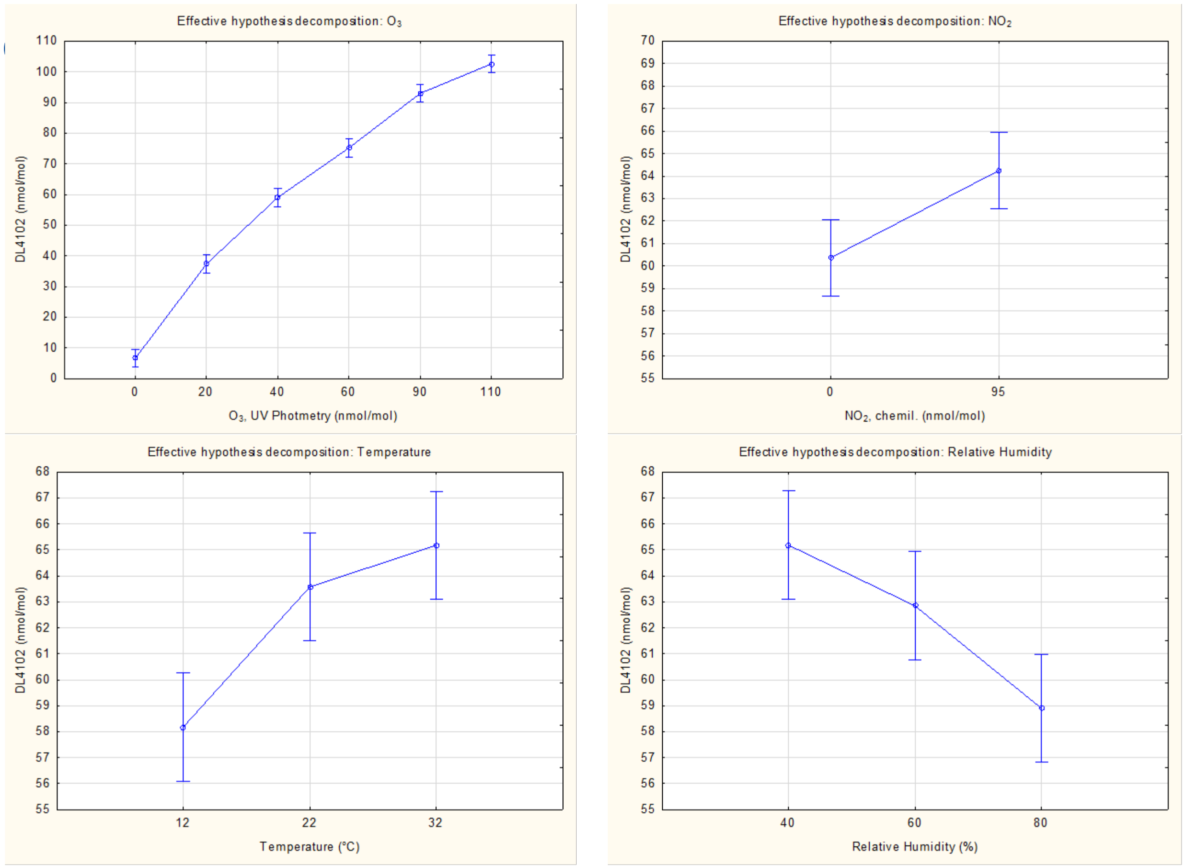
108 experiments

NO_2 sensors: 7 NO_2 levels x 2 O_3 levels x 3 Temp. x 3 Rel. Hum.

