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J R C T E C H N I C A L R E P O R T S

# Report of laboratory and in-situ validation of micro-sensor for monitoring ambient air pollution

NO9: CairClipNO<sub>2</sub> of  
CAIRPOL (F)

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# **ENV01- MACPoll Metrology for Chemical Pollutants in Air**

**Report of the laboratory and in-situ validation of micro-sensors and evaluation of suitability of model equations.**

**N09: CairClipNO<sub>2</sub> of CAIRPOL (F)**

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*Task 4.3: Testing protocol, procedures and testing of performances of sensors (JRC, MIKES, INRIM, REG-Researcher (CSIC))*



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<b>1</b>	<b>TASK 4.3: TESTING PROTOCOL, PROCEDURES AND TESTING OF PERFORMANCES OF SENSORS (JRC, MIKES, INRIM, REG-RESEARCHER (CSIC)).....</b>	<b>7</b>
1.1	“LABORATORY AND IN-SITU VALIDATION OF MICRO-SENSORS” AND “REPORT OF THE LABORATORY AND IN-SITU VALIDATION OF MICRO-SENSORS (AND UNCERTAINTY ESTIMATION) AND EVALUATION OF SUITABILITY OF MODEL EQUATIONS” .....	8
1.2	TIME SCHEDULE AND ACTIVITIES .....	8
1.3	PROTOCOL OF EVALUATION.....	9
1.4	GAS SENSOR TESTED WITHIN MACPOLL.....	11
<b>2</b>	<b>SENSOR IDENTIFICATION .....</b>	<b>11</b>
2.1	MANUFACTURER AND SUPPLIER:.....	11
2.2	SENSOR MODEL AND PART NUMBER:.....	11
2.3	DATA PROCESSING OF THE SENSOR.....	11
2.4	AUXILIARY SYSTEMS SUCH AS POWER SUPPLY, TEST BOARD AND DATA ACQUISITION SYSTEM. ....	12
2.5	PROTECTION BOX AND/OR SENSOR HOLDER USED WITH THE MATERIAL USED FOR ITS PREPARATION.....	12
<b>3</b>	<b>SCOPE OF VALIDATION.....</b>	<b>13</b>
<b>4</b>	<b>LITERATURE REVIEW: .....</b>	<b>14</b>
<b>5</b>	<b>LABORATORY EXPERIMENTS .....</b>	<b>15</b>
5.1	EXPOSURE CHAMBER FOR TEST IN LABORATORY .....	15
5.2	GAS MIXTURE GENERATION SYSTEM .....	18
5.3	REFERENCE METHODS OF MEASUREMENTS.....	18
5.3.1	<i>Methods</i> .....	18
5.3.2	<i>Quality control</i> .....	19
5.3.3	<i>Homogeneity</i> .....	19
<b>6</b>	<b>METROLOGICAL PARAMETERS .....</b>	<b>19</b>
6.1	RESPONSE TIME .....	19
6.2	PRE-CALIBRATION.....	22
6.3	REPEATABILITY, SHORT-TERM AND LONG TERM DRIFTS .....	23
6.3.1	<i>Repeatability</i> .....	24
6.3.2	<i>Short term drift</i> .....	24
6.3.3	<i>Long term drift</i> .....	26
<b>7</b>	<b>INTERFERENCE TESTING.....</b>	<b>29</b>
7.1	GASEOUS COMPOUNDS.....	29
7.1.1	<i>Ozone – O<sub>3</sub></i> .....	31
7.1.2	<i>Nitrogen monoxide – NO</i> .....	32
7.1.3	<i>Carbon monoxide – CO</i> .....	33
7.1.4	<i>Carbon dioxide – CO<sub>2</sub></i> .....	33
7.1.5	<i>Sulphur dioxide – SO<sub>2</sub></i> .....	34
7.1.6	<i>Ammonia – NH<sub>3</sub></i> .....	34
7.2	AIR MATRIX.....	35
7.3	HYSTERESIS.....	38
7.4	METEOROLOGICAL PARAMETERS.....	40
7.4.1	<i>Humidity and Temperature</i> .....	40
7.4.2	<i>Wind velocity effect</i> .....	43
7.4.3	<i>Ambient pressure effect</i> .....	46
7.5	EFFECT OF POWER SUPPLY .....	46
7.6	CHOICE OF TESTED INTERFERING PARAMETERS IN FULL FACTORIAL DESIGN.....	47



<b>8</b>	<b>EXPERIMENTAL DESIGN .....</b>	<b>48</b>
8.1	DATA AND MODEL .....	48
8.2	UNCERTAINTY ESTIMATION .....	52
<b>9</b>	<b>FIELD EXPERIMENTS .....</b>	<b>54</b>
9.1	MONITORING STATIONS.....	54
9.2	SENSOR EQUIPMENT .....	55
9.3	CHECK OF THE SENSOR IN LABORATORY .....	56
9.4	FIELD RESULTS .....	57
<b>10</b>	<b>DISCUSSION CONCLUSION .....</b>	<b>62</b>
<b>11</b>	<b>APPENDIX A: TECHNICAL DATA SHEET CAIRCLIP NO<sub>2</sub>.....</b>	<b>64</b>
<b>12</b>	<b>APPENDIX B: RESPONSE TIME STEPS .....</b>	<b>65</b>
<b>13</b>	<b>APPENDIX C: EVALUATION OF CAIRCLIP NO<sub>2</sub> DURING THE OZONE CAMPAIGN.....</b>	<b>67</b>



## 1 Task 4.3: Testing protocol, procedures and testing of performances of sensors (JRC, MIKES, INRIM, REG-Researcher (CSIC))

The aim of this task was to validate NO<sub>2</sub> and O<sub>3</sub> cheap sensors under laboratory and field conditions. Based on the recommendations of the review of sensors (Task 4.1), the graphene sensors and a limited number of sensor types and air pollutants were chosen. At the beginning of the validation a testing protocol was drafted, which was improved and refined during the process of validation experience. This task provided the information needed for estimating the measurement uncertainty of the tested sensors. Further, procedures for the calibration of sensors able to ensure full traceability of measurements of sensors to SI units were also drafted.

The laboratory work package endeavours to find a solution to the current problem of validation of sensors. In general, the validation of sensors is either carried out in a laboratory using synthetic mixtures, or at an ambient air monitoring station with real ambient matrix. Generally, these results are not reproducible at other sites than the one used during validation. In fact, sensors are highly sensitive to matrix effects, meteorological conditions and gaseous interferences that change from site to site.

Commonly, the validation generally performed by sensor users consists in establishing the minimum parameter set of sensors to describe their selectivity, sensitivity and stability. Since, this feature is generally not reproducible from site to site, it was proposed in this project to extend the validation procedure by establishing simplified model descriptions of the phenomena involved in the sensor detection process. Both laboratory experiment in exposure chambers and fine tuning of these models during field experiments were carried out in this project.

The sensors were exposed to controlled atmospheres of gaseous mixtures in exposure chambers. These laboratory controlled atmospheres consisted of a set of mixtures with several levels of NO<sub>2</sub>/O<sub>3</sub> concentrations, under different conditions of temperature and relative humidity and including the main gaseous interfering compound.

### Description of work:

- The tested sensors were selected by CSIC and JRC. The development of the protocol for the evaluation of sensors was carried out by CSIC and JRC. INRIM and MIKES carried out the initial laboratory evaluations of the new NO<sub>2</sub> graphene sensors. JRC carried out the experimental test of the selected O<sub>3</sub> and NO<sub>2</sub> commercial sensors and JRC and the REG-Researcher (CSIC) performed the evaluation of their test results. After laboratory tests, the commercial O<sub>3</sub> and NO<sub>2</sub> sensors were tested at field sites under real conditions by JRC.
- Along the different step of the project, the protocol for evaluation of sensors was improved by CSIC and JRC based on the test results and the technical feasibility of the experiments.
- The controlled atmospheres of the INRIM and MIKES tests were designed to evaluate the linearity of graphene sensors at different NO<sub>2</sub> levels (5) and their stability with respect to temperature (3 levels) and/or relative humidity (3 levels) at constant NO<sub>2</sub> level.
- JRC performed laboratory tests to determine the parameters of the NO<sub>2</sub> and O<sub>3</sub> model equations (task 4.1) using full or partial experimental design of influencing variables (identified in task 4.1). In any case, the controlled atmosphere included at least 5 levels of air pollutants, 3 levels of air pollutants and 3 levels of relative humidity and 2 levels of the chemical interference evidenced in task 4.1.
- CSIC and JRC applied the protocol of evaluation to the commercial sensors with determination of their metrological characteristics: detection limits, response time, poisoning points, hysteresis, etc., measurement uncertainty in laboratory and field experiment.

### Activity summary:

- Selection of suitable sensors for validation (at least 2 commercially available NO<sub>2</sub> sensors, 3 commercially available O<sub>3</sub> sensors and the INRIM and MIKES graphene sensors (**JRC, REG-Researcher (CSIC)**)
- Development of a validation protocol and procedures for calibration of micro-sensors (**CSIC**)



- Laboratory evaluation of the INRIM and MIKES graphene sensors: lab tests of NO<sub>2</sub> level, temperature, humidity, response time and hysteresis **(INRIM)**
- Laboratory evaluation of the INRIM and MIKES graphene sensors (lab tests of NO<sub>2</sub> concentration, response time, warming time and temperature or humidity effect) **(MIKES)**
- Laboratory tests in exposure chamber and at one field site according to the validation protocol **(JRC)**. The site will be representative of the population exposure and should be consistent with the sampling sites in which micro-sensors are likely to be used in future. Unless the bibliographic review will suggest other locations for any reason, the O<sub>3</sub> sensors will be tested at a suburban/rural site (at the JRC). The sampling site for NO<sub>2</sub> will be representative for urban areas or traffic sites where high levels of NO<sub>2</sub> in conjunction with sufficient population density are expected. Nevertheless, the actual location of the field site will be confirmed after the bibliographic review.
- Improvement of graphene sensors based on the results of JRC laboratory tests **(INRIM, MIKES)**
- Estimation of the effect of influencing variables based on laboratory and field tests and evaluation of the suitability of the model equations proposed in 4.1 **(REG-Researcher (CSIC), JRC)**

This task leads to deliverables 4.3.1 -4.3.5.

**1.1 “Laboratory and in-situ validation of micro-sensors” and “Report of the laboratory and in-situ validation of micro-sensors (and uncertainty estimation) and evaluation of suitability of model equations”**

**1.2 Time schedule and activities**

4.3.4	Laboratory and in-situ validation of micro-sensors	JRC	INRIM, MIKES	Data sets	Jul. 2013
4.3.5	Report of the laboratory and in-situ validation of micro-sensors (and uncertainty estimation) and evaluation of suitability of model equations	JRC	INRIM, MIKES, REG-Researcher (CSIC)	Report	Dec. 2013



### 1.3 Protocol of evaluation

This report presents the evaluation of the performances of the CairClip NO<sub>2</sub> sensor according to the MACPoll Validation protocol [1]. The objective of this evaluation is to determine the laboratory and field measurement uncertainties and to compare these uncertainties with the Data Quality Objective (DQO) of the European Air Quality Directive [2] for indicative method. The DQOs correspond to a relative expanded uncertainty. A flow chart depicting the procedure for the validation of sensors is given in

Figure 1.

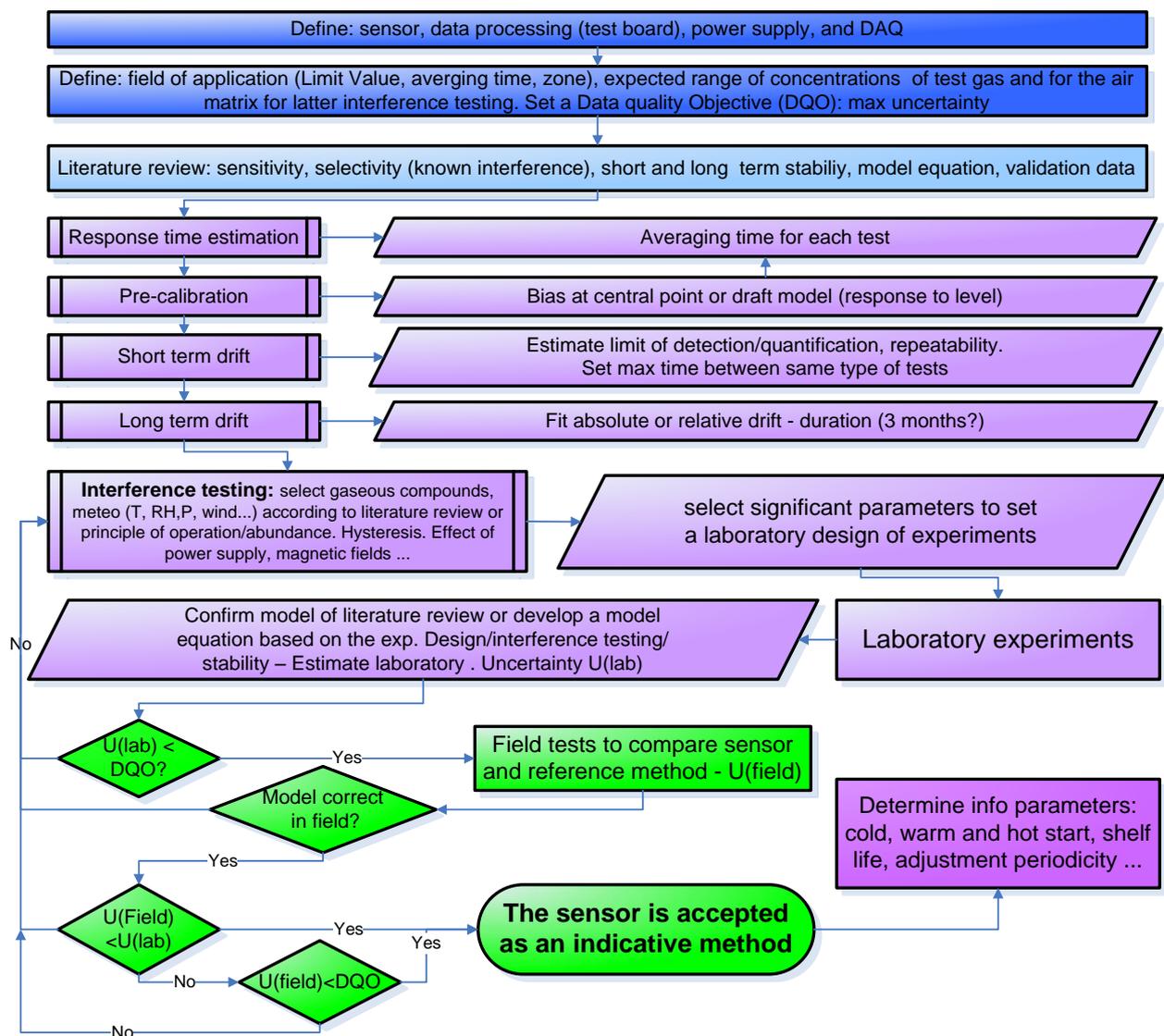


Figure 1: Protocol of evaluation of sensor

<sup>1</sup> Spinelle L, Alexandre M, Gerboles M. Protocol of evaluation and calibration of low-cost gas sensors for the monitoring of air pollution. EUR 26112. Luxembourg (Luxembourg): Publications Office of the European Union; 2013. JRC83791.

<sup>2</sup> Directive 2008/50/EC of the European Parliament and the Council of 21 May 2008 on ambient air quality and cleaner air for Europe



**Table 1: Matrix of laboratory tests carried out in exposure chamber under controlled conditions**

	Tests	Temperature, °C	Relative humidity, %	Comment
1	Response Time	Central value	Central value	Three times: 0 to 80 % of Full Scale and 80% of FS to 0
2	Pre-calibration	Central value	Central value	At least 3 levels including 0, LV, IT, AT, CL, LAT and UAT
3	Repeatability, short-long term drifts			
3-1	Repeatability	Central value	Central value	0 and 80 % of LV, 3 repetitions every averaging time
3-2	Short term drift	Central value	Central value	0, 50 % and 80 % of LV, 3 repetitions per day for 3 consecutive days
3-3	Long term drift	Central value	Central value	0, 50 % and 80 % of LV, repeated every 2 weeks during 3 months
4	Interference testing			
4-1	Gaseous interference	Central value	Central value	Interfering gaseous compound at 0 and central value in ambient air, test gas at 0 and LV
4-2	Air matrix	Central value	Central value	Zero air, laboratory air and ambient air at 0 and LV
4-3	Temperature	From central value-10 °C to central value +10 °C by step of 5 °C	Central value	At LV
4-4	Humidity	Central value	From central value-20% to central value +20% by step of 10%	At LV
4-5	Hysteresis	Central value	Central value	Increasing-decreasing-increasing concentration cycles of the pre-calibration levels
4-6	Pressure	Central value	Central value	overpressure 10 mbar and under pressure 5 mbar
4-7	Power supply effect	Central value	Central value	At LV test under 210, 220 and 230 V
4-8	Wind velocity	Central value	Central value	from 1 to 5 m/s (needed?)
4	Validation/modelling			
4-1	Lab experiments (model)	Central value $\pm$ 10°C, central value, if significant	Central value $\pm$ 20%, central value, if significant	0, LV, AT for each significant parameter: temperature and humidity (levels) and interference (2 levels)
4-2	Field experiment			At an automatic station equipped with reference methods of measurement
5	Additional information			
5-1	Cold start, warm start, hot start	Central value	Central value	At LV

*CL: Critical levels for the protection of the vegetation, FS: Full Scale, IT/AT: Information and alert thresholds, LAT/UAT: Lower and upper assessment threshold, LV: Limit values or target value, Central value: average temperature or humidity typical in the field of application*

Table 1 gives a list of all the tests for the evaluation of micro-sensors included in the protocol [1]. Even when the DQO cannot not be met, the application of the protocol is still of interest as the method produces a full estimation of laboratory and field measurement uncertainty which demonstrates the performance of the sensor.



## 1.4 Gas sensor tested within MACPoll

Within MACPoll, Work Package 4, eleven models of nitrogen dioxide (NO<sub>2</sub>) sensors were selected for evaluation (see Table 2). Hereafter, we report the results of the evaluation of the nitrogen dioxide sensor of Cairpol (see yellow background on Table 2) which is an amperometric sensor with 3 electrodes.

**Table 2: List of NO<sub>2</sub> sensors selected for the MACPoll validation programme.**

N°	Manufacturer	Model	Type	Data acquisition
NO1	Unitec s.r.l	NO2 Sens 3000	Res.	Analogic voltage of transmitter board
NO2	αSense	NO <sub>2</sub> sensors NO2-B4	4 Elect.	Analogic Voltage of transmitter board
NO3	Citytech	Sensoric NO2 3E 50	3 Elect.	Analogic Voltage
NO4	Citytech	Sensoric NO 3E 100	3 Elect.	Analogic Voltage
NO5	Citytech	A3OZ EnviroceL	4 Elect.	No testing board existing?
NO6	e2V	MiCS-2710 sensor	Res.	Analogic Voltage
NO7	e2V	MiCS 4514 sensor	Res.	Analogic Voltage
NO8	Figaro	TGS 2201	Res.	No testing board existing?
NO9	Cairpol	CairClip NO2	3 Elect.	Analogic Voltage of transmitter board embedded in the sensor
NO10	MIKES	Graphene sensor	Res.	
NO11	INRIM	Graphene sensor	Res.	

3 Elect. and 4 Elect.: amperometric, 3 or 4 electrode sensor, Res.: resistive sensor

## 2 Sensor Identification

### 2.1 Manufacturer and supplier:

CAIRPOL, ZAC du Capra, 55, avenue Emile Antoine, 30340 Méjannes les Alès – France, Tel: +33 (0)4 66 83 37 56, Fax: +33 (0)4 66 61 82 53, [info@cairpol.com](mailto:info@cairpol.com), [www.cairpol.com](http://www.cairpol.com)

### 2.2 Sensor model and part number:

Sensors CairClip NO<sub>2</sub> ANA, s/n CNB0311120002 (used for the field experiments) and CNB0311120001 (used in the laboratory experiments). The sensors were not calibrated by the manufacturer. The manufacturer adds that these sensors were preliminary version still in development. The main issue encountered in there laboratories was an effect on the position on the sensor response. Those issues have been solved in the final version of the sensor.

CairClip NO<sub>2</sub> ANA was also added in the O<sub>3</sub> experiments to get details about the O<sub>3</sub> interference on this NO<sub>2</sub> sensor and filter. Two sensors were tested: s/n CCB0306120003 (used for the field experiments) and s/n CCB030120004 (used in the laboratory experiments). As for the previous sensors, these were not previously calibrated by the manufacturer. The results obtained for these two sensors will be integrated in Appendix C: Evaluation of CairClip NO<sub>2</sub> during the ozone campaign. but will not be included in the Design of experiment.

Options included: dongles USB (red for switching off, see Figure 2, and green used as a basis for the sensor), filters, USB cable and USB power supply.

### 2.3 Data processing of the sensor

No info was available about any embedded data processing system that may change with other model of the sensor. As it will be detailed in the pre-calibration (see 6.2) the manufacturer as the capacity to set different calibration lines and thresholds.

## 2.4 Auxiliary systems such as power supply, test board and data acquisition system.

- Power supply: a power supply TracoPower ESP18-05SN 5V-3.6 A was used both for the laboratory tests and for the fields tests (the power supply sent by Cairpoll was not used)
- Test board used: no needs for a test board, CairClip sensors include a 5V analogic output on their USB connector.
- Data acquisition: for the laboratory experiments, the data acquisition is performed by means of special JRC LabView software developed to manage data acquisition of sensor responses and gaseous references values and other parameters such as temperature, humidity (see 2.5.1). It consisted of a NI USB-6009 acquisition system from National Instrument with a periodicity of data acquisition of 100Hz and an average data acquisition every minute without filtering.

## 2.5 Protection box and/or sensor holder used with the material used for its preparation

Laboratory tests: No protection box was used but it was wrapped in a Teflon tape to avoid reaction with gaseous compounds (see Figure 2). It has been carefully checked that the Teflon tape was not placed in front of the inlet of the sensor in order to not interfere with the sensor response.



**Figure 2:** Left: ClairClip sensors prepared for laboratory test. View of the CairClip sensor; upper right: view of the CairClip sensor; bottom right: example sensors in the exposure chamber

Field campaign: CairClip NO<sub>2</sub> was put into a PVC box mainly to protect it from direct rain. The largest part as possible of the sensor was put outside the box as seen on Figure 3.



*Figure 3: CairClip NO<sub>2</sub> installed in a PVC box at the field monitoring site*

### 3 Scope of validation

This validation report aims at demonstrating that the gas sensor satisfies the Data Quality Objective DQO for NO<sub>2</sub> Indicative Method of measurements at a target level (LV).

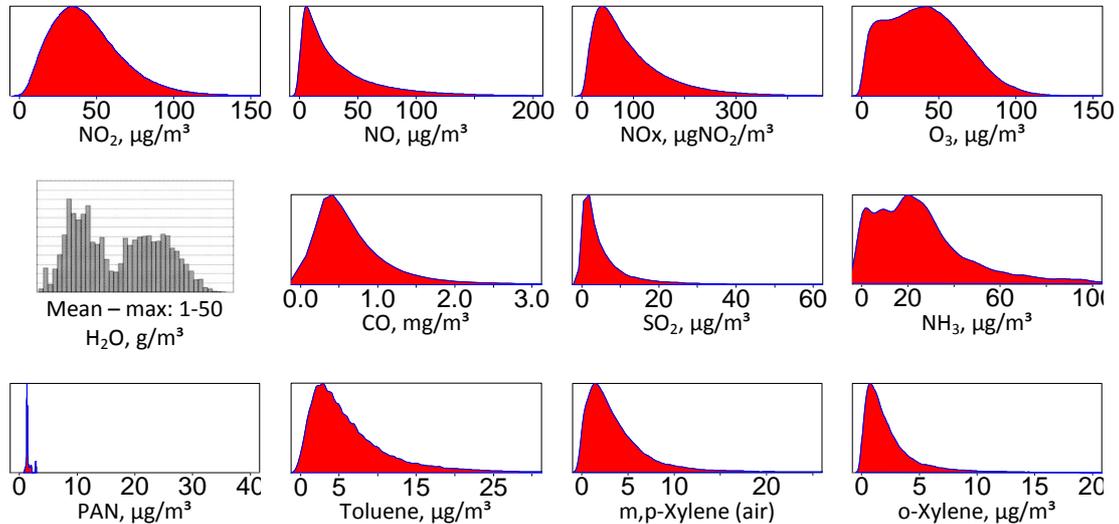
- the DQO consists of a relative expanded uncertainty of 25 % in the region of the Target Value (LV)
- the LV corresponds to 200 µg/m<sup>3</sup> or 100 nmol/mol
- the LV is defined as a 1-hour mean value hourly mean of NO<sub>2</sub> in ambient air. Consequently, an averaging time of one hour is mandatory for the sensor. Other important values defined in the Directive are the alert thresholds (AT): 400 µg/m<sup>3</sup> (200 nmol/mol), the lower and upper assessment threshold (LAT/UAT): 100 µg/m<sup>3</sup> (50 nmol/mol) and 140 µg/m<sup>3</sup> (70 nmol/mol). The lowest value is the yearly average with 40 µg/m<sup>3</sup> (20 nmol/mol)
- it was planned to validate the sensor in the following micro-environment: traffic and background type of station with urban/suburban areas since they corresponds to zones where NO<sub>2</sub> monitoring is mandatory.

Using several on-line databases and literature sources, was established to set down the expected air composition in different micro-environments, more details are given in [3]. Using this table, the full scale of the nitrogen dioxide gas sensor was set to 150 nmol/mol with main mode at 50 nmol/mol. Major gas molecules in urban/suburban areas appears to be O<sub>3</sub>, CO, NO.

<sup>3</sup> MACPoll, WP4, Selection of suitable micro-sensors for validation, D4.3.1 , vs 1, Mar 2012



**Table 3: Ambient air composition for NO<sub>2</sub> and other gaseous compounds at traffic station, urban/suburban areas form the Airbase EUsar and TTorchs database. Daily data are reported.**



Further to this information it was decided to:

- set the full scale to 75 % of the alert threshold: 300 µg/m<sup>3</sup> (about 150 nmol/mol) taking into consideration the distribution of NO<sub>2</sub> (see Table 3).
- it will be important to check the interference of abundant compounds: O<sub>3</sub>, NO, CO.
- the average temperature and relative humidity will be set to 22 °C and 60 %, respectively.

It is worth reminding that before using the sensor based on the validation data included in this report, it should be ascertained that the sensor is applied in the same configuration in which it was tested here. This requires using the same data acquisition and processing, the same protection box and calibration type. The sensor shall be submitted to the same regime of QA/QC as during evaluation. In addition, it is strongly recommended that sensors results are periodically compared side-by-side using the reference method.

In this report, all calculations were conducted using R (R Development Core Team, 2012). Data exploration was applied following Zuur et al. (2010). The presence of outliers was investigated using Cleveland dotplots, collinearity was assessed using multi-panel scatterplots, Pearson correlation coefficients and variance inflation factors (VIF).

#### 4 Literature review:

Category under which the gas sensor falls:

- the sensor behaves as a black-box without the user knowing the model equation used for the transformation of sensor response into NO<sub>2</sub> values,
- the company does not supply information about the relevant data treatment and processing that is applied and the model equation used for the transformation of the sensor responses into NO<sub>2</sub> values
- the objective of this evaluation protocol is the validation of the sensor NO<sub>2</sub> values with the possibility to establish a correction function with the test results of the evaluation protocol.

No info was found on the internet about the performance of this sensor

model equation: since no info is available, it is assumed that the model should be linear (NO<sub>2</sub> = a + b.Rs). The manufacturer gives an equation for transforming the voltage output V of the sensor into a concentration unit which is NO<sub>2,nmol/mol</sub> = (V<sub>mV</sub> - 100)/10



- known interference, the manufacturer gives advices about  $\text{Cl}_2$  and  $\text{O}_3$ . It is unlikely that  $\text{Cl}_2$  can be present in sufficient quantity to modify sensor responses. The effect of  $\text{Cl}_2$  on the sensor will not be studied.  $\text{O}_3$  is known to be the main gaseous interfering compound of  $\text{NO}_2$  sensors
- previous field implementation and comparison with reference method: no info available

The manufacturer gave some information about the short and long term stability and other metrological parameters (repeatability, linearity):

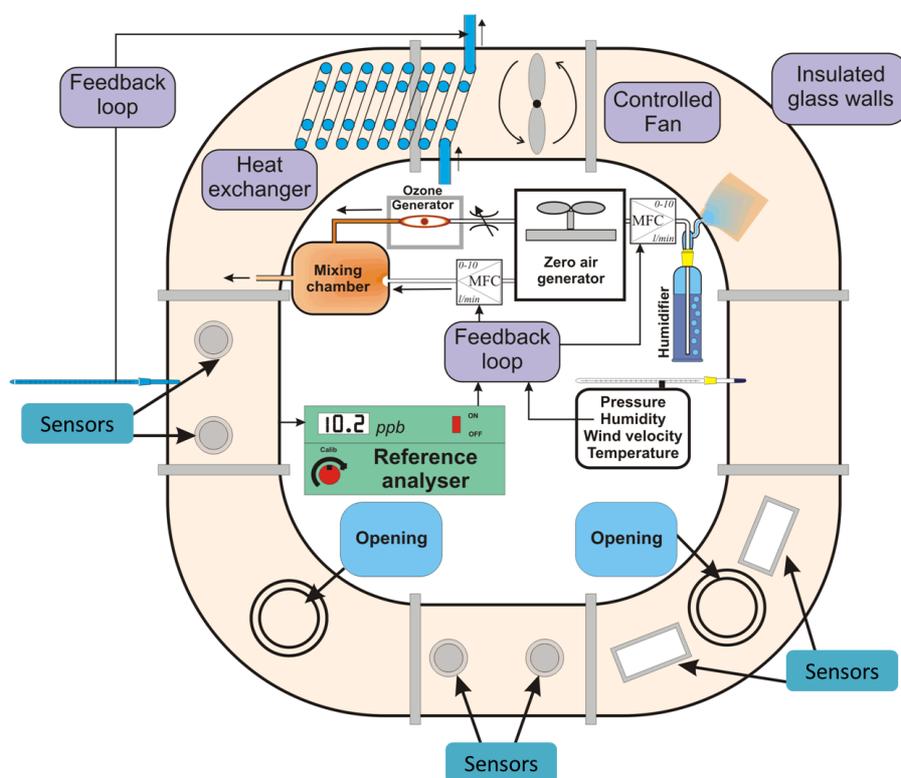
- Full scale: 0-250 nmol/mol (0-240 nmol/mol analog)
- Limit of detection: 20 ppb
- Repeatability at zero: +/- 7 ppb
- Repeatability à 35% of FS : +/- 20 ppb
- Linearity: < 10%
- Short term drift for zero: < 5 ppb/24hr
- Short term drift of sensitivity: <1% FS/24hr
- Long term drift for zero: < 10ppb/month
- Long term drift of sensitivity: < 2% FS/month
- Rise time ( $t_{10-90}$ ): <90s (180 s with important HR change)
- Fall time ( $t_{10-90}$ ): < 90s (180 s with important HR change)
- Effect of interference:  $\text{Cl}_2$  about 80 %, possible interference from  $\text{O}_3$  if high concentration.
- Conditions of use : -20°C to +40°C / 10 to 90% HR without condensation, 1013 mbar +/- 200 mbar
- Maximum concentration (short time): 50ppm
- Annual limit concentration (average on 1 hr): 780ppm
- Recommended storage: Temperature between 5°C and 20°C, relative humidity >15% without condensation, ambient free from  $\text{O}_3$ .

