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

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OPEN SESSION COST on New Sensing Technologies for Air Quality Monitoring Brescia, Italy, 10 September 2014 Engineering Campus, University of Brescia Via Branze, 38, Brescia, Italy

Projects at JRC about sensors for air pollution monitoring

- Two EURAMET Joint Research Projects - European Metrology Research Programme. Objective: do sensors meet the data quality objective for ambient air monitoring as indicative methods according to the European Legislation?
- MACPoll (Metrology of ambient air pollution monitoring) from 1-Jun-14 to 31-May-14: Validation of commercially available O_3 and NO_2 sensors and cluster of sensors. Micro-environment: O_3 rural background and NO_2 urban background sites
- KEY-VOC (1-Oct 2014 to 31-Sept 2017): validation targeted on sensors-based devices for VOCs measurements (mainly benzene)
- A research project on the development of a multi-sensor platform (O3, NO2, NO and CO)

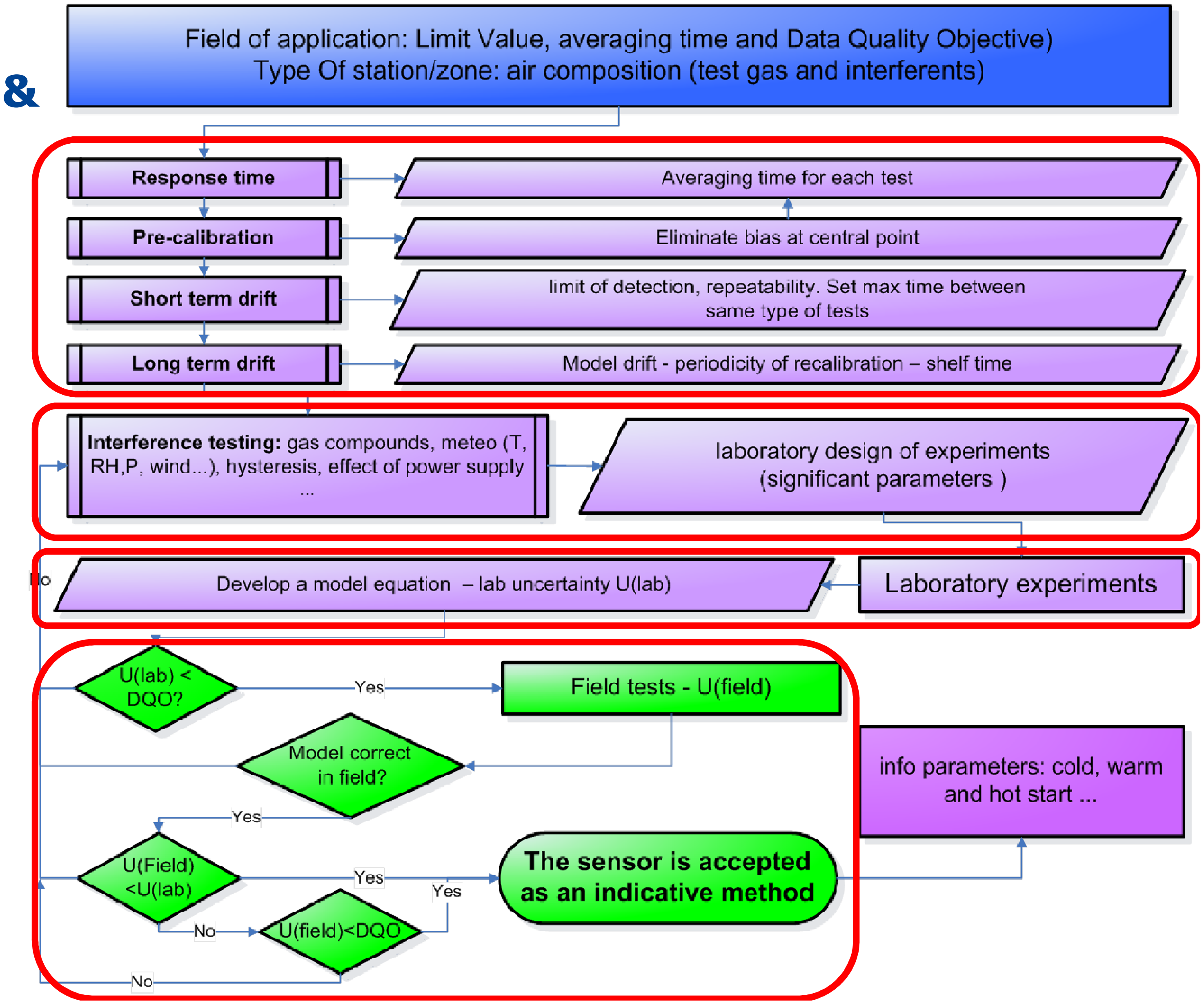
Data Quality Objectives (DQO) of the European Air Quality Directive

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

Manufacturer	Model	Type
Unitec s.r.l – IT	O_3 Sens 3000	Resistive
Ingenieros Assessores – SP	NanoENvi mote and MicroSAD datalogger, with Oz-47 sensor	Resistive
αSense - UK	O_3 sensors (O3B4)	4 electrodes
Citytech – G	Sensoric 4-20 mA Transmitter Board with O3E1 sensor	3 electrodes
Citytech – G	Sensoric 4-20 mA Transmitter Board with O3E1F sensor	3 electrodes
CairPol – F	CairClip O3	3 electrodes
e2V – CH	MiCS-2610 sensor and OMC2 datalogger,	Resistive
e2V – CH	MiCS Oz-47 sensor and OMC3 datalogger	Resistive
IMN2P – FR	Prototype WO3 sensor with MICS-EK1 Sensor Evaluation Kit	Resistive
FIS - J	SP-61 sensor and evaluation test board	Resistive

Manufacturer	Model
Unitec s.r.l – IT	Sens 3000
Ingenieros Assessores – SP	NanoENvi mote and MicroSAD datalogger, unidentified sensor probably e2v-MICS sensor
αSense – UK	NO_2 sensors (B4)
Citytech – G	Sensoric 4-20 mA Transmitter Board with 3E50/3E100 sensor
MIKES – FI	Prototype graphene sensors
CairPol – F	CairClip NO2/O3 - filtered

Evaluation & Validation Protocol[1]



Field of application: Limit Value, averaging time and Data Quality Objective)
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Pre-calibration – Eliminate bias at central point

Short term drift – limit of detection, repeatability. Set max time between same type of tests

Long term drift – Model drift - periodicity of recalibration – shelf time

Interference testing: gas compounds, meteo (T, RH,P, wind…), hysteresis, effect of power supply …

laboratory design of experiments (significant parameters)

Laboratory experiments

Develop a model equation – lab uncertainty U(lab)

U(lab) < DQO? – Yes – Field tests - U(field)

Model correct in field?

U(Field) <U(lab)

U(field)<DQO

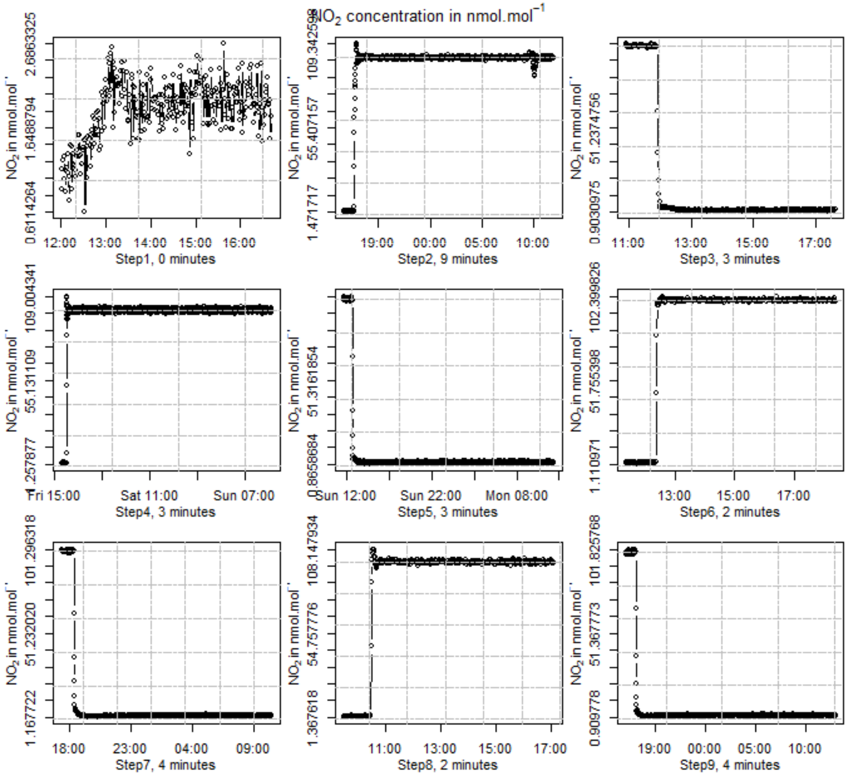
The sensor is accepted as an indicative method

info parameters: cold, warm and hot start …

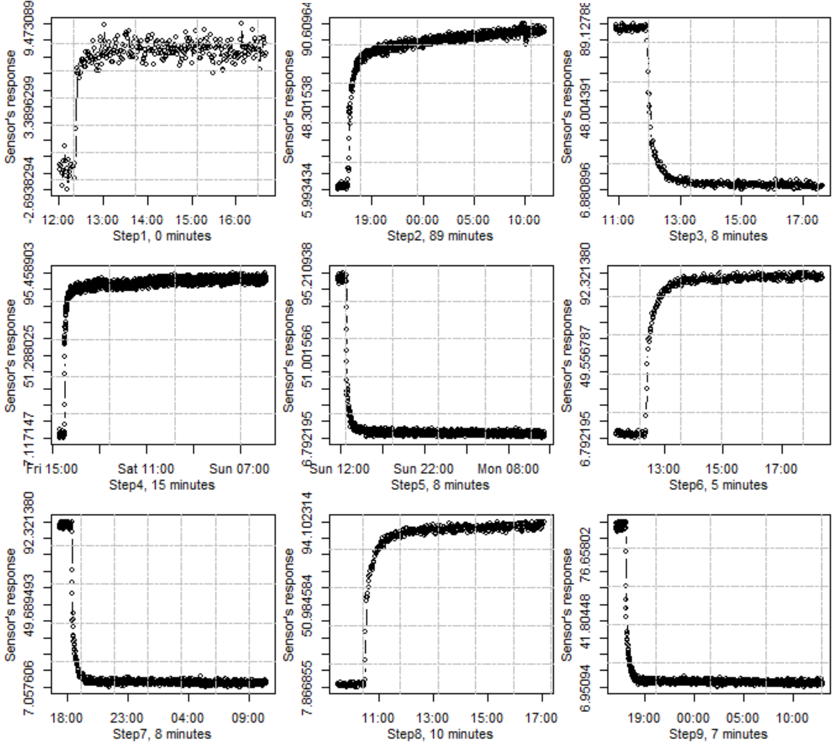
[1] Spinelle L, Aleixandre M, Gerboles M. Protocol of evaluation and calibration of low-cost gas sensors for the monitoring of air pollution. EUR 26112.

Metrological parameters

1 – Response Time



NO2_Chem, uncalibrated sensor responses



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	Unitec, Sens3000	33 '	66 '	50 '	**Rise: 33’** **Fall: 47’** **Ave: 40’**
	e2V, MICS-2610	0.3 '	10 '	5 '	
	FIS, SP-61	57'	54'	56'	
	Ingenieros Assessores, NanoEnvi	8 '	13 '	10 '	
	e2v, OMC3	20 ‘	25 ‘	23 ‘	
	e2v, OMC2	> 116 ‘	> 177 ‘	> 146 ‘	
	e2v, MICS_Oz47	19 '	27'	23'	
	IMN2P, WO_3	6.5 '	13 '	10 '	
Elec	Citytech, O3 3E1F + Test Panel	1.5 '	0.5 '	1 '	**Rise: 1’** **Fall: 1,7’** **Ave: 1,3’**
	Citytech, O3E1 + 4-20mA Board	0.8 '	1.8 '	1.3 '	
	AlphaSense, O3-B4	2.3 '	0.8 '	1.5 '	
	Cairclip O_3/NO_2	2.6 '	0.8 '	1.7 '	

Metrological parameters

2 – Pre-calibration

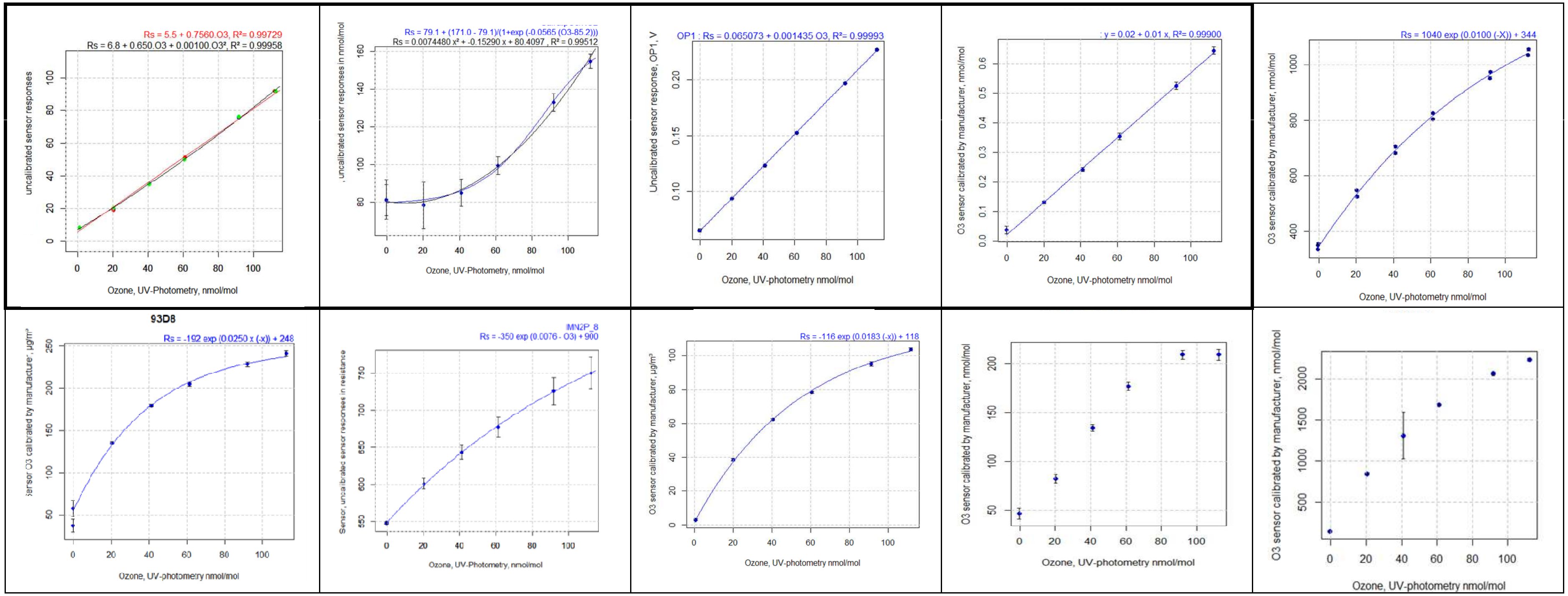
	NO_2	Name	Fitting equation
Elect	AlphaSense, NO2-B4	Chem_1	Linear Linear
	AlphaSense, O3-B4 *	Chem_2	Linear
	Citytech, NO2 3E50	Chem_3	Linear Linear
	Citytech, NO 3E100 *	Chem_4	Not Linear to NO_2
	CairClip NO2	Chem_5	Linear
Mox	e2V, MiCS-2710	Res_1	Nearly Linear
	e2V, 4514	Res_2	Log/Parabolic

	O_3	Name	Fitting equation
MOx	Unitec, Sens3000	Res_1	Exponential
	e2V, MICS-2610	Res_2	Log
	FIS, SP-61	Res_3	~Sigmoid
	Ingenieros Assessores, NanoEnvi	Res_4	Exponential decay
	e2v, OMC3	Res_5	Log
	e2v, OMC2	Res_6	Log
	e2v, MICS_Oz47	Res_7	Log
	IMN2P, WO_3	Res_8	Parabolic /log
Elec	Citytech, O3 3E1F + Test Panel	Chem_1	Linear
	AlphaSense, O3-B4	Chem_3	Linear
	Cairclip O_3/NO_2	Chem_4	Linear (once parabolic)
	Cairclip NO_2 *	Chem_5	Parabolic to O_3