126 experiments

European Commission

Design of Experiment



108 experiments

126 experiments

Multiple analysis of Variance (MANOVA)

Multiple Linear Regression (MLR)

$$Sr_{DL4102} = 17.3_{\pm 4.5} + 0.84_{\pm 0.02} \times [O_3] + 0.36_{\pm 0.11} \times [T] - 0.16_{\pm 0.06} \times [RH] + 0.0039_{\pm 0.024} \times [NO_2]$$

Design of Experiment

O_3 sensors: 6 O_3 levels x 2 NO_2 levels x 3 Temp. x 3 Rel. Hum. — **108 experiments**

NO_2 sensors: 7 NO_2 levels x 2 O_3 levels x 3 Temp. x 3 Rel. Hum. — **126 experiments**

Laboratory model:

$$Sr_{DL4102} = 17.3_{\pm 4.5} + 0.84_{\pm 0.02} \times [O_3] + 0.36_{\pm 0.11} \times [T] - 0.16_{\pm 0.06} \times [RH] + 0.0039_{\pm 0.024} \times [NO_2]$$

Laboratory uncertainty:

- GUM method

$$\boldsymbol{U}^2(O3) = \mathbf{2}.\sum \left(\frac{\partial O3}{\partial X_i}\right)^2 u^2(X_i)$$

- sum of Variance

$$var\left(\sum_{i=1}^{n} X_i\right) = \sum_{i=1}^{n} var(X_i)$$

Design of Experiment

Laboratory uncertainty

NO_2	U_c^2						
Chem_1	U_{lof}^2	$+ U(O3)^2$	$+ U(T)^2$	$+ U(RH)^2$			$+ cst^2$
	U_{lof}^2	$+ U(O3)^2$		$+ U(RH)^2$			$+ cst^2$
Chem_2 *	U_{lof}^2	$+ U(O3)^2$	$+ U(T)^2$	$+ U(RH)^2$			$+ cst^2$
Chem_3	U_{lof}^2	$+ U(O3)^2$	$+ U(T)^2$				$+ cst^2$
	U_{lof}^2	$+ U(O3)^2$	$+ U(T)^2$	$+ U(RH)^2$	$+ U(NO)^2$		$+ cst^2$
Chem_4 *	U_{lof}^2	$+ U(O3)^2$	$+ U(T)^2$				$+ cst^2$
Chem_5	U_{lof}^2	$+ U(O3)^2$					$+ cst^2$
Res_1	U_{lof}^2	$+ U(O3)^2$	$+ U(T)^2$				$+ cst^2$
	U_{lof}^2	$+ U(O3)^2$	$+ U(T)^2$				$+ cst^2$
Res_2	U_{lof}^2	$+ U(O3)^2$	$+ U(T)^2$		$+ U(NO)^2$	$+ U(CO)^2$	$+ cst^2$

$$U_c^2{}_{Chem\_5} = 3.2^2 + 11.0^2 + 5.02^2 \Rightarrow U_{c,Chem\_5} = 12,51$$