Personal communication of the manufacturer: a Membrapor sensor is used in the CairClip gas sensor. The  $\text{NO}_2$  sensor includes an ozone filter that was not made of indigo (not blue), no more info. The characteristics of the  $\text{O}_3$  filter of the CairClip $\text{NO}_2$  ANA could be explained by the manufacturer.

## 5 Laboratory experiments

### 5.1 Exposure chamber for test in laboratory

The gas sensors are evaluated in the JRC exposure chamber. This chamber allows the control of  $\text{NO}_2$  and other gaseous interfering compounds, temperature, relative humidity and wind velocity (see Figure 4). The exposure chamber is an “O”-shaped ring-tube system, covered with dark insulation material. The exposure chamber can accommodate the  $\text{NO}_2$  micro-sensors directly inside the “O”-shaped ring-tube system.



**Figure 4: Exposure chamber for micro-sensors used in laboratory**

A special LabView software was developed for controlling the exposure chamber and for easy programming of a set of experiments under different controlled conditions: temperature, humidity, wind velocity,  $\text{NO}_2$  and gaseous interfering compounds. It allowed setting criteria for the stability of each parameter and for duration of each step (see Figure 5). The software was also able to manage data acquisition and all results (exposure conditions and sensors responses) were collected in Access database for latter data treatment. The data acquisition system had a frequency of acquisition of 100 Hz and average over one minute where stored.

The software was able to set initial values for all parameters controlling the generation of gaseous compounds ( $\text{NO}_2$  main gas and interfering compounds), temperature, humidity and wind velocity according to the targets set in the programming worksheet (see Figure 5). During experiments, an automatic system (feed-back loop) used the reference measurements of gaseous compounds, temperature, humidity and wind speed to auto-correct the gas mixture generation system, temperature controlling cryostat and wind velocity to reach the target conditions (see the logical graph in Figure 5 and Figure 6).

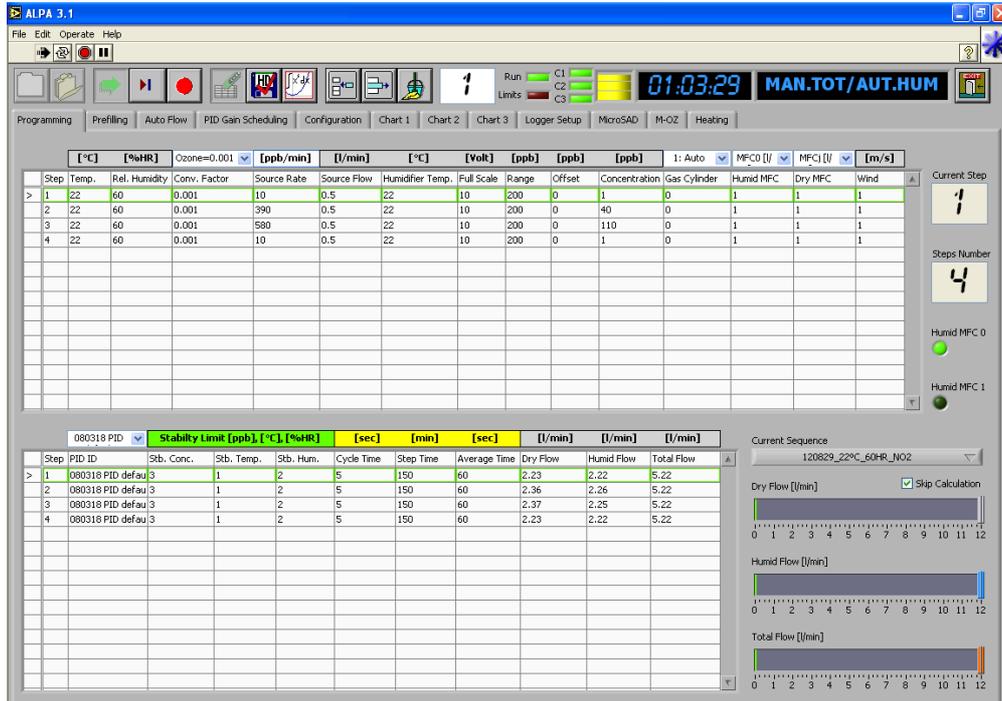


Figure 5: Example of programming of conditions

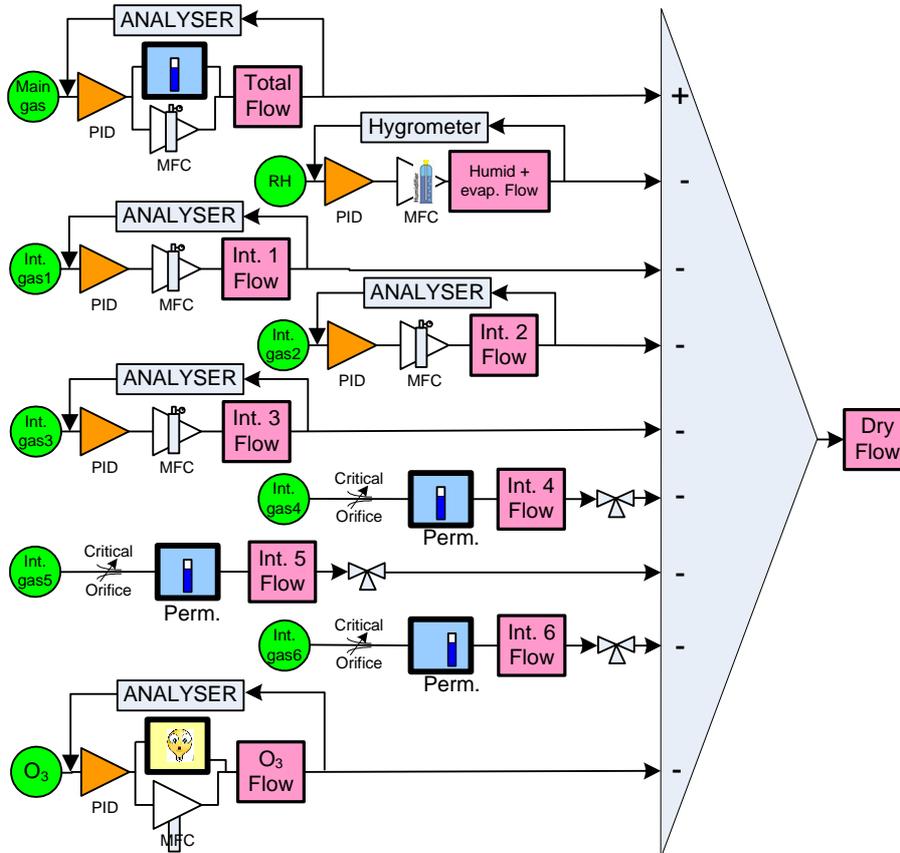


Figure 6: Feedback loops of the exposure chamber control system



## 5.2 Gas mixture generation system

NO<sub>2</sub> was produced by two different methods:

- using permeation tubes from KinTec (G) and Calibrage (F),
- and the dynamic volumetric method using thermal mass flow controllers from certified highly concentrated cylinders (Air Liquide, about 60 µmol/mol of NO<sub>2</sub>). To modify the main concentration NO<sub>2</sub> in the exposure chamber, the software was using a PID able to modify the total flow inside. The gas cylinder was used as an adaptable source of NO<sub>2</sub> to reach higher concentration.

Mixtures of gaseous interference were generated with an in-house designed Permeation system, using NH<sub>3</sub>, SO<sub>2</sub>, HNO<sub>3</sub> permeation tubes from AeroLaser (DE), KinTec (G) and Calibrage (FR) that were weighed every 3 weeks. CO mixtures were directly generated by dynamic dilution from highly concentrated cylinders from Air Liquide. For generating O<sub>3</sub>, two MicroCal 5000 Umwelttechnik MCZ GmbH (G) generators were used. These generators are equipped with UV lamps that dissociated O<sub>2</sub> molecules into reactive O\* atoms that later combine with O<sub>2</sub> molecule to form O<sub>3</sub>. The quantity of O<sub>3</sub> depends on the intensity of the current applied to the UV lamp and the total flow of zero air of the generator which is adjusted by a mass flow controller.

For the response time experiment, the controlled conditions in the exposure chamber shall be established after the minimum time (a few minutes). Seen the internal volume of the exposure chamber (about 120 L), it was decided to use the automatic bench that ERLAP uses for the European intercomparison exercises of the National Reference Laboratories of Air Pollution [4] that can generate mixture with a flow of about 100 L/min.

## 5.3 Reference methods of measurements

### 5.3.1 Methods

NO/NO<sub>x</sub>/NO<sub>2</sub> was monitored using Thermo Environment 42 C chemiluminescence analyser, calibrated against certified gas cylinder from Air Liquide.

Other gaseous compounds were recorded to ease understanding sensors results:

- NO/NO<sub>x</sub>/NO<sub>2</sub>: Thermo Environment 42 C chemiluminescence analyser, calibrated against a permeation system for NO<sub>2</sub> and a NO working standard consisting of a gas cylinder at low concentration (down to 50 nmol/mol) certified against a Primary Reference Material of NMI VSL – NL
- O<sub>3</sub>: Thermo Environment TEI 49C UV-photometer, calibrated against an O<sub>3</sub> primary standard (TEI Model 49 C Primary Standard, Thermo Environmental Instruments) cross-checked against a long-path UV photometer (National Institute of Standards and Technology, reference photometer n° 42, USA).
- SO<sub>2</sub>: Environment SA AF 21 M, calibrated with a working standard consisting of gas cylinder at low concentration (down to 50 nmol/mol) certified against a Primary Reference Material of NMI VSL - NL. The calibration of the analyser was confirmed by cross-checking with a permeation method.
- CO: Thermo Environment 48i-TLE NDIR analyser, calibrated with a CO working standard consisting of a gas cylinder at low concentration (down to 50 nmol/mol) certified against a Primary Reference Material of NMI VSL - NL.
- CO<sub>2</sub>: an infra-Red sensor, Gascard NG 0-1000 µmol/mol (Edinburg Sensors – UK) was used. This sensor includes pressure correction and temperature compensation. The sensor was calibrated with a CO<sub>2</sub> cylinder (369 ppm for Air Liquide) and zero air obtained from an ultra-pure Nitrogen cylinder.

4 For example: M. Barbieri and F. Lagler, Evaluation of the Laboratory Comparison Exercise for SO<sub>2</sub>, CO, O<sub>3</sub>, NO and NO<sub>2</sub>, 11th-14th June 2012, EUR 25536, ISBN 978-92-79-26844-1, ISSN 1831-9424, doi:10.2788/52649, [ftp://ftp\\_erlap\\_ro:3rlapsyst3m@s-jrciprvm-ftp-ext.jrc.it/ERLAPDownload.htm](ftp://ftp_erlap_ro:3rlapsyst3m@s-jrciprvm-ftp-ext.jrc.it/ERLAPDownload.htm)



The sampling line of each gas analyser was equipped with a Naflyon dryer to avoid interference from water vapour on O<sub>3</sub>, NO<sub>x</sub>, SO<sub>2</sub> and CO analyser.

In addition, some other parameters were recorded and/or controlled using:

- Three refrigerated/Heating Circulators were used to regulate the temperature of the exposure chamber. One cryostat (Julabo (G) Model SP-FP50) was used to control the temperature inside the exposure chamber, another one (Julabo (G) Model HE-FP50) for the surface of the O-shaped glass tube and the last one (Julabo (G) Model HE-FP50) was devoted to the control of temperature of the humid and dry air flows. These cryostats used a laboratory calibrated pt-100 probe placed inside the exposure chamber.
- Two KZC 2/5 sensors from TERSID-It (one with ISO 17025 certificate) were used to control temperature and relative humidity. One sensor was used to monitor in real-time using our LabView software, the second one was used to register these parameter.
- One Testo 445 sensor (Testoterm – G) with a temperature and relative humidity probe was used as a control interface to check values inside the chamber.
- One Testo 452 sensor (Testoterm – G) with a temperature and relative humidity probe was used as a reference sensor and to monitor temperature and relative humidity.
- One wind velocity probes based on hot-wire technology was used to monitor wind velocity during tests.
- One pressure gauge DPI 261 from Druck (G) was used to monitor pressure inside the exposure chamber
- Fan ventilator placed in the chamber, Papst (G) model, DV6224, 540 m<sup>3</sup>/hr.
- An in-house developed permeation system able to accommodate 8 permeation cells with carrier flows about 200 ml/min with critical orifices (Calibrage SA, (F)). Each permeation cells were dipped in a water bath (Haake (G) W26 Thermostatic Circulating Water Bath with Haake E8 Controller). The temperature of each cell was set at 40 °C. The permeation tubes were weighed every three weeks. The permeation cells were filled with NO<sub>2</sub>, SO<sub>2</sub>, NH<sub>3</sub> and HNO<sub>3</sub> permeation tubes manufactured by KinTec (G) and Calibrage (F).

### **5.3.2 Quality control**

During the experiments, the analysers were monthly checked using a certified gas cylinder from Air Liquide. The O<sub>3</sub> analyser was monthly checked using a portable O<sub>3</sub> generator SYCOS KTO 3 (Ansyco, GmbH - G) certified against the laboratory primary standard (NIST n°42). The NO<sub>2</sub>, SO<sub>2</sub> and CO analysers were calibrated once a month using cylinders certified by the ERLAP laboratory. ERLAP is ISO-17025 accredited (ACCREDIA-IT, n°1362) for the measurement of O<sub>3</sub>, NO<sub>2</sub>, SO<sub>2</sub> and CO according to EN 14625:2012, EN 14211:2012, EN 14212:2012 and EN 14626:2012, respectively.

### **5.3.3 Homogeneity**

The homogeneity of exposure conditions in the chamber was investigated during several tests. The influence of humidity on the Thermo Environment 42 C was eliminated by using a nafion dryer.

## **6 Metrological parameters**

### **6.1 Response time**

The response time of sensors was estimated by  $t_{0-90}$  and  $t_{90-0}$  (the time needed by the sensor to reach 90 % of the final stable value), after a sharp change of test gas level from 0 to 80 % of the full scale (FS) (rise time) and from 80 % of FS to 0 (fall time). Four determinations of rise and fall



$t_{90}$  were performed, see Table 4. The averaging time of the NO<sub>2</sub> TE42C analyser was set to 60 sec.

**Table 4: Response time measurements**

Step	Test gas	RH	T	Interference	Notes
1	0 nmol/mol	60 %	22 °C	none	Until stable response
2	100 nmol/mol	60 %	22 °C	none	Until stable response
3	0 nmol/mol	60 %	22 °C	none	Until stable response
4	100 nmol/mol	60 %	22 °C	none	Until stable response
5	0 nmol/mol	60 %	22 °C	none	Until stable response
6	100 nmol/mol	60 %	22 °C	none	Until stable response
7	0 nmol/mol	60 %	22 °C	none	Until stable response
8	100 nmol/mol	60 %	22 °C	none	Until stable response
9	0 nmol/mol	60 %	22 °C	none	Until stable response

Any change of all influencing variables of influence (see the list of the monitored variables in Table 5) would result in overestimation of the response time of sensors. Therefore these parameters were kept as stable as possible. Table 5 shows that the Relative Standard Deviations (RSD) of temperature, humidity rate, pressure and O<sub>3</sub> were within 1% at 80 % of FS and less than 0.5 nmol/mol at zero. The only possible influencing variable that could not be regulated while measured was ambient pressure. Table 6 shows the response times of the sensor (with the response time of the analyser already subtracted) compared to the ones of the reference measurements.

**Table 5: Response time experiment, stability of physical parameters during experiments. Temperature is in degree Celsius, relative humidity is in %, pressure is in hPa, O<sub>3</sub>, NO<sub>2</sub> and NO are in nmol/mol.**

	Step 1	Step 2	Step 3	Step 4	Step 5	Step 6	Step 7	Step 8	Step 9
NO <sub>2</sub> , nmol/mol	2.0 ± 0.2	100.0 ± 0.6	1.9 ± 0.3	100.0 ± 0.7	2.0 ± 0.4	100.0 ± 0.5	2.0 ± 0.3	100.0 ± 0.8	2.0 ± 0.2
NO, nmol/mol	5.8 ± 0.1	8.6 ± 0.1	6.4 ± 0.2	9.3 ± 0.2	6.2 ± 0.1	8.2 ± 0.1	5.9 ± 0.1	8.1 ± 0.1	5.7 ± 0.1
Temperature, °C	22.0 ± 0.1	21.9 ± 0.1	22.0 ± 0.1	21.9 ± 0.1	22.0 ± 0.1	22.0 ± 0.1	22.0 ± 0.1	22.0 ± 0.1	22.0 ± 0.1
Humidity, %	60.0 ± 0.1	60.0 ± 0.1	60.0 ± 0.1	60.0 ± 0.1	60.0 ± 0.1	60.0 ± 0.1	60.0 ± 0.1	60.0 ± 0.1	60.0 ± 0.1
Pressure, hPa	970.3 ± 0.1	983.5 ± 0.2	984.9 ± 0.2	991.5 ± 0.3	970.8 ± 0.3	969.7 ± 0.2	977.9 ± 0.2	979.1 ± 0.1	984.0 ± 0.1
O <sub>3</sub> , nmol/mol	0.0 ± 0.2	0.0 ± 0.2	0.0 ± 0.2	0.0 ± 0.2	0.0 ± 0.2	0.0 ± 0.2	0.0 ± 0.1	0.0 ± 0.1	0.0 ± 0.1
Time length, in min	273	118	339	2565	1418	357	955	389	1181

**Table 6: Sensor's response time ( $t_{90}$ ) in minutes compared to the chemiluminescence analyser response time ( $t_{90}$ ) in the exposure chamber.**

$t_{0.90}$ or $t_{90.0}$	Step 2	Step 3	Step 4	Step 5	Step 6	Step 7	Step 8	Step 9
	Rise	Fall	Rise	Fall	Rise	Fall	Rise	Fall
NO <sub>2</sub> , chemiluminescence	9	3	3	3	2	4	2	4
CairClipNO <sub>2</sub>	80	5	12	5	3	4	8	7

The estimated response times in this experiment are likely slightly underestimated because the response time of the chemiluminescence analyser was subtracted while the sensors started responding to the concentration change before the end of the analyser response time.

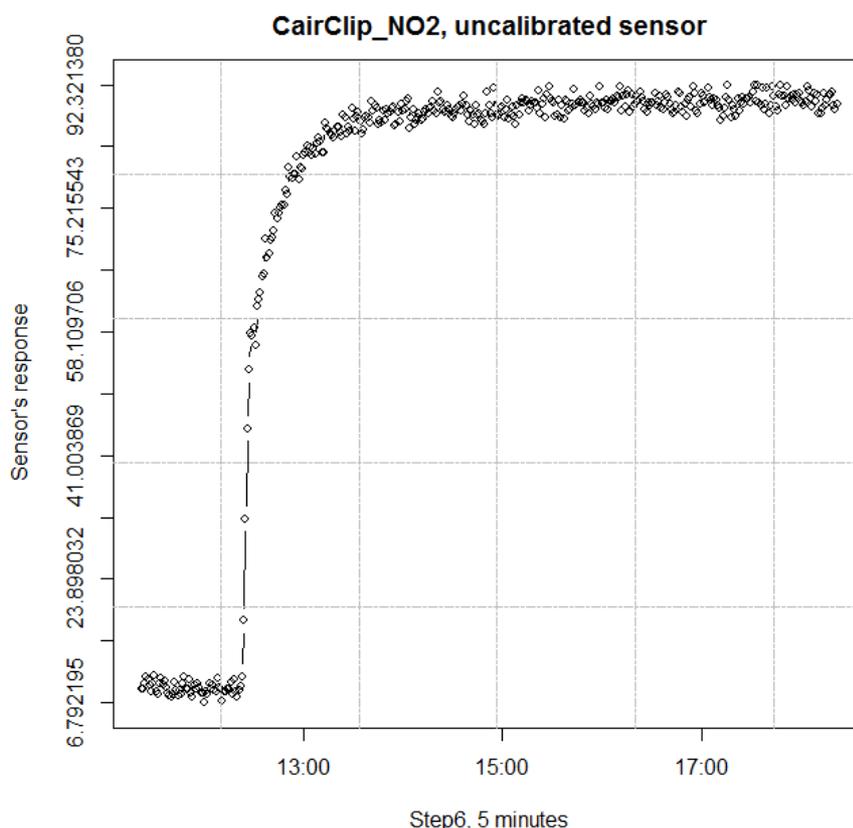
The response time of the gas sensor was longer than the one of the NO<sub>2</sub> analyser. In particular, step 2 which showed a very high  $t_{90}$  was not representative since step1 was very short and the flow of the generation system was not sufficient in step 2. Step 2 was discarded. The general behaviour of the sensor response shows an effect of adsorption and desorption of NO<sub>2</sub> molecules,



as the sensor never reach a stable value like the one observed during the longest exposure in step 2 (Figure 7). According to the manufacturer this behaviour can be due to a conditioning effect.

In average and excluding step 2 from the calculation, the response time of the CairClip NO<sub>2</sub> sensor was about 6 minutes 20 sec. As requested in the evaluation protocol [1], the  $t_{90}$  of the sensor is less than  $\frac{1}{4}$  of the required averaging time of one hour. Compared to the majority of the tested sensors, the CairClip NO<sub>2</sub> showed a short response time.

In average, the sensor is faster in fall condition (5 minutes  $\frac{1}{4}$ ) than in rise condition (around 7 minutes 40 sec). This is mainly link to the adsorption and desorption of NO<sub>2</sub> molecules inside the inner filter. Even though, this difference exceeds 10 %, it is assumed that this difference (about two minutes) will not affect significantly an hourly average even at background stations and at traffic stations provided that NO<sub>2</sub> concentrations slowly change (more than 2 min 20 sec).



**Figure 7: CairClip NO<sub>2</sub> response to 100 nmol/mol of NO<sub>2</sub> during the step number 6 of the response time evaluation.**

The EN standards for measuring NO<sub>2</sub> stated that measuring instruments should produce individual measurements that are not influenced by previous individual measurements provided that two individual measurements are separated by at least four response times [5, 3.16]. Applying the same idea to sensors, all following tests should last for at least  $6.33 \times 4 = 25$  minutes plus the stabilisation time of the exposure chamber. However, because of other slower sensors, it was decided to have each lasting for 150 minutes, well longer than the response time of the CairClip sensors.

<sup>5</sup> EN 14625:2005 'Ambient air quality - Standard method for the measurement of the concentration of ozone by ultraviolet photometry'



The CairClip sensors are to some extent suitable for mobile monitoring, being able to deliver 25 minute averages. However, micro-environment where air pollutants changes with a periodicity of a few minutes (e. g. in front of traffic light or with rapid indoor/outdoor moves) shall be excluded.

## 6.2 Pre-calibration

The objective of this experiment was to check if the transformation of sensor responses into air pollutant concentration does not include any bias at the mean temperature and relative humidity. The full scale of the sensor was previously defined at 150 nmol/mol. More test levels were used based on the following pattern 80, 40, 60, 0, 50, 20, 95% of the full scale. The order of the tests was randomised to take into account possible hysteresis effect for the CairClip NO<sub>2</sub> (see Table 7).

The controlled conditions (NO<sub>2</sub>, NO, O<sub>3</sub>, estimated NH<sub>3</sub>, T, RH and P) and sensor responses were averaged over the last hour of test in the exposure chamber. The experiment went on for 150 minutes once stabilisation of exposure conditions was reached.

Temperature and humidity, which were suspected to affect the sensor response, were kept under control with relative standard deviation (RSD) of about 2 % while it is not possible to control atmospheric pressure (and less than 0.5 nmol/mol at 0 nmol/mol). The temperature and relative humidity of the test were set at 22°C and 60 %. The NO<sub>2</sub> was generated both from gas cylinder and permeation tubes resulting in production of a small amount of NO (no effect of NO, see 7.1.2).

**Table 7: Experimental conditions for pre-calibration experiments of the CairClip NO<sub>2</sub> ANA**

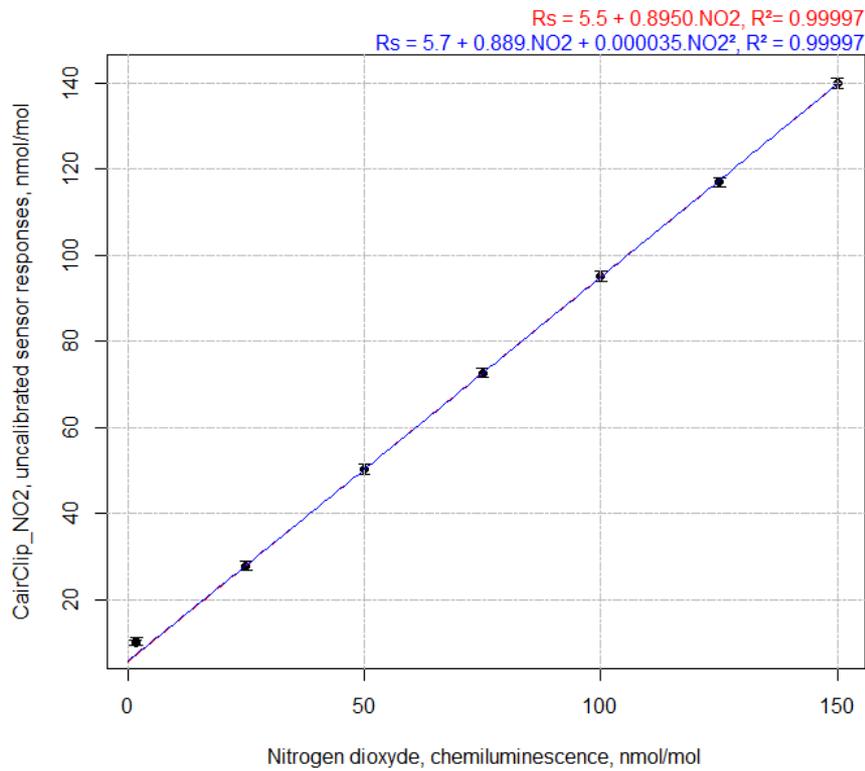
NO <sub>2</sub> Test levels, nmol/mol	NO, nmol/mol	T, °C	RH, %	Pressure, hPa	Interference	Comments
125.0 ± 0.6	10.9 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	980.9 ± 0.2	None	
50.0 ± 0.4	11.5 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	979.9 ± 0.1	None	LAT
100.0 ± 0.5	8.2 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	982.4 ± 0.2	None	LV
1.8 ± 0.3	4.7 ± 0.1	21.9 ± 0.1	60.0 ± 0.1	985.2 ± 0.1	None	
75.0 ± 0.6	9.1 ± 0.1	21.9 ± 0.1	60.0 ± 0.1	985.1 ± 0.1	None	~ UAT
25.0 ± 0.3	5.8 ± 0.1	21.9 ± 0.1	60.0 ± 0.1	985.1 ± 0.2	None	~ DQO
150.0 ± 0.8	10.5 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	983.6 ± 0.1	None	

In normal use, the sensor would behave as a black box, the sensor being calibrated by the manufacturer. However; the manufacturer sent us two un-calibrated sensors. Therefore, the results of this experiment were used to calibrate the sensor (see Figure 8) instead of confirming the manufacturer calibration.

Figure 8 show that CairClip NO<sub>2</sub> has a linear response in the range 0 to 150 nmol/mol with a slope of 0.895 and an intercept of 5.469 nmol/mol. The zero value wasn't considered in the linear model even if the standard deviation was the lowest of the all experimentation. The pre-calibration function was established by plotting sensor responses versus reference values measured by the Thermo Environment 42 C analyser at stable conditions 22 °C and 60 % of relative humidity. Each steps lasted for 150 minutes once the condition of NO<sub>2</sub> concentrations, temperature and humidity were reached. The average of the last 60 minutes is plotted.



### Pre-calibration of CairClip\_NO2



**Figure 8: Initial calibration of the sensor at 22°C.**

A standard uncertainty of the lack of fit of the calibration function is estimated using Eq. 1 where  $\rho_{max}$  is the maximum residual of the Using a linear model, the CairClip NO<sub>2</sub> has a maximum residual of 0.4 nmol/mol,  $u(\text{lof})$  is found to be equal to 0.3 nmol/mol. Figure 8 shows that a second order linear regression was not found significant.

$$u^2(\text{lof}) = \rho_{max,LV}^2 / 3 \quad \text{Eq. 1}$$

In all the cases,  $u(\text{lof})$  is small enough to be consistent with the DQO.  $u(\text{lof})$  will not be included into the estimation of the laboratory uncertainty since the standard uncertainty of lack of fit of the experimental design/modelling (see 0) will already include the standard uncertainty of the lack of fit of the calibration function.

