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EVALUATION OF MICRO-SENSORS TO MONITOR OZONE IN AMBIENT AIR

Michel Gerboles and Daniela Buzica,
Joint Research Centre, Institute for Environment and Sustainability, Transport and Air Quality Unit, Via E. Fermi, I – 21027 Ispra (VA)

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Contact information
Address: Michel Gerboles, Joint Research Centre, Via E. Fermi, TP 442, I – 21027 Ispra (VA)
E-mail: michel.gerboles@jrc.it
Tel.: +39 0332 785652
Fax: +39 0332 789931

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SUMMARY

Micro-sensors are very small sensors with physical dimensions in the sub-micrometer to millimetre range used to monitor ozone (O_3) in ambient air. They can be based on the variation of the resistance of a semi-conductor or a miniaturized electrochemical cell able to deliver a current varying with the level of the pollutant of interest. In the last years, some technological progress took place and a few commercial sensors are now available in the market. In fact, micro-sensors represent a promising technology in several fields of application: monitoring of O_3 in ambient air, rapid mapping of air pollution over small area, validation of dispersion models, evaluation of exposure of population, emissions monitoring and forest monitoring.

However, due to reliability problems there is a hesitancy to apply these sensors for air pollution monitoring. The suitability of these sensors is here evaluated, hereafter. One electrochemical cell (O3E1) and two semi-conductors (SENS3000 and OMC2), all commercially available, were selected for evaluation of their response time, warming time needed after a cold start, linearity and drift over time. Also, the effect of NO_2 interference, wind velocity, temperature and humidity on the response of sensors is presented. The tests were carried out in our laboratory using an exposure chamber and at one rural field site.

The electrochemical cells (O3E1) did not need a long warming time after a cold start. They reached 99 % of their final value after about 2 hours. On the opposite, the semi-conductor based sensors needed a long warming time. One day was more than enough with the exception of one of the SENS3000. Once the sensors were warm enough their response time to a square wave was about 20 minutes, here also with the exception of one of the SENS3000.

The precision of the semi-conductor based sensors (OMC2 and SENS 3000) expressed in terms of relative standard deviation was constant and better than 2 % for minute average with O_3 ranging between 0 and 90 ppb. However, for O3E1, the relative standard deviation was higher than 5 %. The limits of quantifications were found to be less than 0.5 ppb for OMC2, 2 ppb for SENS3000 and about 30 ppb for O3E1. These figures decrease strongly if half an hour averages are considered. For example the limit of quantification of O3E1 goes down to about 5.5 ppb.

Under laboratory conditions, the linearity of sensors was quite questionable: the OMC2 was found linear but the slopes and intercepts of the regression lines were found completely different according to temperature and humidity of the measured O_3 mixtures. Moreover for O3E1 and SENS3000, the responses were also often curved instead of being linear. In particular, all sensors were found extremely dependent to the relative humidity when O_3 and temperature were kept constant with their responses decreasing with an increase relative humidity.

Apart from temperature and humidity, the results of the laboratory experiments showed that the electrochemical cells (O3E1) were found to be sensitive to NO_2 and wind velocity. SENS3000 was little influenced by wind velocity while OMC2 was not sensitive by both parameters.

The results of the field tests are in contradiction with some of these findings. For O3E1, the main interferences were NO_2 and wind velocity. However, it was not possible to demonstrate any influence of temperature and humidity. In fact, as from one side O_3 in ambient air was strongly correlated with humidity and temperature and on the other side O3E1 was calibrated using O_3 in ambient air, it is likely that any potential influence of temperature and relative humidity on O3E1 was already accounted for by the calibration of O3E1 with O_3. This remark remains valid also for OMC2 and SENS300. The simple calibration of O3E1 with O_3 did not give good results when applied to another time-series of O3E1/O_3. By using a NO_2 correction the agreement between O3E1 and O_3 improved. An attempt to use multi-regression analysis did not bring much improvement while increasing the quantity of needed input data to wind velocity and humidity. A rapid estimation of the uncertainty of O3E1 for hourly averages gave at 30 ppb an expanded uncertainty of 7.4 ppb (about 25 %).

For SENS300, using the manufacturer model yielded some curved responses with huge difference compared to O_3 measured by UV photometry. A first attempt to normalize SENS3000 to O_3 and to correct for temperature was carried out. These corrections were successful with the dataset used for modelling but did not give satisfaction when applied to another set of data used for validation. Better results were obtained by fitting the coefficients of the model equation proposed by the manufacturer to

O_3. Similar and good agreements were observed both with the modelling dataset and the dataset used for validation. The fitting of new coefficients of the model is likely to be needed for any new site with different meteorological conditions. As for O3E1, a rapid estimation of the uncertainty of SENS3000 would give at 30 ppb an expanded uncertainty of 6.8 ppb (about 23 %).

For OMC2, using the manufacturer model also produced some slightly curved responses with high differences compared to O_3 measured by UV photometry. As for SENS3000, best results were obtained by fitting of the coefficients of the model equation proposed by the manufacturer. Similar and good agreements were observed both with the modelling dataset and the dataset used for validation. The same conclusion as for SENS300 applies for OMC2 as well: the new coefficients of the model are likely to be valid only for the sampling site of this study and it may be required to fit new coefficients at each new sampling site and/or for different seasons over the year. A rapid estimation of the uncertainty of OMC2 for hourly averages would give at 30 ppb an expanded uncertainty of 4.8 ppb (about 16 %).

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VALIDATION OF MICRO-SENSORS TO MONITOR OZONE IN AMBIENT AIR

1 INTRODUCTION

Micro-sensors have been tested to monitor ozone (O_3) in ambient air at concentrations of a few 10s of ppb since the end of the 80s[1,2,3,4]. However, due to reliability problems there is a hesitancy to apply these sensors for air pollution monitoring. Sensors have to be efficient, accurate, sensitive and reliable in addition to being small and inexpensive. Moreover, in the last years, some technological progress took place and a few commercial sensors are now available in the market. The suitability of these sensors has to be evaluated for air pollution monitoring under the requirements of the new Air Quality European Directive[5]. In fact, micro-sensors represent a promising alternative to diffusive samplers[6] for monitoring O_3 in ambient air. Diffusive sampling is generally used in alternative to Ultra-Violet photometry[7], the O_3 reference method of measurement. The major advantages of micro-sensors compared to diffusive samplers are their short response time and their capacity to produce real time value without the need for analysis after sampling. Micro-sensors could be implemented in several fields of application:

- O_3 monitoring in ambient air and survey of the limit/target values of the Air Quality Directive;
- rapid mapping of air pollution over small area: the small price of the micro-sensors and the absence of needed maintenance allow using simultaneously a lot of sensors; connecting the sensors to wireless networks creates many other applications for example providing near-to-real-time mapping of air pollution.
- validation of models of air pollution dispersion;
- evaluation of exposure of population (especially if coupled with GPS positioning system);
- fast response emissions monitoring, for example in mobile laboratory;
- forest monitoring, for example determination of real time O_3 profile (Eddy correlation cannot be evaluated with micro-sensors because of their long response time);

A sensor is a device that converts a non-electrical physical or chemical quantity, such as gas concentration, into an electrical signal. Micro-sensors are very small sensors with physical dimensions in the sub-micrometer to millimetre range. They are generally based on the variation of the resistance of a semi-conductor that changes with the concentration of the pollutant being monitored or a miniaturized electrochemical cell able to deliver a current varying with the level of the pollutant of interest. This current is in general generated by a reaction of oxido-reduction. The output signal of the micro-sensors needs be converted into concentration using a known equation that is generally supplied by the micro-sensor manufacturer. Micro-machined metal oxide semi-conductors form perhaps the largest family of micro-sensors because of their widespread availability.