U_{lof}^2 → 3.2^2; $U(O3)^2$ → 11.0^2; cst^2 → 5.02^2

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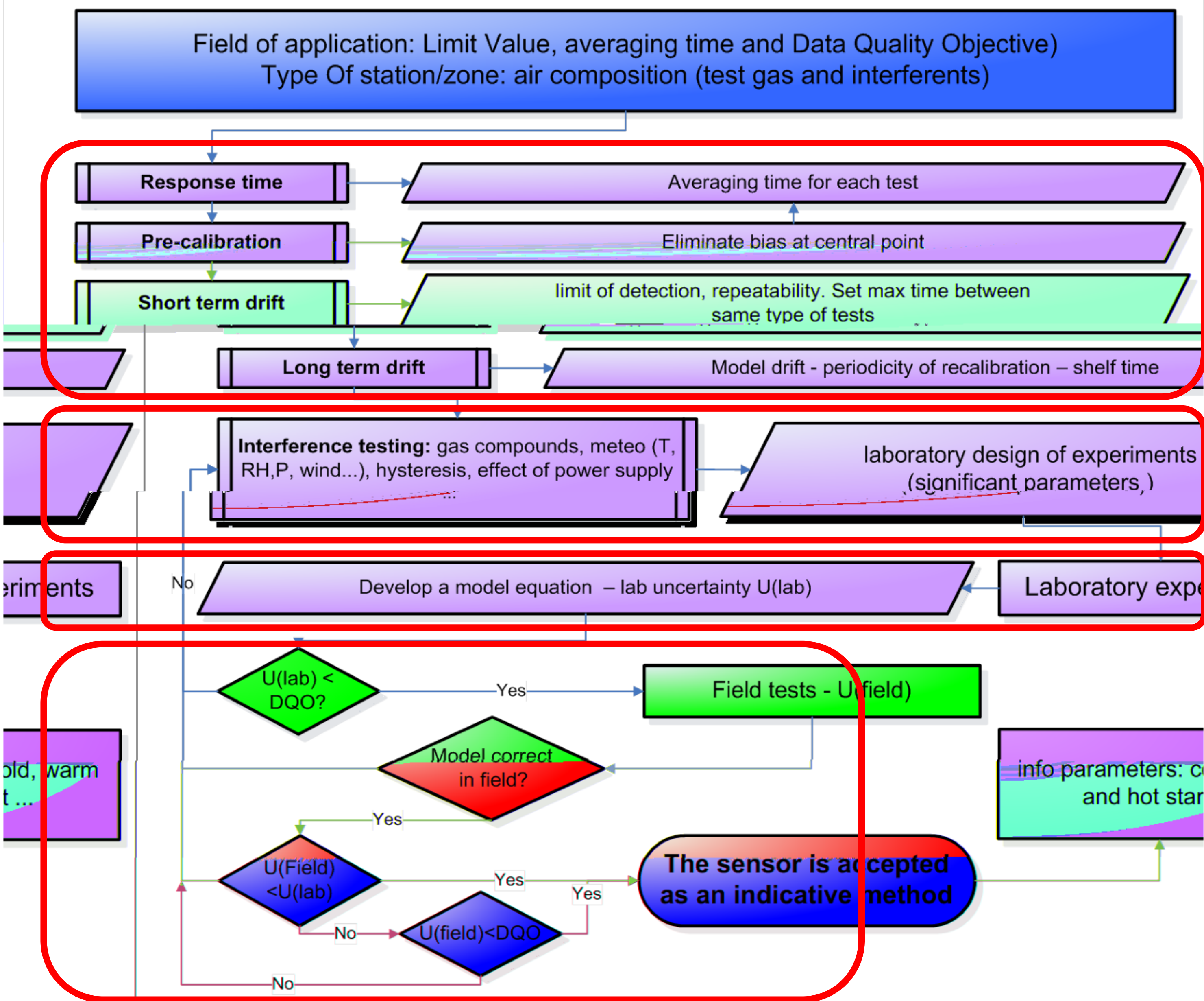
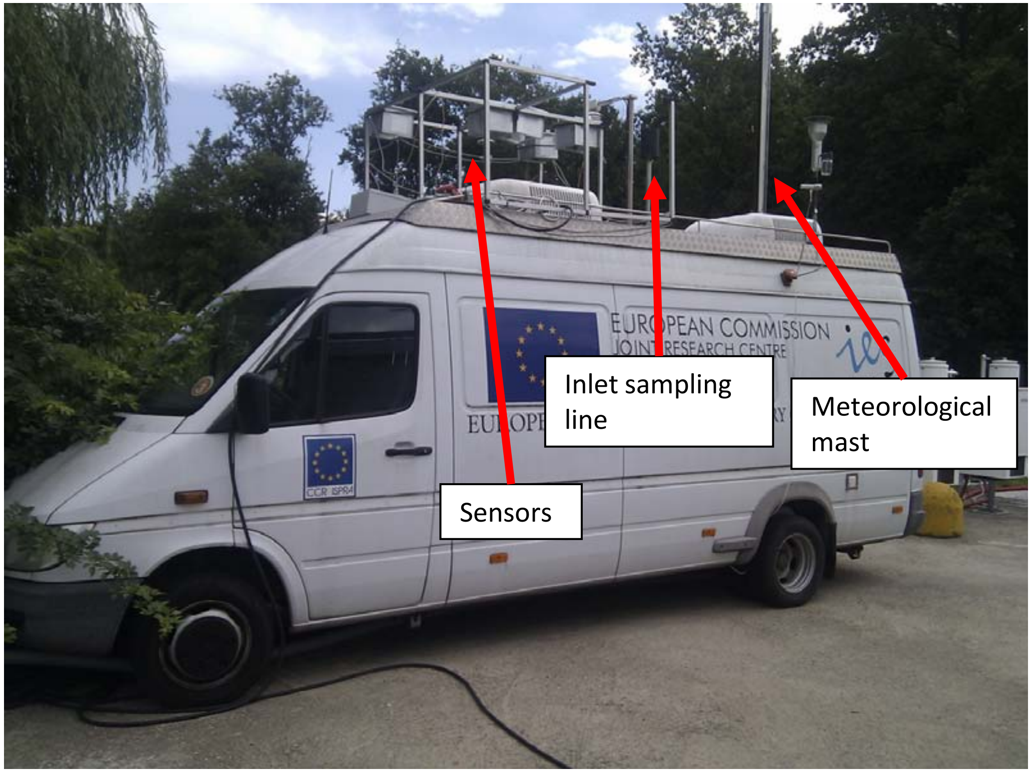