In all the following tests the pre-calibration will be applied on request on the manufacturer unless mentioned. Eq. 2 should be used to correct the Rs to a calibrated value.

$$R_{s,cal} = \frac{R_s - 5.47}{0.895} \quad \text{Eq. 2}$$

### 6.3 Repeatability, short-term and long term drifts

The repeatability, short-long term drifts and long term drifts of the sensor are determined by calculating the standard deviation of sensor values for 3 consecutive averaging time periods, three consecutive days and every 2 weeks during three months of use, respectively.

The repeatability figure imposes limits on the accuracy of the calibration and allows estimating the limit of detection and limit of quantification of the sensor. The short term stability is used to set the maximum time between similar tests or the contribution of the short term stability to the



measurement uncertainty. The long term stability is used to set the periodicity of recalibration and maximum time between similar tests. If a trend in the long term drift is identified, it might be included into the model equation or later treated as sources of uncertainty.

### 6.3.1 Repeatability

The repeatability of the sensor's response was determined by calculating the standard deviation of sensor values for 3 consecutive averaging time periods (one hour) when the sensor was measuring at 0 and 100 nmol/mol under repeatability conditions. All parameters suspected to have an effect on the sensor response (test gas, O<sub>3</sub>, temperature and humidity) were kept under control with relative standard deviation of about 2 %. Each measurement lasted for 150 minutes (6.1). The controlled conditions (NO<sub>2</sub>, NO, O<sub>3</sub>, estimated NH<sub>3</sub>, T, RH and P) and sensor responses were averaged over the last hour of test in the exposure chamber. The experiment went on for 150 minutes once stabilisation of exposure conditions was reached. The calculation of the standard deviation of repeatability is carried out using the following equation:

$$s_r = \sqrt{\frac{\sum(R_i - \bar{R})^2}{N - 1}} \quad \text{Eq. 3}$$

Where  $R_i$  is each measurement,  $\bar{R}$  is the mean sensor response and  $N$  the number of measurements.

**Table 8: standard deviation of repeatability figures at 0 and at 100 nmol/mol of NO<sub>2</sub> with mean and standard deviation of parameters**

	NO <sub>2</sub> (nmol/mol)	NO (nmol/mol)	O <sub>3</sub> (nmol/mol)	T (°C)	Rel. Hum. (%)	P (hPa)	CairClip NO2 (nmol/mol)
Mean ± s (N=22)	2.0 ± 0.1	6.2 ± 0.6	-0.4 ± 0.2	21.9 ± 0.1	60.0 ± 0.2	982 ± 7	4.2 ± 0.3
Mean ± s (N=41)	100.0 ± 0.1	8.8 ± 0.4	-0.7 ± 0.5	21.9 ± 0.1	60.0 ± 0.1	993 ± 2	94.8 ± 1.7

The standard deviations of repeatability are given in Table 8. The repeatability of sensor measurements, the likely difference between two measurements made under repeatability conditions, is computed as  $2\sqrt{2}s_r$  where  $s_r$  is the standard deviation of repeatability 100 nmol/mol of NO<sub>2</sub>. For CairClip NO<sub>2</sub>, this gives a repeatability of:

- 4.8 nmol/mol for 100 nmol/mol

The limit of detection and limit of quantification, estimated as  $3s_r$  and  $10s_r$  where  $s_r$  is the standard deviation of repeatability for the blank value:

- 0.9 nmol/mol for the limit of detection
- 3.0 nmol/mol for the limit of quantification

### 6.3.2 Short term drift

For the short term drift, several measurements were carried out at zero, 50 %, 100 % and 150 % of the LV on several consecutive days (between 12 and 36 hours between the first and the second measurements). The averaging of sensor responses at 0, 50, 100 and 150 nmol/mol were calculated over the last hour of stable conditions of NO<sub>2</sub>, temperature and relative humidity while each steps lasted for 150 min long after stabilisation. Stabilisation was defined by the difference between the objective levels and actual measurements of less than 2 nmol/mol for NO<sub>2</sub>, 1°C and 1 % of relative humidity (this is valid throughout this report). The short term stability was estimated using Eq. 4.

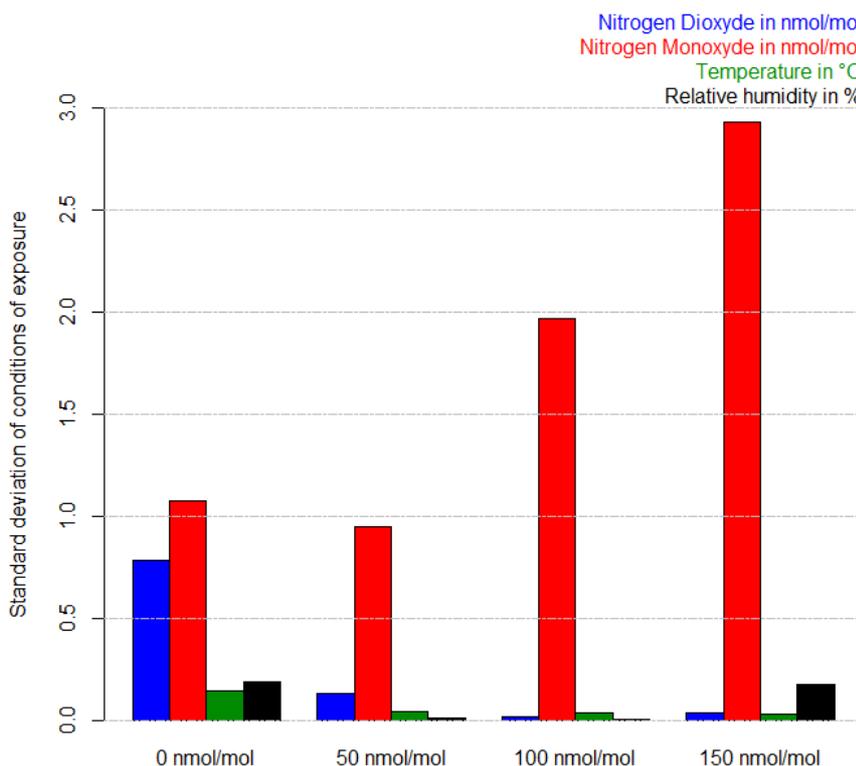


$$D_{ss} = \frac{\sum_1^{N9} |R_{s,after} - R_{s,berfore}|}{N} \quad \text{Eq. 4}$$

where  $R_s$  are the sensor responses (calibrated as in 6.2) at 0, 50, 100 and 150 nmol/nmol at  $t_0$  (before) and 24 hours after (after);  $N$  is the number of pairs of measurements. Experiments for which  $O_3$  was higher than 5 nmol/mol were not considered.

The responses of the  $NO_2$  sensor were transformed following the calibration function established in the pre-calibration experiment (see 6.2). The controlled conditions ( $NO_2$ ,  $NO$ ,  $O_3$ , estimated  $NH_3$ ,  $T$ ,  $RH$  and  $P$ ) and sensor responses were averaged over the last hour of test in the exposure chamber. The experiment went on for 150 minutes once stabilisation of exposure conditions was reached.

During the experiment all parameters suspected to have an effect on the sensor response (test gas, temperature, humidity test values and other possible influencing) were kept under control. The standard deviation of  $NO_2$ ,  $NO$ , temperature and humidity are given in Figure 9 which shows that the maximum standard deviation were found at 0 nmol/mol with 0.8 nmol/mol for  $NO_2$ , 0.2 °C for temperature and 0.2 % for relative humidity.  $NO$  shows a higher standard deviation, especially at 150 nmol/mol of  $NO_2$  with 2.9 nmol/mol due to an internal reactivity of our source of  $NO_2$ .

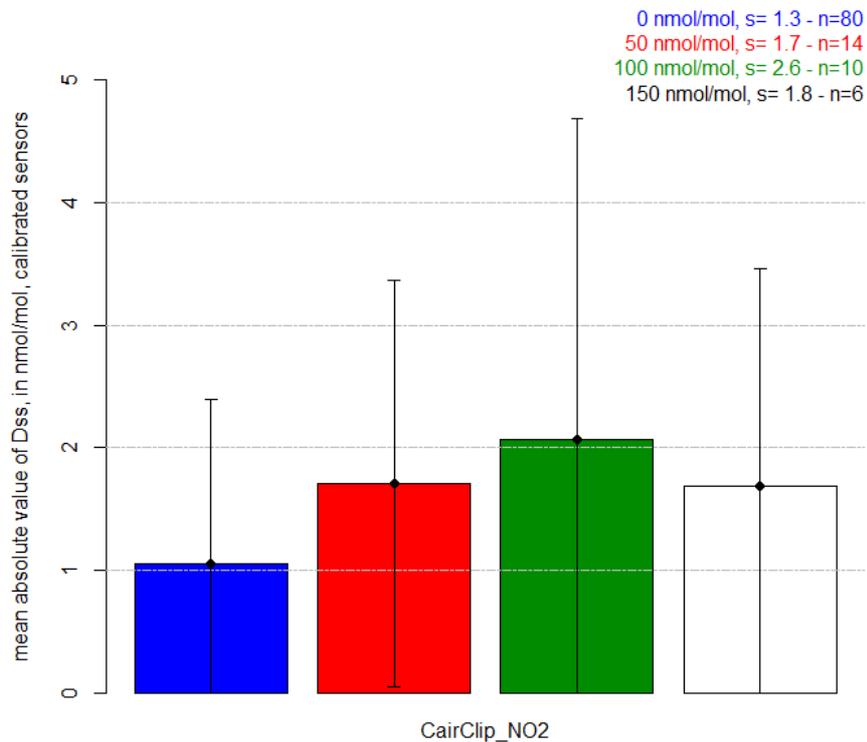


**Figure 9: Stability of  $NO_2$ , temperature and relative humidity in the exposure chamber during the short term drift experiments**

The stability of  $NO_2$ , temperature and humidity was found low enough to use simple standard deviations of  $D_{ss}$  as an indication of the contribution of the short term stability to the measurement uncertainty Eq. 5.

$$u^2(D_{ss}) = \frac{\sum_{i=1}^k (n_i - 1) s_i^2}{\sum_{i=1}^k (n_i - 1)} \quad \text{Eq. 5}$$

The results of these tests for the CairClip  $NO_2$  are given in Figure 10 which gives the number of replicate estimation of  $D_{ss}$  at each concentration level ( $n$ ).



**Figure 10: Short term drift for CairClip NO<sub>2</sub> sensors at 4 NO<sub>2</sub> levels. Each bar represents the absolute mean differences between D<sub>ss</sub> at t and t + 24 hours, the errors bars corresponds to the standard deviation of D<sub>ss</sub>**

Since  $D_{ss}$  looks similar for the 4 levels, the best estimation of the short term drift consists in the average of  $D_{ss}$  at 0, 50, 100 and 150 nmol/mol with uncertainty calculated using Eq. 5 where  $s_i$  represents the standard deviation of the absolute difference between the sensor responses  $|R_{s,after} - R_{s,before}|$ :

- $D_{ss} = 1.6$  nmol/mol and  $u(D_{ss}) = 1.4$  nmol/mol

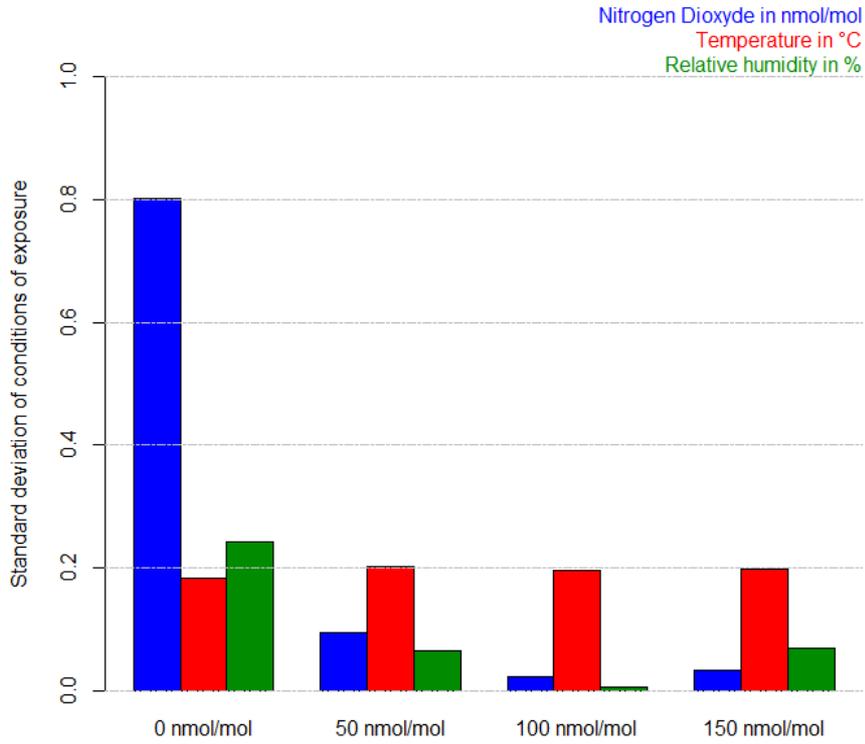
Since for the CairClip NO<sub>2</sub>,  $D_{ss}$  (1.6 nmol/mol) is lower than the repeatability of the sensor responses (see 6.3.1), the maximum duration of experiments can be set last for 48 hours.

### 6.3.3 Long term drift

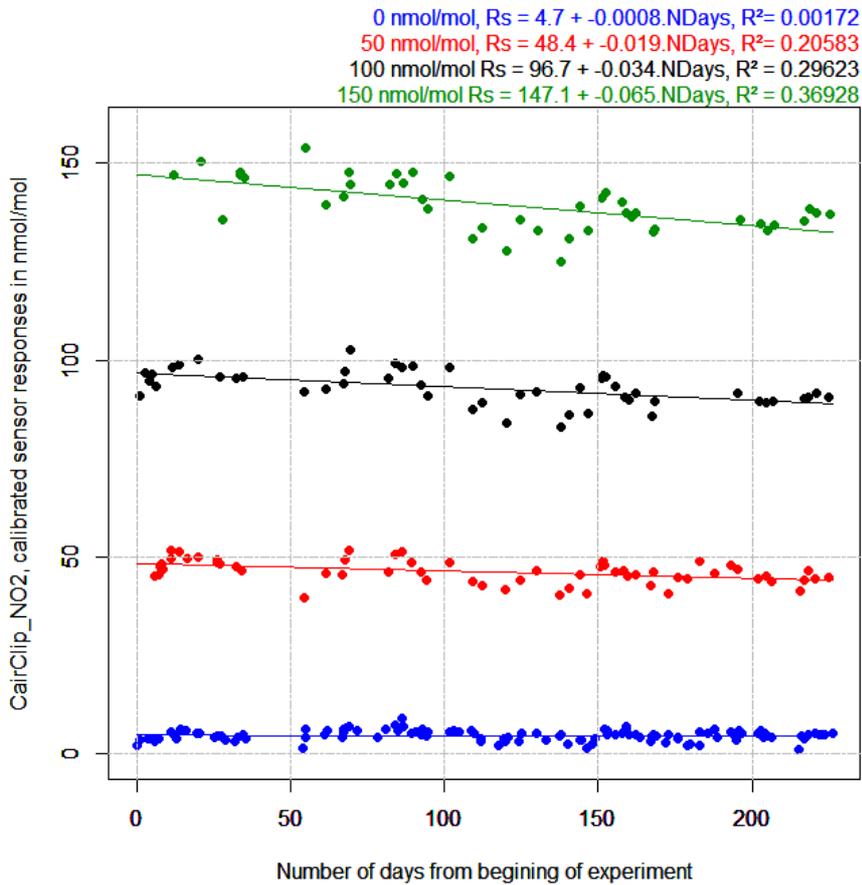
For the long term drift, a similar approach was carried out over a longer time span, measuring about once a week. The long term drift stability was estimated with the same method as the short term stability except that the differences were estimated between  $t_0$  and the end of all laboratory experiment (268 days).

The responses of the NO<sub>2</sub> sensor were transformed following the calibration function established in the pre-calibration experiment (see 6.2). The controlled conditions (NO<sub>2</sub>, NO, O<sub>3</sub>, estimated NH<sub>3</sub>, T, RH and P) and sensor responses were averaged over the last hour of test in the exposure chamber. The experiment went on for 150 minutes once stabilisation of exposure conditions was reached.

During the experiment all parameters suspected to have an effect on the sensor response (test gas, temperature, humidity, test values and other possible influencing) were kept under control.  $D_{ss}$  for NO<sub>2</sub>, temperature and humidity were calculated using Eq. 4. They are given in Figure 11 which shows that the maximum  $D_{ss}$  were found at 0 nmol/mol with 0.8 nmol/mol for NO<sub>2</sub> and 0.3 % for relative humidity. The temperature shows a stable  $D_{ss}$  around 0.2 °C for all steps.



**Figure 11: Stability of NO<sub>2</sub>, temperature and relative humidity in the exposure chamber during the long term drift experiments**



**Figure 12: Long term stability of CairClip NO<sub>2</sub> sensors**



For the CairClip NO<sub>2</sub>, long term drift are given in Figure 12. The slope of the regression line for 0 nmol/mol was not significant suggesting that the sensor does not undergo any drift. For the 3 other levels, the slope increases with the concentration. According to the manufacturer's comment, this increase in slope is proportional to the concentration with a coefficient of 1.8. The drift affects only the slope of the sensor. The manufacturer adds that the long term drift is already taken into account by the sensor during its working time and that such kind of behaviour have been observed with sensors that have not been always switched on. Our experiment showed a maximum drift of 5.8%. Therefore, it is necessary to add the influence of the long term drift in the final design of experiment. The contribution of the long term stability to the sensor measurement can be characterised using a linear model, as shown on Figure 13.

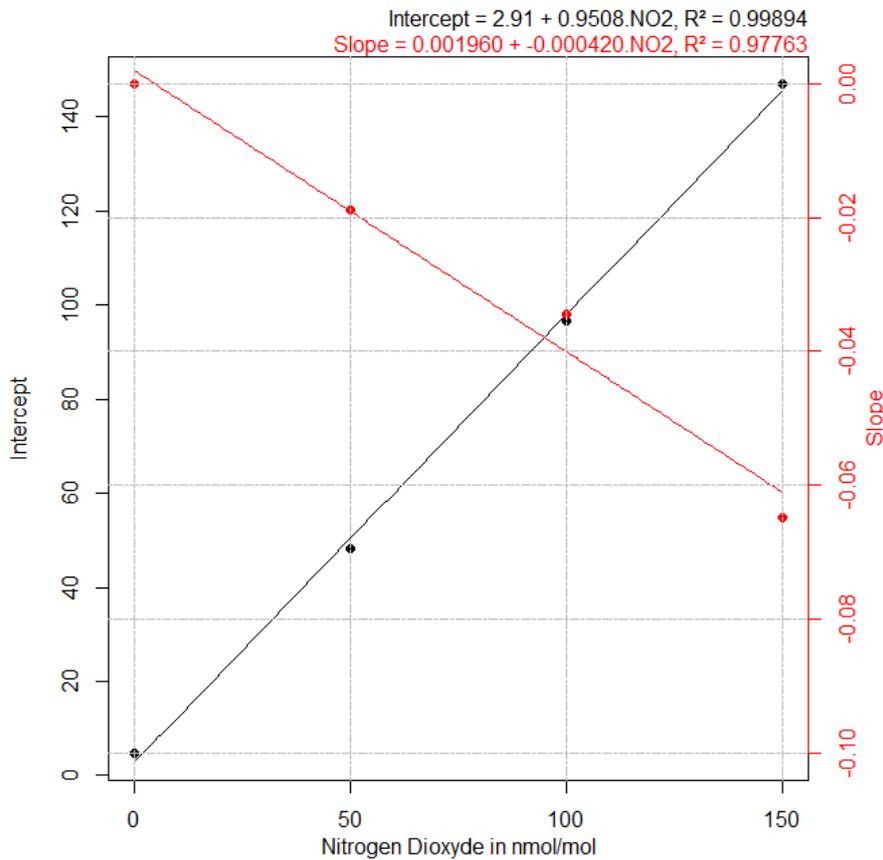


Figure 13: Contribution of the long term stability to the sensor measurement over the levels

To the selected data will be applied a correction function depending of the NO<sub>2</sub> level and the number of days after the beginning of the experiment (Eq. 6):

$$R_{s,corr} = R_s - (2.0 \cdot 10^{-3} - 4.2 \cdot 10^{-4} \cdot NO_2) \cdot NDays \quad \text{Eq. 6}$$

Where  $R_{s,corr}$  is the sensor response corrected for the long term drift,  $R_s$  is the sensor's response,  $NO_2$  is the level of NO<sub>2</sub> and  $NDays$  is the time difference from the initial calibration in days.

As the stability of NO<sub>2</sub>, temperature and humidity was found low enough (see Figure 11) and assuming a rectangular distribution of the sensor response between the initial value and the final value, the contribution of the long term drift to the measurement uncertainty can be estimated using Eq. 5 with which  $u(D_{ls})$  was found equal to 3.6 nmol/mol. Eq. 7 can be used to set a periodicity of re-calibration based on the contribution of the total drift and the residuals of models  $\epsilon$ . For example, the highest contribution is found after 220 days at the 150 nmol/mol of NO<sub>2</sub> level and



is equal to 4.0 nmol/mol. If the model equation is applied, the uncertainty only consists of only the residuals of the regression lines.

$$u^2(D_{ls}) = \frac{(0.00042 NO_2 NDays)^2}{12} + \varepsilon^2 \quad \text{Eq. 7}$$

## 7 Interference testing

### 7.1 Gaseous compounds

Sensors generally suffer from cross sensibility to other gaseous species that may have a positive or negative effect on the sensor response. Further to the literature review of all NO<sub>2</sub> sensors, and the technical feasibility of testing such gas, the compounds presented in Table 9 were selected for the interference testing. The level of the interfering compounds were selected taking into account either the average level of the gaseous interference in the selected micro-environment (see deliverable D4.3.1 of MACPoll project, "Selection of suitable micro-sensors for validation"), its maximum value or another more convenient level, which are to be expected to be present in rural ambient air at background sites.

**Table 9: Interference testing conditions**

	O <sub>3</sub> , nmol/mol		NO, nmol/mol		SO <sub>2</sub> , nmol/mol		CO, μmol/mol		CO <sub>2</sub> , μmol/mol		NH <sub>3</sub> , nmol/mol	
Level	Low	High(int)	Low	High(int)	Low	High(int)	Low	High(int)	Low	High(int)	Low	High(int)
Interfering compound	0	50	0	100	0	~ 25	0	~ 8000	Purified air	400	0	± 85
Level	Low	High(c <sub>t</sub> )	Low	High(c <sub>t</sub> )	Low	High(c <sub>t</sub> )	Low	High(c <sub>t</sub> )	Low	High(c <sub>t</sub> )	Low	High(c <sub>t</sub> )
NO <sub>2</sub> , nmol/mol	0	50	0	50	0	50	0	50	0	50	0	50
Temperature, °C	22		22		22		22		22		22	
Relative humidity, %	60		60		60		60		60		60	

The influence of each gaseous interfering compound was determined separately with all influencing variables kept constant during tests. The tests were carried out at the mean temperature and relative humidity and in absence of other interference. After adjustment of the analyser (NO<sub>2</sub> and one for interfering compound apart for NH<sub>3</sub> for which we relied on gravimetric values), the full procedure including four steps was carried out:

- the sensor was exposed to a low level of NO<sub>2</sub> followed by a high level either with or without interfering compound: sensor's responses will be named Y<sub>0</sub> and c<sub>t</sub> respectively. The level of NO<sub>2</sub> was taken equal to 50 nmol/mol, corresponding to the LAT;
- this scheme was then repeated at a high level of interfering compound (int), first without NO<sub>2</sub> and finally with a mixture of NO<sub>2</sub> and interferent gas: sensor's responses will be named Y<sub>z</sub> and Y<sub>ct</sub> respectively.

The mixtures were supplied for a time period equal to one independent measurement, and, following this, three individual measurements will then be taken of the sensor responses. The level of the mixtures of the test gas and gaseous interfering compounds were measured using reference methods of measurement with a low uncertainty of measurements (uncertainty of less than 5 %) traceable to (inter)nationally accepted standards (see 5.3).

The influence quantity of an interfering compound at zero (Y<sub>int,z</sub>) and at level ct (Y<sub>int,ct</sub>) are calculated using Eq. 8 and Eq. 9. Eq. 10 gives the influence quantity of the interferent Y<sub>int,LAT</sub>.

$$Y_{int,z} = Y_z - Y_0 \quad \text{Eq. 8}$$



$$Y_{int,ct} = Y_{ct} - c_t \quad \text{Eq. 9}$$

$$Y_{int,LAT} = (Y_{int,ct} - Y_{int,z}) \frac{LAT}{c_t} + Y_{int,z} \quad \text{Eq. 10}$$

Usually air pollutants distributions approach a log normal distribution, with the exception of O<sub>3</sub> distribution. Table 3 shows that the distribution for O<sub>3</sub> can be approximated using a rectangular distribution. The standard uncertainty associated to the interferent,  $u(int)$ , can be calculated according to Eq. 11 where  $C_{imax}$  is the maximum concentration of interfering compound present in the micro environment,  $C_{imin}$  is its minimum value, M is the population median and DoE is the level of the gaseous interfering compound during the laboratory experiments used to establish a sensor model. In this equation it is supposed that M, the mode of the distribution is never corrected and it is accounted as a bias in the equation.

$$u(int) = \left| \frac{Y_{int,LAT}}{int} \right| \cdot \sqrt{(M - DoE)^2 + \frac{(C_{imax} - C_{imin})^2}{12}} \quad \text{Eq. 11}$$

$$u(int) = \left| \frac{Y_{int,z}}{int} \right| \cdot \sqrt{(M - DoE)^2 + \frac{C_{imax}^2}{12}} \text{ or} \quad \text{Eq. 12}$$

$$u(int) = \left| \frac{Y_{int,ct}}{int} \right| \cdot \sqrt{(M - DoE)^2 + \frac{C_{imax}^2}{12}}$$

When it is not possible to estimate  $Y_{int,z}$  and/or  $Y_{int,ct}$ , for example the interference of NO on O<sub>3</sub> cannot be estimated because of the oxidation of NO in NO<sub>2</sub> or when  $Y_{int,z}$  was sometimes doubtful because of the higher variability of the sensor at 0 nmol/mol of NO<sub>2</sub> level. In this case, the simple approach given in paragraph 8.5.6 of ISO 14956:2002 based on the determination of the sensitivity coefficient b (difference of sensor responses divided by the extent of the interfering compound level at one level) was applied (Eq. 12).

The table hereafter gives a summary of the effect of all tested interfering compounds. For ozone two periods have been taken into account: the first exposure of the sensor to 50nmol/mol of O<sub>3</sub> was made at the beginning of the experiment, when the filter was the most efficient. The second was done after the whole set of experiment. It shows that only O<sub>3</sub>, during the second exposure, had the most significant effect on the NO<sub>2</sub> CairClip sensor, the uncertainty for the rest of the compounds being within the repeatability of the measurements.



**Table 10: Summary of results of interference testing for all interfering compounds, the units are the one of the interfering compounds except for the sensitivity coefficient (*b*) which is in nmol/mol per nmol/mol (or  $\mu\text{mol/mol}$  for CO) of the interfering compounds**

Interfering compounds	$Y_0$	$Y_z$	$c_t$	$Y_{ct}$	int	$Y_{int,z}$	$Y_{int,ct}$	$Y_{int,LAT}$	$C_{imin}$	$C_{imax}$	<i>b</i>	$u(int)$	
$O_3$ , nmol/mol	1 <sup>st</sup>	3.0	/	46.3	45.8	51.0	/	-0.5	-0.5	0	60	-0.010	0.32
	2 <sup>nd</sup>	2.3	23.2	44.3	71.3	50.9	20.9	27.0	27.8			0.531	17.2
NO, nmol/mol	4.8	5.0	40.6	39.9	100.0	0.2	-0.7	-0.9	0	80	-0.007	0.31	
CO, $\mu\text{mol/mol}$	4.2	2.0	44.8	41.7	8.17	-2.2	-3.1	-3.2	0	2	-0.001	0.44	
CO <sub>2</sub> , $\mu\text{mol/mol}$	4.5	4.1	41.4	45.0	-377.0	-0.4	3.6	4.4	350	450	0.009	0.26	
SO <sub>2</sub> , nmol/mol	4.4	3.5	45.9	45.6	22.8	-0.9	-0.3	-0.2	0	10	-0.013	0.07	
NH <sub>3</sub> , nmol/mol	5.8	3.2	48.0	45.3	~ 85	-2.5	-2.8	-2.9	0	90	-0.032	1.68	

### 7.1.1 Ozone – $O_3$

In this interference test,  $O_3$  was generated using two UV generators (see 5.2). The results of the tests are given in Table 11. The responses of the CairClip  $NO_2$  sensor were transformed using the calibration function established in the pre-calibration experiment (see 6.2). The controlled conditions ( $NO_2$ , NO,  $O_3$ , T, RH and P) and sensor responses were averaged over the last hour of experiment. The experiment went on for 150 minutes once stabilisation of exposure conditions was reached. The interference effect and contribution to the measurement uncertainty are given in Table 10 together with the maximum value and  $C_{imax}$  and  $C_{imin}$  the maximum and minimum values of the interferences present in the ambient gas in the selected micro-environment.