The Air Quality Directive requires an averaging time of 8 hours when monitoring O_3 in ambient air for the target value and 1 hour for the alert threshold. It is expected that the response time of micro-sensors allow sampling with these averaging times on the contrary to diffusive samplers[8]. Model validation and forest monitoring for which O_3 is likely to be measured over several hours can be easily achieved using

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[1] *T. Takada, Ozone detection by In2O3 thin film gas sensor. In: T. Seiyama, Editor, Chem. Sensor Technology vol. 2 (1989), pp. 59–70 Kodansha, Tokyo/Elsevier, Amsterdam*

[2] *Enrico Traversa, Yoshihiko Sadaoka, Maria Cristina Carotta and Giuliano Martinelli, Environmental monitoring field tests using screen-printed thick-film sensors based on semiconducting oxide, Sensors and Actuators B, Vol. 65, 1-3, 2000, 181-185*

[3] *Andreas Schütze, N. Pieper and J. Zachejab, Quantitative ozone measurement using a phthalocyanine thin-film sensor and dynamic signal evaluation, Sensors and Actuators B: Chemical, Vol. 23, 2-3, 1995, 215-217*

[4] *Michel Bobbia, Veronique Delmas, 'Honfleur, utilisation de micro-capteurs pour mesurer l'ozone, 22 mai au 27 aout 2003", Air Normand, Observatoire de la qualité de l'air/ALPA-REMAPPA, Rapport d'étude nº E01-01,* http://www.airnormand.asso.fr

[5] *Directive 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, Official Journal of the European Union L 152/1*

[6] *Cox, R.M., 2003. The use of passive sampling to monitor forest exposure to O_3, NO_2 and SO_2: a review and some case studies. Environmental Pollution 126, 301-311.*

[7] *European Standard, 2005. EN 14625, Ambient Air Quality e Standard Method for the Measurement of the Concentration of Ozone by Ultraviolet Photometry. Brussels, Belgium.*

[8] *Gerboles, M., Buzica, D., Amantini, L., Lagler, F., 2006. Laboratory and field comparison of measurements obtained using the available diffusive samplers for ozone and nitrogen dioxide in ambient air. Journal of Environmental Monitoring 8, 112-119.*

micro-sensors. However, for mobile measurement systems (i. e. monitoring of population exposure or with a mobile laboratory), a short response time of micro-sensors is necessary to avoid artefact from sampling. In fact, in this study, the response time of micro-sensors is investigated. Moreover, warming time after a cold start, linearity, drift over time and the effect of NO_2 interference, wind velocity, temperature and humidity on the response of sensors are presented. The comparison of the responses of these samplers versus UV photometry is investigated both under controlled conditions using an exposure chamber and under field conditions. All sensors used in the study are commercially available. O_3 is determined according to the specifications of the manufacturers, without modification of the model equation proposed by the manufacturers.

2 SELECTION OF TESTED SENSORS

Further to a literature and WEB survey several sensors were selected (see Figure 1). It has to be noticed that so far none of them has in built battery system. They all need connection to power supply and GPS/GM connection for positioning and data transfer that would be needed for monitoring the exposure population to O_3.

2.1 O3E1 Electrochemical cell (Sensoric - G),

The O3E1 (see Figure 1-a) is an amperometric electrode sensor cell using an organic gel electrolyte, equipped with a Transmitter Board. This small device converts the raw sensor signal of the O_3 electrochemical sensor cell into a standard 4-20 mA output or into a 40-200 mV voltage output. The sensor is calibrated by the manufacturer (Sensoric, Bonn - Germany, now owned by City Technology Ltd - UK) in the range 0 – 1000 ppb. The Transmitter Board has on-board temperature compensation and allows the use of an optional external temperature sensor for temperature compensation. The sensor is normally used for environmental and indoor air monitoring. The transmitter board allows the user to calibrate with two points (zero and span). However, during this study it was impossible to successfully carry out this calibration.

The manufacturer provides some validation data proposed by in the sensor data sheet. The sensors are distributed in Italy by Technosens (I – Bergamo). The manufacturer suggests a linear relationship between the O_3 in ambient air and the voltage measured at the output of the cell allowing a two points calibration of the cell. Sensoric also produces micro-sensors for CO and NH_3. The price of an O3E1 sensor without protective box or data logging is about 350 Euro.

2.2 SENS3000 semi-conductor based sensor (UNITEC - I)

The SENS3000[9] is a thick film solid state sensor placed in anodized aluminium case. The sensible surface of the sensor is a semiconductor oxide (the metal oxide type is not disclosed by the manufacturer) made of nano-particles of the size of 200 µm. The first reaction which happens on the surface of the sensor is the absorption of the atmospheric oxygen and the consequent charge transfer from the semiconductor to the oxygen molecule. The second reaction is related to the specific gas to be measured, which while linking to the oxygen molecule allows the electron to be released in the conduction band of the semiconductor. Taking the current signals from the sensor, the direct concentration of the specific gas in atmosphere can be measured. Selectivity and precision are reached using special semiconductor oxides with appropriate filters. The output analogic signal from the sensor needs to be converted into concentration using a known function. The conversion of output signal from the sensor into O_3 was computed using the function given by the supplier:

$$O_3\,[\mu g/m^3] = -31.6 + 5330.9 \,.\, X^{-0.598} \qquad (1)$$

Where X is the voltage given by the SENS3000 sensor in mV. The formula is the same for all the SENS3000 supplied by UNITEC. The SENS3000 sensor is equipped with a miniaturized fan that sucks the air in and takes it to the semi-conductor. It was expected that the fan would reduce the response time. The price of a SENS3000 sensor without protective box or data logging is about 2000 Euro. Unitec manufactures sensors for O_3 (see Figure 1-b) and also for NOx, NO_2, CO and Benzene.

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[9] www.unitec-srl.com

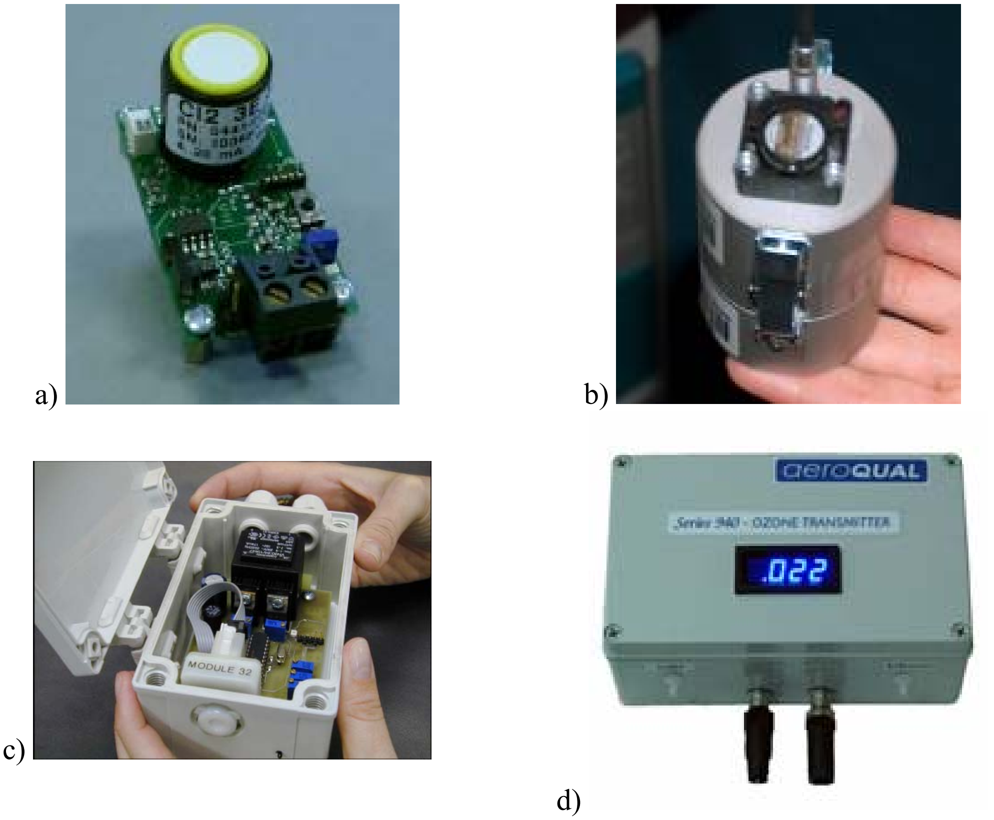
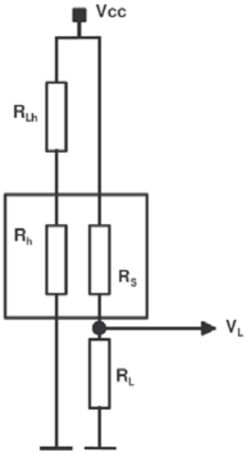