Application in Field



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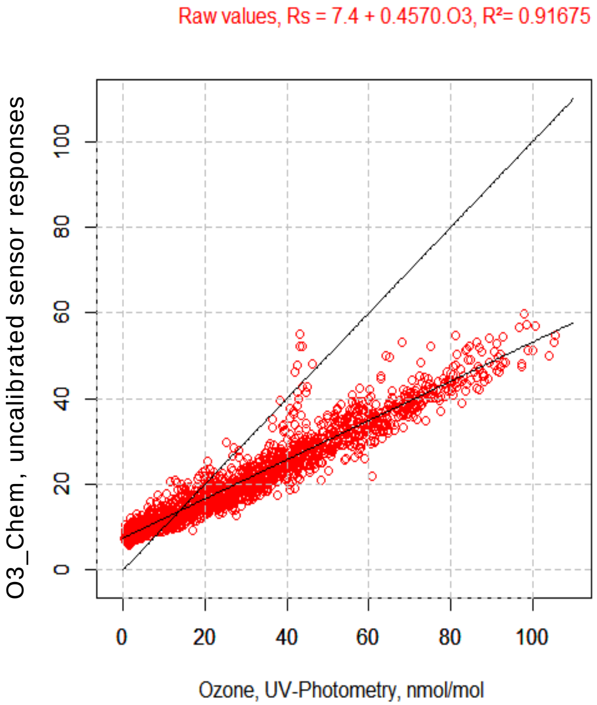
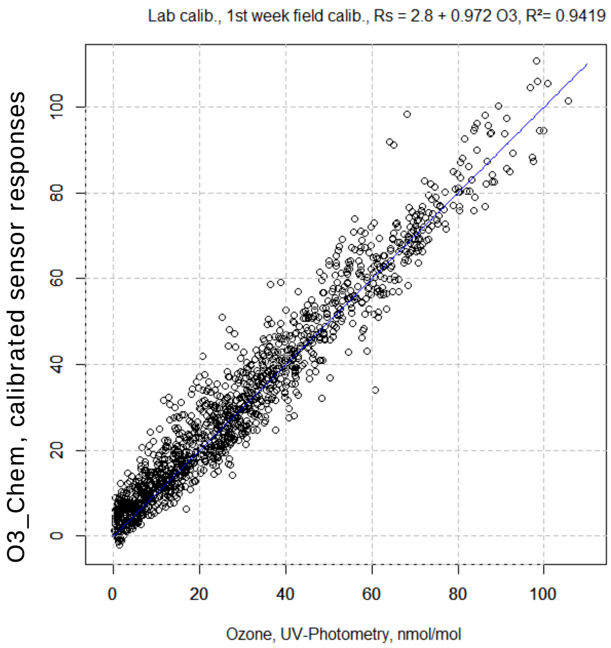