**Table 11: Test conditions for the  $O_3$  interference testing conditions and sensors responses for the CairClip  $NO_2$  sensors**

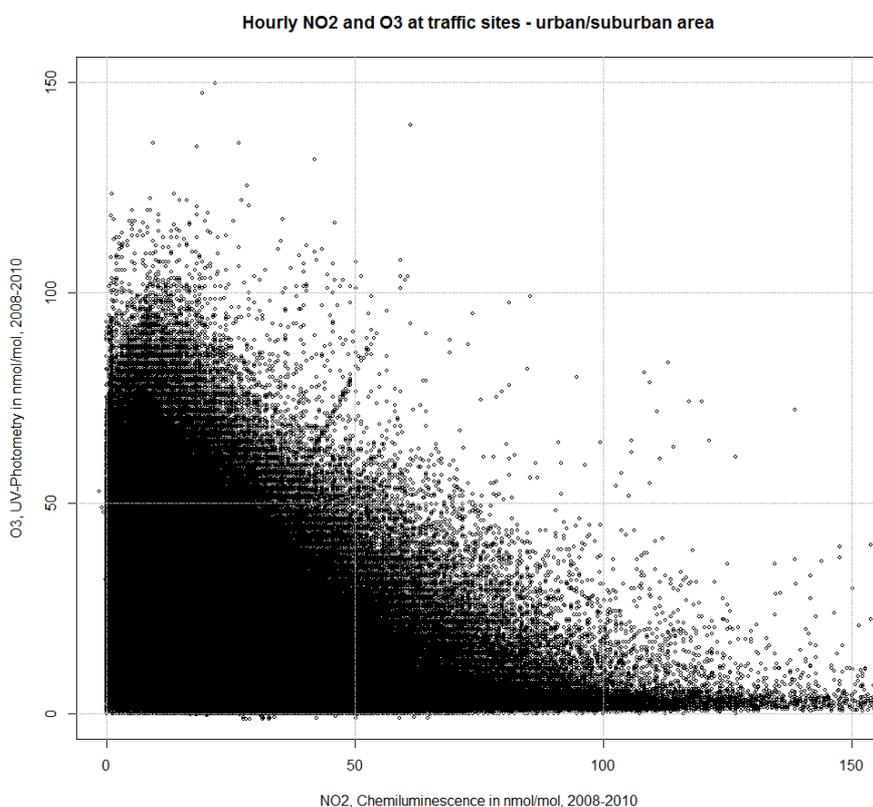
	CairClip $NO_2$ , mol/mol	$NO_2$ , nmol/mol	NO, nmol/mol	$O_3$ , nmol/mol	T, °C	RH, %	P, hPa
First calculation based the first exposure to ozone							
$Y_0$	$3.0 \pm 0.8$	$0.9 \pm 0.2$	$1.9 \pm 0.1$	$0.0 \pm 0.1$	$21.9 \pm 0.1$	$60.0 \pm 0.1$	$998 \pm 0.1$
$c_t$	$45.6 \pm 1.1$	$50.0 \pm 0.2$	$5.0 \pm 0.1$	$0.0 \pm 0.1$	$22.0 \pm 0.1$	$60.0 \pm 0.1$	$987 \pm 0.1$
$Y_{ct}$	$45.1 \pm 1.4$	$49.9 \pm 0.2$	$1.7 \pm 0.1$	$51.0 \pm 0.3$	$21.9 \pm 0.1$	$60.0 \pm 0.1$	$987 \pm 0.5$
Second calculation did after the whole set of experiment							
$Y_0$	$2.3 \pm 1.1$	$1.2 \pm 0.2$	$1.9 \pm 0.1$	$0.5 \pm 0.2$	$21.9 \pm 0.1$	$60.0 \pm 0.1$	$993 \pm 0.1$
$c_t$	$44.3 \pm 1.0$	$50.0 \pm 0.4$	$6.1 \pm 0.2$	$0.4 \pm 0.2$	$22.0 \pm 0.1$	$60.0 \pm 0.1$	$991 \pm 0.1$
$Y_z$	$23.2 \pm 1.4$	$1.2 \pm 0.2$	$1.5 \pm 0.1$	$50.9 \pm 0.2$	$22.0 \pm 0.1$	$60.0 \pm 0.1$	$993 \pm 0.1$
$Y_{ct}$	$71.3 \pm 1.2$	$50.0 \pm 0.3$	$1.9 \pm 0.1$	$50.9 \pm 0.4$	$22.0 \pm 0.1$	$60.0 \pm 0.1$	$991 \pm 0.1$

During the first test, the CairClip  $NO_2$  didn't show any cross sensitivity to  $O_3$  as shown in Table 11 in which the sensor response stay unchanged whereas the increase of  $O_3$ . During the second exposure carried out after the whole set of experiment, including exposure to  $O_3$ , the sensor show a highest response when exposed to a mixture of  $NO_2$  and  $O_3$ . This is due to the decrease of the efficiency of the  $O_3$  filter. To evaluate the interference effect, it was decided to use the result of the second exposure.

Taking into account the second test,  $O_3$  is the gaseous components with the higher cross-sensitivity for the CairClip  $NO_2$ . It is important to remember that in ambient air,  $NO_2$  and  $O_3$  are correlated and therefore all couple of values do not have the same probability. In fact, Figure 14



shows the scatter plot between hourly NO<sub>2</sub> and O<sub>3</sub> for all traffic sites in urban/suburban areas between 2007-2010, for the following countries: BG, CH, CY, DE, DK, ES, FR, GB, GR, HU, IE, IT, LU, PL, RO, SE, SI. This graph shows a correlation coefficient of  $r = -0.52$ .



**Figure 14: Relationship between hourly NO<sub>2</sub> and O<sub>3</sub>, all traffic sites – urban/suburban areas in 2007-2010, for the following countries BG, CH, CY, DE, DK, ES, FR, GB, GR, HU, IE, IT, LU, PL, RO, SE, SI**

### 7.1.2 Nitrogen monoxide – NO

In this interference test, NO was generated using a highly concentrated NO cylinders (Air Liquide 9468D  $62.3 \pm 1.2 \mu\text{mol/mol}$ ) diluted with the zero air generator of the exposure chamber and controlled by MFC (0-100 mL/min). The results of the tests are given in Table 12. The responses of the CairClip NO<sub>2</sub> sensor were transformed following the calibration function established in the pre-calibration experiment (see 6.2). The controlled conditions (NO<sub>2</sub>, NO, O<sub>3</sub>, T, RH and P) and sensor responses were averaged over the last hour of test in the exposure chamber. The interference effect and contribution to the measurement uncertainty are given in Table 10 together with the maximum value and  $C_{\text{imax}}$  and  $C_{\text{imin}}$  of the selected micro-environment.

**Table 12: Test conditions for the NO interference testing conditions and sensors responses for the CairClip NO<sub>2</sub> sensors**

	CairClip NO <sub>2</sub> , mol/mol	NO <sub>2</sub> , nmol/mol	NO, nmol/mol	O <sub>3</sub> , nmol/mol	T, °C	RH, %	P, hPa
$Y_0$	$4.8 \pm 1.1$	$3.2 \pm 0.2$	$2.8 \pm 0.1$	$0.5 \pm 0.2$	$21.9 \pm 0.1$	$60.0 \pm 0.1$	$1000 \pm 0.1$
$c_t$	$40.6 \pm 1.4$	$50.0 \pm 0.3$	$4.1 \pm 0.1$	$0.5 \pm 0.2$	$21.9 \pm 0.1$	$60.0 \pm 0.1$	$1001 \pm 0.1$
$Y_z$	$5.0 \pm 1.2$	$6.0 \pm 0.5$	$100.0 \pm 0.3$	$0.2 \pm 0.2$	$22.0 \pm 0.1$	$60.0 \pm 0.1$	$998 \pm 0.1$
$Y_{ct}$	$39.9 \pm 1.3$	$50.0 \pm 0.5$	$100.0 \pm 0.4$	$0.1 \pm 0.2$	$22.0 \pm 0.1$	$60.0 \pm 0.1$	$993 \pm 0.1$

The results of this experiment showed that NO has no significant influence on CairClip NO<sub>2</sub> sensor.



### 7.1.3 Carbon monoxide – CO

In this interference testing, CO was generated using a highly concentrated CO cylinder (1998±40 µmol/mol, Air Liquide-Messer Griesheim 1898G) diluted with zero air of the exposure chamber and controlled by the MFC (0-100 mL/min). These tests were carried out at a high level of CO corresponding to the CO limit value of the European air quality directive (8 µmol/mol).

The results of the tests are given in Table 13. The responses of the CairClip NO<sub>2</sub> sensor were transformed following the calibration function established in the pre-calibration experiment (see 6.2). The controlled conditions (NO<sub>2</sub>, NO, O<sub>3</sub>, CO, T, RH and P) and sensor responses were averaged over the last hour of test in the exposure chamber. The interference effect and contribution to the measurement uncertainty are given in Table 10 together with the maximum value and C<sub>imax</sub> and C<sub>imin</sub> of the selected micro-environment.

**Table 13: Test conditions for the CO interference testing conditions and sensors responses for the CairClip NO<sub>2</sub> sensors**

	CairClip NO <sub>2</sub> , mol/mol	NO <sub>2</sub> , nmol/mol	NO, nmol/mol	O <sub>3</sub> , nmol/mol	CO, nmol/mol	T, °C	RH, %	P, hPa
Y <sub>0</sub>	4.2 ± 1.4	1.5 ± 0.1	2.1 ± 0.1	0.5 ± 0.2	2961 ± 9.7	22.0 ± 0.1	60.0 ± 0.1	993 ± 0.1
c <sub>t</sub>	44.8 ± 1.2	50.0 ± 0.3	3.5 ± 0.1	0.7 ± 0.4	2968 ± 6.1	21.9 ± 0.1	60.0 ± 0.1	990 ± 0.1
Y <sub>Z</sub>	2.0 ± 0.9	0.7 ± 0.2	11.3 ± 0.4	0.1 ± 0.2	8153 ± 13.2	22.0 ± 0.1	60.0 ± 0.1	994 ± 0.1
Y <sub>ct</sub>	41.7 ± 1.2	50.0 ± 0.3	11.8 ± 0.3	0.3 ± 0.2	8182 ± 85.1	21.9 ± 0.1	60.0 ± 0.1	992 ± 0.1

The results of this experiment seem to show that CO had no influence on CairClip NO<sub>2</sub> sensor, even if the sensor response tends to diminish. It is likely that this effect is caused by a decrease of NO<sub>2</sub> (0.8 nmol/mol) or by a sensor drift at zero level of about 2 nmol/mol rather than a CO effect. But *u(int)*, showed in Table 10, is much smaller than the repeatability so it will not be taking into account as interfering parameters in the full factorial design of experiment.

### 7.1.4 Carbon dioxide – CO<sub>2</sub>

The interference tests were carried out at the mean temperature and relative humidity and in the absence of any other variation from other known interfering compounds. In this interference testing, two experiments were carried out: one with air dilution of the zero air of the exposure chamber including of the CO<sub>2</sub> and one using zero air filtered for CO<sub>2</sub>. A FTIR Purge Gas Generator (85 lpm, Parker-Balston, USA) was used to filter CO<sub>2</sub> down to less than 1 µmol/mol). The differences of sensor response during the two tests were then observed.

The results of the tests are given in Table 14. The responses of the CairClip NO<sub>2</sub> sensor were transformed following the calibration function established in the pre-calibration experiment (see 6.2). The controlled conditions (NO<sub>2</sub>, NO, O<sub>3</sub>, CO<sub>2</sub>, T, RH and P) and sensor responses were averaged over the last hour of test in the exposure chamber. The interference effect and contribution to the measurement uncertainty are given in Table 10 together with the maximum value and C<sub>imax</sub> and C<sub>imin</sub> of the micro-environment.

**Table 14: Test conditions for the CO<sub>2</sub> interference testing conditions and sensors responses for the CairClip NO<sub>2</sub> sensors**

	CairClip NO <sub>2</sub> , mol/mol	NO <sub>2</sub> , nmol/mol	NO, nmol/mol	O <sub>3</sub> , nmol/mol	CO <sub>2</sub> , nmol/mol	T, °C	RH, %	P, hPa
Y <sub>0</sub>	4.5 ± 1.4	1.6 ± 0.1	2.2 ± 0.1	1.0 ± 0.3	398.9 ± 3.9	22.0 ± 0.1	60.0 ± 0.1	989 ± 0.2
c <sub>t</sub>	41.4 ± 1.4	50.0 ± 0.2	3.3 ± 0.1	1.0 ± 0.4	396.5 ± 3.6	22.0 ± 0.1	60.0 ± 0.1	989 ± 0.1
Y <sub>Z</sub>	4.1 ± 1.1	1.3 ± 0.1	2.1 ± 0.1	1.0 ± 0.2	16.8 ± 0.2	22.0 ± 0.1	60.0 ± 0.1	989 ± 0.1
Y <sub>ct</sub>	45.0 ± 1.4	50.0 ± 0.2	3.4 ± 0.1	1.0 ± 0.2	24.7 ± 0.2	22.0 ± 0.1	60.0 ± 0.1	989 ± 0.2

The results of this experiment showed that CO<sub>2</sub> had no influence on CairClip NO<sub>2</sub> sensor.



### 7.1.5 Sulphur dioxide – SO<sub>2</sub>

In this interference testing, SO<sub>2</sub> was generated using permeation tubes from Calibrage (FR). These tests were carried out at a low level of SO<sub>2</sub> higher than the maximum value observed in traffic station and urban/suburban areas. To assure the maximum stability of SO<sub>2</sub> level, the total flow inside the exposition chamber was fixed during all experiment.

The results of the tests are given in Table 15. The responses of the CairClip NO<sub>2</sub> sensor were transformed following the calibration function established in the pre-calibration experiment (see 6.2). The controlled conditions (NO<sub>2</sub>, NO, O<sub>3</sub>, SO<sub>2</sub>, T, RH and P) and sensor responses were averaged over the last hour of test in the exposure chamber. The interference effect and contribution to the measurement uncertainty are given in Table 10 together with the maximum value and C<sub>imax</sub> and C<sub>imin</sub> of micro-environment.

**Table 15: Test conditions for the SO<sub>2</sub> interference testing conditions and sensors responses for the CairClip NO<sub>2</sub> sensors**

	CairClip NO <sub>2</sub> , mol/mol	NO <sub>2</sub> , nmol/mol	NO, nmol/mol	O <sub>3</sub> , nmol/mol	SO <sub>2</sub> , nmol/mol	T, °C	RH, %	P, hPa
Y <sub>0</sub>	4.4 ± 1.3	1.0 ± 0.1	1.8 ± 0.1	1.0 ± 0.3	0.0 ± 0.5	22.0 ± 0.1	60.0 ± 0.1	987 ± 0.1
c <sub>t</sub>	45.9 ± 1.1	50.0 ± 0.2	3.1 ± 0.1	1.0 ± 0.4	0.0 ± 0.5	21.9 ± 0.1	60.0 ± 0.1	984 ± 0.1
Y <sub>z</sub>	3.5 ± 1.1	1.9 ± 0.5	2.2 ± 0.1	0.0 ± 0.2	17.5 ± 1.6	21.9 ± 0.1	60.0 ± 0.1	987 ± 0.1
Y <sub>ct</sub>	45.6 ± 1.2	50.0 ± 0.4	5.5 ± 0.1	0.0 ± 0.3	28.0 ± 0.6	22.0 ± 0.1	60.0 ± 0.1	1003 ± 0.1

The results of this experiment showed that SO<sub>2</sub> had no significant influence on the CairClip NO<sub>2</sub> sensor.

### 7.1.6 Ammonia – NH<sub>3</sub>

In this interference test, NH<sub>3</sub> was generated using permeation tubes from AeroLaser (DE). To assure the maximum stability of NH<sub>3</sub> level and as we cannot measure the NH<sub>3</sub> concentration during the all experiment, the total flow inside the exposition chamber was kept constant. NH<sub>3</sub> was later estimated based on gravimetric values and flow measurements.

The tests were carried out at the mean temperature and relative humidity and in absence of other interfering compounds. Two steps of experiment were carried out: first, the sensor was exposed to a mixture of zero air and NO<sub>2</sub> and second, adding a constant concentration of NH<sub>3</sub>.

The results of the tests are given in Table 15. The responses of the CairClip NO<sub>2</sub> sensor were transformed following the calibration function established in the pre-calibration experiment (see 6.2). The controlled conditions (NO<sub>2</sub>, NO, O<sub>3</sub>, estimated NH<sub>3</sub>, T, RH and P) were averaged over the last hour of test in the exposure chamber. The interference effect and contribution to the measurement uncertainty are given in Table 10 together with the maximum value and C<sub>imax</sub> and C<sub>imin</sub> of the selected micro-environment.

**Table 16: Test conditions for the NH<sub>3</sub> interference testing conditions and sensors responses for the CairClip NO<sub>2</sub> sensors**

	CairClip NO <sub>2</sub> , mol/mol	NO <sub>2</sub> , nmol/mol	NO, nmol/mol	O <sub>3</sub> , nmol/mol	NH <sub>3</sub> , nmol/mol	T, °C	RH, %	P, hPa
Y <sub>0</sub>	5.8 ± 1.2	2.0 ± 0.1	2.3 ± 0.1	1.0 ± 0.2	0	22.0 ± 0.1	60.0 ± 0.1	1000 ± 0.1
c <sub>t</sub>	48.0 ± 1.3	50.0 ± 0.2	3.1 ± 0.1	1.0 ± 0.2	0	22.0 ± 0.1	60.0 ± 0.1	997 ± 0.1
Y <sub>z</sub>	3.2 ± 1.4	0.9 ± 0.1	2.9 ± 0.1	0.0 ± 0.2	~ 85	22.0 ± 0.1	60.0 ± 0.1	994 ± 0.1
Y <sub>ct</sub>	45.3 ± 1.5	50.0 ± 0.2	4.7 ± 0.1	0.0 ± 0.2	~ 85	22.0 ± 0.1	60.0 ± 0.1	993 ± 0.1

The results of this experiment showed that NH<sub>3</sub> had little influence on the CairClip NO<sub>2</sub> sensor as the response tends to diminish. Table 10 shows that *u(int)* is lower than the repeatability therefore it will not be taken into account as interfering parameters in the full factorial design of experiment.



## 7.2 Air Matrix

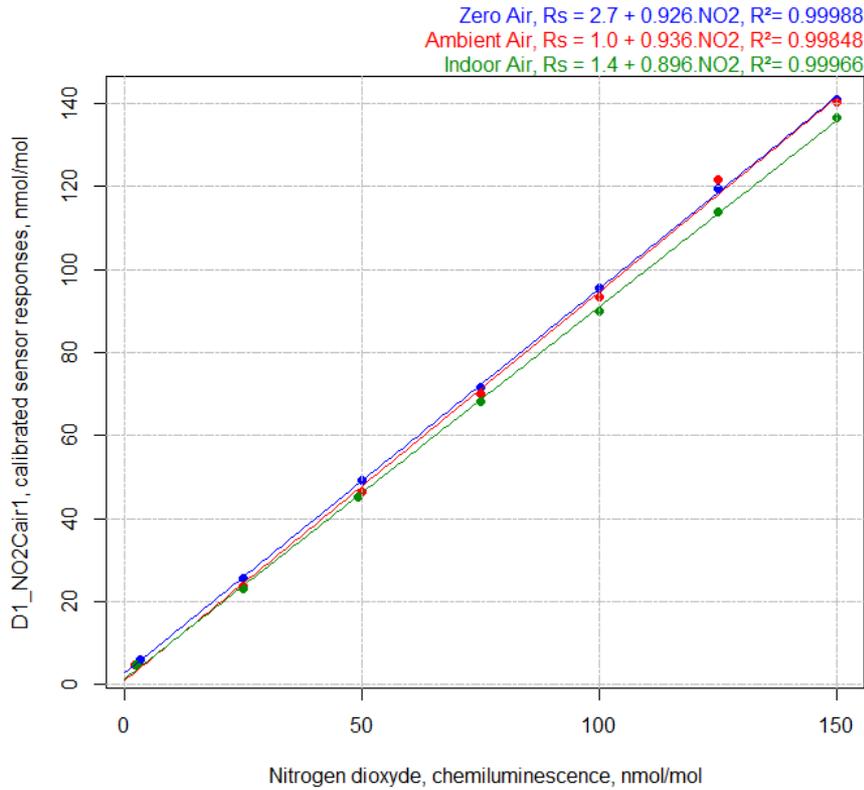
To evaluate the influence of the air matrix on the sensor values, tests were performed at pre-calibration levels using 3 different air matrixes: zero air (filtered air), a mixture of zero air and ambient air and a mixture of zero air and indoor air. For the ambient air and indoor air experiments a constant air flow of outside and inside our building was injected in the exposure chamber. The air was sampled using a low volume samplers (LVS, Derenda 3.1 samplers - G) also used to filter the bulk air from particulate matter with a European PM<sub>10</sub> sampling head. The air was sampled just outside our laboratory (near a small parking lot) for the ambient air experiment and inside our laboratory for the indoor air experiment. The LVS sampling inlets was cleaned before sampling. The flow of the LVS was adjusted to 1 m<sup>3</sup>/hr (around 16 l/min) and regulated to 12 l/min using a cross pattern needle valve. All parameters suspected to have an effect on the sensor response (test gas, O<sub>3</sub>, temperature and humidity) were kept under control with relative standard deviation of about 2 % (see Table 17).

The responses of the NO<sub>2</sub> sensor were transformed following the calibration function established in the pre-calibration experiment (see 6.2). The controlled conditions (NO<sub>2</sub>, NO, O<sub>3</sub>, estimated NH<sub>3</sub>, T, RH and P) and sensor responses were averaged over the last hour of test in the exposure chamber. The experiment went on for 150 minutes once stabilisation of exposure conditions was reached.

**Table 17 : Experiments conditions for Air Matrix interference experiments**

CairClip NO <sub>2</sub> , mol/mol	NO <sub>2</sub> Test levels, nmol/mol	NO, nmol/mol	T, °C	RH, %	Pressure, hPa	Zero Air, l/min	Comments
119.4 ± 1.5	125.0 ± 0.4	3.9 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	993.2 ± 0.1	9.4	Filtered air
49.1 ± 1.7	50.0 ± 0.3	3.2 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	993.4 ± 0.1	8.8	
95.5 ± 1.1	100.0 ± 0.4	3.7 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	933.6 ± 0.1	9.3	
6.0 ± 1.0	3.2 ± 0.2	2.5 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	997.1 ± 0.1	11.1	
71.5 ± 1.2	75.0 ± 0.4	3.1 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	995.8 ± 0.2	12.9	
25.6 ± 1.3	25.0 ± 0.2	2.6 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	993.2 ± 0.2	11.8	
141.0 ± 1.0	150.0 ± 0.5	4.1 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	993.6 ± 0.1	9.1	
121.6 ± 1.4	125.0 ± 0.5	3.4 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	996.8 ± 0.1	2.4	Ambient air ~ 12 l/min
46.3 ± 1.3	50.0 ± 0.3	4.3 ± 0.1	21.9 ± 0.1	60.0 ± 0.1	997.6 ± 0.1	2.8	
93.4 ± 1.4	100.0 ± 0.4	5.0 ± 0.1	21.9 ± 0.1	60.0 ± 0.1	996.9 ± 0.1	2.4	
4.7 ± 0.8	2.1 ± 0.2	2.7 ± 0.2	21.9 ± 0.1	58.8 ± 0.3	1001.8 ± 0.1	19.8	
69.9 ± 0.9	75.0 ± 0.4	4.1 ± 0.1	21.9 ± 0.1	60.0 ± 0.1	996. ± 0.17	6.4	
23.9 ± 1.2	25.0 ± 0.3	3.4 ± 0.1	21.9 ± 0.1	60.0 ± 0.1	997.2 ± 0.1	6.6	
140.3 ± 1.3	150.0 ± 0.6	4.0 ± 0.1	22.0 ± 0.1	60.5 ± 0.2	994.9 ± 0.3	3.0	
113.9 ± 1.4	125.0 ± 0.5	5.2 ± 0.2	21.9 ± 0.1	60.0 ± 0.1	1001.1 ± 0.1	2.6	Indoor air ~ 12 l/min
45.2 ± 1.4	49.3 ± 0.5	4.6 ± 0.1	21.9 ± 0.1	60.0 ± 0.1	1000.8 ± 0.1	2.7	
90.0 ± 1.6	100.0 ± 0.5	5.1 ± 0.1	21.9 ± 0.1	60.0 ± 0.1	1000.9 ± 0.1	3.4	
4.9 ± 1.0	2.3 ± 0.2	2.9 ± 0.1	22.0 ± 0.1	60.0 ± 0.3	1002.7 ± 0.4	17.0	
68.1 ± 1.2	75.0 ± 0.3	4.3 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	997.7 ± 0.1	4.9	
22.9 ± 1.4	25.0 ± 0.2	3.6 ± 0.1	21.9 ± 0.1	60.0 ± 0.1	998.3 ± 0.1	5.3	
136.4 ± 1.0	150.0 ± 0.5	5.4 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	997.3 ± 0.1	3.2	

Figure 15 presents the sensor responses to the 7 levels under the 3 air matrix.



**Figure 15: Effect of air matrix on ClairClip NO<sub>2</sub> sensor**

The uncertainty contribution  $u(D_{matrix})$  was calculated by first fitting a linear model (Eq. 13) for each type of dilution air: zero air, ambient air and indoor air (see Figure 15). In the equations,  $R_s$  is the response of the sensor, calibrated according to the pre-calibration equation Eq. 2,  $a$  and  $b$  are the parameters of the linear model and  $c_c$  the reference measurements of the test gas.

$$R_s = a + b \cdot c_c \quad \text{Eq. 13}$$

$$R_s = 2.7 + 0.926 NO_2, R^2 = 0.99988 \quad \text{Zero Air}$$

$$R_s = 1.0 + 0.936 NO_2, R^2 = 0.99848 \quad \text{Ambient Air}$$

$$R_s = 1.4 + 0.896 NO_2, R^2 = 0.99966 \quad \text{Indoor Air}$$

Then Eq. 14 allows determining  $c_r$ , the corrected sensor response calculated using Eq. 13.

$$c_r = \frac{R_s - a}{b} \quad \text{Eq. 14}$$

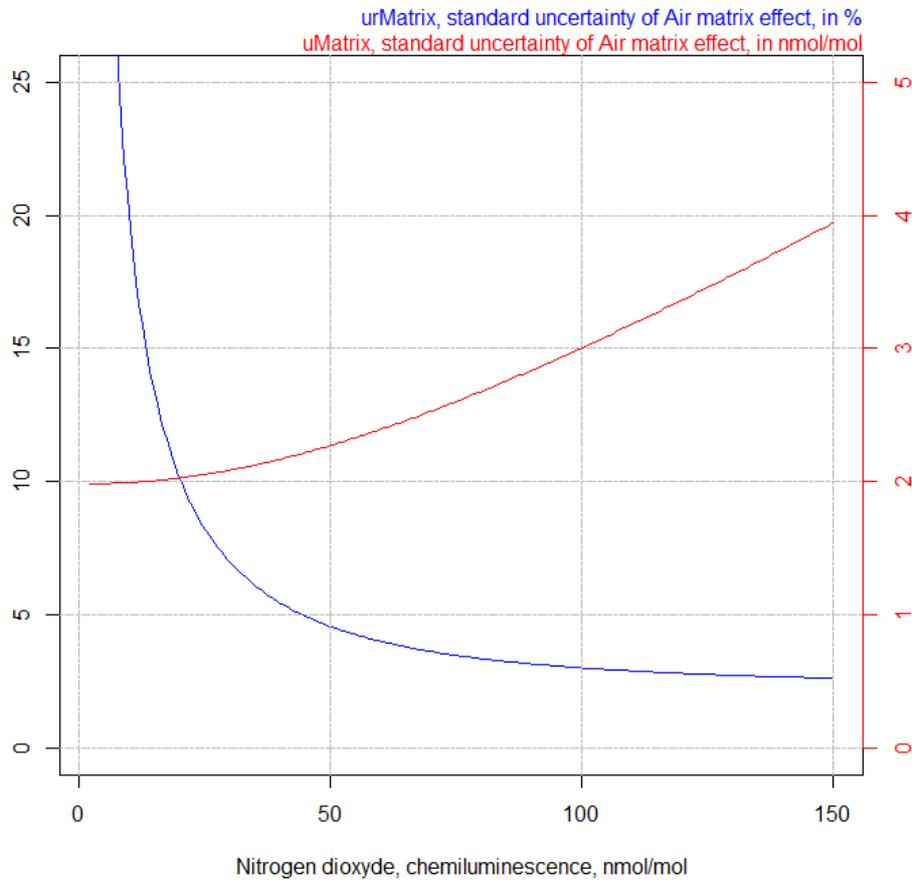
Eq. 15 gives  $u_{r,Matrix}$ , the relative combined uncertainty due to the air matrix effect where  $S_r$  is the repeatability of the sensor response and  $s$  denotes the standard deviation of the parameters between parentheses determined using their scattering in the three linear models for zero air, ambient air and indoor air dilution.

$$u_{r,Matrix}^2 = \frac{u(c_r)^2}{c_r^2} = \frac{S_r^2 + s^2(a) + s^2(b) \cdot c_r^2}{b^2 \cdot c_r^2} \quad \text{Eq. 15}$$



$$u_{r,Matrix}^2 = \frac{1.02^2 + 0.93^2 + 0.02^2 \cdot c_r^2}{0.92^2 \cdot c_r^2}$$

Figure 16 shows  $u_{r,Matrix}$  as a function of  $c_r$ , the sensor corrected NO<sub>2</sub> level. At the limit value (100nmol/mol),  $u_{r,Matrix} = 3.02\%$  which correspond to a standard uncertainty  $u_{Matrix} = 3.02$  nmol/mol. Even if this value is higher than the repeatability, the influence of the air matrix on the sensor values will not be consider in the final model as it is already included in each single gaseous interfering compounds.



**Figure 16: Evolution of  $u_{r,Matrix}$  and  $u_{Matrix}$  as a function of the concentration of NO<sub>2</sub>**

The variability of the sensor's response can be represented using  $D_{matrix}$  given by Eq. 16.  $R_s$  represents the sensor's response to the different air matrixes: filtered, indoor and ambient air matrix.

$$D_{matrix} = \frac{\sum_1^N |R_{s,matrix} - R_{s,filtered}|}{N} \quad \text{Eq. 16}$$

$$D_{matrix,Amb} = 1.78 \text{ nmol/mol} \quad \text{Ambient Air}$$

$$D_{matrix,Ind} = 3.80 \text{ nmol/mol} \quad \text{Indoor Air}$$

$$D_{matrix} = 2.79 \text{ nmol/mol} \quad \text{Average ambient and indoor air}$$



### 7.3 Hysteresis

The sensors can present some hysteresis as the order of the measurements can influence the responses. To evaluate the hysteresis effect, we carried out an exposure of the sensor following the experimental conditions presented in Table 18.