Figure 1: Microsensors used to monitor ozone in ambient air: a) chemical sensor "O3 3E1" of Sensoric with Transmitter Board, b) SENS3000 of UNITEC, c) OMC2 sensors manufactured by MicroChemical Systems MICS and d) Series 940 – ozone transmitter manufactured by AEROQUAL

2.3 OMC2 semi-conductor based sensor (MicroChemical Systems MICS - CH)



The OMC2 sensors (see Figure 1-c) are already implemented by several laboratories in France[10]. This instrument was designed for real time O_3 monitoring and has a recording capability of up to 220 days of the average O_3 concentration at 15 minute intervals in outdoor environments. Taking the signals from the sensor, the direct concentration of the specific gas in atmosphere can be measured. Selectivity and precision are reached using special semiconductor oxides with appropriate filters. The conversion of output analogic signal from the sensor into O_3 is carried out using the function given by the supplier:

$$O_3 = x_0 + x_1 R_S + x_2 R_S^2 + x_3 R_S^3 \qquad (2)$$

$$R_S = R_L \frac{V_{cc} - V_L}{V_L} e^{K(T-25)} \qquad (3)$$

Where O_3 is the ozone concentration in ppb, x_3, x_2, x_1 and x_0 are parameters specific to each OMC2 sensor that are given by the manufacturer and R_S is the measured resistance. R_S is normalized to 25ºC using equation 3 where R_L is the load resistance (generally 470 ohms), V_{cc} is the supply voltage (5.0 V), V_L is the measured voltage, T is the ambient air temperature in ºC and K is the coefficient of the temperature correction (generally 0.05). R_{LH} is used to limit the power consumption of the sensor and to regulate the temperature of the sensitive layer (the target temperature for O_3 detection is 400°C).

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[10] *www.cea-technologies.com/article/pdf/num_74.pdf and Cecile Raventos, Utilisation des microcapteurs : bilan et retour d'expérience, 2006, INERIS – DRC – AIRE-74769-nº0837/CRa,*

The OMC2 sensor has a membrane in front of the sensitive surface of the semi- conductor. Consequently, it was expected that the O_3 molecules would slowly reach the active surface of the semi-conductor since they first have to diffuse through the membrane. This passive system of diffusion may produce long response time to be evaluated later on in the report. The price of an OMC2 sensor including protective box, data logging and data transfer software is about 1000 Euro.

2.4 Series 940 – ozone transmitter

The sensor (see Figure 1-d) was supplied by UNITEC and manufactured by Aeroqual (NZ). It consists of a semi-conductor based sensor (Aeroqual-NZ). Unfortunately, the sensor arrived too late to be included in this study and will be tested at a later stage. The price of a Series 940 sensor with protective box, data logging and data transfer is about 350 Euro.

2.5 Other manufacturers

- A few semi-conductor based sensors and an exposition board were also purchased from Microsens/Silsens (CH). However the software supplied by Microsens/Silsens for exchanging data between the acquisition system and the sensor did not work properly. While asked, the technical department of Microsens/Silsens did not give information and support on how to use their software. Therefore these sensors were not tested. Further potential manufacturers were contacted without success:
- LASMEA[11] (Clermont Ferrand – F), a laboratory specialized on gas sensors based on organic semi-conductor of phtalocyanine, was invited to participate to the study. However the laboratory was not able to supply a commercially available sensor used to monitor O_3.
- Pirelli Labs (Milan – I) produces a newly designed sensor based on semi-conductor according to a research carried out at the University of Ferrara (it seems that the SENS3000 is based on the same technology). A confidential validation report issued by ARPA was sent to us[12]. The sensor should be distributed by SARTEC (I). Pirelli Labs was not willing to include their new sensor in this study.
- Figaro Technologies, a well known company in the field of gas sensors was contacted but no sensor for O_3 in the range of ambient concentration was available.

3 Design of experiment

3.1 Laboratory tests

3.1.1 Exposure chamber

Micro-sensors were evaluated in an exposure chamber. This chamber allows the control of O_3 and additional gaseous interference, temperature, relative humidity and wind velocity (see Figure 2). The exposure chamber is an “O”-shaped ring-tube system, covered with dark insulation material. For generating $O_{3,}$ a MicroCal 5000 Umwelttechnik MCZ Gmbh (G) generator was used. The exposure chamber can accommodate the O_3 micro-sensors directly inside the “O”-shaped ring-tube system.

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[11] *J. Bruneta, A. Pauly, L. Mazet, J.P. Germain, M. Bouvet, B., Malezieux, Improvement in real time detection and selectivity of phthalocyanine gas sensors dedicated to oxidizing pollutants evaluation”, Thin Solid Films 490 (2005) 28 – 35, oi:10.1016/j.tsf.2005.04.015*

[12] *Giuseppe CASTROFINO, Michele D’ANGELO, Vorne GIANELLE, Marco PIGA, RAPPORTO SINTETICO SPERIMENTAZIONE MONITORAGGIO QUALITA’ DELL’ARIA, Pirelli Labs, Agenzia Regionale per la Protezione dell’Ambiente della Lombardia*

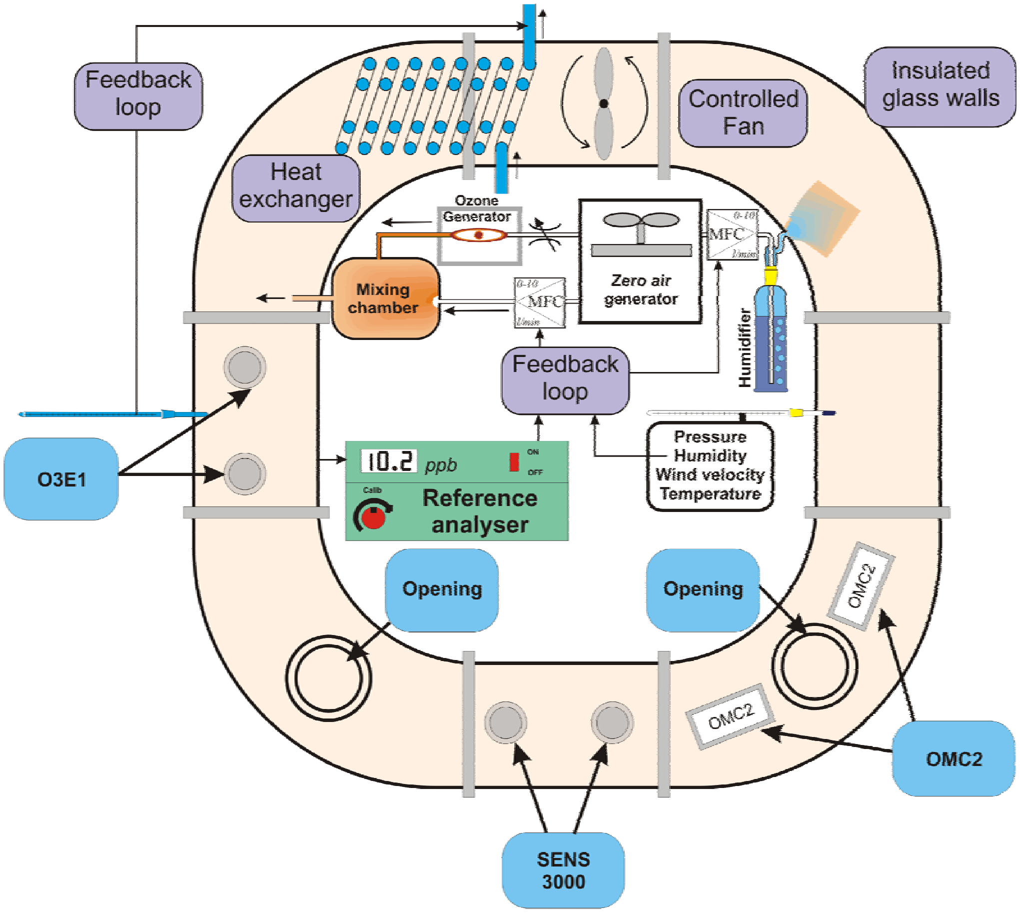

Figure 2: Exposure chamber for micro-sensors used in laboratory

O_3 was monitored using a Thermo Environment TEI 49C UV-photometer. The analyser was calibrated before the experiments using an O_3 primary standard (TEI Model 49 C Primary Standard, Thermo Environmental Instruments) cross-checked against a long-path UV photometer (UMEG GmbH, G). During the experiments, the analyser was submitted to control checks using a portable O_3 generator SYCOS KTO 3 (Ansyco, GmbH) certified against the primary standard. The homogeneity of exposure conditions in the chamber shall be investigated in all tests. The influence of humidity on the TEI 49C was evaluated and corrected where needed. The data acquisition system had a frequency of acquisition of 100 Hz and average over one minute where stored.