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

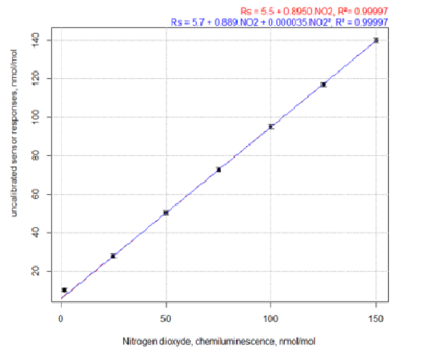
Metrological parameters (Rs = f(O_3 or NO_2))

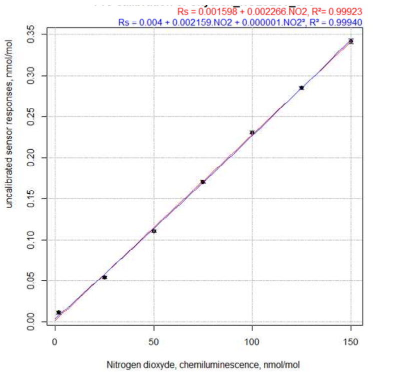
2 – Pre-calibration O_3

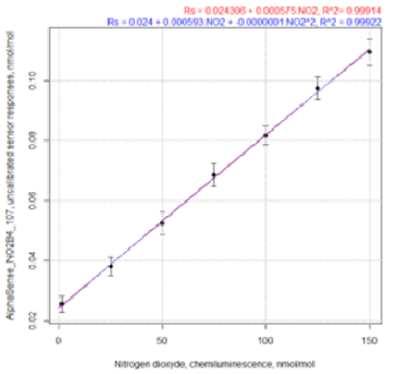


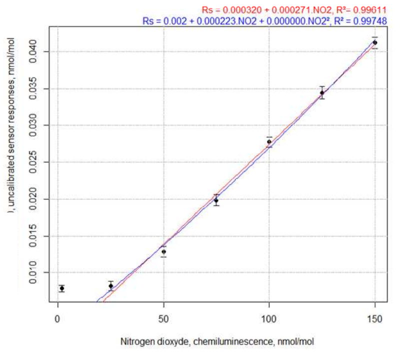
Metrological parameters

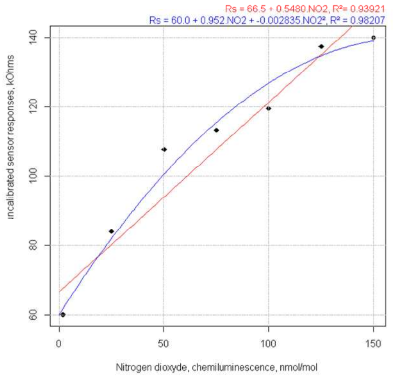
2 – Pre-calibration NO2

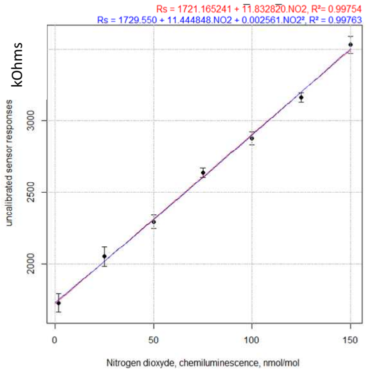


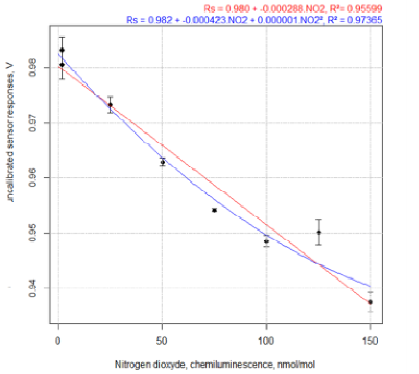












Metrological parameters

3 – Repeatability

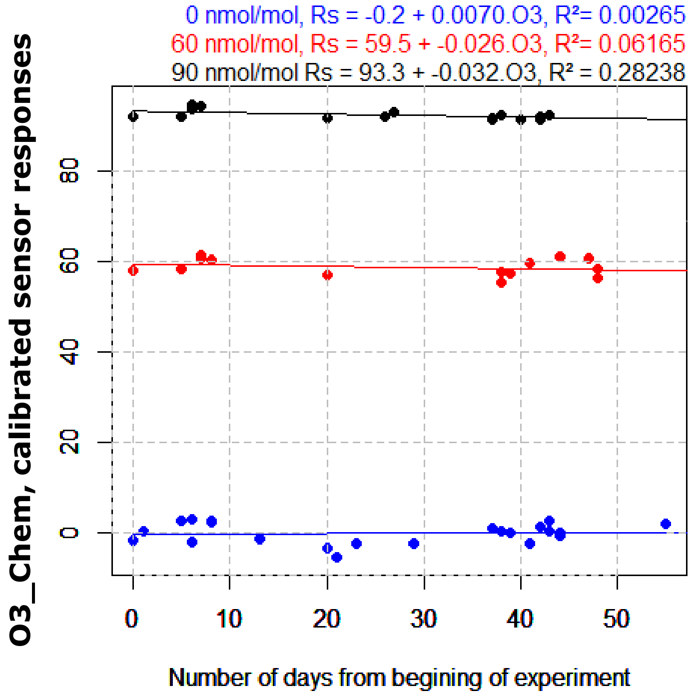
4 – Short term Drift

NO_2	Repeatability (nmol/mol)	Short term Drift (nmol/mol)
Chem_1	3.6	4.0
	5.2	5.47
Chem_2 *	3.6	4.31
Chem_3	0.8	1.43
	1.7	1.07
Chem_4 *	2.5	2.08
Chem_5	2.7	1.60
Res_1	4.7	24 kOhms
	5.5	26 kOhms
Res_2	8.3	15 kOhms

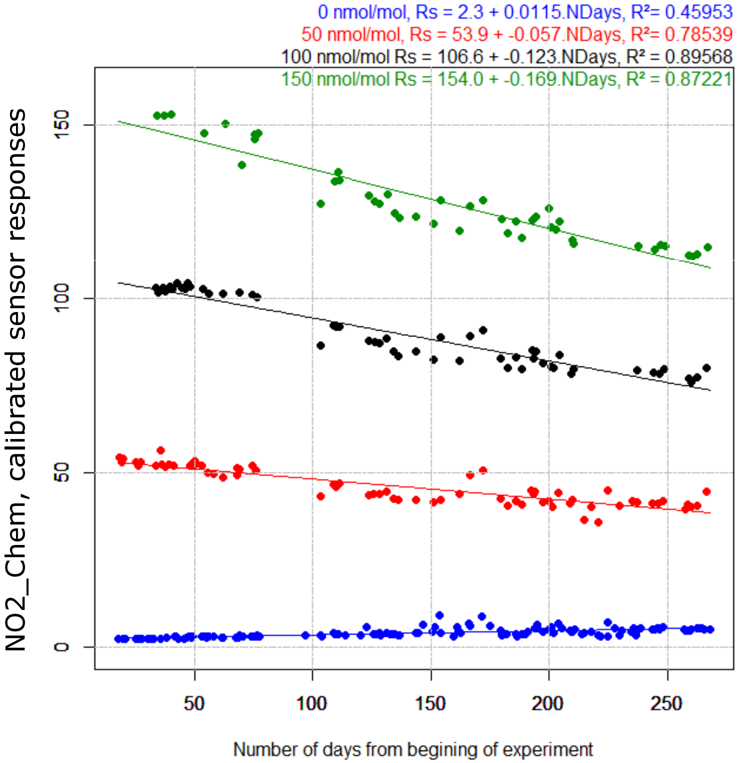
O_3	Repeatability (nmol/mol)	Short term Drift (nmol/mol)
Res_1	3.9	3.4
Res_2	2.8	3.5
Res_3	13.7	12.4
Res_4	2.0	2.1
Res_5	2.4	2.3
Res_6	2.8	3.5
Res_7	2.4	2.3
Res_8	2.6	2.6
Chem_1	1.3	1.3
Chem_3	0.9	2.1
Chem_4	1.2	2.7

Metrological parameters

5 – Long term Drift



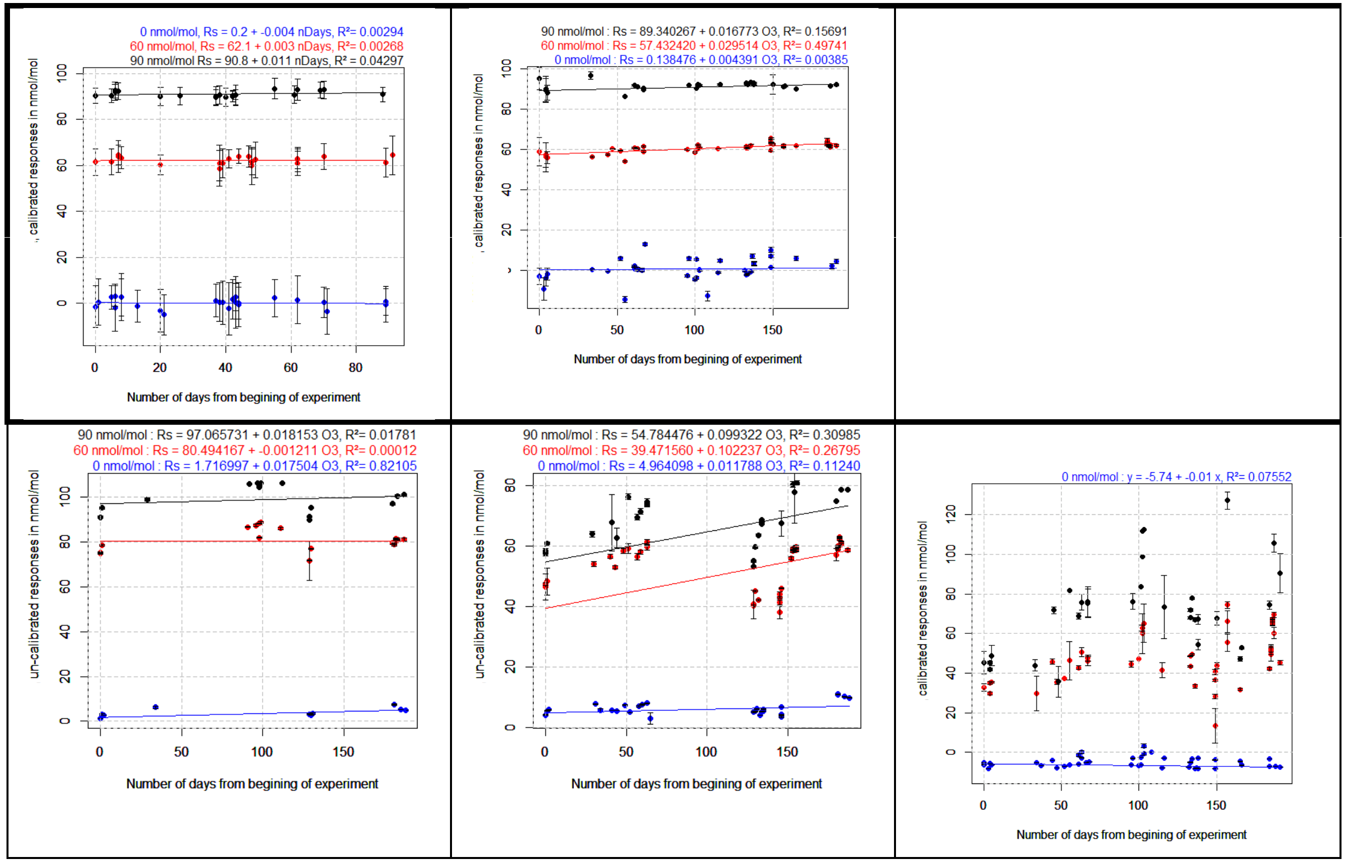
D_{ls} = 1.7 ± 1.9 nmol/mol



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

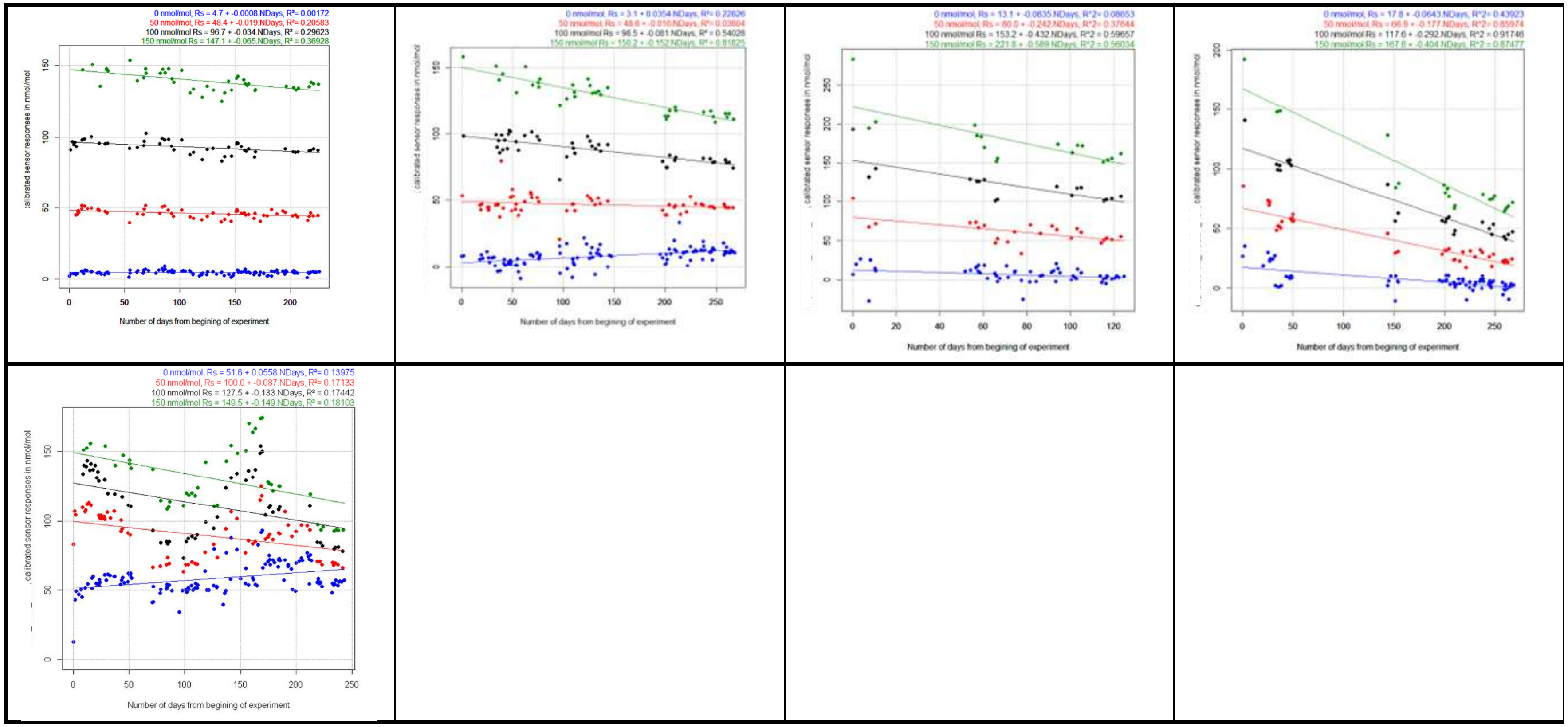
Metrological parameters (Rs = f(O_3 or NO_2))