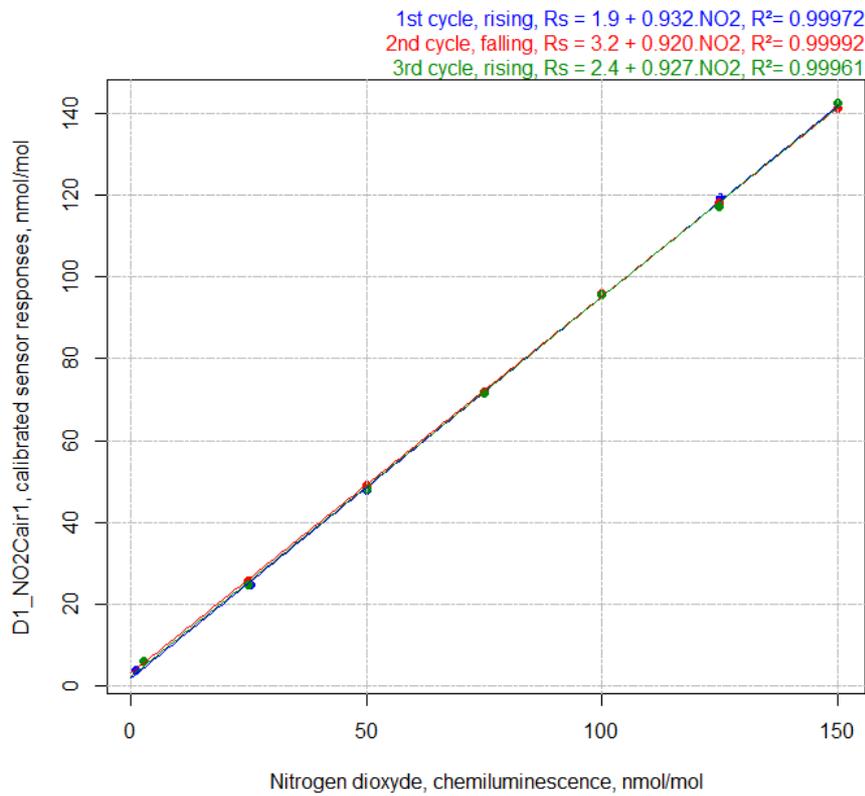
The responses of the NO<sub>2</sub> sensor were transformed following the calibration function established in the pre-calibration experiment (see 6.2). The controlled conditions (NO<sub>2</sub>, NO, O<sub>3</sub>, estimated NH<sub>3</sub>, T, RH and P) and sensor responses were averaged over the last hour of test in the exposure chamber. The experiment went on for 150 minutes once stabilisation of exposure conditions was reached.

All parameters suspected to have an effect on the sensor response (test gas, O<sub>3</sub>, temperature and humidity) were kept under control with relative standard deviation of about 2 %.

**Table 18 : Experiments conditions for Hysteresis experiment**

CairClip NO <sub>2</sub> , mol/mol	NO <sub>2</sub> Test levels, nmol/mol	NO, nmol/mol	T, °C	RH, %	Pressure, hPa	Interference	Comments
3.9 ± 1.1	1.0 ± 0.1	1.6 ± 0.1	22.0 ± 0.1	58.3 ± 0.1	994.4 ± 0.1	None	1st cycle, rising
24.7 ± 1.1	25.5 ± 0.2	2.3 ± 0.1	22.0 ± 0.1	58.6 ± 0.2	996.6 ± 0.1	None	
47.7 ± 1.4	50.0 ± 0.3	2.9 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	996.3 ± 0.1	None	
71.5 ± 1.2	75.0 ± 0.4	3.1 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	995.8 ± 0.2	None	
95.5 ± 1.1	100.0 ± 0.4	3.7 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	993.6 ± 0.1	None	
119.4 ± 1.5	125.0 ± 0.4	3.9 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	993.2 ± 0.1	None	
141.0 ± 1.0	150.0 ± 0.5	4.1 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	993.6 ± 0.1	None	
118.1 ± 1.6	125.0 ± 0.5	4.0 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	993.6 ± 0.2	None	2nd cycle, falling
95.9 ± 1.0	100.0 ± 0.3	3.9 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	993.0 ± 0.1	None	
72.0 ± 1.0	75.0 ± 0.4	3.3 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	993.9 ± 0.1	None	
49.1 ± 1.7	50.0 ± 0.3	3.2 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	993.4 ± 0.1	None	
25.6 ± 1.3	25.0 ± 0.2	2.6 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	993.2 ± 0.2	None	
6.2 ± 1.0	2.8 ± 0.1	2.4 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	991.3 ± 0.1	None	3rd cycle, rising
24.8 ± 1.0	25.0 ± 0.2	2.5 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	991.3 ± 0.1	None	
48.0 ± 1.5	50.0 ± 0.3	3.0 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	991.4 ± 0.1	None	
71.5 ± 1.2	75.0 ± 0.5	3.2 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	992.9 ± 0.1	None	
95.7 ± 1.3	100.0 ± 0.4	3.7 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	991.9 ± 0.1	None	
116.9 ± 1.6	125.0 ± 0.5	4.0 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	992.8 ± 0.1	None	
142.5 ± 1.3	150.0 ± 0.6	4.2 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	994.9 ± 0.3	None	

Figure 17 presents the sensor responses when exposed to the hysteresis experiment.



**Figure 17: Effect of hysteresis on CairClip NO<sub>2</sub> sensor**

Using Eq. 13 to Eq. 15, we can calculate the uncertainty by first fitting a model to each part of the hysteresis cycle.

$$R_s = 1.9 + 0.932 NO_2, R^2 = 0.99972 \quad \text{1st cycle, rising}$$

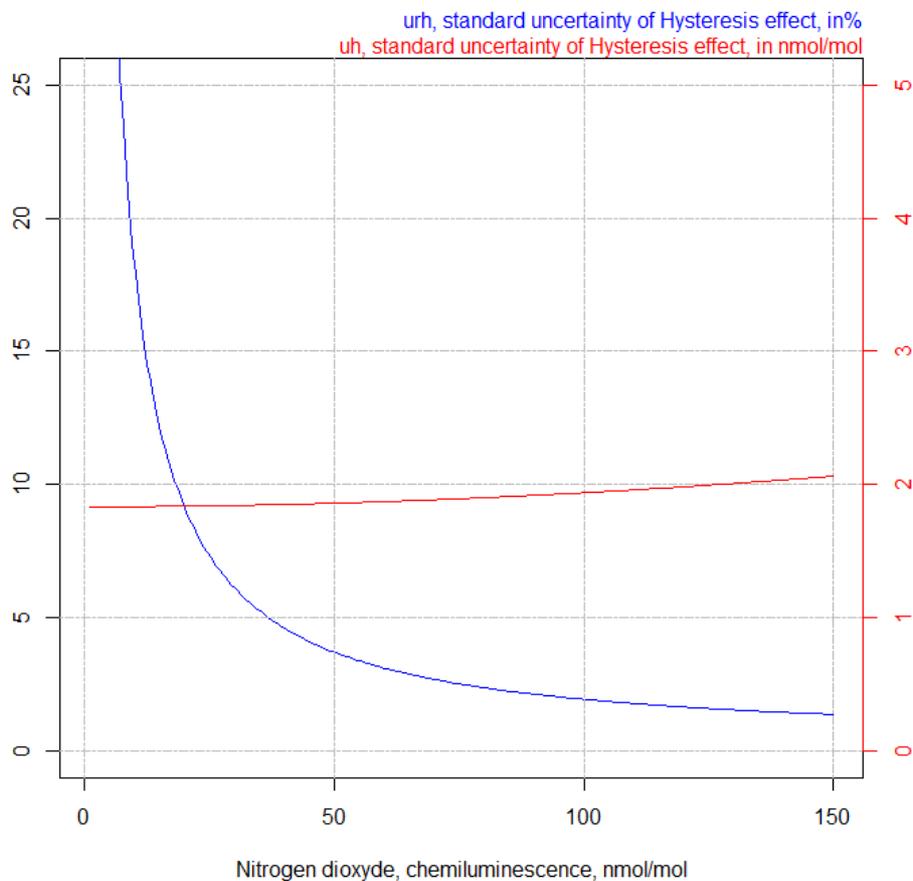
$$R_s = 3.2 + 0.920 NO_2, R^2 = 0.99992 \quad \text{2nd cycle, falling}$$

$$R_s = 2.4 + 0.927 NO_2, R^2 = 0.99961 \quad \text{3rd cycle, rising}$$

Eq. 17 gives  $u_{r,h}$ , the relative combined uncertainty due to the hysteresis effect where  $u(R_s)$  is the repeatability of the sensor response and  $s$  denotes the standard deviation of the parameters between parentheses determined using their scattering in the three linear models for the 3 part of the hysteresis cycle.

$$u_{r,h}^2 = \frac{u(c_r)^2}{c_r^2} = \frac{S_r^2 + s^2(a) + s^2(b) \cdot c_r^2}{b^2 \cdot c_r^2} \quad \text{Eq. 17}$$

$$u_{r,h}^2 = \frac{1.02^2 + 0.65^2 + 0.01^2 \cdot c_r^2}{0.93^2 \cdot c_r^2}$$



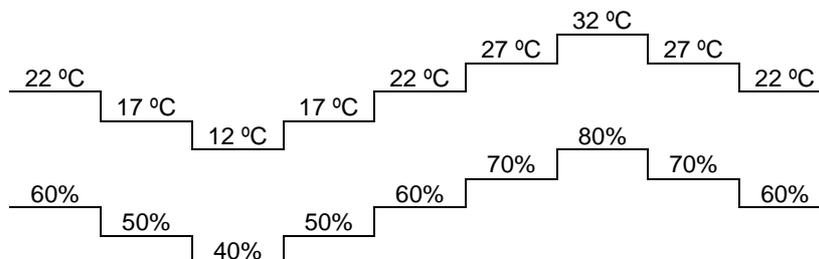
**Figure 18: Evolution of  $u_{r,h}$  and  $u_h$  as a function of the concentration of  $NO_2$**

Figure 18 shows  $u_{r,h}$  as a function of  $c_r$ , the sensor corrected  $NO_2$  responses.  $u_{Matrix}$  stay rather stable in the whole range of concentration. At the limit value (100nmol/mol),  $u_{r,Matrix} = 1.94 \%$  which correspond to a standard uncertainty  $u_{Matrix} = 1.94 \text{ nmol/mol}$ . The sensor does not suffer from hysteresis effect so that hysteresis effect will not be considered in the final model.

## 7.4 Meteorological parameters

### 7.4.1 Humidity and Temperature

To determine the influence of temperature and humidity on the sensor's response, we carried out two hysteresis loops in a row of 5 levels of each parameter according to Figure 19.



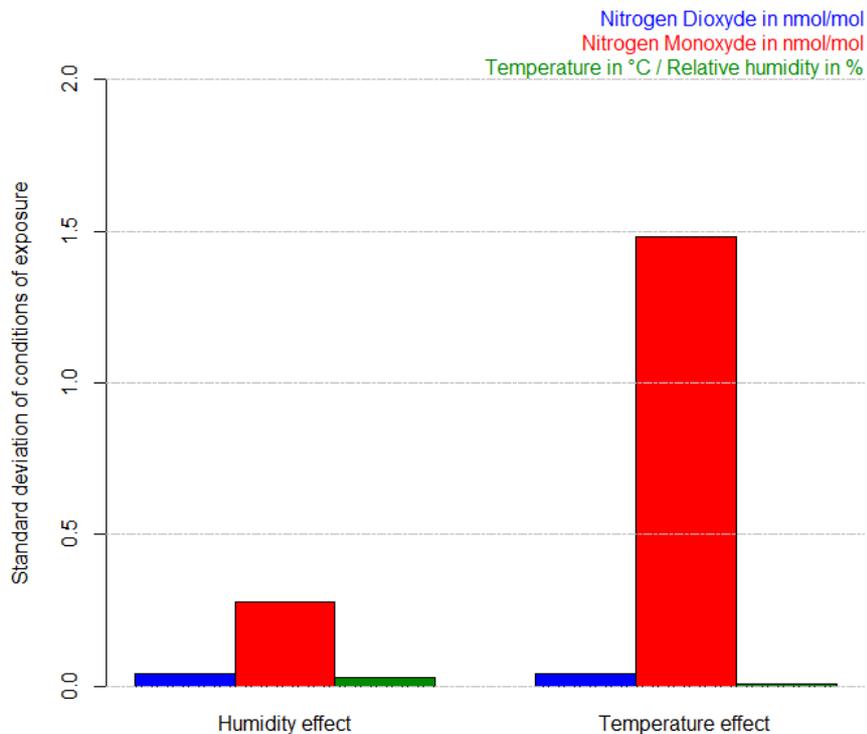
**Figure 19: Testing of temperature and humidity effect**

The responses of the  $NO_2$  sensor were transformed following the calibration function established in the pre-calibration experiment (see 6.2). The controlled conditions ( $NO_2$ ,  $NO$ ,  $O_3$ , estimated  $NH_3$ ,  $T$ ,  $RH$  and  $P$ ) and sensor responses were averaged over the last hour of test in the exposure



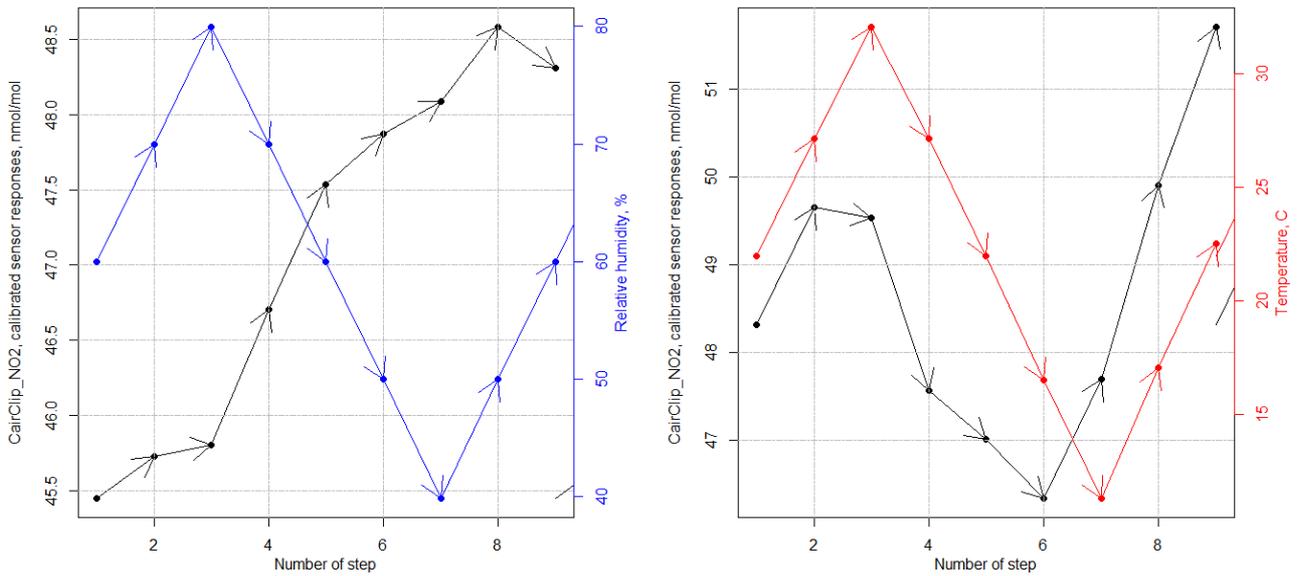
chamber. The experiment went on for 150 minutes once stabilisation of exposure conditions was reached.

All other parameters suspected to have an effect on the sensor response (test gas, O<sub>3</sub>, temperature or humidity) were kept under control with relative standard deviation of about 2 %, as shown on Figure 20.



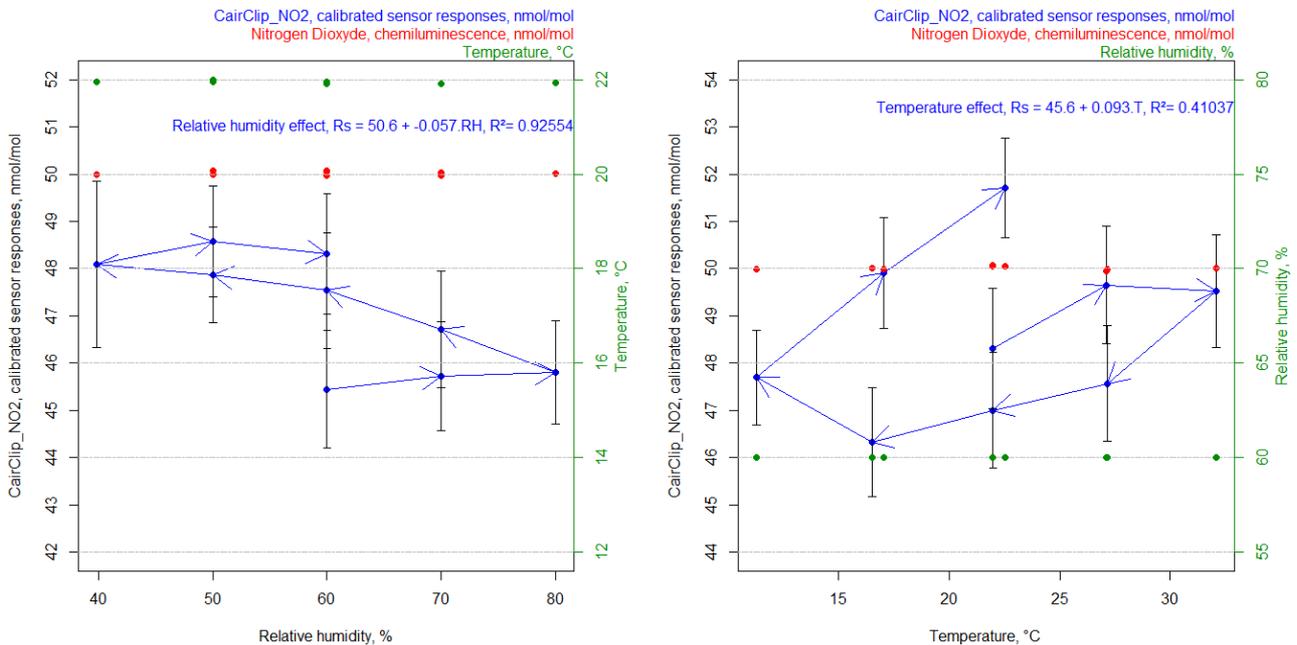
**Figure 20: Stability of NO<sub>2</sub>, NO and temperature or relative humidity during Humidity and Temperature effect experiment**

Figure 21 shows the evolution of the sensor's response over the humidity and temperature effect exposure. Regarding temperature, the sensor showed a slight hysteresis effect. In fact, the sensor responses showed a delay from test level to test level. For example, the sensor responses kept on increasing one step after the maximum temperature and conversely The sensor showed a minor effect against relative humidity, as the sensor response tend to slightly increase over the different step.



**Figure 21: Temporal evolution of the sensor's response toward relative humidity (left) and temperature (right) over the different exposure step.**

The influences of temperature and humidity on the sensor responses are shown in Figure 22. CairClip NO<sub>2</sub> shows a highest sensibility toward temperature than humidity.



**Figure 22: Sensitivity of CairClip NO<sub>2</sub> sensor toward relative humidity (left) and temperature (right).**

Actually we observed a dependence of the sensor's response versus relative humidity and temperature. Against relative humidity, the sensor's response seems to increase step by step while against temperature, the response follows an hysteresis shape. In the temperature test, the highest sensor response at 22 °C is likely an outlier. Assuming a linear dependence, the measurement uncertainty,  $u(x)$  arising from change of temperature and relative humidity was estimated using Eq. 18 using the sensitivity coefficient (the slope of the regression lines) for both



influencing variables and adding a contribution from the hysteresis of temperature and humidity corresponding to the maximum deviation to the regression lines or preferably the one at the LV.

$$u(x) = \left( b^2 \frac{(X_{max} - X_{min})^2}{3} + \frac{\rho_{max,LV}^2}{3} \right)^{1/2} \quad \text{Eq. 18}$$

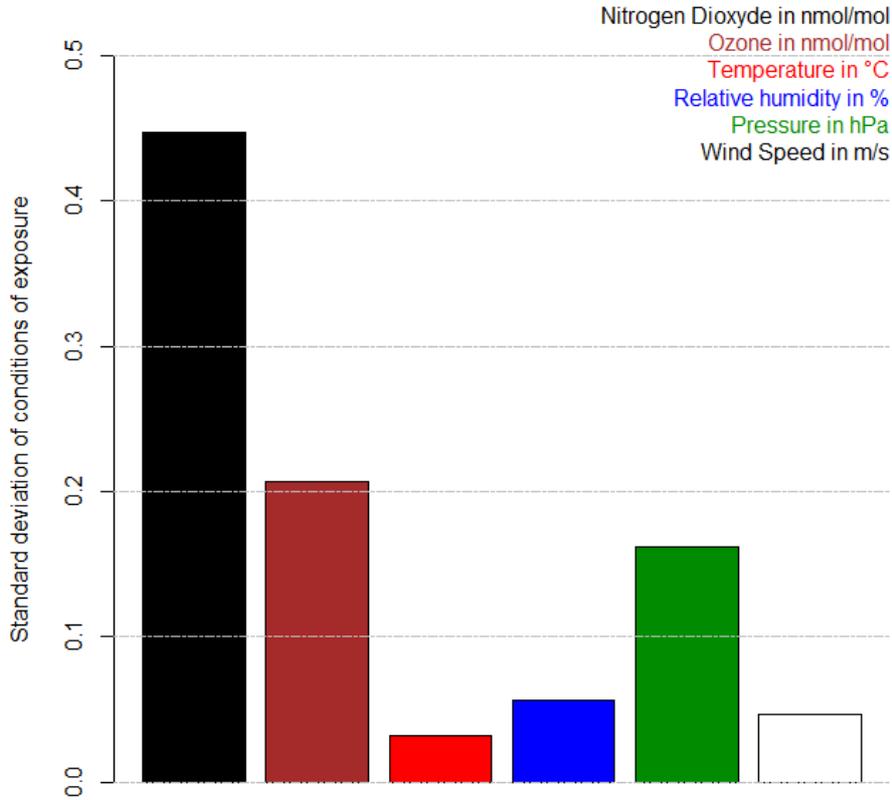
Where  $X$  is the tested parameter,  $b$  is the slope of the regression line of the sensor responses versus temperature and humidity,  $X_{max}$  and  $X_{min}$  the maximum and minimum values encountered in real ambient for parameter  $x$  and  $\rho$  is the maximum residuals between the regression line and the sensor responses or the one at the LV.

Assuming a relative humidity range between 30 and 95 %, the maximum residual of the linear fit being 0.3 nmol/mol at the LAT, the contribution of the relative humidity effect was  $u(RH) = 2.2$  nmol/mol without correction of the sensor for the relative humidity effect and  $u(RH) = 2.1$  nmol/mol with correction of the relative humidity effect with its regression equation.

Assuming a temperature range between 15 and 45 °C, the maximum residual of the linear fit being 1.0 nmol/mol at the LAT, the contribution of the temperature effect was  $u(T) = 1.7$  nmol/mol without correction of the sensor for the temperature effect and  $u(T) = 1.6$  nmol/mol with correction of the temperature effect with its regression equation.

#### **7.4.2 Wind velocity effect**

The effect of wind velocity on the sensor responses was also evaluated. To determine the influence of wind velocity on the sensor's response, we carried out a 4-level experiment between 1 m/s to 4 m/s with step of 1 m/s. The NO<sub>2</sub> level was set to 100 nmol/mol (hourly LV of the Directive). The responses of the NO<sub>2</sub> sensor were transformed following the calibration function established in the pre-calibration experiment (see 6.2). The controlled conditions (NO<sub>2</sub>, NO, O<sub>3</sub>, estimated NH<sub>3</sub>, T, RH and P) and sensor responses were averaged over the last hour of test in the exposure chamber. The experiment went on for 150 minutes once stabilisation of exposure conditions was reached. All other parameters suspected to have an effect on the sensor response (test gas, O<sub>3</sub>, temperature or humidity) were kept under control with relative standard deviation of about 2 %, as shown on Figure 23.



**Figure 23: Stability of NO<sub>2</sub>, temperature and relative humidity in the exposure chamber during the wind velocity experiments**

Figure 24 shows the effect of wind velocity on the sensor's response. The sensor responses increased with wind velocity and the maximum difference was 3.7 nmol/mol between 1 m/s and 3.8 m/s. Even though Figure 24 shows that the sensor responses are parabolic, we used a linear model to estimate the uncertainty resulting from wind velocity changes. Eq. 19 and Eq. 20 were applied to estimate the sensitivity coefficient of the sensors to changes in the wind velocity and the contribution of this parameter to the measurement uncertainty of the sensor,  $u(WV)$ , with sensor response  $C_{Xn}$  at  $X_n$ ,  $X_{max}$  and  $X_{min}$  the max and min values of the tested velocities.

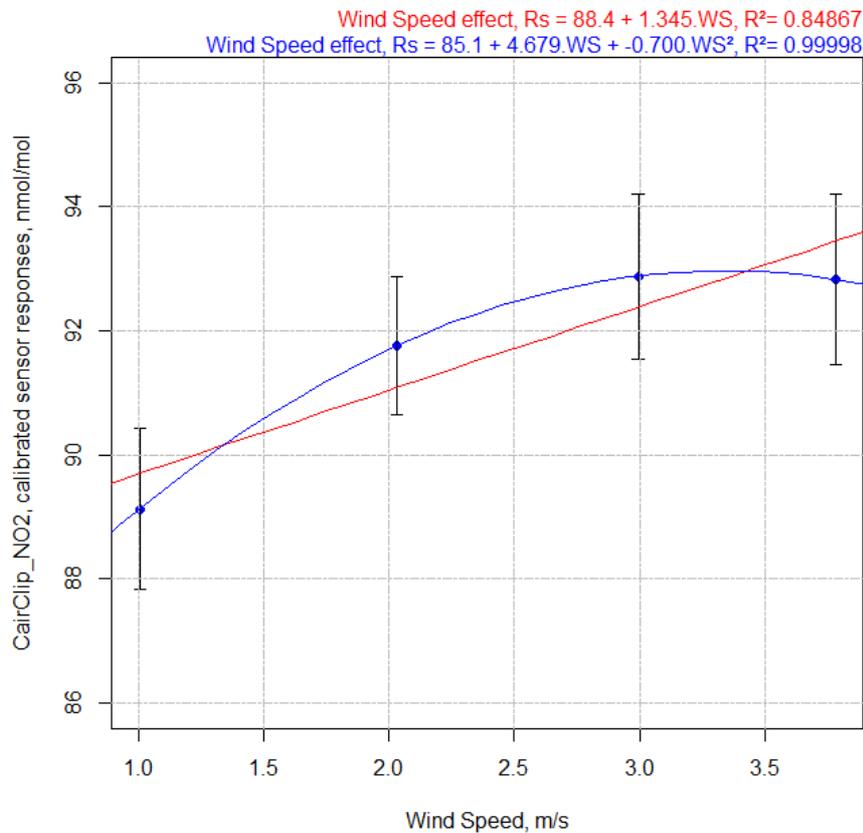
$$\frac{\Delta C}{\Delta X} = \left| \frac{C_{X2} - C_{X1}}{X_2 - X_1} \right| \quad \text{Eq. 19}$$

$$u(X_p) = \sqrt{\left| \frac{C_{X2} - C_{X1}}{X_2 - X_1} \right|^2 \cdot \frac{(X_{max} - X_{min})^2}{3}} \quad \text{Eq. 20}$$

The sensitivity coefficient  $\Delta C / \Delta WV$  and the standard uncertainty  $u(X_{WV})$  were calculated assuming a change of wind velocity in the range 0.5 to 5 m/s. For CairClip NO<sub>2</sub>  $\Delta C / \Delta WV = 1.3$  (nmol/mol)/(m/s) and  $u(X_{WV}) = 3.5$  nmol/mol.



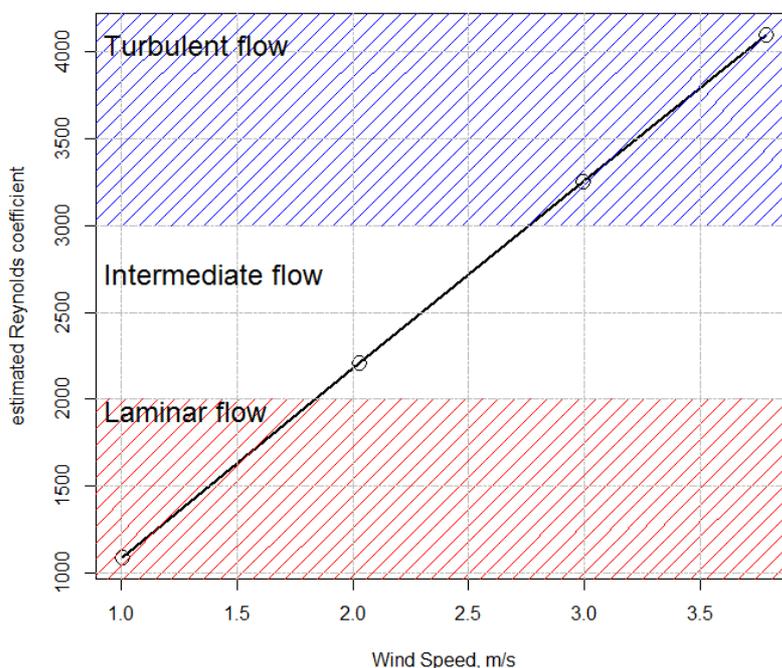
### CairClip\_NO2 wind velocity effect



**Figure 24: Effect of Wind speed on the sensor responses at 100 nmol/mol**

With the Reynolds formula, it is possible to estimate the type of flow inside the exposure chamber against wind velocity. Figure 25 shows the value of the estimated Reynolds coefficient during the wind velocity test. Below 2 m/s, the flow in the exposure chamber can be considered as laminar. Above this speed, the flow is turbulent and it's not possible to determine the real wind velocity around the sensor.