3.1.2 Warming period after cold start

MICS, the manufacturer of OMC2 micro-sensors recommends 12 hours of waiting period before considering the response of the OMC2 as valid, after a cold start. The manufacturer explains that the sensible surface of the sensor undergoes a first reaction that is the absorption of the atmospheric oxygen and the consequent charge transfer from the semiconductor to the oxygen molecule. The second reaction is related to O_3, which while linking to the oxygen molecule allows the electrons to be released in the conduction band of the semiconductor.

To evaluate the warming period of the O3E1, OMC2 and SENS3000, pairs of cold micro-sensors (switched off) were exposed to a stable conditions of O_3 (about 200 µg/m^3), temperature (25 ºC) and relative humidity (between 62 and 66 %) in the exposure chamber and then switched on. Table 1 and Figure 3 shows the warming period for all the tested micro-sensors. For the 1st OMC2 (ref. 1!183), 90 % of the final value was reached after 5 hours, 95 % after 10 hours and 99 % after about 16 hours. For the 2nd OMC2 (ref. 4?47), 90 % of the final value was reached after half an hour, 95 % after 2 hours and 99 % after about 15 hours. For the 1st SENS3000 (ref 56B-B12), stability of the sensor was not reached after 17 hours. For the 2nd SENS3000 (ref 88B C010), 90 % of the final value was reached after half an hour, 95 % after 6 hours and 99 % after about 16 hours. For the 1st O3E1 (P/N 1531-031-65109,

Table 1: Warming period, time needed by the sensors to reach 90, 95 and 99 % of O_3 in the exposure chamber after a cold stat

Micro-sensors	90 % of final value	95 % of final value	99% of final value
OMC2 - 1	5 hours	10 Hours	16 hours
OMC2 – 2	½ hour	2 hours	15 hours
SENS3000 - 1			> 17 Hours
SENS3000 - 2	½ hour	6 hours	16 hours
O3E1 - 1	3 min	40 min	2 and ½ hours
O3E1 - 2	3 min	20 min	2 hours

S/N10665401-613), 90 % of the final value was reached after 3 min, 95 % of the final value was reached after 40 min while 99 % of the final value was reached after 2 and half hours. For the 2nd O3E1 (S/N 10665408-613), 90 % of the final value was reached after 3 min, 95 % of the final value is reached after 20 min while 99 % of the final value was reached after 2 hours. In this experiment, the electrochemical sensors shows a shorter response time (within 3 min for 90% of the final value, up to 40 min for 95 % and up to 2 and half hours for 99 %) compared to the micro-sensors based on semi-conductor. One shortcoming of these latter sensors is that they show different response times for the same model of sensor. With the exception of one of the SENS3000 which was not stabilized at the end of this experiment yet, the other semi-conductor sensors needed less than one day of stabilization after a cold start while the electrochemical cells are ready after less than 3 hours. In the following experiments, all evaluations are carried out after a pre-warming of the sensors for at least 48 hours (this is referred as a warm-start afterwards).

3.1.3 Response time to a change of concentration of ozone

To evaluate the response time of the micro-sensors, a rapid change of O_3, between 0 and 210 µg/m³, was achieved. The time that the sensors needed to reach 90 % of the final value was used to estimate their response time. The rapid change of concentration of O_3 was made possible by connecting the exposure chamber with the outlet of an O_3 generator delivering 100 l/min with the desired O_3. The exposure chamber had an internal volume of about 120 l. The UV-photometer showed that O_3 in the chamber could reach 90 % of its final value within 4 min.

In the 1st experiment (see Figure 16 in annex 1), O_3 was initially at 100 ppb and was decreased to nearly 0 ppb for two hours. Then, O_3 was increased to 100 ppb for 4 hours and then decrease to 0 ppb for 75 min. Finally O_3 was increased again to 100 ppb and the whole experiment was stopped during the rising step. The SENS3000 appeared much slower than the OMC2 and O3E1 in the fall step. The response of the O3E1 sensors showed higher noise than the one of OMC2 and SENS3000 and thus their response signals had to be fitted using a moving average (5-minute averages). Table 2 shows the lag time (from 0 to 10 % of the final value), rise time (from 10 to 90 % of the final value) and response (from 0 to 90 % of the final value) for this experiment. The response time of the micro-sensors is not corrected for the time that O_3 needed to reach stability in the exposure chamber. This time could be estimated by the response time of the UV-photometer (TECO in Table 2) to reach 100 ppb. During the whole experiment, the temperature in the chamber was accurately controlled and remained stable since all air gas mixtures were injected at the ambient temperature (22.5 ºC), the value at which the exposure chamber was temperature controlled. On the opposite, all air streams were directly injected in the exposure chamber without pre-adjustment of the humidity condition of the chamber. This lack of pre-adjustment of humidity yielded variable conditions of relative humidity during the whole experiment. It is likely that this change of humidity condition is responsible for the long response time during the rise step (up to 2 and a half hours, see Table 2) especially longer for O3E1 compared with the cold start experiment. The smaller response time of the fall step is likely to be caused by more stable condition of relative humidity.