Calibration + Model



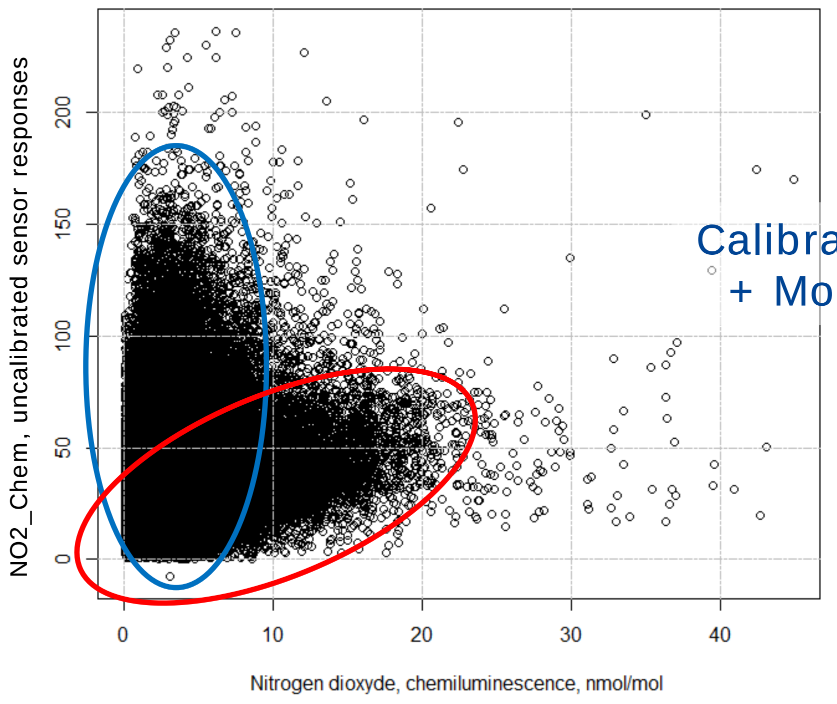
Calibration: first week of exposure

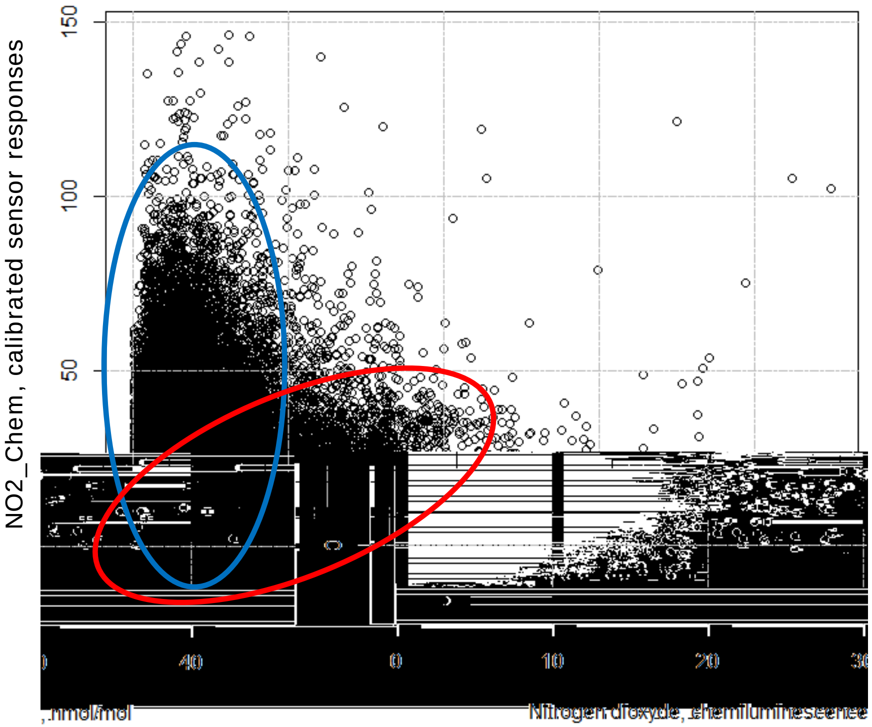
Model: Laboratory model

Expanded relative uncertainty
(Guidance to Demonstration of Equivalence)