It is likely that the sensitivity coefficient and the standard uncertainty are overestimated because turbulent flows are more likely than laminar ones both reducing the sensitivity coefficient and the range of possible wind velocity.



**Figure 25: Flow type depending on the wind speed**

Even if the influence of wind velocity might be significant, the CairClip NO<sub>2</sub> sensor contains an internal microfan that permanently sends a fixed flow to the sensor. Taking into account that in field conditions the flow is mainly turbulent and in order to ensure an efficient flow inside the exposure chamber, we set wind velocity at around 3.2 m/s for the design of experiment. When reporting these results, the manufacturer informed that the wind effect strongly depends on the direction of the wind and the precise positioning of the sensor whose microfan can be disturbed (resistance to pressure of the fan). Cairpoll recommends using their sensor protective box called Cairbox.

### 7.4.3 Ambient pressure effect

During the first experiment we observe that the level of NO<sub>2</sub> and NO were strongly affected by ambient air coming into our exposition chamber and by a cycling increase of concentration during daytime. To avoid this dependence we chose to seal all possible leaks to maintain a constant but slight overpressure. That way all experiments were carried out in overpressure, even if the mean pressure was still dependant from the ambient pressure.

### 7.5 Effect of power supply

The effect of power supply on the sensor responses was tested at 3 levels of voltage (210, 220 and 230 V) while all other parameters suspected to have an effect on the sensor response (test gas, O<sub>3</sub>, temperature or humidity) were kept under control. In this experiment, the power supply of the sensor was changed using a variable generator (rheostat) model Rheothor ADB. The results of the test are given in Table 19.

The responses of the NO<sub>2</sub> sensor were transformed following the calibration function established in the pre-calibration experiment (see 6.2). The controlled conditions (NO<sub>2</sub>, NO, O<sub>3</sub>, estimated NH<sub>3</sub>, T, RH and P) and sensor responses were averaged over the last hour of test in the exposure chamber. The experiment went on for 150 minutes once stabilisation of exposure conditions was reached. All other parameters suspected to have an effect on the sensor response (test gas, O<sub>3</sub>, temperature or humidity) were kept under control with relative standard deviation of about 2.



**Table 19: Effect of change of voltage on the sensor responses and conditions of exposure with average and standard deviation for each parameter during the experiments.**

Tension V	CairClip NO <sub>2</sub> , mol/mol	NO <sub>2</sub> , nmol/mol	NO, nmol/mol	O <sub>3</sub> , nmol/mol	T, °C	RH, %	P, hPa
210	89.1 ± 1.4	100.0 ± 0.6	3.5 ± 0.1	1.0 ± 0.2	22.0 ± 0.1	60.0 ± 0.1	1006 ± 0.2
220	88.8 ± 1.3	100.0 ± 0.6	3.4 ± 0.1	1.0 ± 0.2	22.0 ± 0.1	60.0 ± 0.1	1007 ± 0.1
230	89.6 ± 1.0	100.0 ± 0.5	3.5 ± 0.1	-1.0 ± 0.2	22.0 ± 0.1	60.0 ± 0.1	1005 ± 0.1

Eq. 21 and Eq. 22 were applied to estimate the sensitivity coefficient of the sensors to change in the power supply and the contribution of this parameter to the measurement uncertainty of the sensor,  $u(X_V)$ , where  $X_V$  is the tested tension, with sensor response  $C_{XV}$  at  $X_V$ ,  $X_{Vmax}$  and  $X_{Vmin}$  the max and min values.

$$\frac{\Delta C}{\Delta X} = \left| \frac{C_{X2} - C_{X1}}{X_2 - X_1} \right| \quad \text{Eq. 21}$$

$$u(X_V) = \left| \frac{C_{X2} - C_{X1}}{X_2 - X_1} \right| \cdot \frac{X_{Vmax} - X_{Vmin}}{\sqrt{3}} \quad \text{Eq. 22}$$

The sensitivity coefficient for CairClip NO<sub>2</sub> is found to be 0.03 nmol/mol/V and assuming a change of tension in the range of 20 Volts results in a standard uncertainty of  $u(V)$  equal to 0.35 nmol/mol. Change in voltage is not significant as this value is much smaller than the repeatability of sensor responses.

#### 7.6 Choice of tested interfering parameters in full factorial design

The major cross sensitivities showed by the CairClip NO<sub>2</sub> were in order of magnitude: aging O<sub>3</sub> filtering, long-term drift, relative humidity and temperature and wind velocity. All the results are resumed in Table 20. The experimental design will included tests based on the effect of O<sub>3</sub>, temperature and humidity which were found significant for the majority of the other sensors tested within MACPoll even though the CairClip NO<sub>2</sub> compensation system for humidity was found effective.

Among the remaining factors:

- regarding uncertainty, the effect of wind velocity was found significant especially at velocity below 2 m/s even if the influence for the whole range of variation was in the same order of the repeatability. Nevertheless it is unlikely that during field measurement wind velocity would be measured and latter corrected. Consequently, wind velocity can only be estimated and taken into account when estimating the measurement uncertainty of the sensor results.
- finally the long term drift was found significant and link to the NO<sub>2</sub> concentration and elapsed time since the first calibration. Eq. 6 will be used in the model equation of the sensor response as well as the pre-calibration curve.



**Table 20: Summary of effect of all tested parameters with sensitivity coefficient and standard uncertainty**

Parameters	Can be controlled?	Can be corrected?	$\Delta C/(\Delta X)$ ( $\mu$ or n) mol/mol/Xunit	Standard uncertainty at LV
Laboratory calibration, nmol/mol	No	Yes	f(NO <sub>2</sub> )	0.3
Repeatability	No	Not needed	-	1.7
Short term drift, after 1 day	No	Not needed	-	1.4
Long term drift, per days	Periodic calibration?	Yes	$2.0 \cdot 10^{-3}$ - $4.2 \cdot 10^{-4}$ NO <sub>2</sub>	< sqrt( $4.0^2 + s(E)^2$ ) or s(E) f(NO <sub>2</sub> )
O <sub>3</sub> , nmol/mol	Already filtered	O <sub>3</sub> sensor needed	0.53 or -0.01*	17.2 or 0.32 + 2.u(O <sub>3</sub> ).u(NO <sub>2</sub> )*
NO, nmol/mol	No	Not needed	-0.009	0.3
CO, $\mu$ mol/mol	No	Not needed	-0.001	0.4
CO <sub>2</sub> , $\mu$ mol/mol	No	Not needed	0.012	0.34
NH <sub>3</sub> , nmol/mol	No	Not needed	-0.033	1.6
SO <sub>2</sub> , nmol/mol	No	Not needed	-0.1	0.1
Matrix effect	No	Within the results of the single interfering compounds	0.92	3.0
Hysteresis of concentration	No	Not needed	0.93	1.9
Relative Humidity in %	It is already controlled	Buffer effect?	0.093	2.2
Temperature, °C	Yes	A T sensor is needed	-0.057	1.7
Wind, m/s	An internal fan is already used	Not needed	1.3	3.5
Pressure, hpa	Test not carried out.			
Power supply, Volt	No	Voltage could be regulated around 220 V if used without battery	0.03	0.35

\*Depends on aging of O<sub>3</sub> filter

## 8 Experimental design

### 8.1 Data and model

A full factorial design of experiments was set up including the 7 levels of NO<sub>2</sub> of the pre-calibration experiment, 3 temperatures (12, 22 and 32 °C) under 3 relative humidities (40, 60 and 80%) and at 2 levels of O<sub>3</sub> (0 and 60 nmol/mol). Table 21 presents the full factorial design of experiments with CairClip NO<sub>2</sub> sensor responses. In order to save time, the order of experiments was randomized only for NO<sub>2</sub> and not for temperature and humidity.

The responses of the NO<sub>2</sub> sensor were transformed following the calibration function established in the pre-calibration experiment (see 6.2). The controlled conditions (NO<sub>2</sub>, NO, O<sub>3</sub>, estimated NH<sub>3</sub>, T, RH and P) and sensor responses were averaged over the last hour of test in the exposure



chamber. The experiment went on for 150 minutes once stabilisation of exposure conditions was reached. The correction for long drift (see 6.3.3) was also applied and no correction link to the wind effect was applied.

The dataset of measurement of the experimental design included the results of the CairClip NO<sub>2</sub> sensor and reference values for NO<sub>2</sub>, O<sub>3</sub>, temperature and relative humidity. Only one data was excluded from our model, the one highlighted in yellow in Table 21, because the O<sub>3</sub> concentration was too high: 39.3 nmol/mol instead of 0.0 nmol/mol as required.

**Table 21: Laboratory experimental design for the in nmol/mol.**

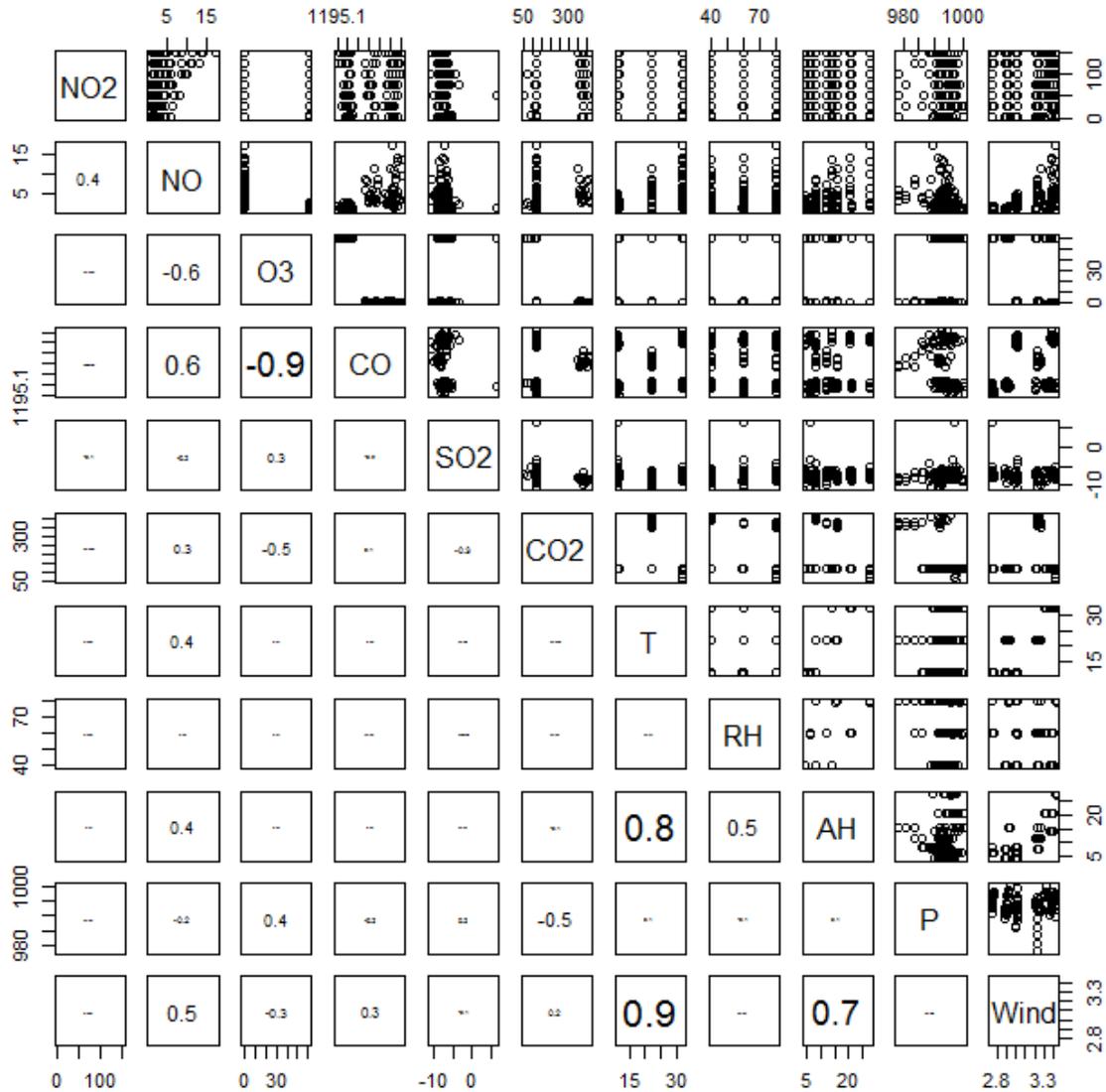
O <sub>3</sub> nmol/mol	Temp. °C	Rel. Hum. %	NO <sub>2</sub> nmol/mol	CairClip NO <sub>2</sub> , nmol/mol	O <sub>3</sub> nmol/mol	Temp. °C	Rel. Hum. %	NO <sub>2</sub> nmol/mol	CairClip NO <sub>2</sub> , nmol/mol
0.4	11.4	40.0	125.0	111.6	61.1	11.4	40.0	125.0	129.3
0.3	11.4	39.9	50.0	48.9	61.1	11.4	40.0	50.0	68.3
0.4	11.8	40.0	100.0	92.5	61.1	11.4	40.0	100.0	106.7
0.6	11.4	40.0	2.2	7.4	61.2	11.4	40.0	2.7	32.3
0.6	11.4	40.0	75.0	67.4	61.1	11.4	40.0	75.0	86.3
0.5	11.4	40.0	25.0	25.7	61.1	11.4	40.0	25.0	48.4
0.3	11.4	40.0	150.0	136.2	61.1	11.4	40.0	150.0	141.2
0.4	11.4	60.0	125.0	114.5	61.1	11.7	60.0	125.0	138.8
0.1	11.4	59.4	50.0	47.3	61.1	11.4	60.0	50.0	70.6
0.2	11.5	60.0	100.0	95.4	61.1	11.4	60.0	100.0	113.7
0.3	11.4	60.0	1.6	5.2	61.1	11.4	60.0	2.0	28.1
0.4	11.4	60.0	75.0	68.9	61.1	11.4	60.0	75.0	91.4
0.2	11.4	58.9	25.0	22.3	61.2	11.4	60.0	25.0	48.1
0.5	11.4	60.0	150.0	141.2	61.1	11.4	60.0	150.0	154.4
0.3	11.5	80.0	125.0	115.2	61.1	11.4	80.0	125.0	133.1
0.3	11.4	80.0	50.0	46.0	61.2	11.5	80.0	50.0	70.5
0.4	11.4	80.0	100.0	92.4	61.1	11.5	80.0	100.0	116.2
0.4	11.4	80.0	1.7	3.6	61.2	11.4	80.0	2.0	26.7
0.3	11.4	80.0	75.0	68.3	61.1	11.4	80.0	75.0	93.4
0.4	11.4	80.0	25.0	21.1	61.2	11.4	80.0	25.0	47.9
0.1	11.4	80.0	150.0	143.2	61.2	11.5	80.0	150.0	162.1
0.1	21.9	40.2	125.0	111.7	61.1	22.0	40.0	125.0	125.3
0.0	21.9	39.9	50.0	48.1	61.2	22.0	40.0	50.0	67.4
0.1	21.9	40.0	100.0	92.8	61.1	22.0	40.0	100.0	106.1
0.0	21.9	39.9	1.9	8.4	61.1	21.9	40.0	2.1	29.9
0.0	21.9	40.2	75.0	70.1	61.2	21.9	40.0	75.0	85.5
0.2	21.9	39.9	25.0	23.4	61.1	22.0	40.0	25.2	48.1
0.3	22.0	40.0	150.0	136.5	61.1	22.0	40.0	150.0	143.5
0.5	21.9	60.0	125.0	117.7	61.1	22.0	60.0	125.1	130.4
0.5	21.9	60.0	50.0	49.3	61.1	22.0	60.0	50.0	64.5
0.2	21.9	60.0	100.0	97.2	61.1	21.9	60.0	100.0	109.3
0.2	21.9	60.0	1.9	6.6	61.1	21.9	60.0	4.2	23.1
0.1	21.9	60.0	75.0	73.5	61.1	21.9	60.0	75.0	85.9
0.0	21.9	60.0	25.0	28.6	61.1	21.9	60.0	25.0	42.2
0.0	21.9	60.0	150.1	147.6	61.1	21.9	60.0	150.0	153.1
0.6	21.9	80.0	125.0	115.3	61.1	22.0	80.0	125.0	131.3
0.2	21.9	80.0	50.0	45.7	61.2	22.0	80.0	50.0	64.3
0.2	21.9	80.0	100.0	92.2	61.1	22.0	80.0	100.0	111.5
0.3	21.9	80.0	1.8	4.3	61.1	22.0	80.0	2.3	20.7
0.2	21.9	80.0	75.0	68.4	61.2	22.0	79.3	75.0	88.4
0.2	21.9	80.0	25.0	21.5	61.1	22.0	80.0	25.0	42.0
0.3	21.9	80.0	148.7	136.9	61.1	21.9	80.0	150.0	146.5



O <sub>3</sub> nmol/mol	Temp. °C	Rel. Hum. %	NO <sub>2</sub> nmol/mol	CairClip NO <sub>2</sub> , nmol/mol	O <sub>3</sub> nmol/mol	Temp. °C	Rel. Hum. %	NO <sub>2</sub> nmol/mol	CairClip NO <sub>2</sub> , nmol/mol
0.0	32.0	39.9	125.0	118.6	61.1	32.1	40.0	125.0	136.3
0.1	32.0	40.0	50.0	51.2	61.1	32.1	40.0	50.0	70.2
0.0	32.0	40.0	100.0	93.8	61.2	32.1	40.0	100.0	112.8
0.2	32.0	40.0	1.9	8.8	61.2	32.1	40.0	4.6	30.1
0.2	32.0	40.0	75.0	68.9	61.2	32.1	40.0	75.0	89.4
0.2	32.0	40.0	25.0	25.4	61.1	32.1	40.0	25.0	47.5
0.0	32.0	40.0	150.0	132.9	61.1	32.1	40.0	150.0	153.6
0.0	32.0	60.0	125.0	121.1	61.1	32.1	60.0	125.0	130.7
0.0	32.0	60.0	50.0	51.7	61.2	32.1	60.0	50.0	66.9
0.1	32.0	60.0	100.0	98.3	61.1	32.1	60.0	100.0	110.5
0.3	32.0	60.0	2.3	8.1	61.2	32.1	60.0	4.3	25.0
0.2	32.0	60.0	75.0	72.4	61.1	32.1	60.0	75.0	88.2
0.0	32.0	60.0	25.0	26.5	61.2	32.1	60.0	25.0	43.6
0.0	32.0	60.0	150.0	144.3	61.1	32.1	60.0	150.0	158.1
0.0	32.0	80.0	125.7	123.1	61.1	32.1	80.0	125.0	133.3
39.3	32.0	80.0	49.8	47.2	61.1	32.1	80.0	50.0	62.7
0.0	32.0	80.0	100.0	100.2	61.1	32.1	80.0	100.0	111.7
0.3	32.0	80.0	1.2	5.8	61.3	32.1	80.0	4.7	19.5
0.3	32.0	79.4	75.0	74.9	61.2	32.1	80.0	75.0	88.2
0.2	32.0	80.0	25.1	25.7	61.1	32.1	80.0	25.0	39.6
0.0	32.0	80.0	150.4	152.0	61.1	32.1	80.0	150.0	165.2

As shows in Figure 26, significant co-linearities were observed between NO and O<sub>3</sub>, between O<sub>3</sub> and CO, between temperature and absolute humidity and between temperature/absolute humidity and wind speed.

The relation between O<sub>3</sub> and NO can be explained by the fact that NO is oxidise in presence of O<sub>3</sub> to give NO<sub>2</sub>. The co-linearity between CO and O<sub>3</sub> can also be explained by a chemical reaction involving those two molecules to form CO<sub>2</sub>. The relation between temperature and absolute humidity is due to the fact that absolute humidity was calculated based on temperature and relative humidity values using the Clausius-Clapeyron equation. Finally wind velocity and temperature/absolute humidity co-linearity (the biggest one) is mainly due to the measurement method of wind velocity (hot wire) and can therefore explain the effect of wind velocity on the wind sensor which is likely an effect of temperature. Since it was chosen to design an experiment with orthogonal factors NO<sub>2</sub>, O<sub>3</sub>, temperature and relative humidity do not present any correlations.



**Figure 26: Co-linearities of covariates within the dataset of the experimental design**

Multiple Linear Regression (MLR) was used to model the sensor responses according to the available covariates within our dataset. Initially, all main effects were included in the MLR and only  $NO_2$  and  $O_3$  were found significant. This is consistent with the results of the single interference testing which show a strong effect of  $O_3$  on the sensor response. The equation giving the sensor responses according to  $NO_2$  and  $O_3$  is given in Eq. 23 with  $R_{S,corr}$  being the sensor response after pre-calibration and corrected in long term drift,  $[NO_2]$  the concentration of nitrogen dioxide and  $[O_3]$  the ozone concentration.

$$R_{S,corr} = 2.89 + 0.91 NO_2 + 0.34 O_3 \quad \text{Eq. 23}$$

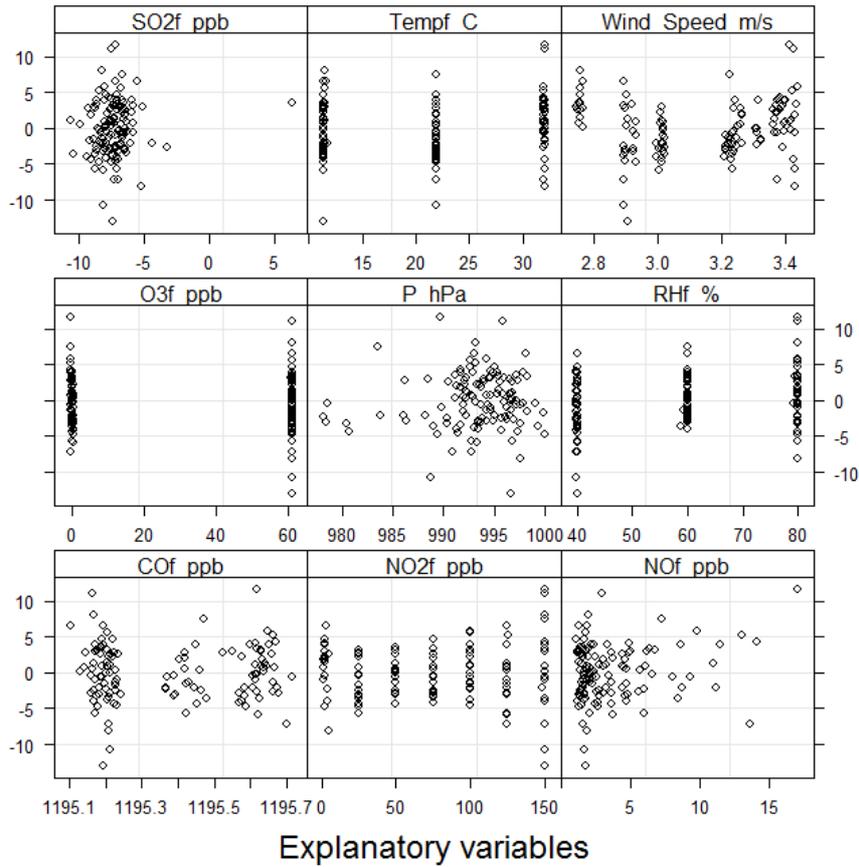
Table 22 gives the multiple analysis of variance which shows that all the effects are highly significant.



**Table 22: Analysis of variance of the model**

Coefficients	Estimate	Standard Error	t-value	Probability (Pr(> t ))
Intercept	2.89	0.90	3.20	0.002
NO <sub>2</sub>	0.91	0.01	91.8	< 2e-16
O <sub>3</sub>	0.34	0.02	16.11	< 2e-16

It was checked that the residuals of the model equation were independent of all available covariates (Figure 27): references values of NO<sub>2</sub>, temperature, relative humidity, O<sub>3</sub>, NO, CO, SO<sub>2</sub>, ambient pressure and wind velocity.



**Figure 27: Residuals towards all possible covariates**

Finally, Eq. 24 can be used to estimate NO<sub>2</sub> from the sensor response, however the sensor response first need to be pre-calibrated  $f(NO_{2,pre-cal})$ . Obviously, the drawback of this equation is that it uses the elapsed time  $Ndays$  and ozone  $O_3$ .

$$NO_2 = \frac{f(NO_{2,pre-cal}) - 2.89 - 0.34 O_3 - 2.0 \cdot 10^{-3} Ndays}{0.91 - 4.2 \cdot 10^{-4} Ndays} \quad \text{Eq. 24}$$

## 8.2 Uncertainty estimation

To estimate the measurement uncertainty it should be possible to use the GUM method (see Eq. 25).

$$u_c^2(O_3) = \sum \left( \frac{\partial O_3}{\partial X_i} \right)^2 u^2(X_i) \text{ and } U = k \cdot u_c \text{ with } k = 2 \quad \text{Eq. 25}$$



However, because our model is complicated (6 variables), it was decided to use the “variance approach”. We will assume that the variance of the measurement is the sum of the variance of individual random variables including the contributions of the lack of fit of the model equation, O<sub>3</sub> interference for the main effect. As decided in 7.6 and according to Table 20, we will add the effect of wind speed, temperature, humidity and NH<sub>3</sub> after having subtracted the repeatability contribution as it is already included in the lack of fit.

**Table 23: Uncertainty after laboratory experiment at the NO<sub>2</sub> limit value (100 nmol/mol)**

Parameters		Model applied + corrections/adjustments		Model not applied without corrections and adjustments
		Correction	Variance <sup>½</sup>	Variance <sup>½</sup>
1	Rs, lack of fit of model	yes	3.9	
2	O <sub>3</sub> in nmol/mol	yes	8.5*	$(0.32^2 - 2.u(O_3).u(NO_2))^{½}$ $(17.2^2 - 2.u(O_3).u(NO_2))^{½**}$
3	Long term drift in nmol/mol	yes	3.7	4.3
4	Relative Humidity in %	no	$(2.2^2 - 1.0^2)^{½}$	$(2.2^2 - 1.0^2)^{½}$
5	Temperature in °C	no	$(1.7^2 - 1.0^2)^{½}$	$(1.7^2 - 1.0^2)^{½}$
6	Wind velocity in m/s	no	$(3.5^2 - 1.0^2)^{½}$	$(3.5^2 - 1.0^2)^{½}$
7	NH <sub>3</sub> in nmol/mol	no	$(1.7^2 - 1.0^2)^{½}$	$(1.7^2 - 1.0^2)^{½}$
$U = 2 \times u_c$ (see Eq. 25)		$u_c = 12.5$ (DQO = 25)		$U = 2 \times 15.8 > DQO$

\*: obtained by difference between the DQO and the other contributions; \*\*: depends on aging of O<sub>3</sub> filter

1. The variance of the lack of fit of the model equation was estimated using the residuals of the MLR. This parameter already includes contribution from the lack of fit of the calibration, the repeatability of sensor responses and its short term drift and hence these parameters are not repeated in the table.
2. In the “Model applied + corrections/adjustments” column the contribution arising from O<sub>3</sub> becomes null. However this implies that O<sub>3</sub> shall be measured to be included in the model equation of the sensor and hence an uncertainty for O<sub>3</sub> measurements cannot be excluded. The standard uncertainty was set by difference between the DQO and the rest of the parameter contribution resulting in a standard uncertainty of 8.5 nmol/mol. This standard uncertainty is for O<sub>3</sub>, taking into account the sensitivity coefficient  $b = 0.5$  of Table 10, the accepted standard uncertainty of the O<sub>3</sub> measurements would be  $8.5/0.5 = 17.0$  nmol/mol (expanded uncertainty  $U = 34.0$  nmol/mol). Conversely, if the sensor values are not corrected for O<sub>3</sub> then the interference estimated in 7.1 is taken into account subtracting the correlation between O<sub>3</sub> and NO<sub>2</sub> observed in field.
3. For the long term drift, the uncertainty showed into the column “Model applied + corrections/adjustments” correspond to the residual standard error of the linear regression at the limit value whereas in the “Model not applied” column it correspond to its standard deviation.
4. It was shown in 7.4.1 that the temperature only affects the sensor by a kind of hysteresis effect to which the repeatability shall be subtracted rather than a systematic effect with a sensitivity coefficient.
5. As for temperature, it was shown that relative humidity and wind velocity were not significant as interferent parameters. These contributions will be included after having subtracted the repeatability rather than a systematic effect with a sensitivity coefficient.



6. As decided in 7.6 and according to Table 20, contribution of  $\text{NH}_3$  will be included after having subtracted the repeatability.