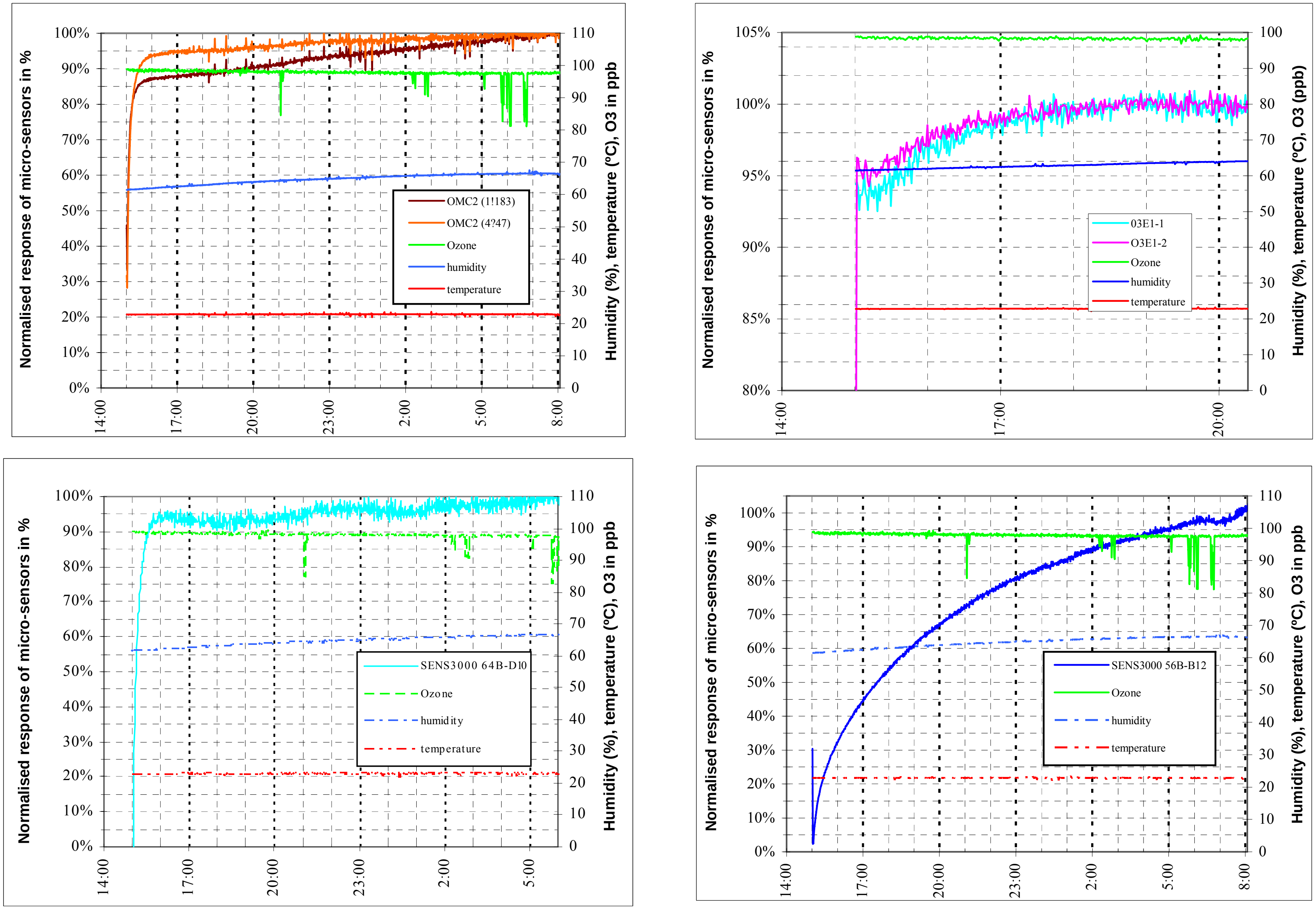

Figure 3: Warming period of simultaneously started micro-sensors (OMC2, SENS3000 and O3E1) exposed to the same conditions after a cold start versus time at constant ozone level (98 ppb), constant temperature (23 ºC) and relative humidity between (32 to 66 %).

Table 2: Lag time, rise time and response for several micro-sensors in the exposure chamber when ozone increase (“Rise” step) and decrease (“Fall” step) between 0 and 100 ppb and unstable relative humidity

		Lag time	Rise time	Response time
		(0 -10 %)	(10 - 90 %)	(0 - 90 %)
Rise	TECO	0:02	0:08	0:10
	OMC2-1	0:02	1:05	1:08
	OMC2-2	0:01	0:57	0:58
	UNITEC-1	0:04	1:12	1:17
	UNITEC-2	0:01	0:40	0:42
	O3E1-1	0:03	2:21	2:25
	O3E1-2	0:02	2:11	2:14
Fall	TECO	0:02	0:08	0:10
	OMC2-1	0:02	0:15	0:17
	OMC2-2	0:02	0:16	0:18
	UNITEC-1	Not stable after 75 min		
	UNITEC-2	Not stable after 75 min		
	O3E1-1	0:04	0:20	0:24
	O3E1-2	0:04	0:18	0:22

To avoid the possible dependence of the response time on the variation of humidity, a 2nd experiment with constant humidity was carried out. In the 2nd experiment, O_3, temperature, relative humidity and wind speed remained constant: 105 ppb, 22 ºC, 42 % and 2.5 m/s, respectively. Figure 17 (in annex 1) shows the responses of the micro-sensors sensors and Table 3 shows the response times. For the O3E1 sensors that gives more noisy values a moving average of 10 minutes was overlaid on the measurements. For the OMC2 and SENS 3000, the response times were calculated using the profile of the sensors response crossing with 10 % and 90 % of the final value lines. For the O2E1, the response time was calculated using the moving average profile crossing with 10 % and 90 % of the final value lines and subtracting 5 minutes to these response times (half of the moving average windows). Table 3 gives the lag time, rise time and response time for each sensor. It is obvious that these values are much smaller than in the 1st experiment when humidity was poorly controlled. Here also, one of the SENS3000 has a longer response time when compared to the other one. On the opposite both O3E1 and OMC2 have similar response times while O3E1 is overestimated of a few minutes by the moving average computation

The SENS3000 is the only sensor using active pumping with a fan. Consequently it was expected that this sensor would react faster than the other sensors. However, it is not the case and the sensors show very different response times for the two SENS3000 sensor: one very slow sensor (56B-B12) while the other one as fast as the other sensors.

The time needed by O_3 in the chamber to reach 100 ppb should be subtracted from the estimated response times. Taking into account that 2 min 48 sec are necessary for O_3 to reach 90 % of the final in an exposure chamber of 120 l in which O_3 is injected at 100 ppb with a flow of 100 l/min, a response time of 22 min will be considered for the next experiments.

Table 3: Lag time, rise time and response for several micro-sensors in the exposure chamber when ozone rises from 0 to 210 µg.m^{-3} in less 4 minutes

	Lag time (0-10 %)	Rise time (10-90 %)	Response time including equilibrium in the chamber (0-90 %)	Response time of sensors (0-90 %)
UV-photometry	2'	2'	4'	1'
OMC2 (1!183)	2'	23'	25'	22'
OMC2 (4?47)	2'	23'	25'	22'
SENS3000 56B-B12	2'	40’	42'	39'
SENS3000 64B-D10	2’	18’	20'	17'
O3E1-1	3'	16'	19'	16'
O3E1-2	3'	19'	21'	18'

Table 4: Conditions of exposure and micro-sensors responses with their relative standard deviations (s) and relative standard deviations (RSD)

O_3 ppb	s ppb	RSD	RH %	s %	RSD	Temp. ºC	s ºC	RSD	OMC2 ppb	s ppb	RSD (1!183)	OMC2 ppb	s ppb	RSD (4?47)	Unitec ppb	s ppb	RSD 56B-B12	Unitec ppb	s ppb	RSD 64B-D10	03E1 ppb	s ppb	RSD	O3E1 ppb	s ppb	RSD
0.1	0.13	99.0%	77.8	0.21	0.3%	14.5	0.28	1.9%	4.7	0.03	0.5%	9.5	0.03	0.3%				3.6	0.03	0.7%	6.1	7.3	118%	5.9	3.8	66%
13.4	0.17	1.3%	78.2	0.20	0.3%	14.4	0.29	2.0%	7.2	0.08	1.1%	12.6	0.09	0.7%	5.3	0.28	5.3%	24.4	0.35	1.4%	20.4	4.8	23.5%	20.0	3.8	19.2%
28.6	0.19	0.7%	78.4	0.21	0.3%	14.4	0.24	1.7%	11.5	0.12	1.1%	17.2	0.14	0.8%	21.0	0.30	1.4%	33.3	0.31	0.9%	37.6	6.0	16.0%	47.8	5.5	11.5%
58.9	0.15	0.3%	78.4	0.20	0.3%	14.4	0.26	1.8%	19.9	0.28	1.4%	25.7	0.31	1.2%	37.4	0.40	1.1%	41.5	0.50	1.2%	72.5	7.4	10.2%	105.0	5.8	5.5%
74.8	0.96	1.3%	78.8	0.57	0.7%	14.6	0.28	1.9%	24.3	0.39	1.6%	30.0	0.42	1.4%	42.3	0.43	1.0%	44.6	0.56	1.2%	83.3	6.9	8.3%	123.2	6.0	4.9%
87.7			78.5	0.18	0.2%	14.4	0.16	1.1%	28.1	0.27	1.0%	33.6	0.30	0.9%	45.6	0.48	1.1%	46.9	0.59	1.3%	92.4	8.5	9.2%	134.6	6.0	4.5%

It can be observed that after a cold start, the O3E1electrochemical sensors reach stability faster than semi-conductors while after a warm start the semi-conductors and electrochemical cells have a similar response time.

3.1.4 Precision under repeatability conditions, limit of detection, limit of quantification

The precision under repeatability conditions of the sensors was estimated at several levels of O_3 concentration keeping the relative humidity (78 %) and temperature (14 ºC) constant. A fraction of the variability of the factors influencing the sensor response (first O_3 but also temperature and humidity) will be included in the variability attributed to the sensors. However, these influencing factors were kept as constant as possible and it is expected that this aspect can be neglected as they remain within 2% (see Table 4 about 2 % of relative standard deviation (RSD) for temperature, 1 % for O_3 and 0.5 % for humidity).