5 – Long term Drift O_3

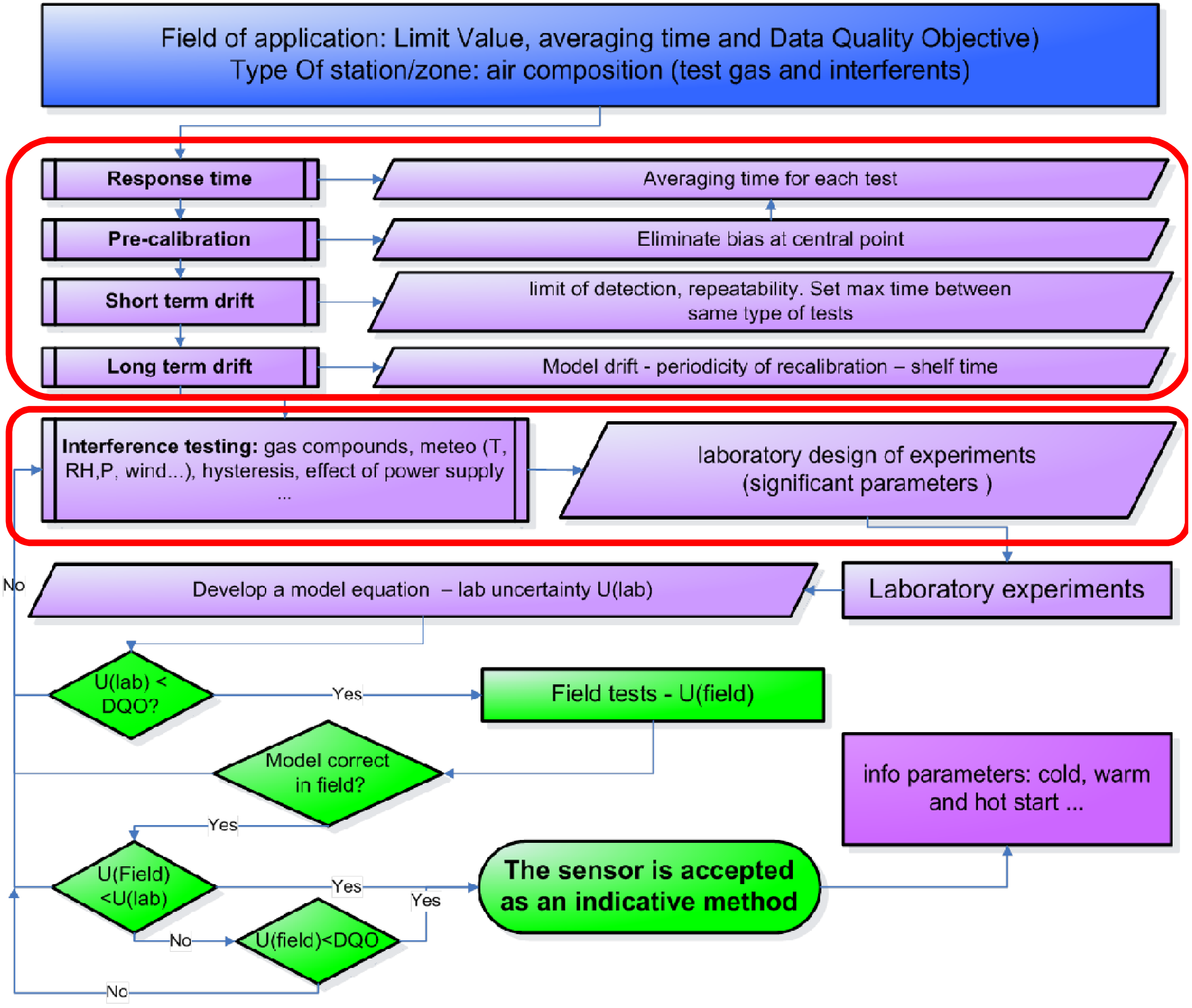


Metrological parameters

5 – Long term Drift NO_2



Evaluation Validation Protocol



Field of application: Limit Value, averaging time and Data Quality Objective)
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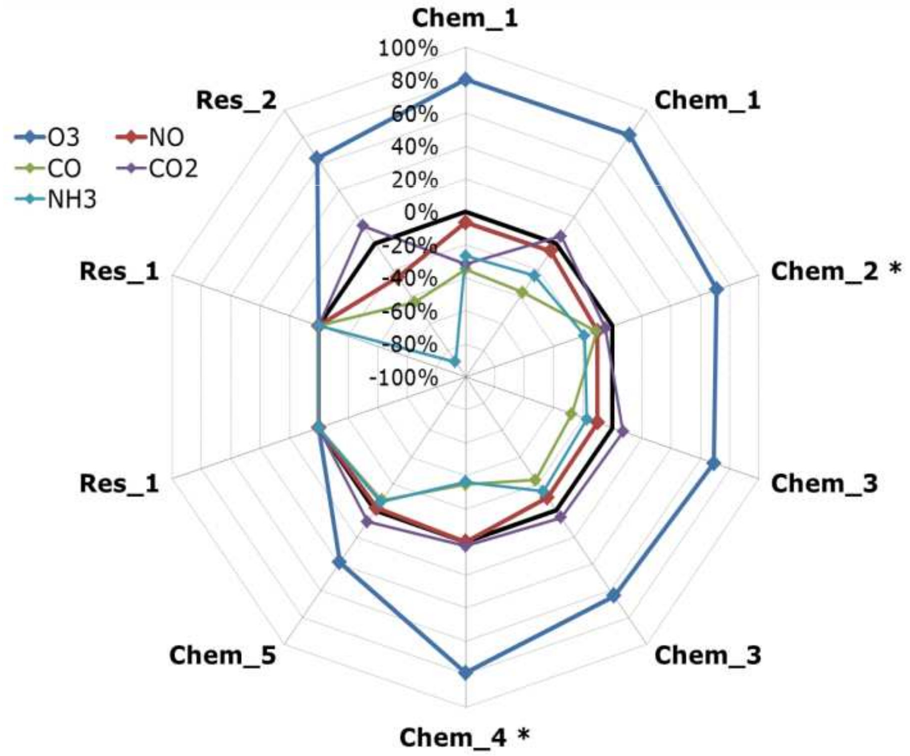
Interfering effect

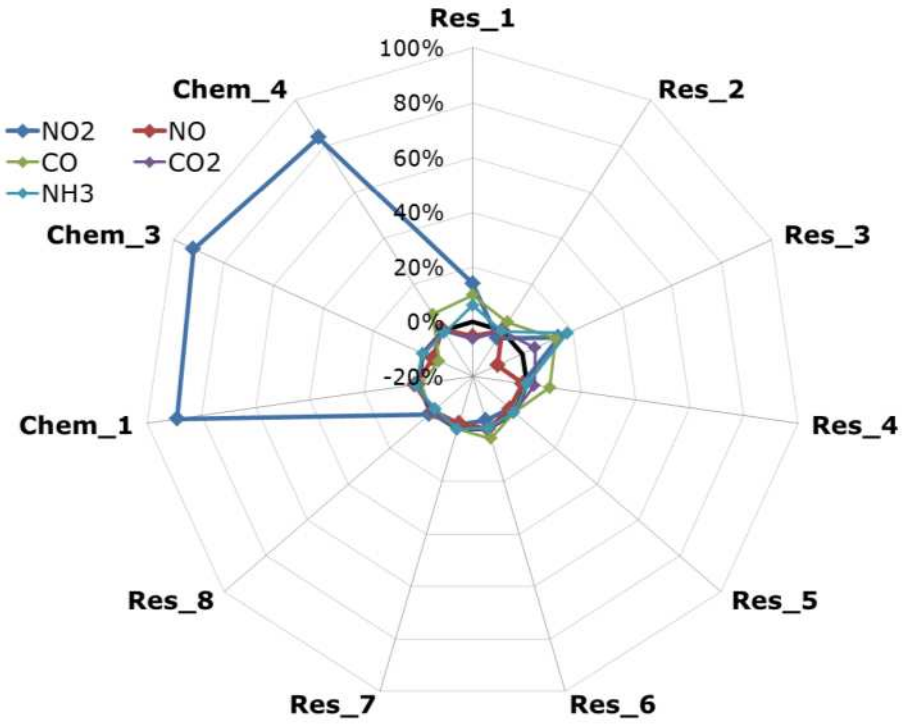
1 – Gaseous compounds

NO_2 sensors



Main interferent gas: O_3

O_3 sensors

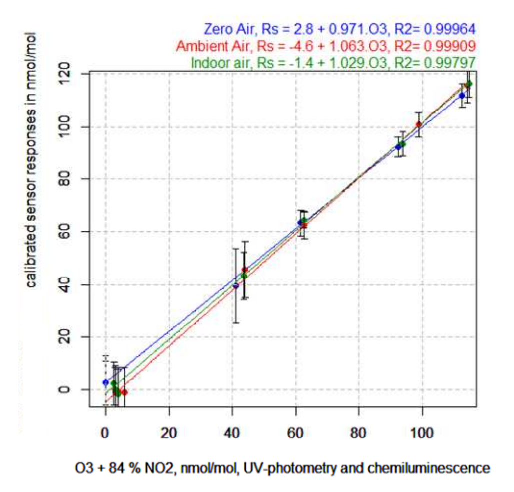


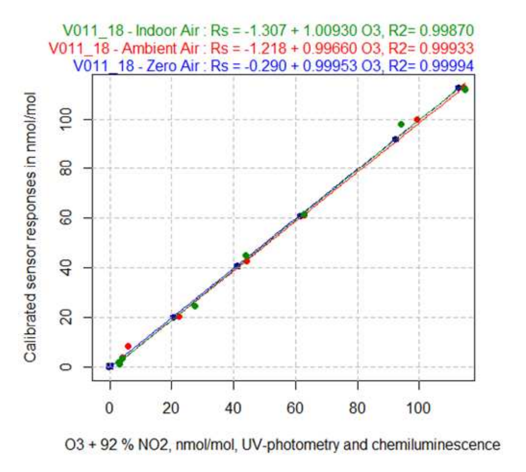
Main interferent gas: NO_2

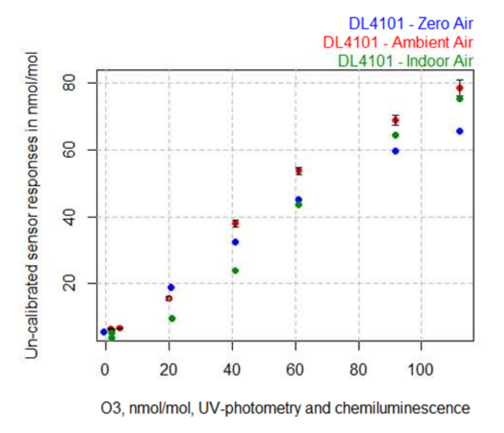
European Commission

Interfering effect

2 – Air Matrix O3







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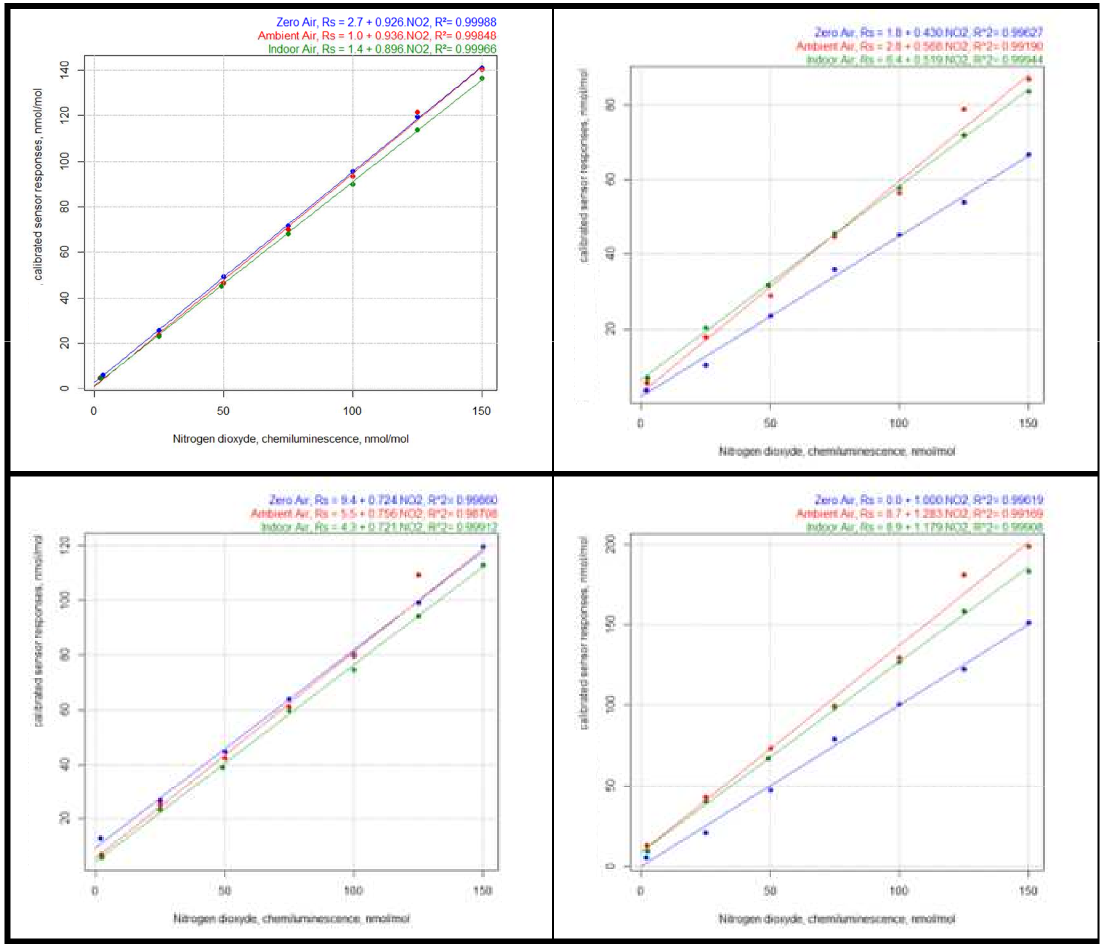
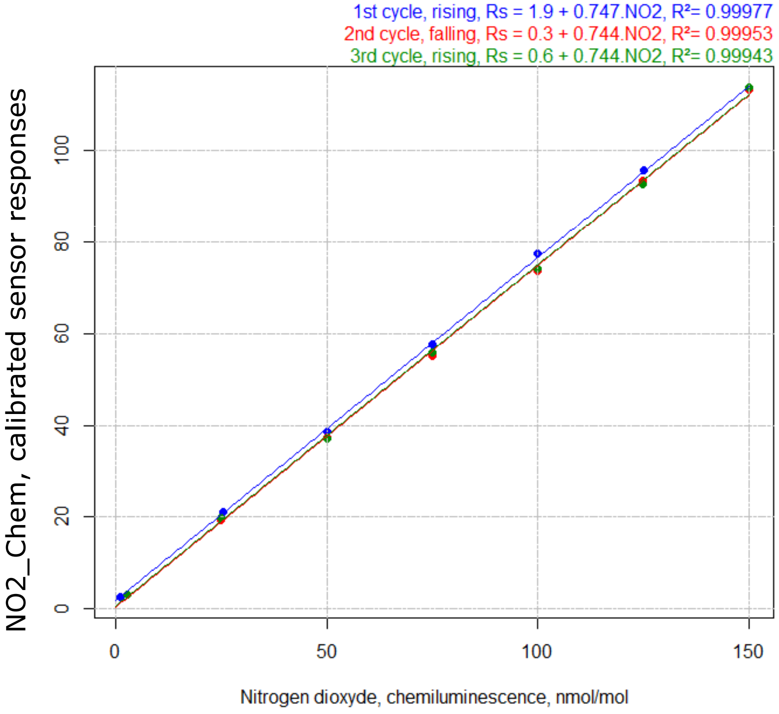