## 9 Field experiments

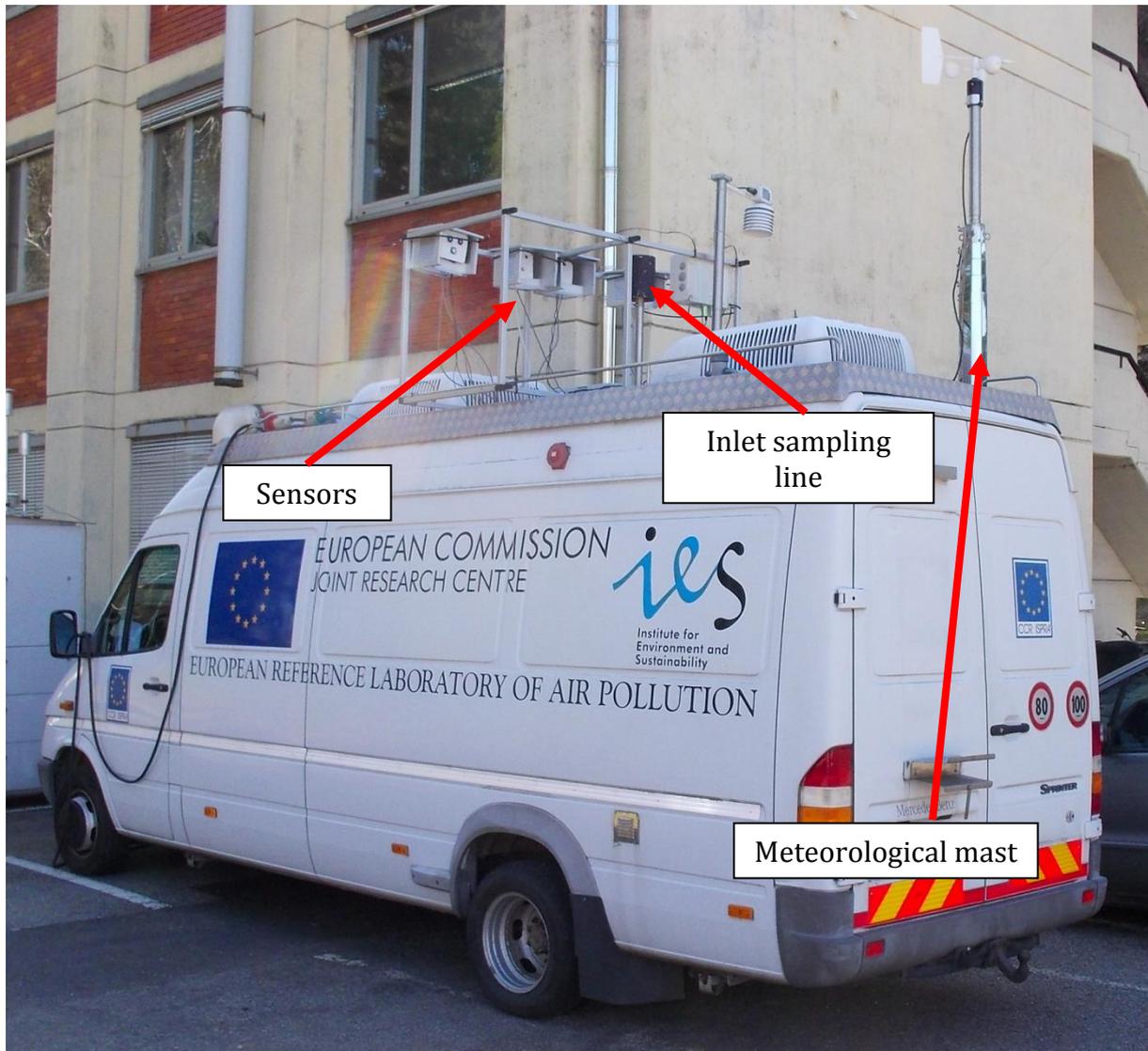
### 9.1 Monitoring stations

The JRC station for atmospheric research (45°48.881'N, 8°38.165'E, 209 m asl) is located by the Northern fence of the JRC-Ispra site, situated in a semi-rural area at the NW edge of the Po valley. The station is several tens of km away from large emission sources like intense road traffic or big factories. The main cities around are Varese, 20 km east, Novara, 40 km south, Gallarate - Busto Arsizio, about 20 km south-east and the Milan conurbation, 60 km to the south-east. Busy roads and highways link these urban centres. Four industrial large source points (CO emissions > 1000 tons / yr) are located between 20 and 50 km E to SE of Ispra. The closest (20 km SSE) emits also > 2000 tons of  $\text{NO}_x$  per year. The aim of the JRC-Ispra station is to monitor the concentration of pollutants in the gas phase, the particulate phase and precipitations, as well as aerosol optical parameters, which can be used for assessing the impact of European policies on air pollution and climate change. Measurements are performed in the framework of international monitoring programs like the Co-operative program for monitoring and evaluation of the long range transmission of air pollutants in Europe (EMEP) of the UN-ECE Convention on Long-Range Transboundary Air Pollution (CLRTAP) and the Global Atmosphere Watch (GAW) Program of the World Meteorological Organization (WMO).

Tests were carried out with the collaboration of ERLAP Laboratory at an air conditioned mobile laboratory that has been installed at the station in replacement of the routine analysers normally installed in the containers of the EMEP station. Gases were sampled using a sampling line (see Figure 28) placed at the top of the roof of the van at about 3.5 m above the ground and on the roof of the mobile laboratory. The sampling line consists in a stainless steel gas inlet with grid protection for rain, insects and dust wh. The stainless steel inlet tube of 4 cm internal diameter with internal PTFE tube that ends with a Teflon manifold of 8 PTFE ports to connect the gas analysers. The sampling line is flushed with ambient air with about 2 second residence time of samples in the sampling line. Each instrument samples from the glass tube with its own pump through a 1/4" PTFE/PFE tube and a 1  $\mu\text{m}$  pore size 47 mm diameter Teflon filter to eliminate particles from the sampled air.

The mobile laboratory was equipped with meteorological sensors and gas analysers which were calibrated in laboratory before the in-situ measurements and then checked every months. Field checks were carried out using zero air in gas cylinders and a span value (internally certified gas cylinders at low concentration for  $\text{NO}/\text{NO}_x$  and  $\text{SO}_2$ , highly concentrated cylinders for CO and ozone generator do  $\text{O}_3$ ). The highest observed drift of calibration was 3 %, consistent with the uncertainty of the working standards used on field. Therefore, no correction of measurements was undergone apart from the discarding values during maintenance and calibration checks.

- Meteorological parameters (ambient temperature, ambient relative humidity, ambient pressure, 10m mast for wind speed and wind direction) a mobile. The mobile laboratory was equipped with:
- Gaseous pollutants: for  $\text{O}_3$  an UV Photometric Analyser Thermo Environment 49C; for  $\text{NO}_2/\text{NO}/\text{NO}_x$  a Chemiluminescent Nitrogen Oxides Analyser Thermo 42C; for CO a non-Dispersive Infrared Gas-Filter Correlation Spectroscopy Thermo 48C-TL, for  $\text{SO}_2$  and UV Fluorescent Analyser Thermo 43C TL



**Figure 28:** Mobile laboratory used in front of the building and after in the provisory EMEP Station at JRC Ispra.

To avoid interference, we made sure that the flow air coming out of the air condition system was blowing far enough from the sensor to avoid any effect on the sensor responses.

## 9.2 Sensor equipment

The same equipment as the one used in laboratory was used:

- Power supply: a power supply TracoPower ESP18-05SN 5V-3.6 A was used both for the laboratory tests and for the fields tests (the power supply sent by Cairpoll was not used)
- Test board used: No needs for a test board, CairClip sensors include a 5V analogic output on their USB connector.
- Data acquisition: the data acquisition is performed by means of special LabView software developed to manage data acquisition synchronously with the gaseous and other parameters such as temperature, humidity (see 2.5.1). It consisted of a NI USB-6009 acquisition system from National Instrument with a periodicity of data acquisition of 100Hz and an average data acquisition every minute without filtering.



### 9.3 Check of the sensor in laboratory

In a first step all the sensors were installed inside the exposure chamber in order to verify their proper functioning and to create a pre-calibration curve before the installation on the field. As for all the experiments of the laboratory study, temperature, relative humidity and other gaseous compounds which were suspected to affect the sensor response, were kept under control with relative standard deviation (RSD) of about 2 %. The temperature and relative humidity of the test were set at 22°C and 60 %.

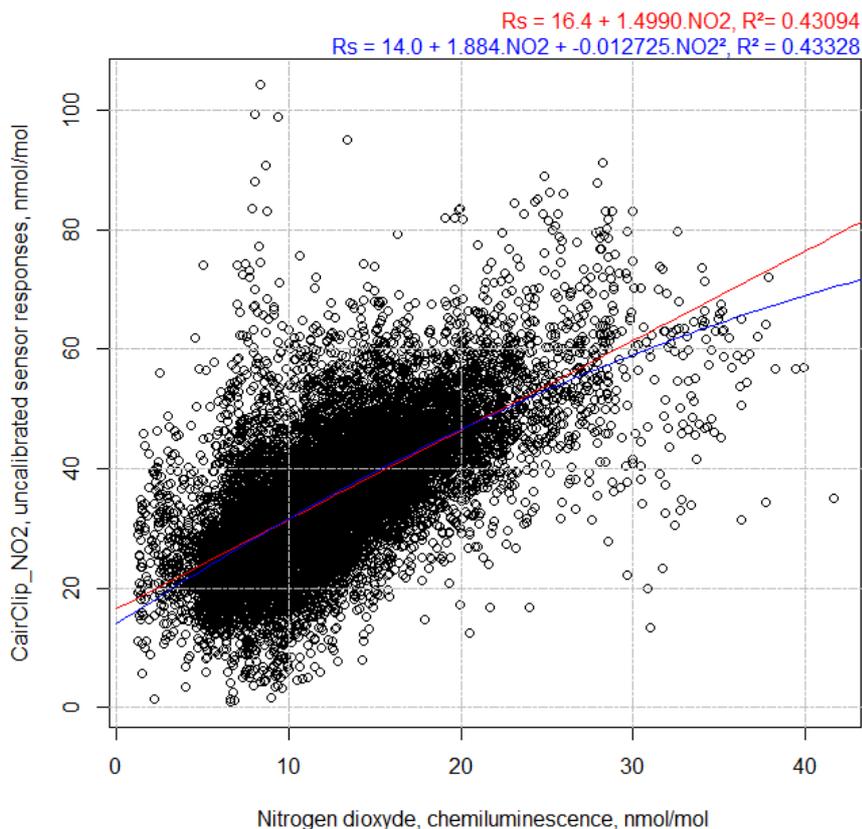
Unfortunately, the two CairClip NO<sub>2</sub> presented an electronic limitation of the signal which has been removed by the manufacturer before the rest of the laboratory and field tests. However, it was decided to use the first 10 days of field exposure to estimate a first calibration curve.

The results of the experiment are given in Figure 29 which shows that a linear regression, as the one used for the laboratory sensor can be used (see Eq. 26).

$$R_{s,cal} = \frac{R_s - 16.4}{1.5} \quad \text{Eq. 26}$$

This pre-calibration function was established by plotting sensor responses versus reference values measured by the TE 42C analyser. Each steps lasted for 150 minutes once the condition of NO<sub>2</sub> concentrations, temperature and humidity were reached. The averages of the last 60 minutes are plotted. In all the following results this pre-calibration is applied before data analysis.

**Pre-calibration of D2\_NO2Cair2**



**Figure 29: Initial calibration of Field CairClip NO<sub>2</sub>**



#### 9.4 Field Results

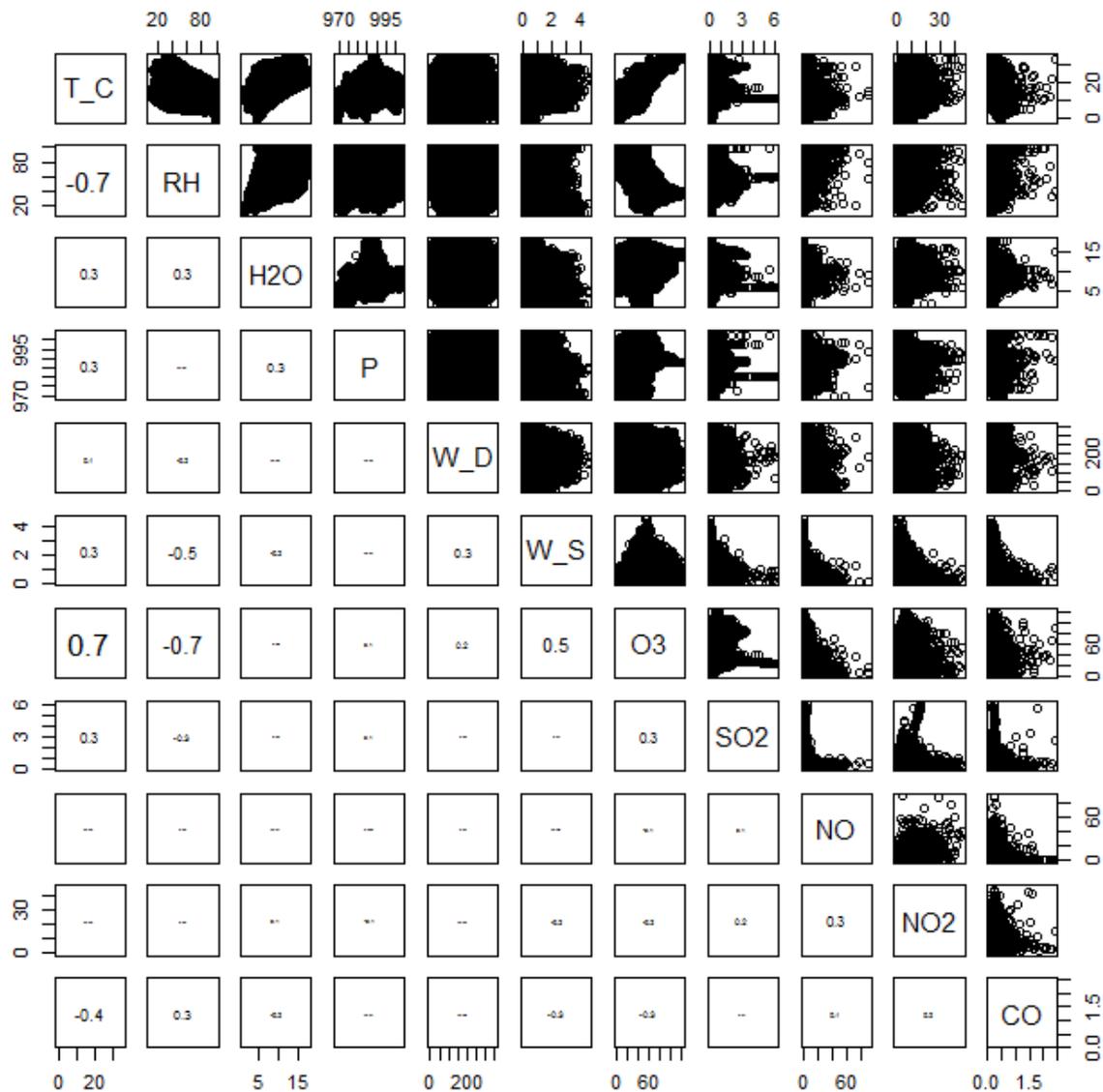
The CairClip NO<sub>2</sub> was installed between 20 March and 21 October 2013. From the beginning to 09 July, the mobile laboratory was placed near our laboratory, in a parking place, to simulate in the best way our micro environment. From the 09 July to the 21 of October, a new location was decided for the mobile laboratory and it was placed in a field inside the Research Centre as far as possible from traffic and building to be representative for a rural area.

Apart from the CairClip NO<sub>2</sub> and other sensors, reference values were registered for O<sub>3</sub>, NO<sub>2</sub> and NO, SO<sub>2</sub>, CO, PM<sub>10</sub>, temperature, relative humidity while absolute humidity was calculated. However, the time series for PM<sub>10</sub> being incomplete it had to be dropped.

Figure 30 and Figure 31 show the co-linearities in the field data set with scatterplots between pairs of parameters (upper matrix plots) and their correlation (lower matrix values) for hourly values of O<sub>3</sub>, NO<sub>2</sub>, NO, and SO<sub>2</sub> in nmol/mol, CO in μmol/mol, temperature in °C (T), relative humidity in % (RH), absolute humidity in mg/m<sup>3</sup> (H<sub>2</sub>O), wind direction in ° (WD), wind velocity in m/s (WV) and pressure in hPa (P). Sens correspond to the uncalibrated CairClip NO<sub>2</sub> values.

Being in field where factors cannot be controlled, collinearities between each other is unavoidable. Figure 30 shows the co-linearities during the first period of the campaign, from 30 March to 09 July 2013. There are strong correlation between O<sub>3</sub>, temperature and relative humidity as expected, making it impossible to include all of these parameters into a regression model. A lower level of correlation can be also observed between O<sub>3</sub> and wind velocity.

Unfortunately, during this time period, NO<sub>2</sub> was not the main gaseous compounds in the ambient air; ozone was present at least as the same levels. The CairClip NO<sub>2</sub> does not show a high correlation with NO<sub>2</sub> but it is correlated with O<sub>3</sub>, temperature and relative humidity as a consequence of the their self-correlation. This correlation is due to the fact that NO<sub>2</sub> concentration stays under 45nmol/mol with a mean concentration equal to 6 nmol/mol whereas the mean concentration of ozone is equal to 35 nmol/mol.

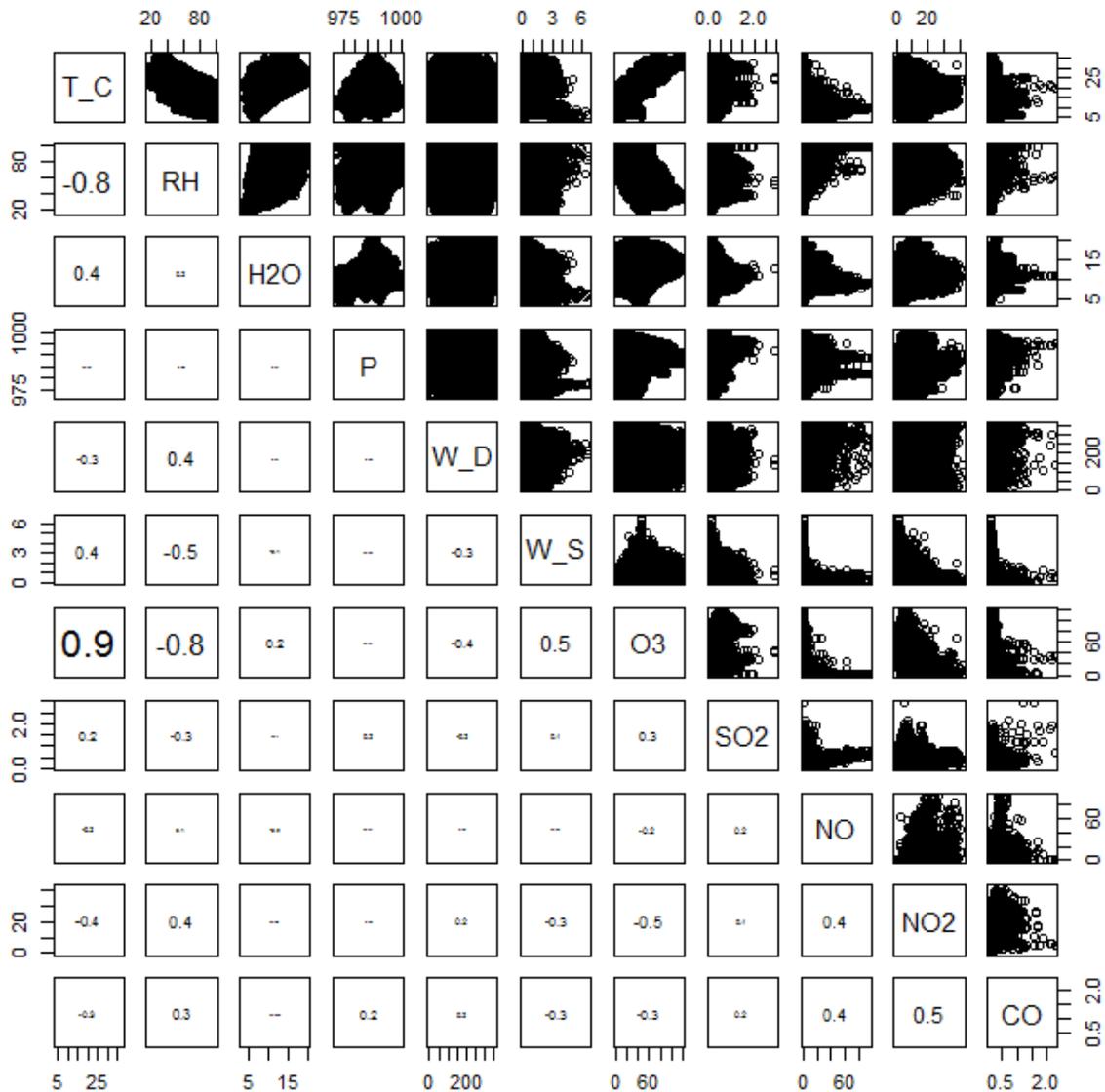


**Figure 30: Co-linearities in the field data set during the first half of the filed campaign: building parking place**

Figure 31 shows the co-linearities during the first period of the campaign, from 05 March to 09 July 2013. We observe the same correlation as the one in Figure 30 with in average a higher coefficient.

There are strong correlation between  $O_3$ , temperature and relative humidity as expected, making it impossible to include all of these parameters into a regression model. A lower level of correlation can be also observed between  $O_3$  and wind velocity.

Unfortunately, during this time period,  $NO_2$  was not the main gaseous compounds in the ambient air; ozone was present at least as the same levels. The CairClip  $NO_2$  does not show a high correlation with  $NO_2$  but it is correlated with  $O_3$ , temperature and relative humidity as a consequence of the their self-correlation.

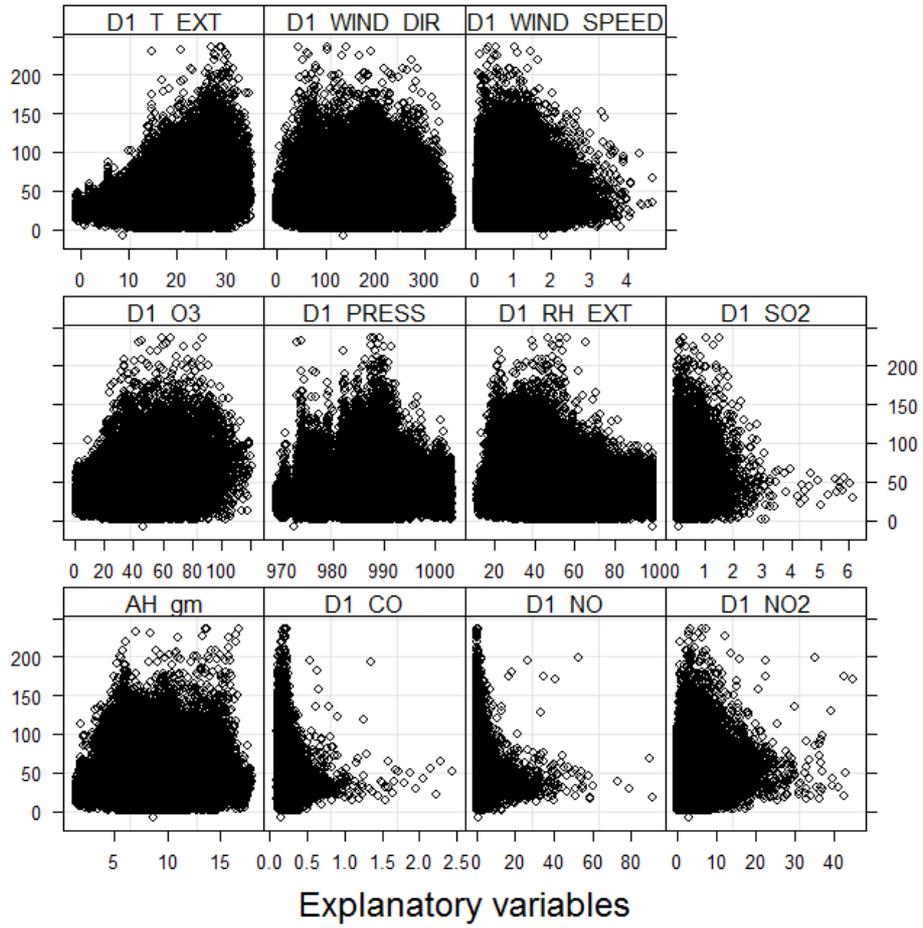


**Figure 31: Co-linearities in the field data set during the second half of the filed campaign: rural area**

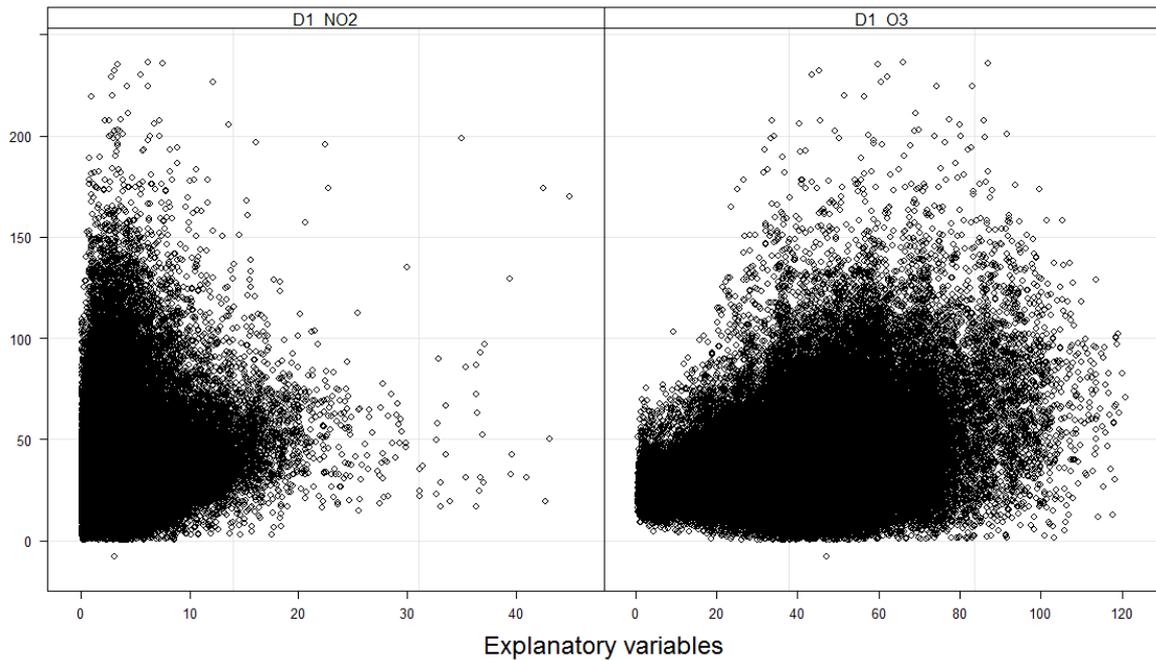
It was decided for the next part of the evaluation to focus on the first time period as it's the one which can better represent our micro-environment.

Figure 32 shows the relationship between sensor response and reference measurement of NO<sub>2</sub>, NO, O<sub>3</sub>, CO, SO<sub>2</sub>, temperature, relative humidity, pressure, wind (both direction and velocity) and absolute humidity. By comparing the sensor response toward NO<sub>2</sub> and O<sub>3</sub> (see Figure 33), it's clearly shows that:

1. O<sub>3</sub> was most of the time present in higher concentration than NO<sub>2</sub> during the field campaign (mean concentration of ozone is equal to 35 nmol/mol whereas NO<sub>2</sub> concentration stays under 45nmol/mol with a mean concentration equal to 6 nmol/mol).
2. CairClip NO<sub>2</sub> seems to be more sensitive to O<sub>3</sub> than NO<sub>2</sub> in those exposure conditions. According to the manufacturer review, this behaviour can be explained by both position-dependent filter and exposure conditions.



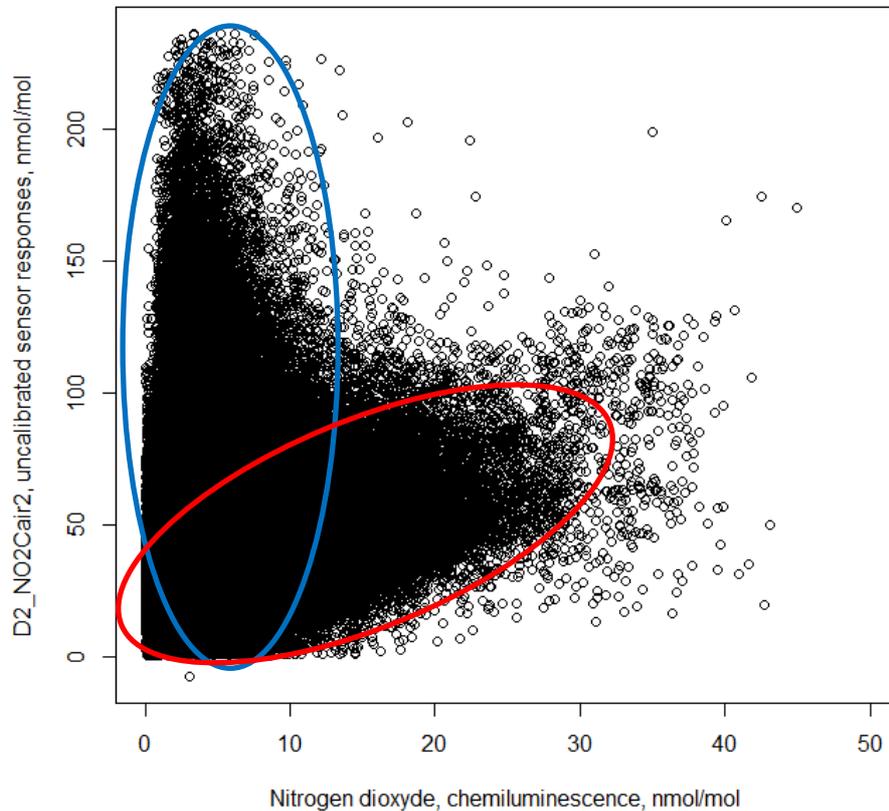
**Figure 32: Relationship between CairClip NO<sub>2</sub> and reference measurements values**



**Figure 33: Relationship between CairClip NO<sub>2</sub> and reference measurements values for NO<sub>2</sub> and O<sub>3</sub>**

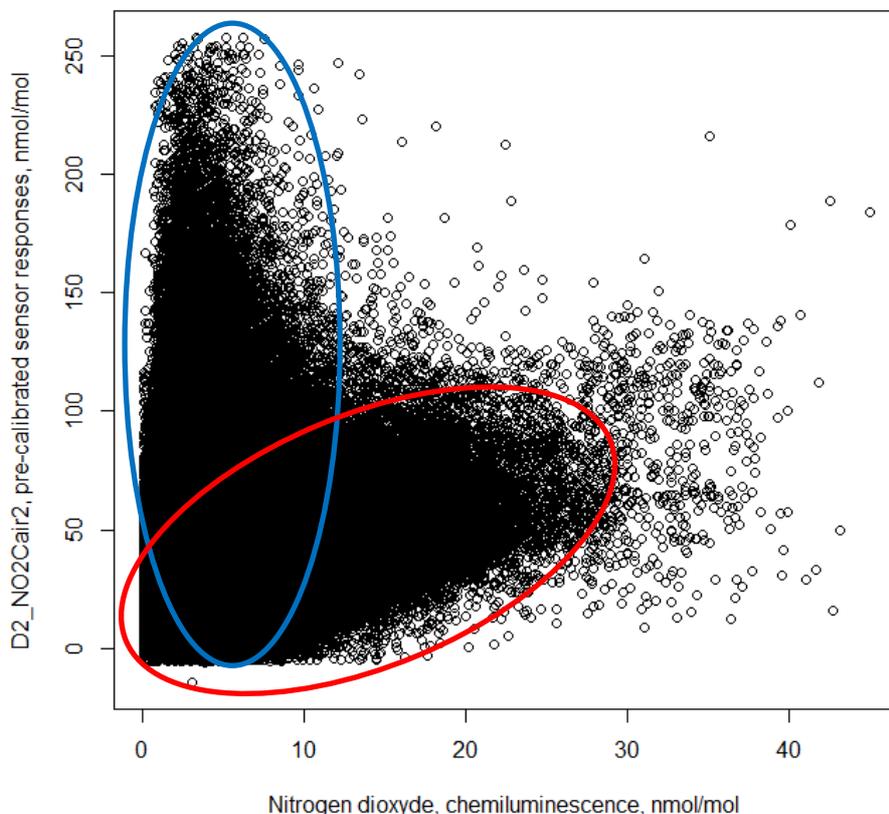


Figure 34 shows the raw sensor responses versus  $\text{NO}_2$  reference values measured by chemiluminescence. It is clearly observable that 2 populations of data are represented: red circle for  $\text{NO}_2$  and blue circle for  $\text{O}_3$ . It was found during the laboratory experiment that  $\text{O}_3$  is the main gaseous interferent of CairClip  $\text{NO}_2$  which explains this dual dependency.