Table 4 gives the standard deviation (s) and RSD of the sensors at different concentrations of O_3. The repeatability was estimated after waiting for more than for 4 response-times (90 min) and was also estimated during 4 times the response time. By observing the relative standard deviations one can notice that the electrochemical cells are more scattered than the semi-conductors based sensors while between the semi-conductors the OMC2 appear more precise especially for O_3 lower than 50 ppb. It can be observed that the standard deviation of semi-conductor sensors are strongly correlated with O_3 (R^2 about 0.85 for OMC2/SENS 3000) while the RSDs are less correlated with O_3. The standard deviation at 0 ppb of O_3 is estimated by regression analysis for each sensor. It is multiplied by 3.3 to compute the limit of detection. The limit of detection represents the smallest concentration of O_3 that can be reliably detected by the sensors. The limit of quantification is calculated as 10 times the standard deviation at 0 ppb. The limit of quantification is the lowest concentration of O_3 that can be quantitatively determined with suitable precision and accuracy. These limits are calculated for one-minute measurements. As Table 5 shows these limits significantly decrease for half-an-hour measurements. The semi-conductor sensors (OMC2 and SENS3000) have much lower limit of detection than the O3E1 electrochemical sensors.

Table 5: Limit of detection and limit of quantification in ppb for all sensors measuring every minute or every half and hour estimated at 14ºC and 78 % of relative humidity

	Limit of detection (ppb)		*Limit of quantification (ppb)*	
	Every minute	Every 30 minutes	Every minute	Every 30 minutes
OMC2 1!183	0.110	0.020	0.33	0.061
OMC2 4?47	0.133	0.037	0.44	0.081
SENS3000 56B12	0.78	0.142	2.35	0.43
SENS3000 64B-D10	0.48	0.088	1.47	0.27
O3E1 – 1	12.2	2.2	37	6.8
O3E1 - 2	8.3	1.52	25	4.6

3.1.5 Linearity

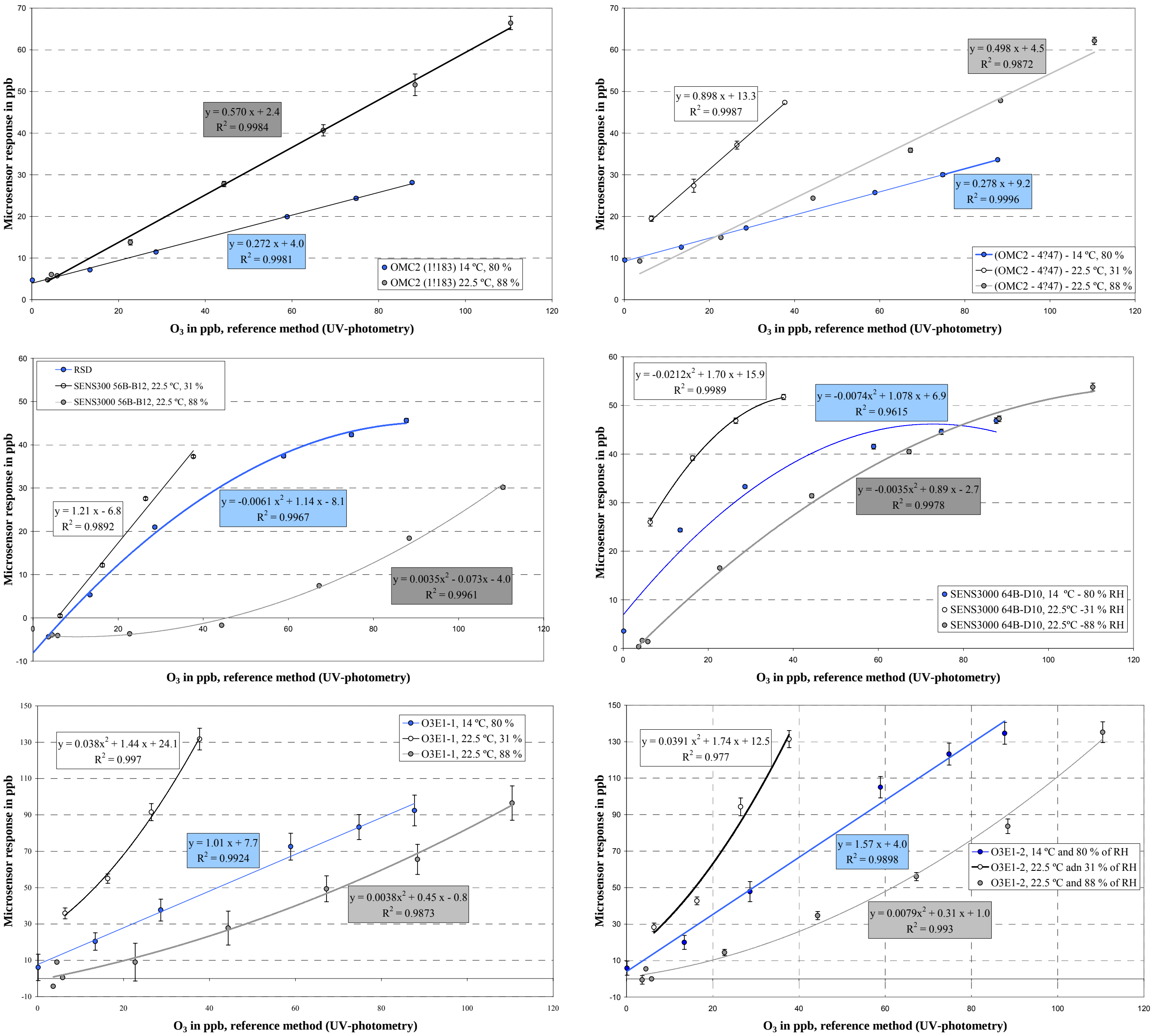

Figure 4: Linearity of micro-sensors at three different temperature and relative humidity conditions (14 ºC/78 %, 22.5/31 % and 22.5/88 %). The error bars represents the standard deviations of the measurements. The two upper graphs represent the OMC2 results, the two middle ones are the SENS3000 results and the two lower ones are the O3E1 results.

All sensors were submitted to a multipoint linearity test at concentrations between 0 and 180 µg/m³ (0 to 88 ppb) at one condition of temperature and humidity (14 ºC and 77 % of relative humidity strictly controlled). For the OMC2 and SENS3000, the calibration function provided by the manufacturer was used even though for OMC2 the calibration was out of date. On the opposite, the O3E1 were calibrated during the warming experiment using two points (0 and 76 ppb at 14ºC and 77 % of relative humidity). The equations were $[O_3]_{ppb} = 1600 - 9676\ V_{Volt}$ and $[O_3]_{ppb} = 492 - 3526\ V_{Volt}$ where V is the response of the sensors in Volt. With these equations a decrease of voltage corresponds to an increase of O_3. The O3E1 were not re-calibrated for the 2-and-a-half months of laboratory experiments.

Figure 4 shows the linearity plots for all sensors with their errors bars representing the standard deviations of measurements at each concentration step. The response of the sensors have been calculated based on a data acquisition every minute during 4 response times (90 minutes) after 4 response times (90’) of stabilisation. Regarding the semi conductors, their results show lower values than the reference values given by UV photometry. This discrepancy is due to an incorrect calibration function but it is not the point of this experiment. The important aspect is that the response of the OMC2s appears linear while the one of the SENS3000s is not linear. The response of the O3E1 seems reasonably linear (R^2 of 0.99 for the tested pair of O3E1) but suffers from higher noise (longer error bars) than the semi-conductors. One has to remember that it is normal that O3E1 response agrees with the UV photometer value since they were used for the linear calibration of these sensors.

3.1.6 Temperature and humidity effects

Further to the evaluation of the response time, it was expected that the semi-conductor is affected by humidity. Consequently, another experiment was carried out in which both O_3 and temperature were kept constant (70 ppb and 25 ºC) while the relative humidity was changed between 28 and 78 %. As the data acquisition system did not work for the 1st OMC2, only the data for the 2nd OMC2 are reported here.