Interfering effect

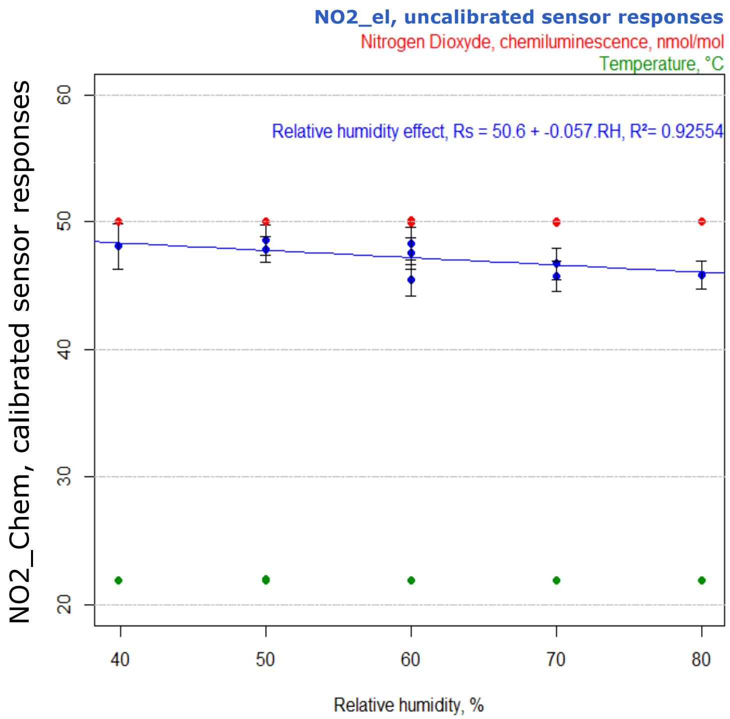
3 – Hysteresis in concentration

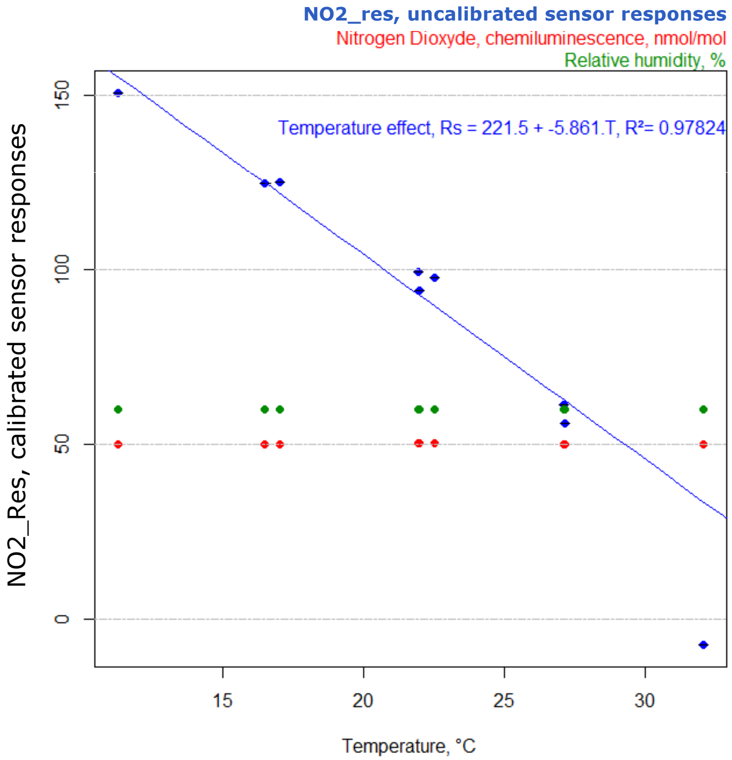
NO_2	Hysteresis (nmol/mol)
Chem_1	< 3.0
	< 10.0
Chem_2 *	< 3.0
Chem_3	< 1.5
	< 1.0
Chem_4 *	< 2.5
Chem_5	< 1.5
Res_1	< 50.0
	< 15.0
Res_2	< 22.0



Interfering effect

3 – Meteorological effect: Relative Humidity / Temperature





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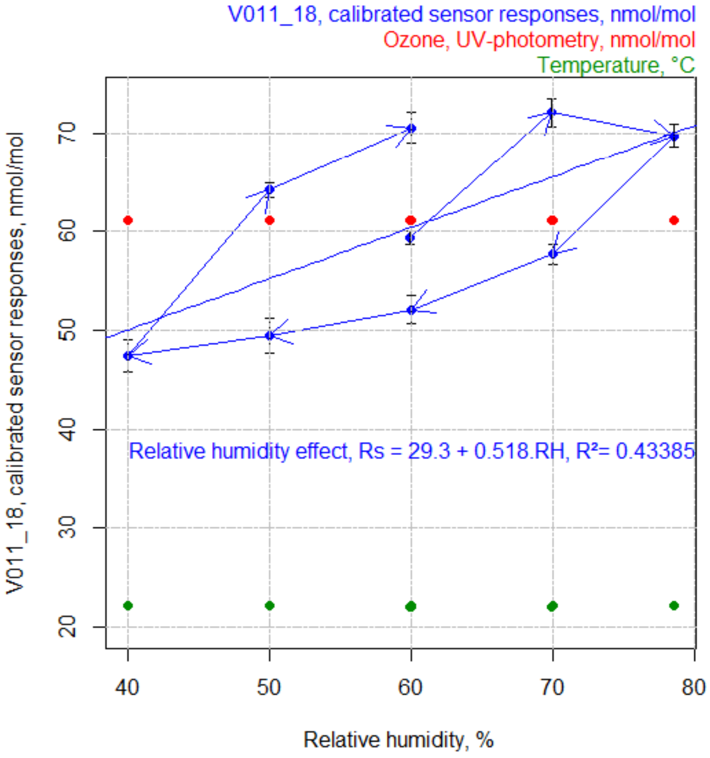
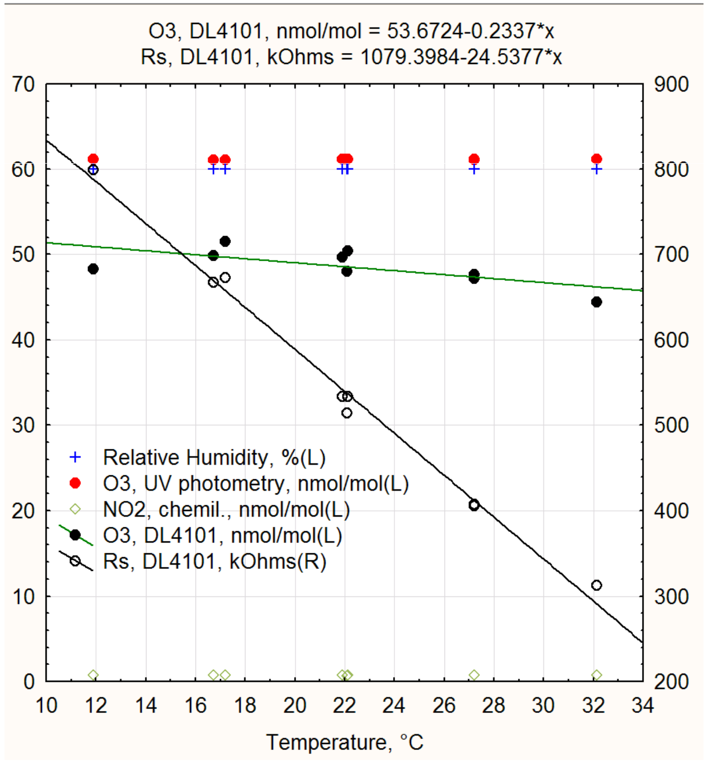
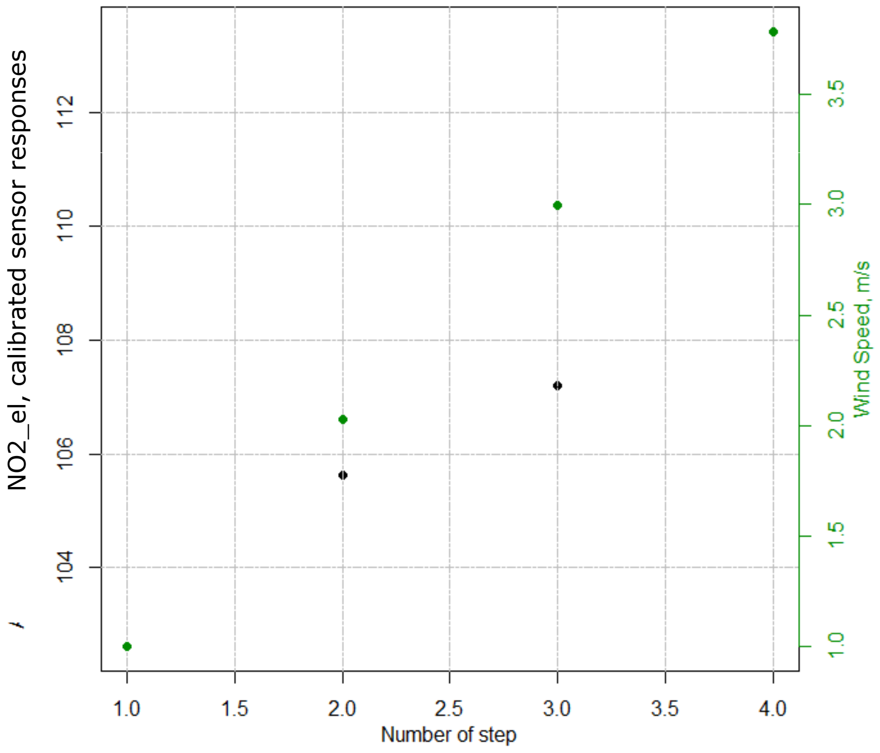
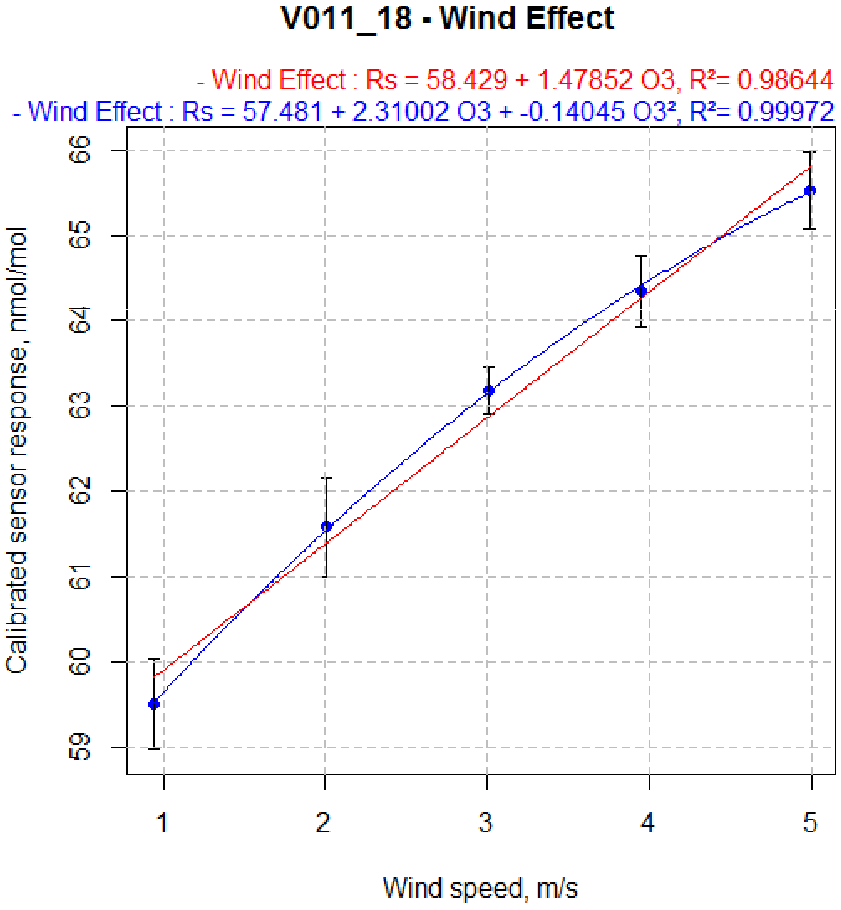




Interfering effect

Meteorological effect: Wind





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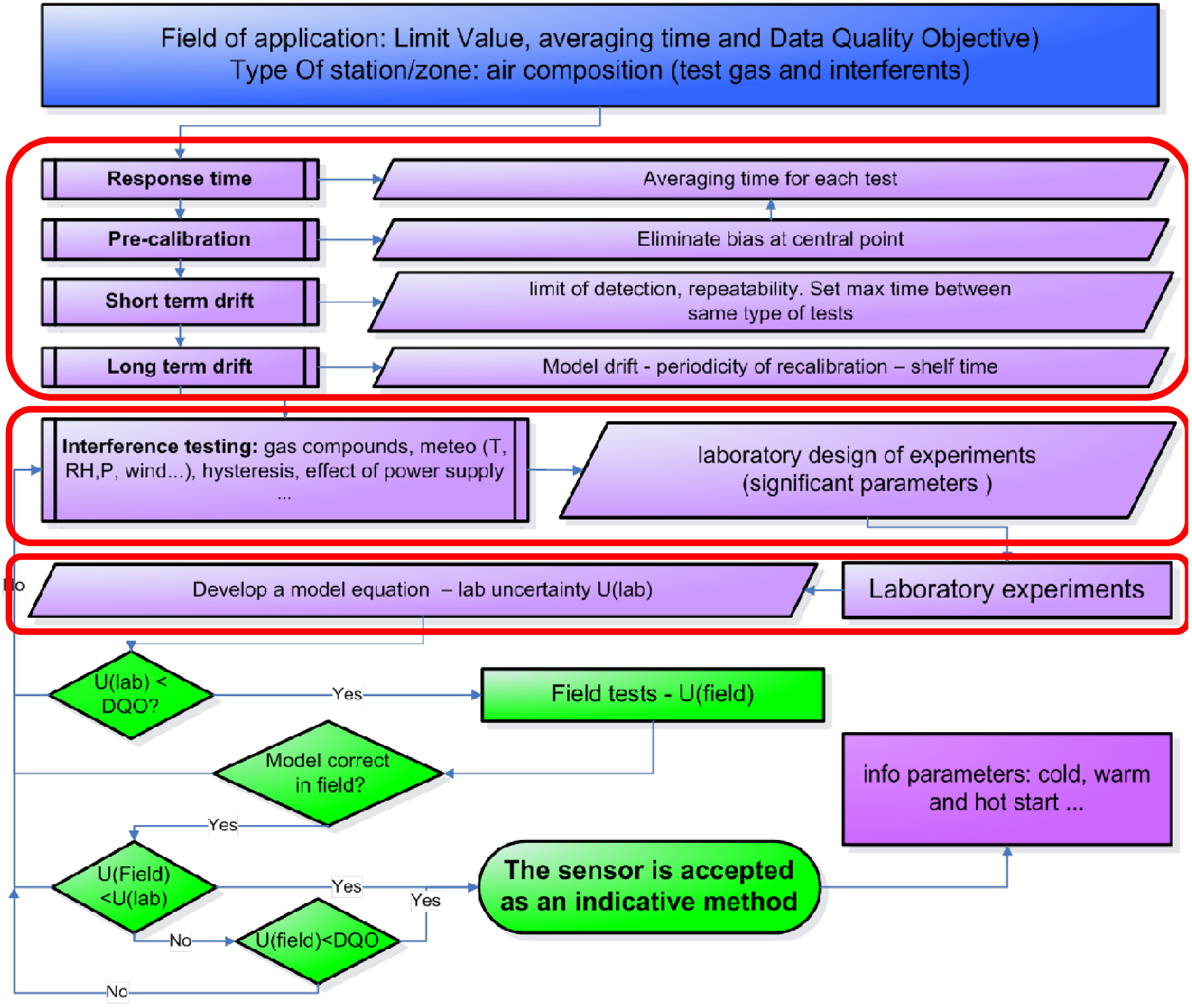