**Figure 34: uncalibrated CairClip  $\text{NO}_2$  versus  $\text{NO}_2$  reference values**

Figure 35 shows the same data set after pre-calibration using the function established with the 10 first days of field exposure (Eq. 26). The improvement acquired by using this pre-calibration are not significantly. It was only possible to reduce the range of response from -5 / 235 nmol/mol to -15 / 145 nmol/mol.



**Figure 35: pre-calibrated CairClip NO<sub>2</sub> versus NO<sub>2</sub> reference values**

Based on this observation and according to the fact that the time period for the field campaign did not correspond to the optimal exposure conditions, it is unnecessary to apply the model found in 8.1 (see Eq. 24) as this model was based on a low level of ozone and on a higher range of NO<sub>2</sub> concentration.

## 10 Discussion conclusion

This evaluation shows that CairClip NO<sub>2</sub>, compared to other sensor, presents advantages regarding sensitivity to temperature and relative humidity. Concerning gaseous interference, the laboratory experiments had shown a high sensitivity to ozone balanced by the use of a very efficient O<sub>3</sub> filter. Even if some other species can be considered as light interferent, they were not considered significant as in the chosen micro-environment the same compounds are not present in such a level of concentration.

The design of the CairClip NO<sub>2</sub> shows that the sensor is intrinsically sensitive to O<sub>3</sub>. In laboratory, a number of experiments showed that the sensor was sensitive to NH<sub>3</sub> but independent from change of CO, CO<sub>2</sub>, NO and SO<sub>2</sub>. The sensor does not suffer from short term drift and doesn't present hysteresis effect when the NO<sub>2</sub> levels changes. However it has been shown that the sensor suffers from an important long term drift. It is slightly dependent to relative humidity and shows a little hysteresis when temperature changes but we cannot conclude towards pressure as the experiment was not feasible in the actual laboratory configuration. Some doubts remain about the sensitivity of the sensor to wind velocity. Power supply change was not found significant.

A sophisticated model equation has been established in laboratory that needs number of exposure days and ozone concentration to estimate NO<sub>2</sub> using the CairClipNO<sub>2</sub> sensors. At high O<sub>3</sub> levels,



when using this model the measurement uncertainty was found lower than the Data Quality Objective of the European Directive for measurement while DQO would not be met without.

Unfortunately, the field campaign was realised in late winter - summer period during which the  $\text{NO}_2$  was lowest than  $\text{O}_3$  in ambient air which lead into the presence of two main population in the Field data that making rather impossible to evaluate the final uncertainty.

However in laboratory the DQO of indicative method of the European Directive is met by the CairClip  $\text{NO}_2$ . Based on the manufacturer review and keeping in mind that the evaluated CairClip  $\text{NO}_2$  sensor was not finalized version, this sensor has shown an interesting behaviour during the laboratory experiments, especially a good linearity of response and a good repeatability. Further to this study, the field of application of the CairClip sensor should be validated for fixed measurement at traffic station in urban/suburban area.



## 11 Appendix A: Technical Data Sheet CairClip NO<sub>2</sub>



### Technical Data Sheet CairClip NO<sub>2</sub> (document prone to modifications)

<b>Range</b>	0-250 ppb (0-240 ppb analog)
Limit of detection <sup>(1, 2)</sup>	20 ppb
Repeatability at zero <sup>(1, 2)</sup>	+/- 7 ppb
Repeatability at 35% of range <sup>(1, 2, 3)</sup>	+/- 20 ppb
Linearity <sup>(1, 2)</sup>	< 10 %
Short term Zero drift <sup>(1, 2, 4)</sup>	< 5 ppb / 24 H
Short term Span drift <sup>(1, 2, 4)</sup>	< 1% FS <sup>(5)</sup> / 24 H
Long term Zero drift <sup>(1, 2, 4)</sup>	< 10 ppb / 1 month
Long term Span drift <sup>(1, 2, 4)</sup>	< 2 % FS <sup>(5)</sup> / 1 month
Rise time (T10-90) <sup>(1, 2)</sup>	< 90 s (180 s if large variation of RH)
Fall time (T10-90) <sup>(1, 2)</sup>	< 90 s (180 s if large variation of RH)
Effect of interfering species <sup>(1)</sup>	Cl <sub>2</sub> : around 80 % possible interferences from O <sub>3</sub> if high concentration
Maximum exposure	50 ppm
Annual exposure limit (1 hour average)	780 ppm (NO <sub>2</sub> )
Annual exposure limit (1 hour average)	180 ppm (O <sub>3</sub> )
Operating conditions	- 20°C to 40°C / 10 to 90 % RH non-condensing 1013 mbar +/- 200 mbar
Recommended storage conditions	Temperature: between 5°C and 20°C Air relative humidity: > 15 % non-condensing Ambient air free from O <sub>3</sub>
Power supply <sup>(6)</sup>	5 VDC / 200 mA (rechargeable by USB via PC or 100 V-240 V / 5 V 0.8 A-1.0 A with adaptor)
Communication interface	USB (RS 232 or UART on demand)
Dimensions	Diameter: 32 mm - Length: 62 mm
Weight	55 g
Protection	IP42 (according IEC60529)
Electrical certification	 Conform to UL Std. 61010-1 Certified to CSA Std. C22.2 N°. 61010-1 
CairSoft Version	CairSoft V3A

<sup>1</sup> According to our operating conditions during tests in laboratory: 20°C +/- 2°C / 50 % RH +/- 10 % / 1013 mbar +/- 5 %

<sup>2</sup> Values possibly affected by exposures to high gradients of concentration

<sup>3</sup> In accordance with the Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe

<sup>4</sup> Full scale continuous exposure

<sup>5</sup> FS = Full Scale

<sup>6</sup> The complete discharge of a device (screen turned off) can lead to a deterioration of its performances

*For an optimal quality of use, please keep the Cairclip in a vertical position in accordance with indications on the device*

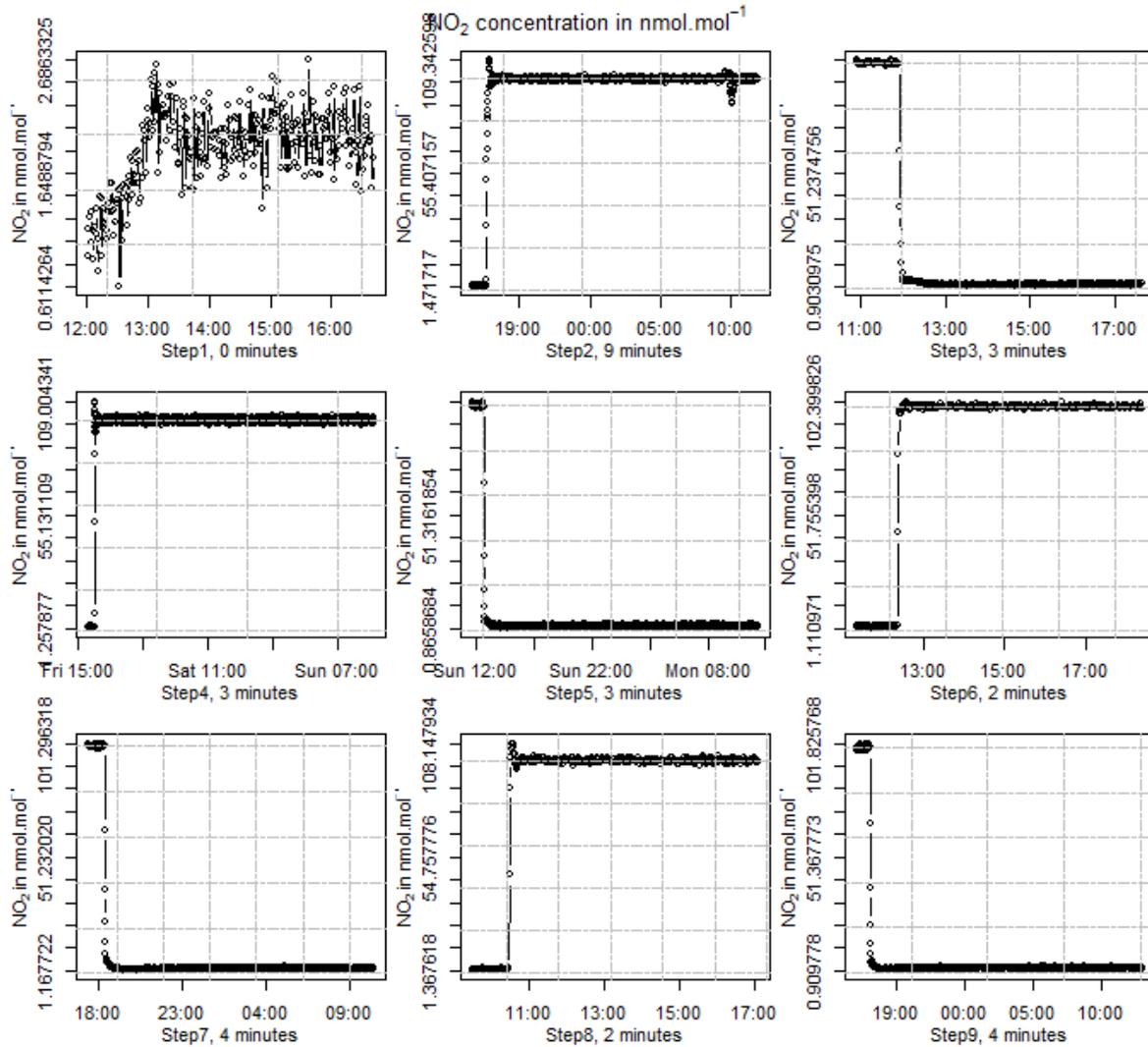
<b><u>Main options</u></b>	CairTub: autonomy 21 days CairNet: wireless connexion & battery powered by solar panel Software: CairSoft, CairMap, CairWeb
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Office : CAIRPOL  
ZAC du Capra  
55, avenue Emile Antoine  
30340 Méjannes les Alès - France

SARL au capital de 354 200€ - N° Siren : 492 976 253

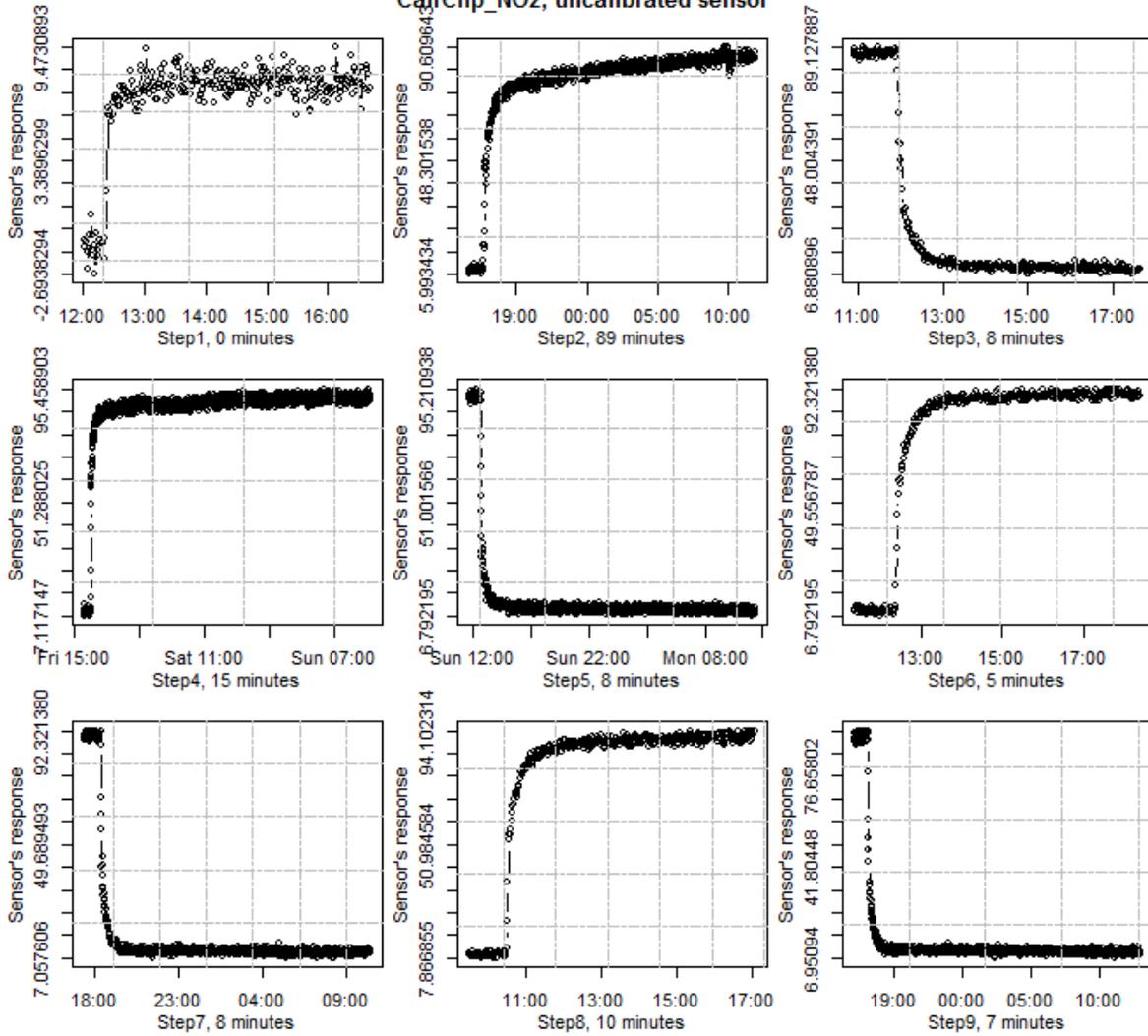
Tel: +33 (0)4 66 83 37 56  
Fax: +33 (0)4 66 61 82 53  
info@cairpol.com  
Web site: www.cairpol.com

## 12 Appendix B: Response time steps



Appendix B, Figure 1: Response time of the whole exposure chamber

CairClip\_NO2, uncalibrated sensor



Appendix B, Figure 2: Response time of CairClip NO<sub>2</sub>

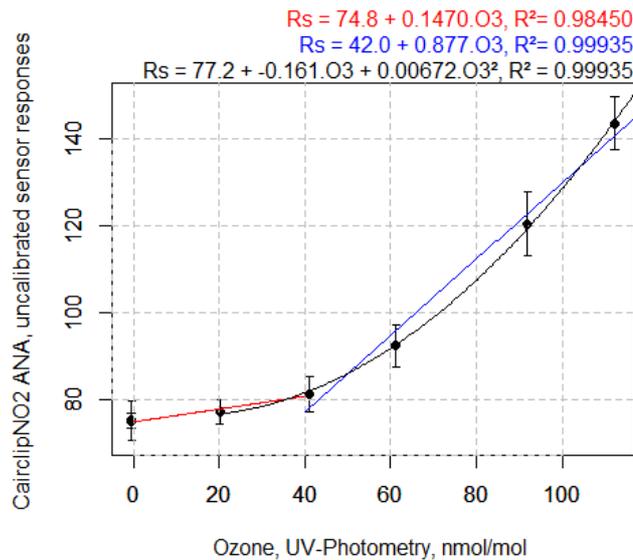


### 13 Appendix C: Evaluation of CairClip NO<sub>2</sub> during the ozone campaign.

Based on the design on the sensor, it was decided in agreement with the manufacturer to add two CairClip NO<sub>2</sub> ANA during the evaluation of ozone sensors to get details about the O<sub>3</sub> interference on this NO<sub>2</sub> sensor and filter: s/n CCB0306120003 (used for the field experiments) and s/n CCB030120004 (used in the laboratory experiments). These sensors were not previously calibrated by the manufacturer.

The evaluation of the time needed by the sensor to reach a stable response was realized at 90 nmol/mol of O<sub>3</sub>. It has been measured a response time of 2 minutes excluding the response time of the reference analyser. In this report we have seen the response time at 100 nmol/mol of NO<sub>2</sub> was about 5 minutes. Even if the response time toward NO<sub>2</sub> is higher, the CairClip NO<sub>2</sub> showed a very good response time compared to the majority of the tested sensors.

Whereas the pre-calibration used during the NO<sub>2</sub> campaign can be easily modeled using a linear model, the pre-calibration to O<sub>3</sub> showed a flattening at low O<sub>3</sub> levels. Figure 1 of Appendix C shows a lowest extent of variation of the sensor responses against ozone than nitrogen dioxide. This decrease is likely due to the ozone filter which was highly effective for ozone concentration lower than 40 nmol/mol while it becomes less effective for higher O<sub>3</sub> levels.



**Appendix C, Figure 1: Initial calibration of CairClip NO<sub>2</sub> at 22°C and 60% relative humidity with errors bars representing the relative standard deviations during the last 60 minutes of measurement**

For the rest of the study, two formulas have been applied for the pre-calibration:

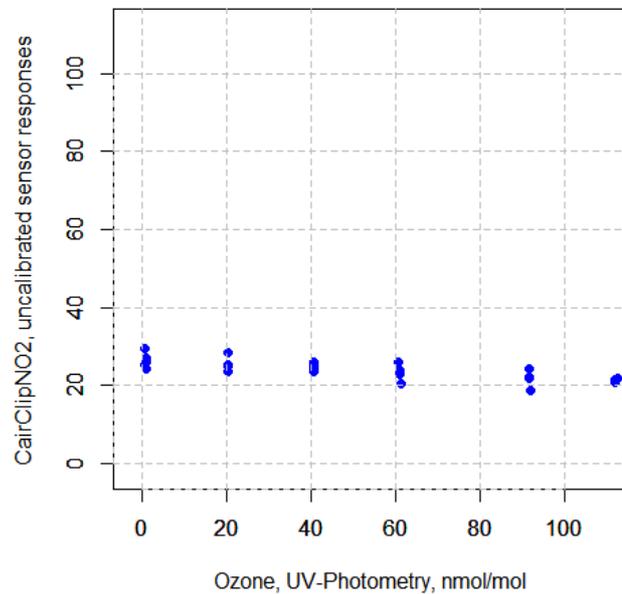
$$O_3 = \frac{Rs - 74.8}{0.147} \quad \text{for } Rs \text{ lower than } 78.6$$

$$O_3 = \frac{0.161 + \sqrt{0.161^2 - 4 \times 0.00672(77.2 - Rs)}}{2 \times 0.00672} \quad \text{for } Rs \text{ higher than } 78.6$$

The same behavior was not observable on the sensor used for field experiment. It was possible to test the sensor in laboratory before installation in field, thus the laboratory check have been postponed to the end of the field experiment. During this experiment, O<sub>3</sub>, NO<sub>2</sub>, temperature and humidity were kept under control. The temperature and relative humidity of the test were set at 22



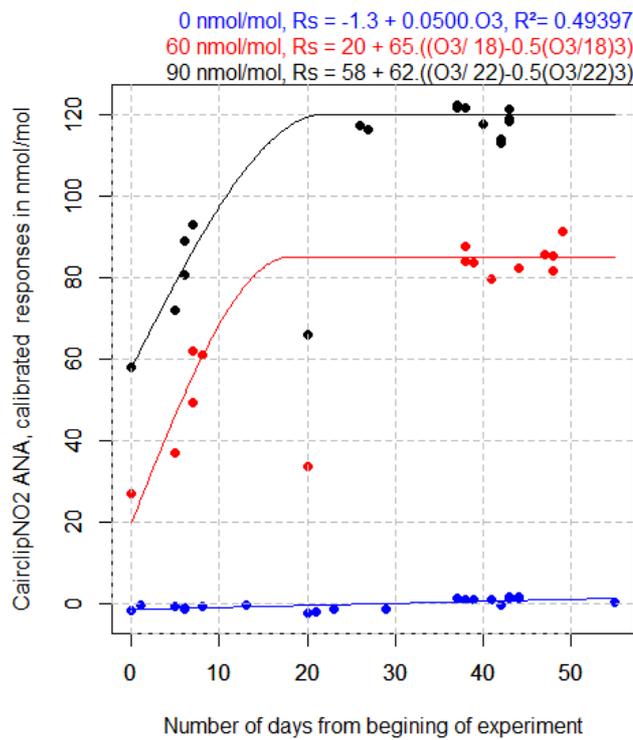
°C and 60 %. The results of the experiment, given in Figure 2 of Appendix C, show a little or no curvature on the sensor responses resulting in the use of a simple linear equation.



**Appendix C, Figure 2: Initial calibration of CairClip NO<sub>2</sub> sensor used for the field experiments of O<sub>3</sub> campaign**

The repeatability of the sensor was calculated using Eq. 3 and was found equal to 4.8 nmol/mol with a high level of ozone whereas it was found equal to 2.7 nmol/mol with high level of NO<sub>2</sub>. In the same way the short term drift,  $D_{ss}$ , evaluated with Eq. 4 is higher when the sensor is exposed to ozone with  $D_{ss} = 4.3$  nmol/mol and an uncertainty  $u(D_{ss}) = 4.8$  nmol/mol. This is likely caused by the saturation of the ozone filter in the CairclipNO<sub>2</sub> as it can be clearly observed Figure 3 of Appendix C on which the filter seems to become saturated after about 30 days.

Regarding the long term drift, the CairClip NO<sub>2</sub> clearly shows that the capacity to filter high levels of ozone decreases over time with sensor responses reaching a plateau after about 20 days. When starting the filter is able to filter about 40 and 32 nmol/mol of O<sub>3</sub> at respectively 60 and 90 nmol/mol. On those both level,  $D_{sl}$  is about 70 nmol/mol. Assuming a rectangular distribution of  $D_{sl}$ , this would correspond to an uncertainty  $u(D_{sl}) = \sqrt{(70^2/3)} = 40.4$  nmol/mol. For informative, Figure 3 of Appendix C give the long term stability of the sensor that can be used to characterised the interference of O<sub>3</sub> overtime

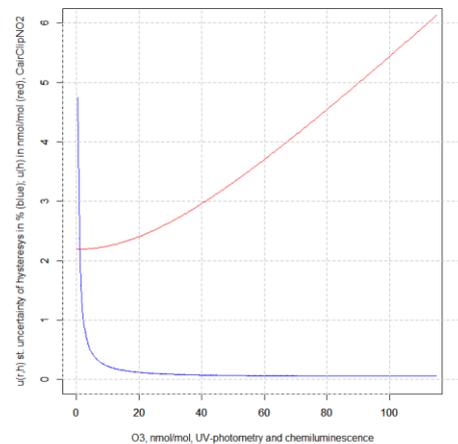
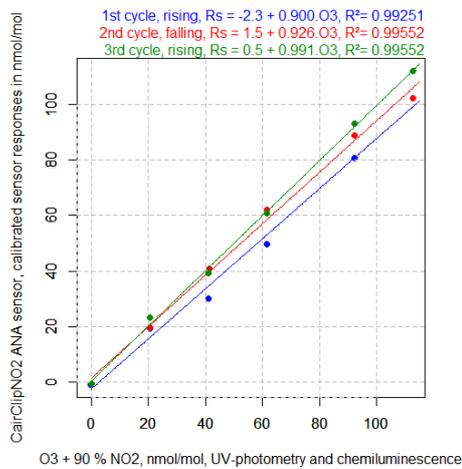


**Appendix C, Figure 3: Long term stability of CairClip NO<sub>2</sub> sensors exposed to O<sub>3</sub>**

It has been shown in 7.3 Hysteresis that the sensor does not suffer from hysteresis effect when exposed to NO<sub>2</sub>. For O<sub>3</sub>, a significant change on the regression line can be observed according to the rising or falling cycle of O<sub>3</sub> levels. The results are given in Table 1 and Figure 4 of this Appendix to know the possible matrix effect of the NO<sub>2</sub> sensor in case of high level of O<sub>3</sub>.

**Appendix C, Table 1: Stability of conditions during the experiments for the determination of hysteresis effect during an exposure to ozone**

O <sub>3</sub> in nmol/mol	NO <sub>2</sub> in nmol/mol	T in °C	RH in %	Pressure in hPa	CairclipNO <sub>2</sub>	Notes
-0.5 ± 0.2	0.4 ± 0.1	22.0 ± 0.03	60.0 ± 0.02	989 ± 0.2	-0.7 ± 1.8	Rise
20.1 ± 0.3	0.4 ± 0.1	22.0 ± 0.03	60.0 ± 0.04	991 ± 0.1	19.5 ± 2.1	
40.7 ± 0.3	0.4 ± 0.3	22.0 ± 0.03	60.0 ± 0.03	991 ± 0.1	30.1 ± 2.7	
61.3 ± 0.2	0.4 ± 0.4	22.0 ± 0.02	60.0 ± 0.04	991 ± 0.1	49.5 ± 5.3	
91.9 ± 0.2	0.2 ± 0.3	22.0 ± 0.03	60.0 ± 0.04	992 ± 0.2	80.6 ± 5.6	
112.4 ± 0.3	0.4 ± 0.2	22.1 ± 0.02	60.0 ± 0.06	992 ± 0.1	102.1 ± 5.9	Fall
91.9 ± 0.3	0.4 ± 0.2	22.0 ± 0.02	60.0 ± 0.04	991 ± 0.2	89.0 ± 7.0	
61.3 ± 0.2	0.4 ± 0.1	22.0 ± 0.02	60.0 ± 0.04	990 ± 0.2	61.9 ± 5.8	
41.0 ± 0.4	0.4 ± 0.1	22.0 ± 0.03	60.0 ± 0.06	989 ± 0.1	41.0 ± 4.2	
20.3 ± 0.3	0.4 ± 0.2	22.0 ± 0.03	60.0 ± 0.06	990 ± 0.1	19.5 ± 2.5	
-0.4 ± 0.2	0.3 ± 0.2	22.0 ± 0.03	60.0 ± 0.03	990 ± 0.1	-0.4 ± 1.8	Rise
20.1 ± 0.3	0.3 ± 0.4	22.0 ± 0.03	60.0 ± 0.03	990 ± 0.1	23.3 ± 2.9	
41.0 ± 0.2	0.2 ± 0.2	22.0 ± 0.02	60.0 ± 0.03	991 ± 0.1	39.3 ± 4.1	
61.3 ± 0.2	0.4 ± 0.2	22.0 ± 0.02	60.0 ± 0.04	992 ± 0.2	60.9 ± 4.8	
92.0 ± 0.3	0.4 ± 0.1	22.1 ± 0.02	60.0 ± 0.03	991 ± 0.1	93.0 ± 7.3	
112.3 ± 0.3	0.4 ± 0.1	22.1 ± 0.02	60.0 ± 0.04	990 ± 0.2	111.9 ± 6.1	



**Appendix C, Figure 4: Effect of hysteresis on CairClip NO<sub>2</sub> sensor and evolution of  $u_{r,h}$  and  $u_h$  as a function of the concentration of O<sub>3</sub>**

During this campaign it has been possible to evaluate the effect of pressure on the sensor responses at 2 levels of ambient pressure (difference about  $\pm 10$  hPa) while other parameters remained constant: O<sub>3</sub> at the LV (60 nmol/mol), mean temperature (22 °C), relative humidity of 50% and without NO<sub>2</sub>. The change of pressure was obtained by:

- first increasing the dilution flow of the generation system of the exposure chamber while carefully eliminating of possible leak of the glass chamber in order to increase ambient pressure
- and second by decreasing the same dilution flow and increasing the aspiration of the output venting of the chamber in order to decrease ambient pressure without allowing for air sample entering into the chamber, e. g. through openings of the chamber.

In average the sensitivity coefficient was found to be 0.19 nmol/mol/hPa and assuming a pressure change extent of 30 hPa results in a standard uncertainty of  $u(P)$  equal to 3.2 nmol/mol. This latter value being slightly smaller than the repeatability, changes in ambient pressure were likely insignificant.



European Commission

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#### Abstract

The aim of this report is to evaluate and validate CairClipO3/NO2 sensors of CAIRPOL within laboratory and field tests under ambient/indoor air conditions corresponding to a specific micro-environment: traffic station, urban/suburban areas. This report presents the evaluation of the performances and determination of the laboratory and field measurement uncertainty of the sensor values, compared to uncertainties fixed by the Data Quality Objective (DQO) of the European Air Quality Directive for indicative method. Further, procedures for the calibration of sensors able to ensure full traceability of measurements of sensors to SI units are developed.

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