19.4% < 30% of the Data Quality Objective

Application in Field





Calibration: first 10 days of exposure

Model: Laboratory model

low NO2 level: field campaign conditions un-adapted to the sensor

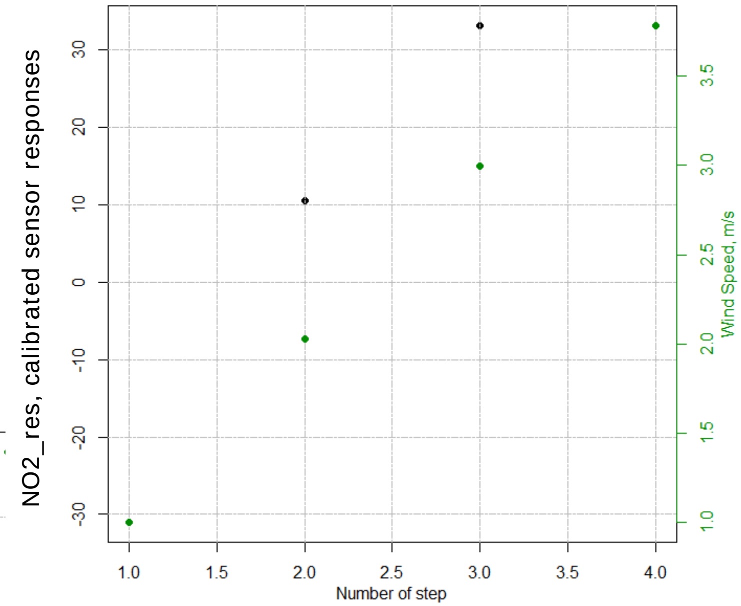
Thank You…

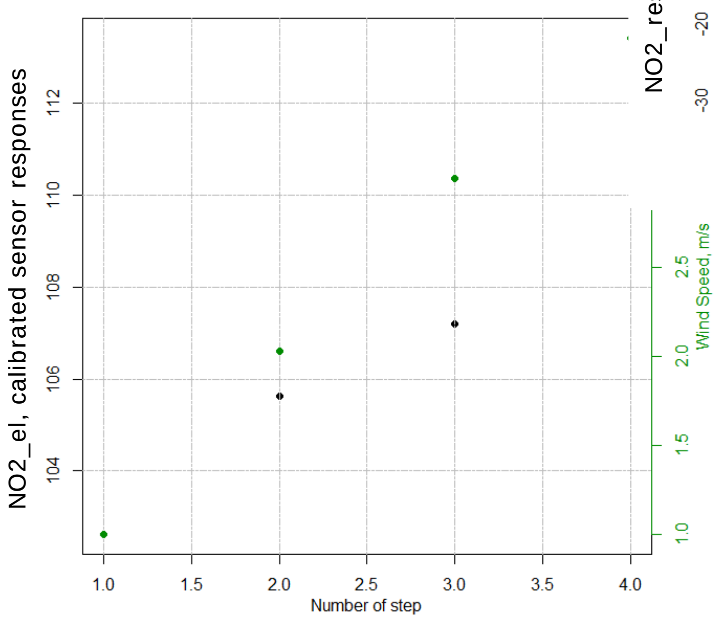
…and come to ask us your questions
at our Live Demonstration

Interfering effect

Meteorological effect: Wind

NO_2	Wind (nmol/mol)
Chem_1	2.66
	1.16
Chem_2 *	0.91
Chem_3	0.48
	0.25
Chem_4 *	0.07
Chem_5	< 3.40
Res_1	0.01
	0.07
Res_2	1.31





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