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Design of Experiment

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**

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

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

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

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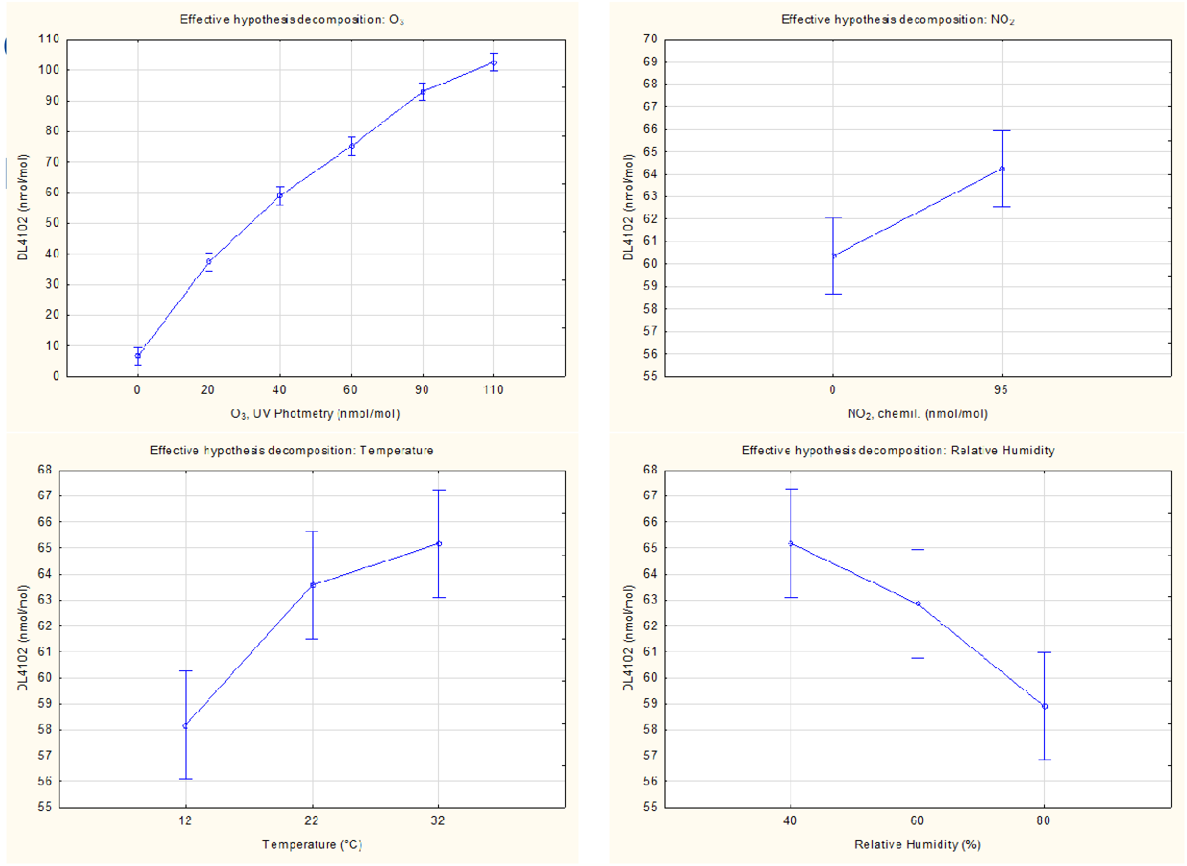


108 experiments

126 experiments

Multiple analysis of Variance (MANOVA)

Multiple Linear Regression (MLR)

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

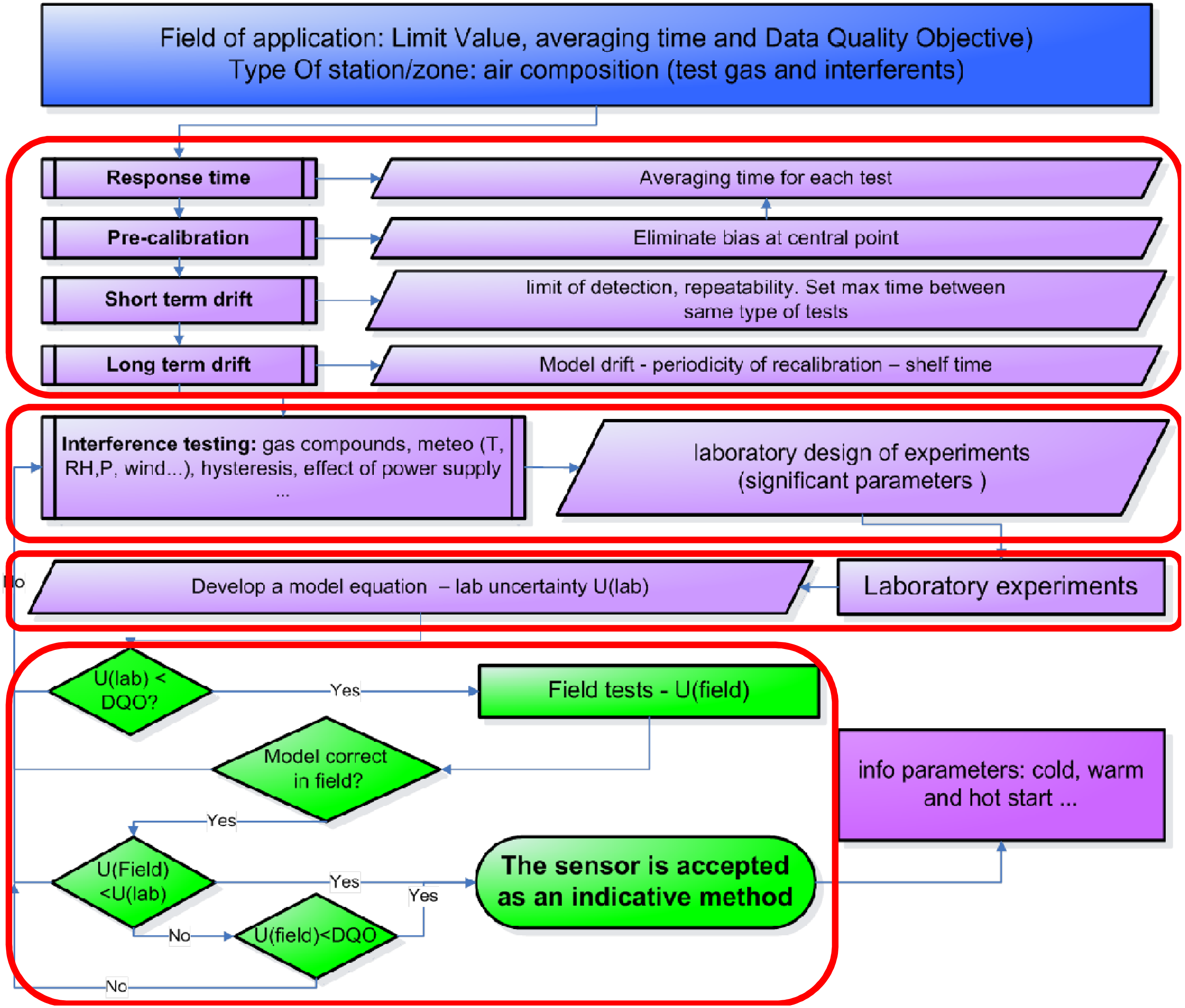
Design of Experiment

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	$+ U(O3)^2$	$+ U(T)^2$		$+ U(NO)^2$	$+ U(CO)^2$	$+ cst^2$

$$U_c^2{}_{Chem\_5} = \underset{U_{lof}^2}{\underset{\nearrow}{3.2^2}} + \underset{U(O3)^2}{\underset{\uparrow}{11.0^2}} + \underset{cst^2}{\underset{\nwarrow}{5.02^2}} \Rightarrow U_{c,Chem\_5} = 12{,}51$$

Evaluation Validation Protocol



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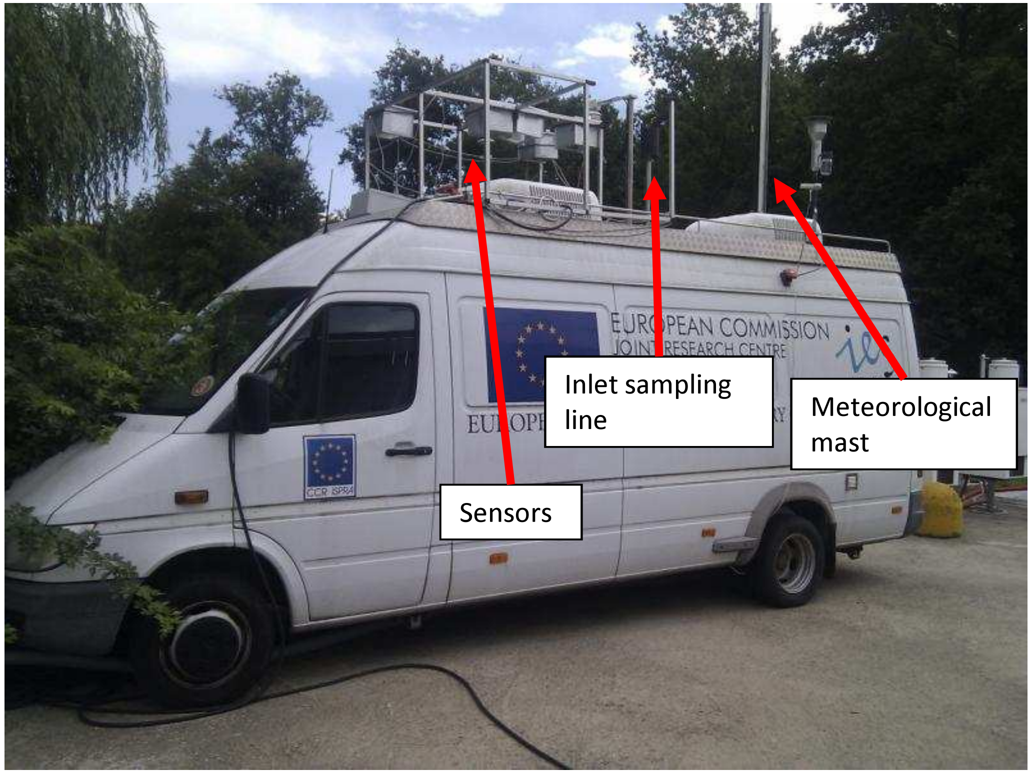
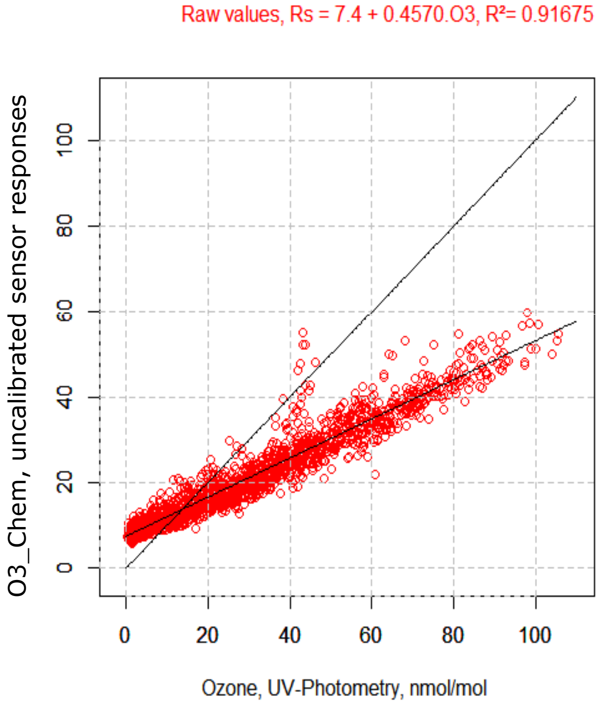
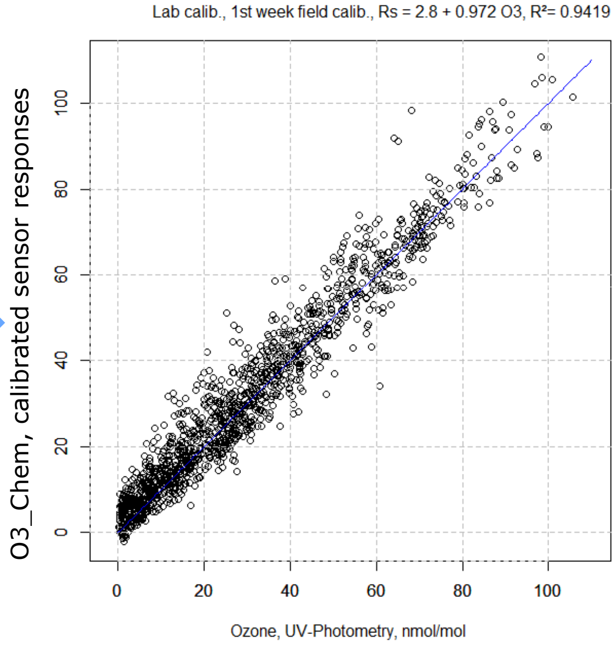
Application in Field



Application in Field O3


Raw values, Rs = 7.4 + 0.4570.O3, R²= 0.91675

Calibration
+ Model


Lab calib., 1st week field calib., Rs = 2.8 + 0.972 O3, R²= 0.9419

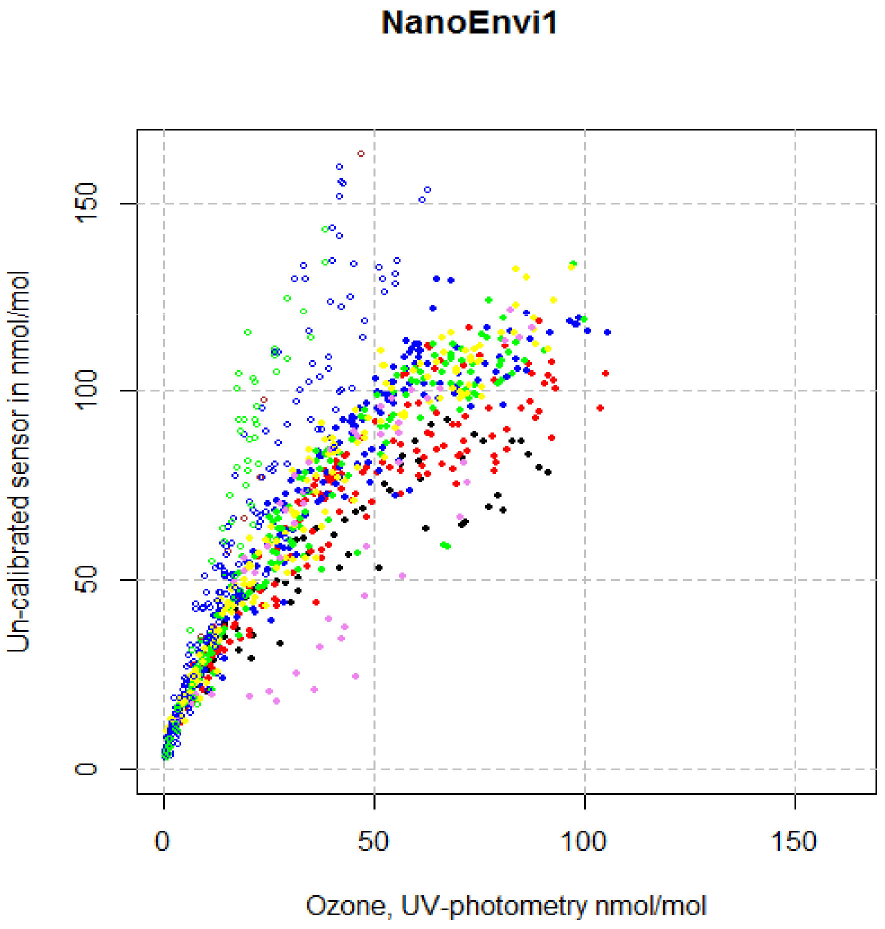
Calibration: first week of exposure

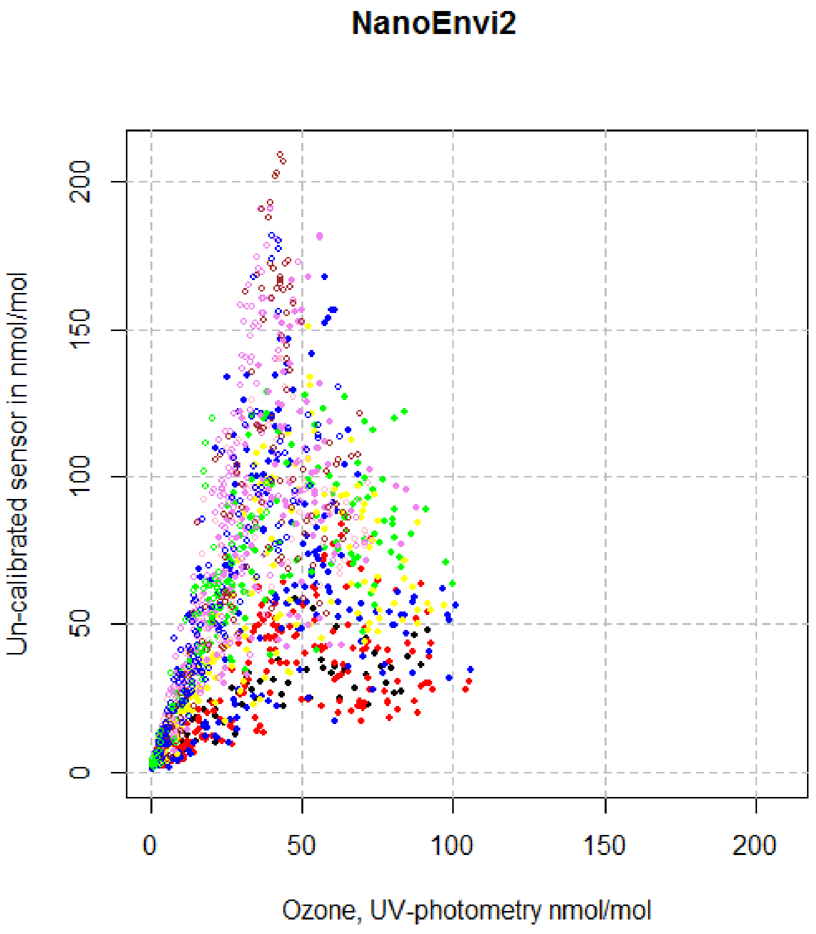
Model: Laboratory model

Expanded relative uncertainty
(Guidance to Demonstration of Equivalence)