Figure 5 shows the strong decrease of the responses of all the sensors versus relative humidity. The response of the sensors at 25ºC for 70 ppb of O_3 decreases of 1.6 % per percentage of relative humidity for the OMC2 (4?47), 0.75 $\%.\%^{-1}$ of relative humidity for the SENS3000 – 56B-B12, 0.26 $\%.\%^{-1}$ of relative humidity for the SENS3000 – 64B-D10, 0.28 $\%.\%^{-1}$ of relative humidity for the O3E1-1 and 0.24 $\%.\%^{-1}$ of relative humidity for the O3E1-2. Figure 5 also shows that two different SENS3000 can react to a different extent to humidity. In fact, the 1st sensor decreases its response of 0.75 % per percentage of relative humidity while the response of the 2nd one only decreases of 0.26 %. This suggests that each sensor may need a specific correction for the effect of humidity. Altogether, Figure 5 shows how important the effect of humidity is when calibrating the sensors. The sensors could be sensitive to relative humidity (an index of vicinity to water condensation) or to the concentration of water vapour molecules (the mass of H_2O molecules per volume unit). Since, in this experiment temperature was kept constant, relative humidity and concentration of water molecules are completely correlated. Consequently, it is not possible to decide if the sensors are sensitive to the relative humidity or to the concentration of water vapour.

It is also observed that the linear relationship describing the decrease of the sensor responses versus relative humidity depends on the temperature condition as well. Figure 4 shows that for all sensors the regression equations are different for the high relative humidity (88 and 80 %) while temperature changed between 14 and 22.5 ºC. In order to confirm this assumption, further experiments under constant humidity and different temperatures are necessary.

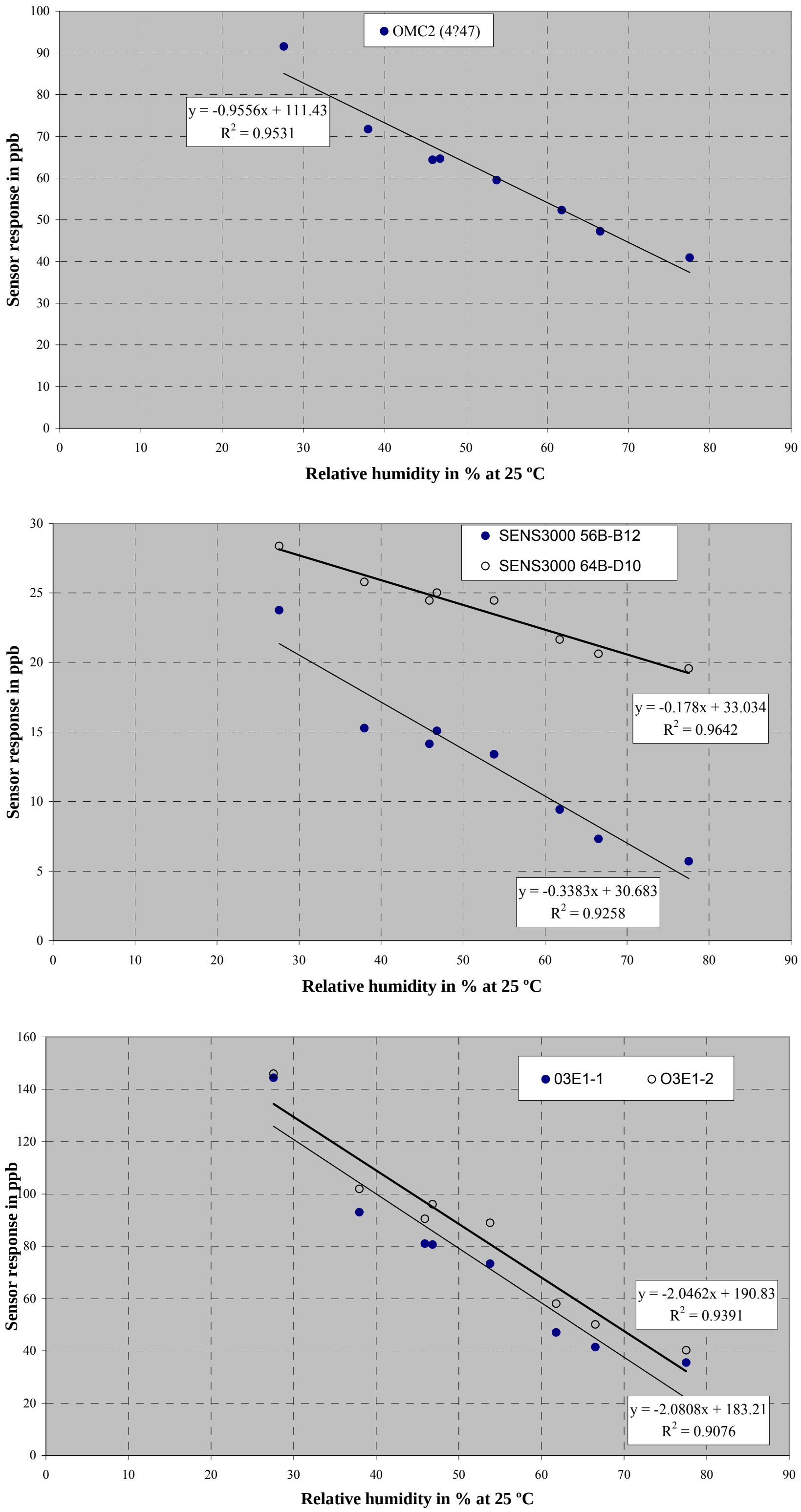

Figure 5: Effect of humidity on the response of sensors at constant temperature (25ºC) and O_3 concentration (70 ppb)

3.1.7 NO_2 Interference

In the chamber, all the sensors were exposed to a gas mixtures with low concentration of O_3 (about 2 ppb) at 22.5 ºC and 82 % of relative humidity. Nitrogen dioxide (NO_2) was generated using a permeation system. First, NO_2 was first kept at 30 ppb and then NO_2 was set to 0.5 ppb. The change of NO_2 level resulted in a change O_3 (from 2 to 4 ppb) and relative humidity level (from 82 to 88 %) as well in the chamber. Figure 6 shows that nevertheless within the uncertainty of this experiment the responses of OMC2 and SENS3000 are not affected by a change of NO_2, at low O_3 concentrations. On the contrary, the responses of O3E1 sensors seem to react to NO_2 as well but in a surprising way: the response signal increases when the NO_2 concentration decreases.

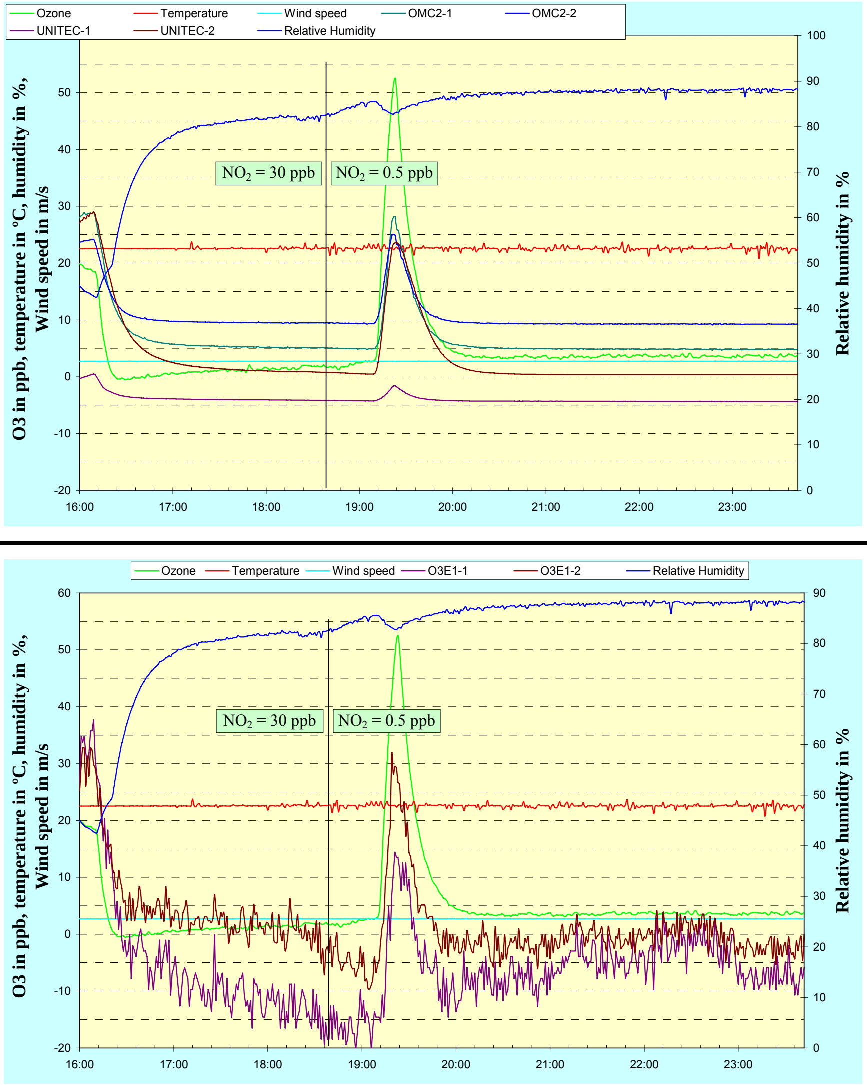

Figure 6: Effect of NO_2 changing from 30 to 0.5 ppb (at the solid line) on the response of ozone sensors with ozone concentration of 2 then 4 ppb, relative humidity of 82 then 88 %, constant wind speed (2.8 m/s) and temperature 22.5 °C