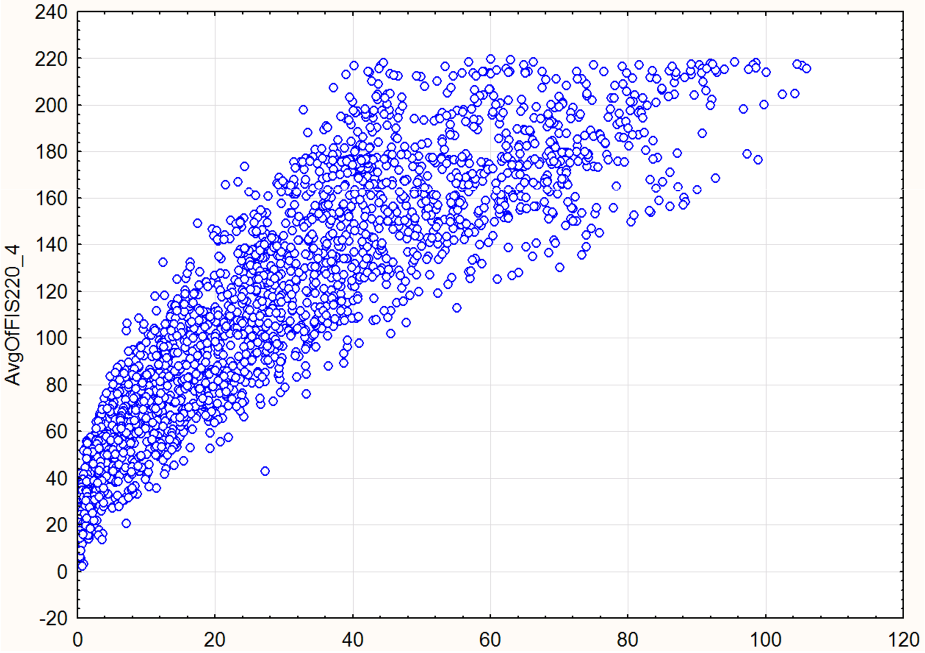
19.4% < 30% of the Data Quality Objective

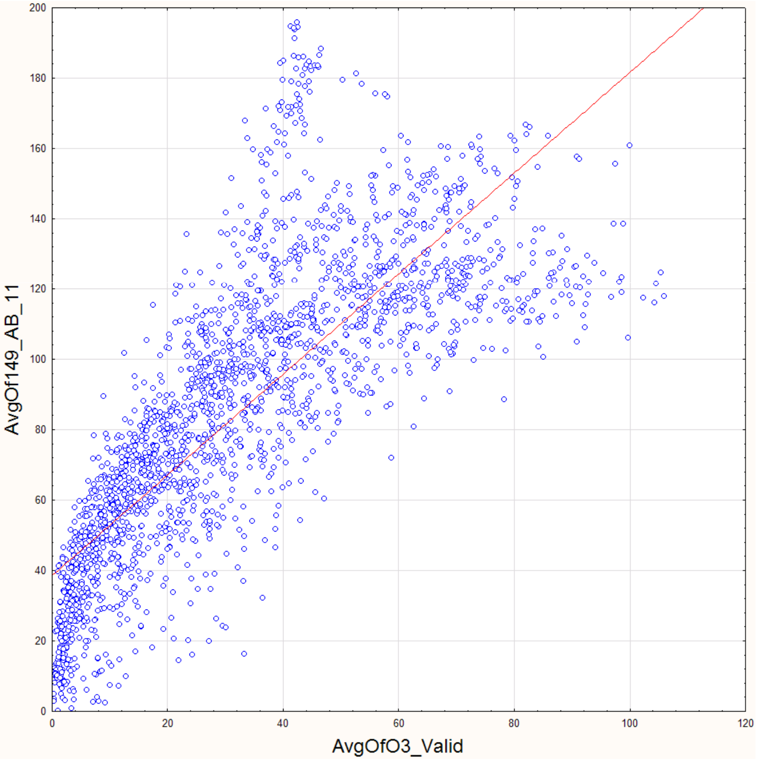
Application in Field O3,



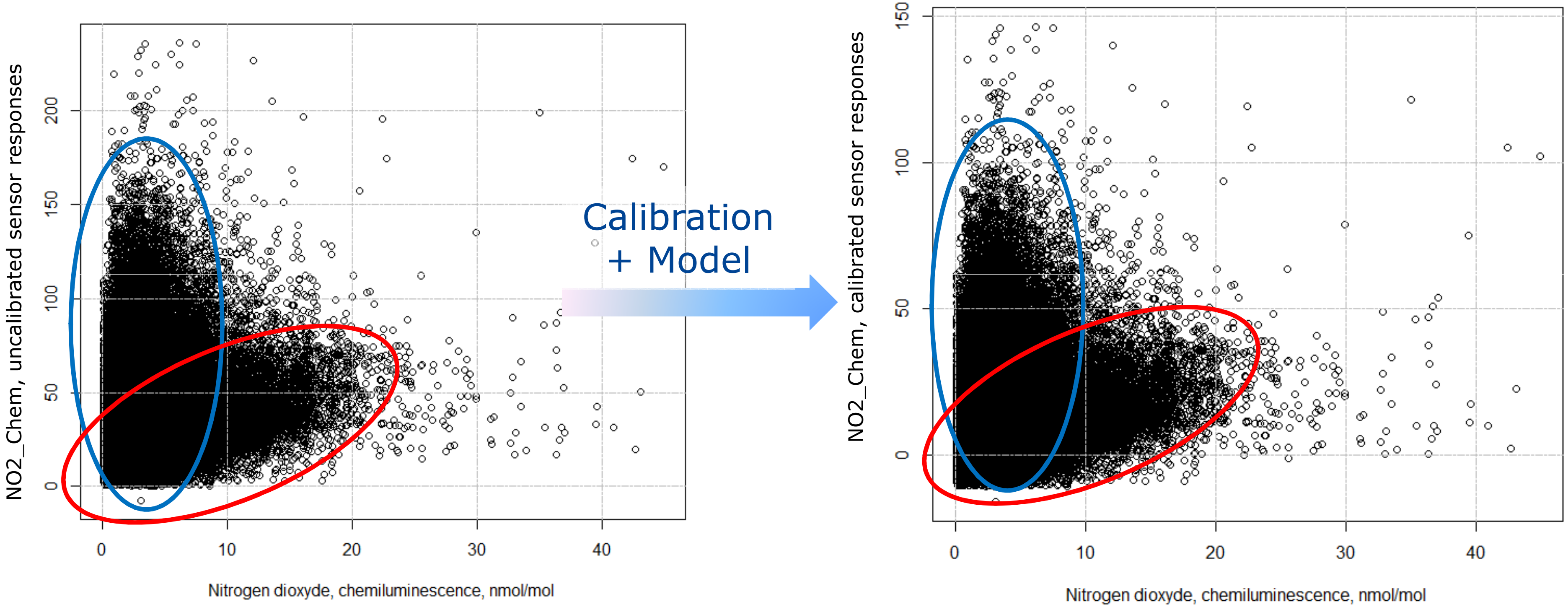


Application in Field O3,





Application in Field, NO2



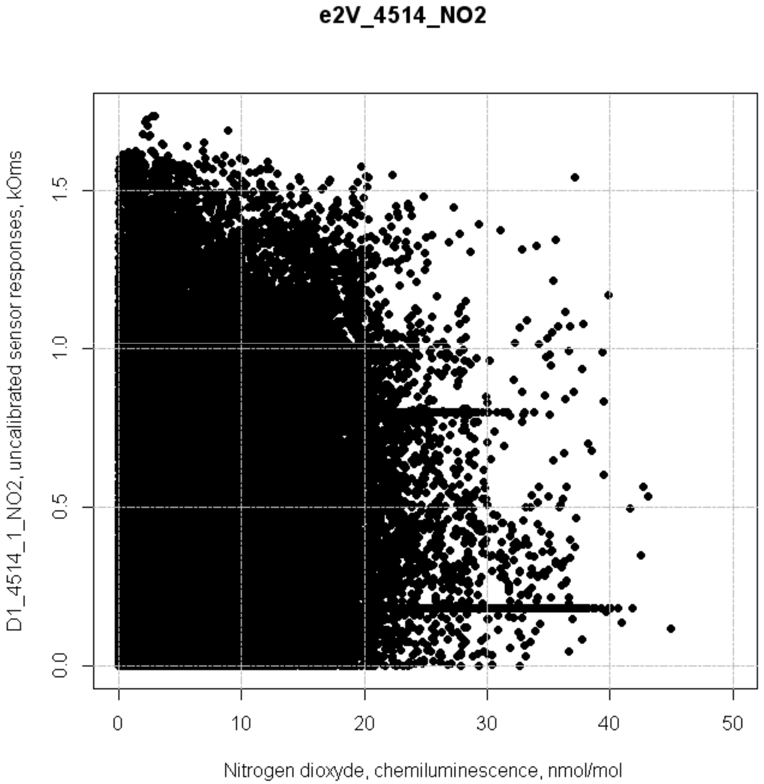
Calibration
+ Model

Calibration: first 10 days of exposure

Model: Laboratory model

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

Application in Field, NO2



Metal oxide sensor: no correlation for NO2

Validation of single sensors

Ozone:

- Chemical: Good: precise, linear, long term stability, little matrix effect, hysteresis and temperature effect

  Less good: interference NO_2, humidity effect

- Resistive: Good: low gaseous interference, precise, sensitive, humidity and temperature effect can be corrected

  Less good: calibration, lack of linearity, long term stability, matrix effect, response time

- DQO: OK for some chemical sensors provided that NO2 interference and humidity effect are solved

- Calibration: only field calibration

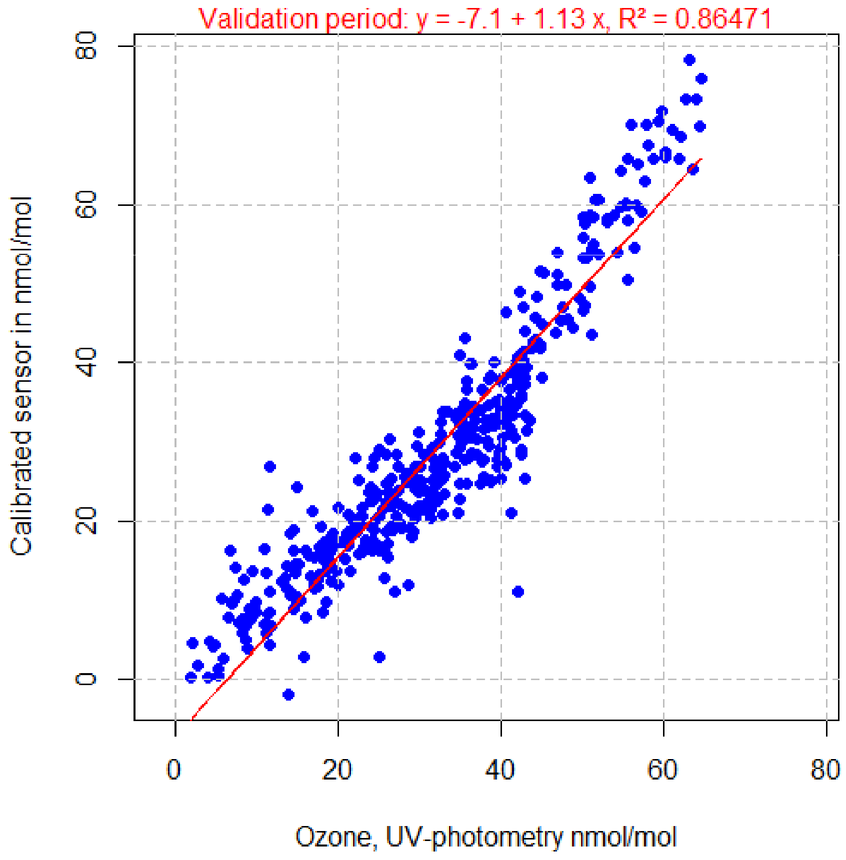
Nitrogen Dioxide: O_3 interference, matrix effect, gaseous interference on resistive sensor – no good field experience at rural sites

Field calibration by linear regression, multi-linear regression and artificial neural network for a cluster of sensors

Linear regression and multiliner regression

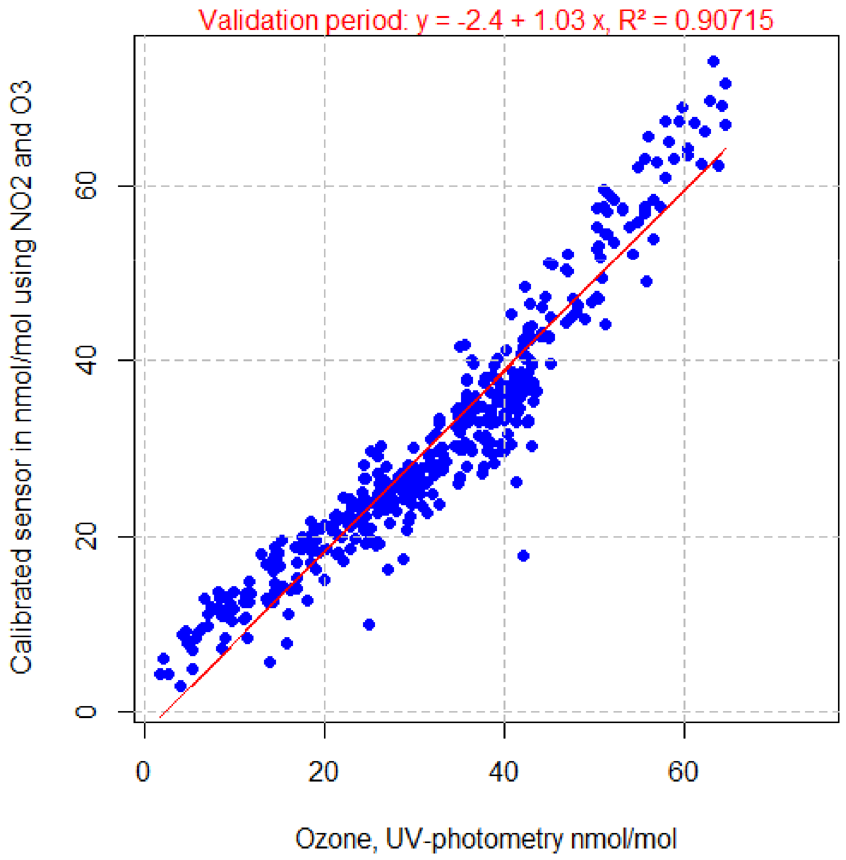
Manufacturer	Model	R^2 of linear regression	Multivariate linear model	R^2
αSense	O3 sensors B4	0.07	O3 = (Rs – bNO$_2$ - cNO$_2$H$_2$O - d)/a	0.49
Citytech	**O3_3E1F**	**0.87**	**O3 = (Rs-bNO$_2$ -c)/a**	**0.91**
CairPol	CairclipO3/NO2	Unknown	O3 = (Rs – bNO$_2$ - c)/a	Unknown
αSense	NO2-B4	0.06	NO2 = (Rs-bO3-cT-dRH-e)/a	0.56
Citytech	NO2 3E 50	0.01	NO2 = (Rs-bO3-cT-dRH-e)/a	0.63
	NO 3E 100	0.05	Unknown	Unknown
e2V	**2710 sensor**	**0.31**	**NO2 = (Rs-bO$_3$.cT-d)/a**	**0.36**
	4514 sensor	**0.34**	**NO2 = (Rs-bO3-cNO-dT)/a**	**0.42**
CairPol	CairClip NO2	0.37	NO2 = (Rs-bO3-c)/a	0.74
Figaro	5042 sensor	0.17	CO = (Rs-bT-cRH-d)/a	0.23
e2V	4514 sensor	0.56		0.58
Edinburgh Sensors	Gascard NG	0.14	CO2 = (Rs-bT-cRH-d)/a	0.47
ELT Sensors	S-100H	0.58		0.62
NASUS αSense	NO2 sensors NO2-A1	0.46	Unknown	Unknown
	NO2 sensors NO2-B4	0.01		
	CO sensor CO-AF	0.09		
	CO sensor CO-B4	0.08		
	SO2 sensor	Unknown		

Linear Regression
O3_3E1F = f(O3)



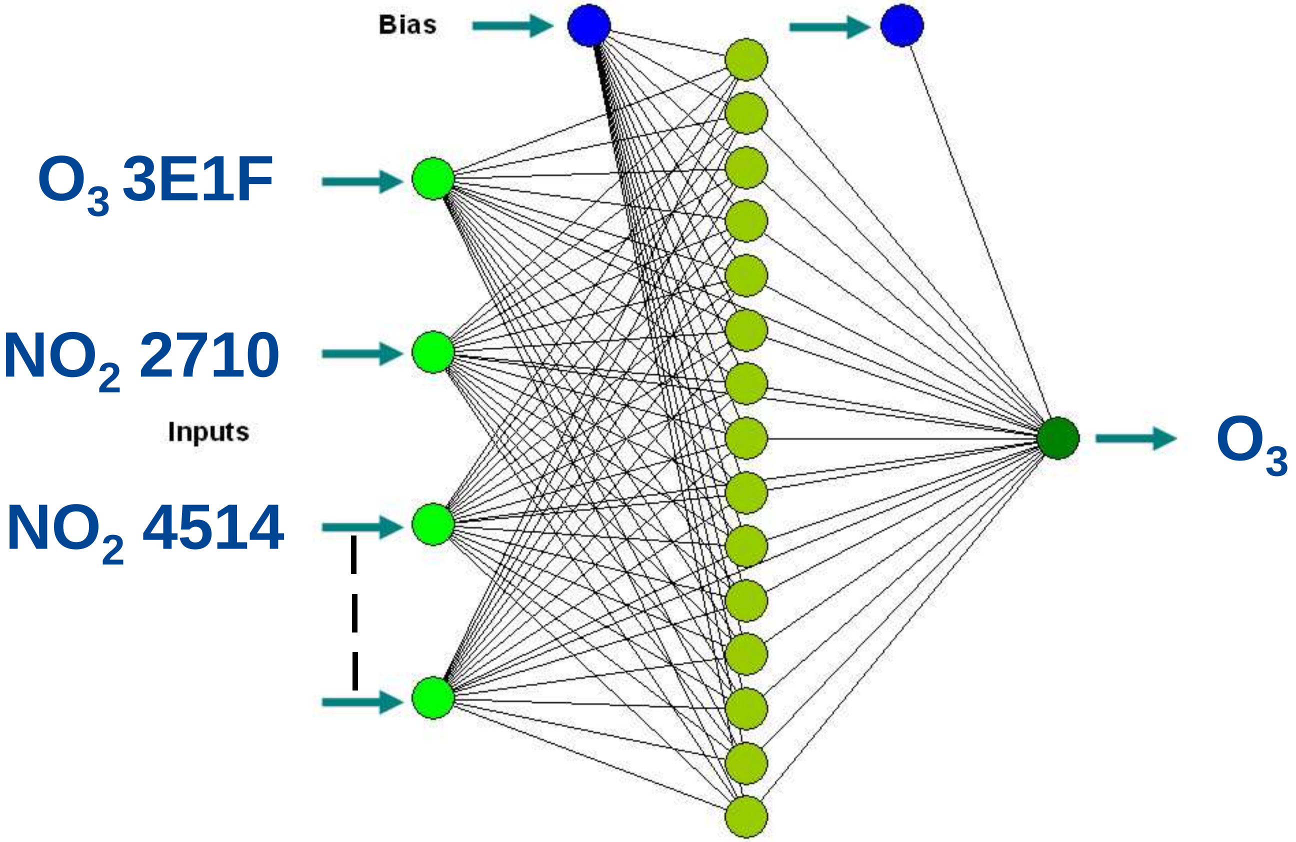
Validation period: y = -7.1 + 1.13 x, R² = 0.86471

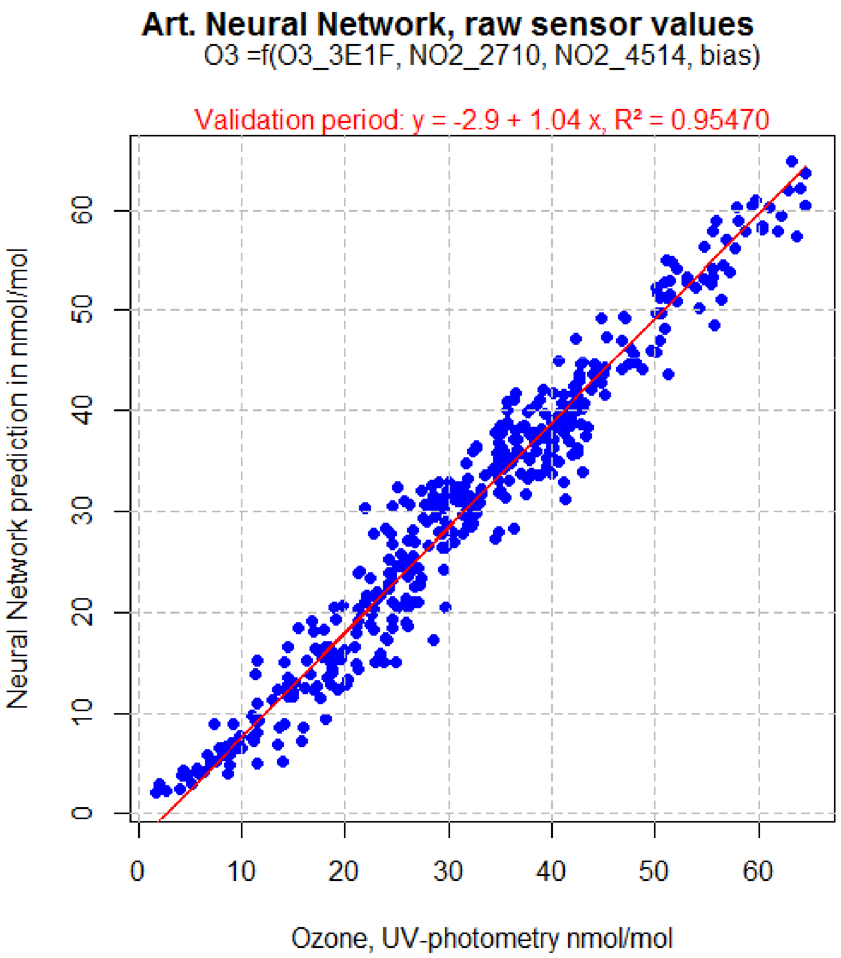
Multi-Linear Regression
O3_3E1F = f(O3, NO2)



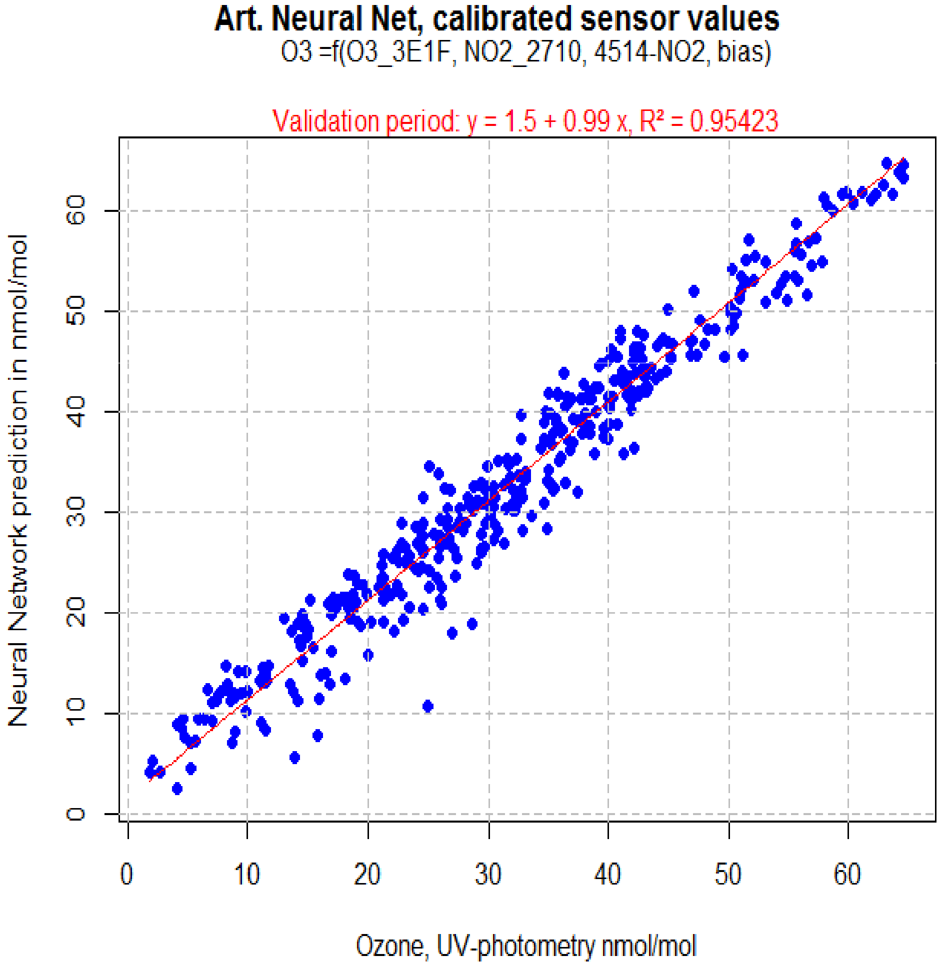
Validation period: y = -2.4 + 1.03 x, R² = 0.90715

Artificial Neural network





Art. Neural Network, raw sensor values
O3 =f(O3_3E1F, NO2_2710, NO2_4514, bias)

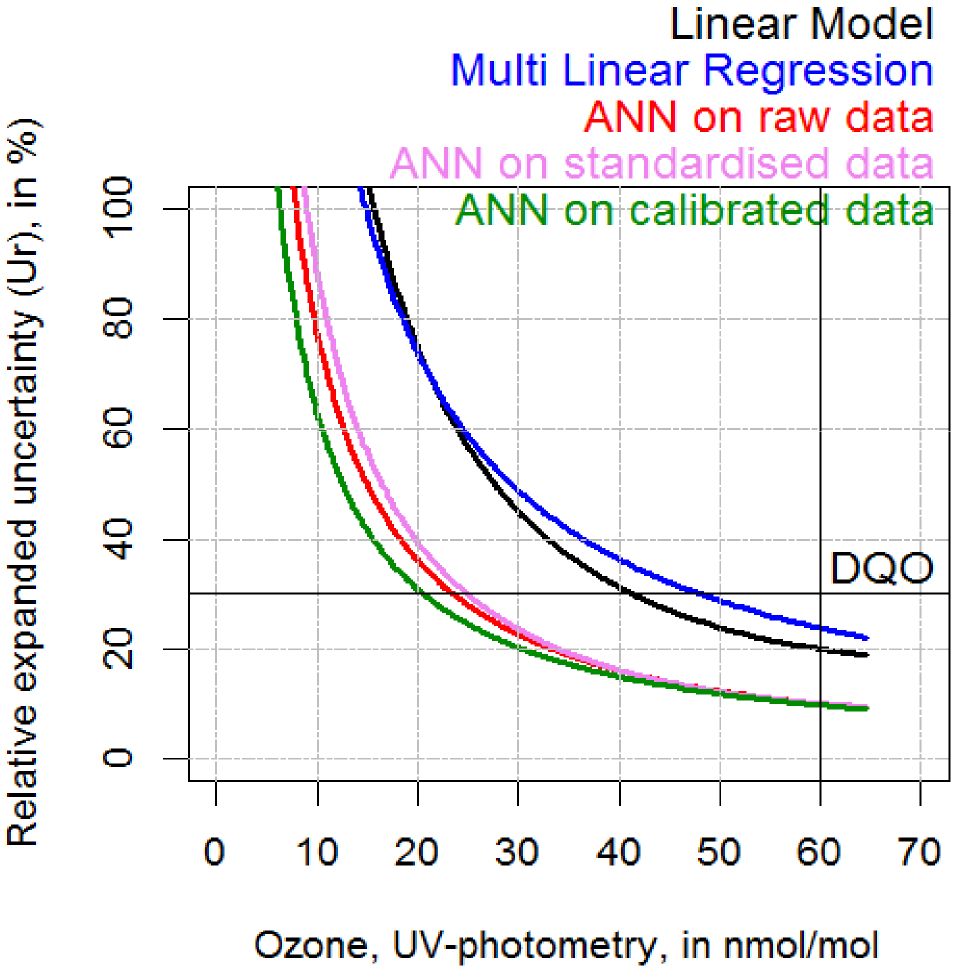


Art. Neural Net, calibrated sensor values
O3 =f(O3_3E1F, NO2_2710, 4514-NO2, bias)

Model Uncertainty

Algorithms	Ambient parameters	Inputs
LM	No	Sensor
MLR	No	Sensor + Reference
ANN	No	Sensors
ANN+Std	No	Sensors
ANN+MLR	No	Sensors

$$U_r(y_i) = 2\left(\sqrt{\frac{RSS}{(n-2)} - u^2(x_i) + [a + (b-1)\cdot x_i]^2}\right) / y_i$$



Modelisation PLS, ANN and physycal model for a cluster of sensors

Physical model

The resistance dependence on the temperature is given by:

$R=R_0 \cdot \exp(T \cdot \beta + \delta)$

R_0 is the resistance known at a reference temperature T_0, T is the temperature, β and δ are parameters that needs to be fitted.

The influence of humidity is given by $R=R_0 \cdot Hd^{\alpha}$

Hd is the humidity in ambient air, R_0 the resistance of the sensor at a reference humidity Hd_0 and α is a parameter that needs to be fitted.

Both equations are combined in :

- $R=R_0 \cdot Hd^{\alpha} \cdot \exp(T \cdot \beta + \delta)$

Calibration methods

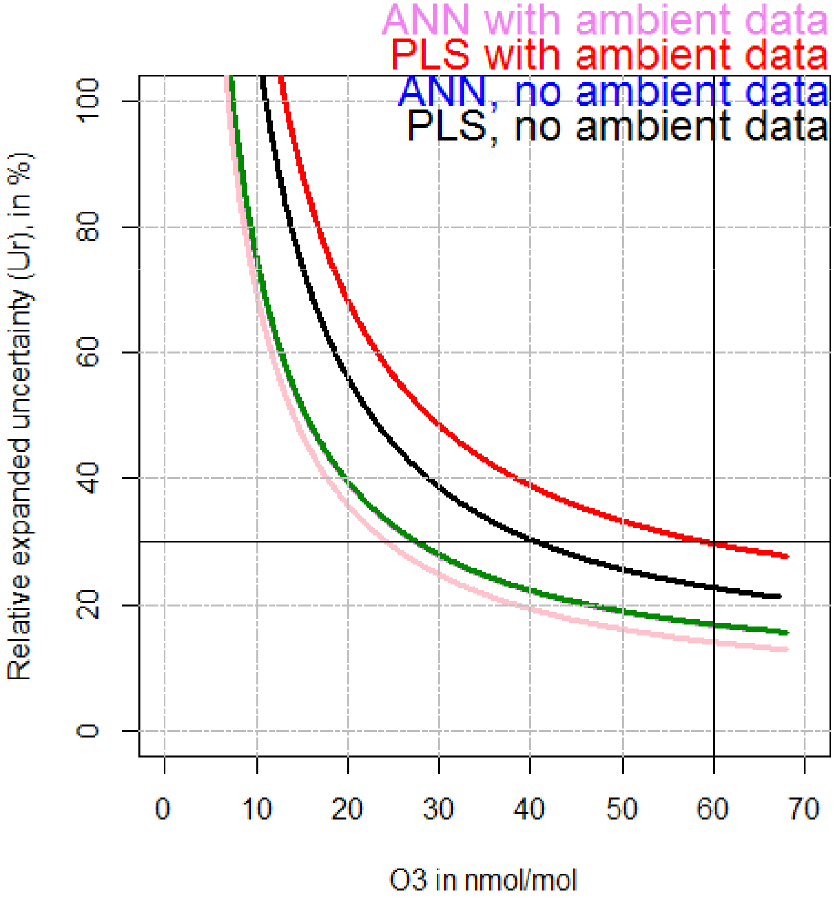
Algorithms	Ambient Parameters	Algorithms used	PLS Inputs	ANN inputs	Training dataset	Validation Dataset
PLS	No	PLS	Sensors	-	70 %	30 %
ANN	No	ANN	-	Sensors	70 %	30 %
PLS + Ambient	Yes	PLS	Sensors, Ambient	-	70 %	30 %
ANN + Ambient	Yes	ANN	-	Sensors, Ambient	70 %	30 %
ANN + PLS	Yes	ANN+PLS	Sensors, Ambient	Sensors, PLS, Ambient	70 %	30 %
ANN + Model	Yes	ANN+Model	-	Sensors, Ambient, Model	70 %	30 %

Model Uncertainty

Algorithms	Ambient parameters	Inputs
PLS	No	Sensors
ANN	No	Sensors
PLS + Ambient	Yes	Sensors + Ambient
ANN + Ambient	Yes	Sensors + Ambient
ANN + PLS	Yes	Sensors + Ambient
ANN + MLR	Yes	Sensors + Ambient+ Model

$$U_r(y_i)=2\left(\sqrt{\frac{RSS}{(n-2)}-u^2(x_i)+[a+(b-1)\cdot x_i]^2}\right)/y_i$$

✓ O_3 NO_2 NO CO CO_2

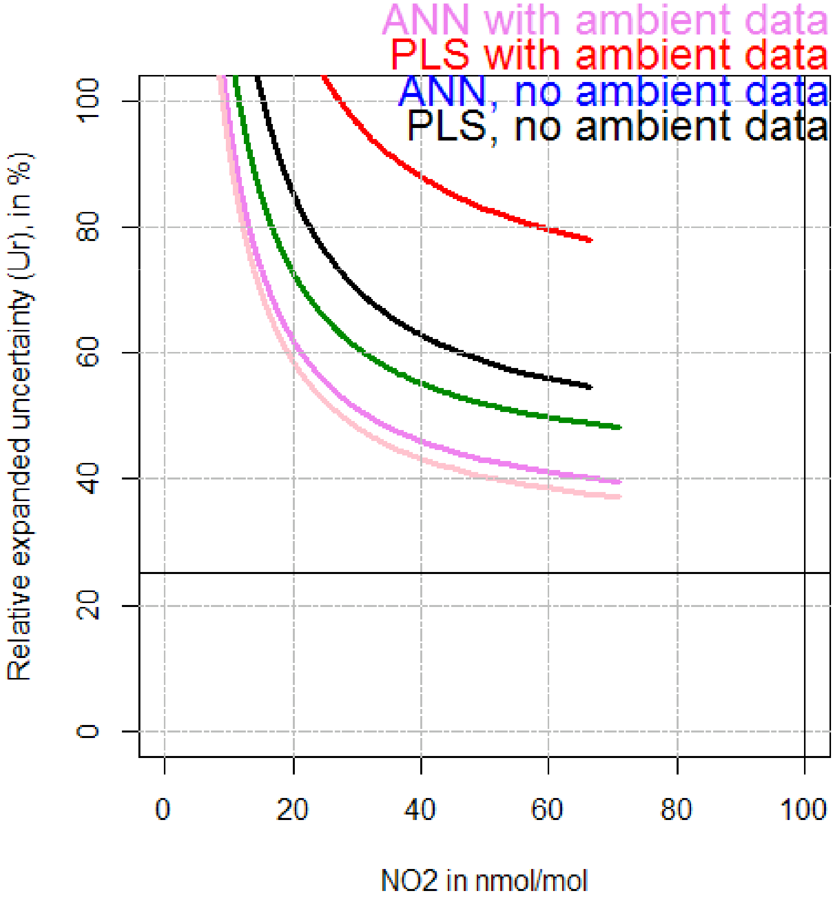


Model Uncertainty

Algorithms	Ambient parameters	Inputs
PLS	No	Sensors
ANN	No	Sensors
PLS + Ambient	Yes	Sensors + Ambient
ANN + Ambient	Yes	Sensors + Ambient
ANN + PLS	Yes	Sensors + Ambient
ANN + MLR	Yes	Sensors + Ambient+ Model

$$U_r(y_i)=2\left(\sqrt{\frac{RSS}{(n-2)}-u^2(x_i)+[a+(b-1)\cdot x_i]^2}\right)/y_i$$

O_3 ✓ NO_2 ✗ NO CO CO_2

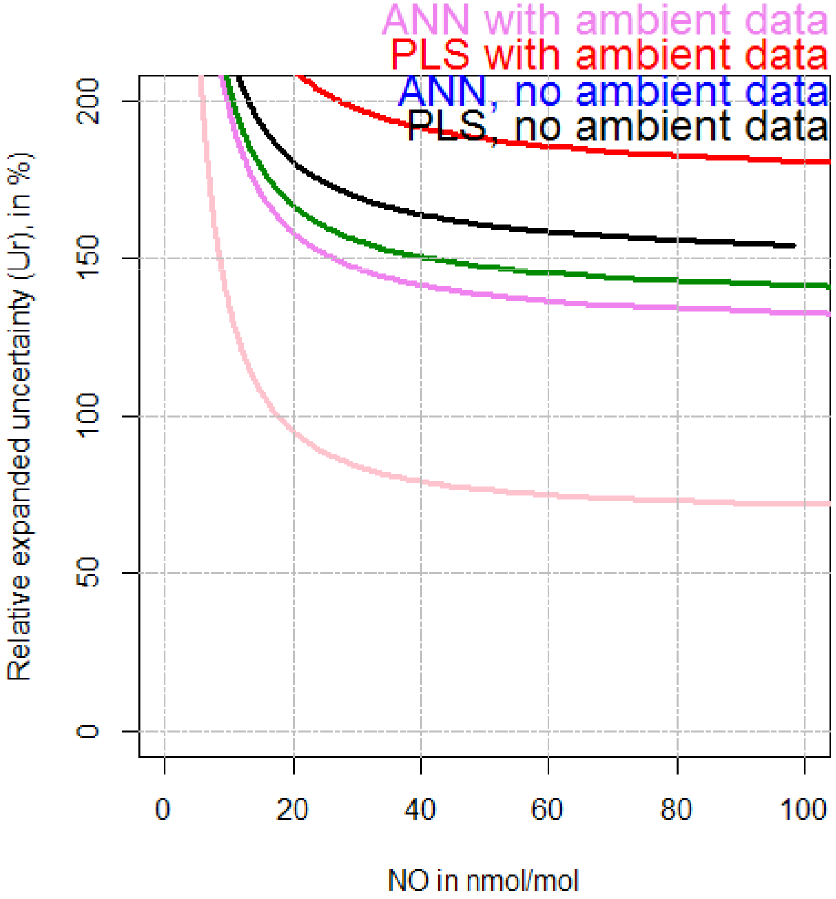


Model Uncertainty

Algorithms	Ambient parameters	Inputs
PLS	No	Sensors
ANN	No	Sensors
PLS + Ambient	Yes	Sensors + Ambient
ANN + Ambient	Yes	Sensors + Ambient
ANN + PLS	Yes	Sensors + Ambient
ANN + MLR	Yes	Sensors + Ambient+ Model

$$U_r(y_i) = 2\left(\sqrt{\frac{RSS}{(n-2)} - u^2(x_i) + [a+(b-1)\cdot x_i]^2}\right) / y_i$$

✓ O_3 ✗ NO_2 ✗ NO CO CO_2

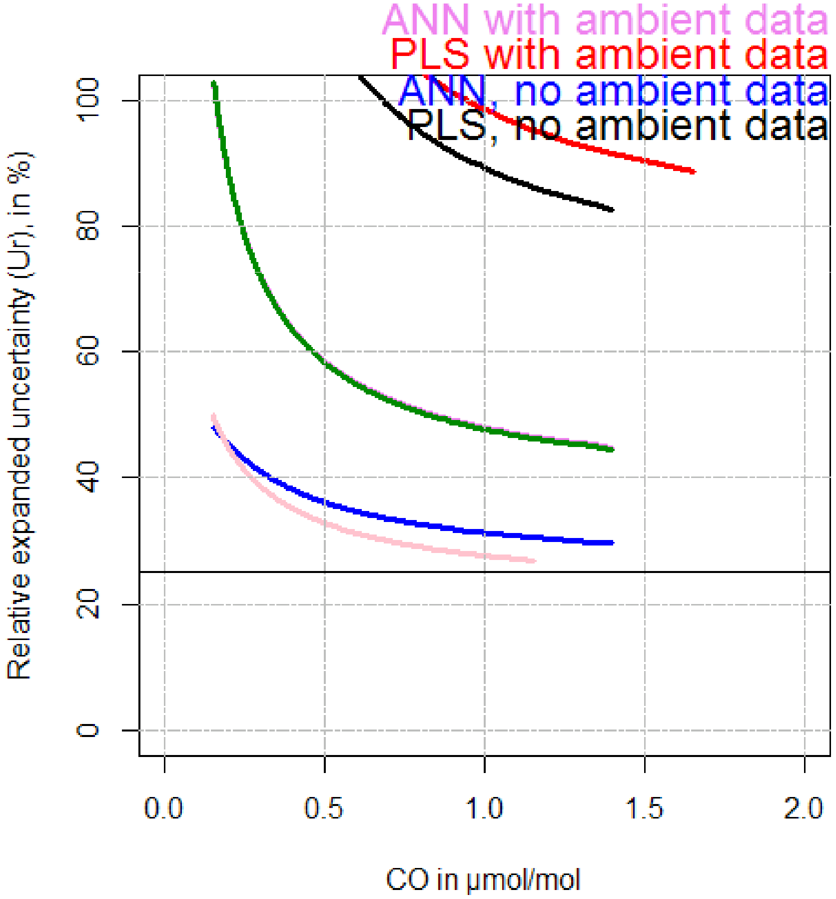


Model Uncertainty

Algorithms	Ambient parameters	Inputs
PLS	No	Sensors
ANN	No	Sensors
PLS + Ambient	Yes	Sensors + Ambient
ANN + Ambient	Yes	Sensors + Ambient
ANN + PLS	Yes	Sensors + Ambient
ANN + MLR	Yes	Sensors + Ambient+ Model

$$U_r(y_i)=2\left(\sqrt{\frac{RSS}{(n-2)}-u^2(x_i)+[a+(b-1)\cdot x_i]^2}\right)/y_i$$

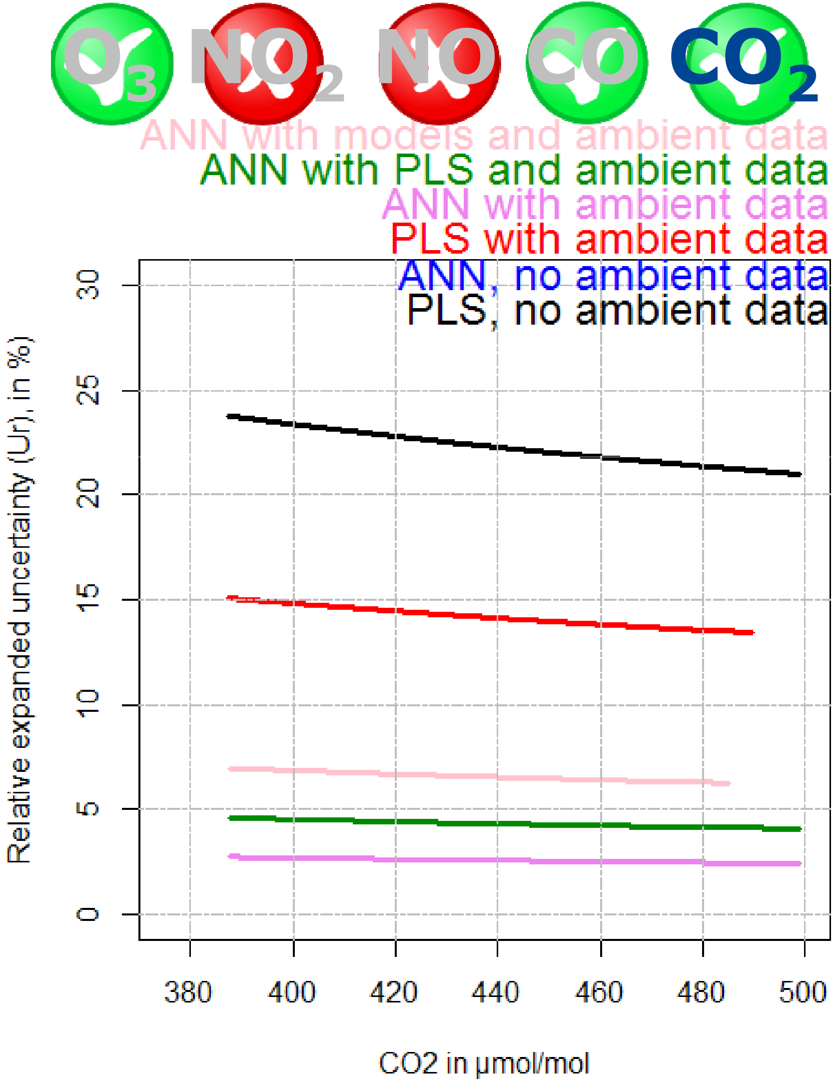
O_3 ✓ NO_2 ✗ NO ✗ CO ✓ CO_2



Model Uncertainty

Algorithms	Ambient parameters	Inputs
PLS	No	Sensors
ANN	No	Sensors
PLS + Ambient	Yes	Sensors + Ambient
ANN + Ambient	Yes	Sensors + Ambient
ANN + PLS	Yes	Sensors + Ambient
ANN + MLR	Yes	Sensors + Ambient+ Model

$$U_r(y_i) = 2\left(\sqrt{\frac{RSS}{(n-2)} - u^2(x_i) + [a+(b-1)\cdot x_i]^2}\right) / y_i$$



Conclusion calibration methods for the whole cluster of sensors

- The DQO for indicative methods can be met for O_3, likely for CO , not for NO_2 (DQO of 35% > 25%). High uncertainty for NO (> 75 %). For CO_2, low uncertainty down to about 3%.
- Multivariate regression gives the highest U (with or without meteo)
- Meteo data does decrease measurement uncertainty for the ANN methods.
- ANN methods: higher R^2 and lower RSS -> lower U
  ANN methods: lower bias to reference data (slopes and intercept nearer to 1 and 0, respectively)
- ANN method with input from the physical model and meteo is generally the best. It may needs corrections of interfering compounds.

Thank You…

Reports at:
ftp://ftp_erlap_ro:3rlapsyst3m@s-jrciprvm-ftp-ext.jrc.it/ERLAPDownload.htm

Or send a mail at

michel.gerboles@jrc.ec.europa.eu