3.1.8 Wind effect

In the exposure chamber, the effect of wind on the sensors was studied by changing the wind velocity between 0.6 and 2.75 m/s in a square wave while the values of O_3, temperature and relative humidity were kept constant at 66 ppb, 25 °C and 55 %, respectively. In fact, it is necessary that O_3, temperature and humidity are kept as constant as possible not to interfere with the estimation of the effect of wind velocity. In this experiment, the data acquisition system did not record the response of the 2nd OMC2. Figure 7 shows the effect of wind velocity on the response of the sensors. First, one can observe that the O3E1 are more affected by wind velocity than the semi-conductor based sensors. It is not clear if this effect is caused by the lack of sufficient barrier of the sensor to turbulent movement of ozone molecules or if it is the kinetic of the red-ox reaction which is affected by the rate at which the O_3 molecules reach the sensor. The response of the SENS3000-1 is slightly affected by wind velocity with behaviour similar to O3E1 sensor. The Unitec-2 appears to be nearly independent to wind velocity while the OMC2 is clearly not affected as its response varies as much as the exposure conditions of O_3 temperature and humidity. Table 6 gives the quantitative differences in % (Δ) between responses of the sensors when the wind velocity changes between 0.6 and 2.8 m/s.

Table 6: Effect of wind velocity on the response of OMC2, SENS3000 and O3E1 with constant O_3, temperature and relative humidity. Δ gives the relative deviations related to the 1st step value. The quoted values are the standard deviations of each parameter

Wind m/s	Δ	O_3 ppb	Δ	humidity %	Δ	Temp. ºC	Δ	OMC2-2 ppb	Δ	SENS3000-1 ppb	Δ	SENS3000-2 ppb	Δ	O3E1-1 ppb	Δ	O3E1-2 ppb	Δ
2.8 ±0.01	0%	65.5 ±0.4	0%	54 ±0.03	0%	25.3 ±0.4	0%	54.5 ±0.8	0%	24.5 ±0.6	0%	47.5 ±1.3	0%	81.6 ±6.0	0%	75.2 ±6.3	0%
0.6 ±0.01	-79%	66.6 ±0.2	2%	54.6 ±0.05	1%	25.1 ±0.1	-1%	53.9 ±0.3	-1%	31.8 ±1.6	29%	50 ±1.2	5%	110.4 ±5.5	35%	110.4 ±4.9	47%
2.8 ±0.01	0%	65.6 ±0.3	0%	54.2 ±0.03	1%	25.3 ±0.1	0%	55.3 ±0.3	2%	26.8 ±0.7	9%	49.1 ±0.9	3%	98.3 ±6.2	20%	93.2 ±4.8	24%
2.8 ±0.01	0%	65.5 ±0.2	0%	53.2 ±0.9	-1%	25.3 ±0.1	0%	56.1 ±0.4	3%	26.7 ±0.6	9%	49.7 ±1.3	5%	86.6 ±6.7	6%	88.1 ±5.8	17%
0.6 ±0.01	-78%	66.9 ±0.2	2%	53.7 ±0.1	0%	25.1 ±0.1	-1%	55.9 ±0.3	3%	33.6 ±0.9	37%	51.6 ±1.2	9%	112.3 ±6.2	38%	117.3 ±4.7	56%

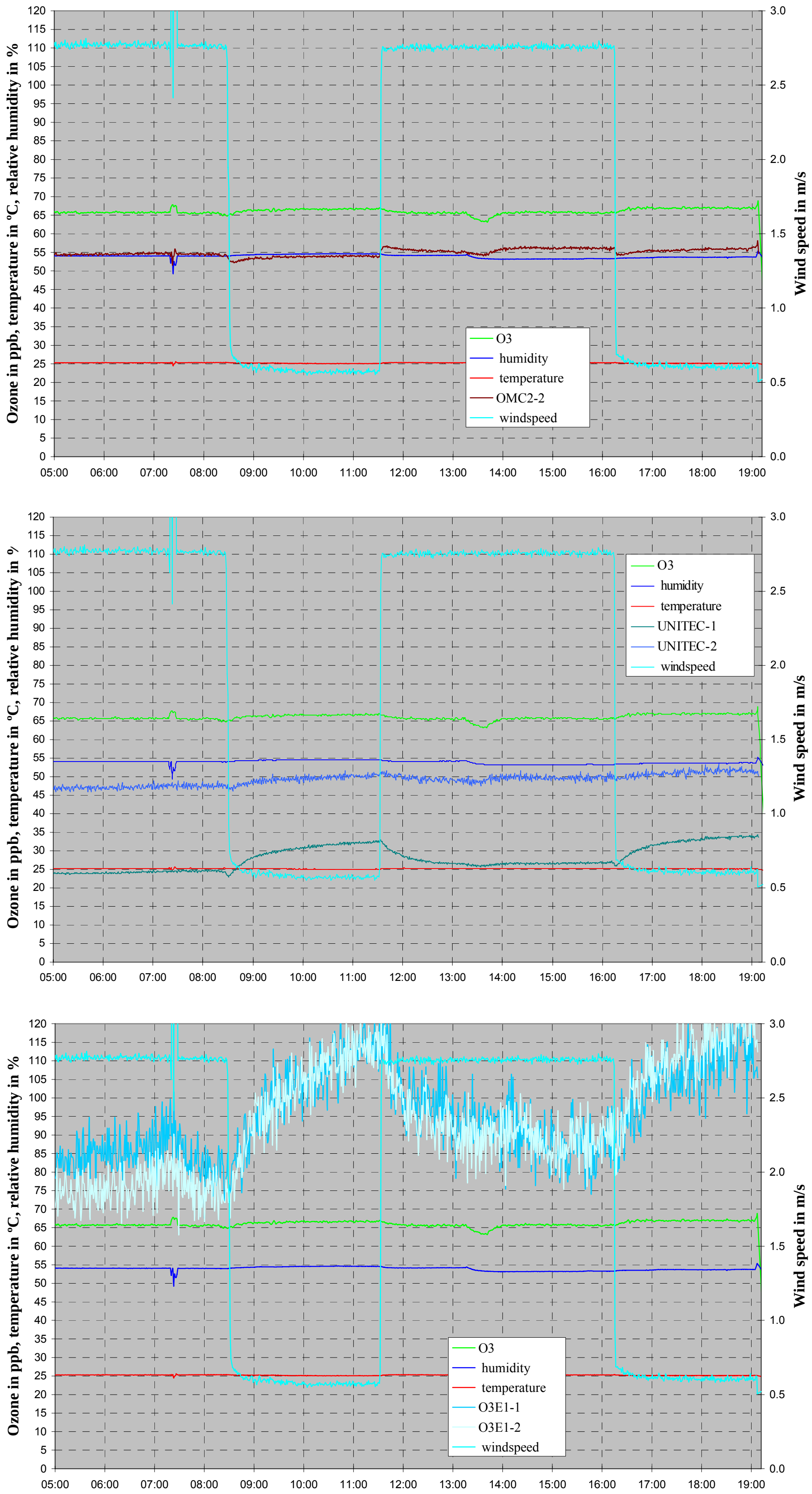

Figure 7: Effect of wind speed

3.2 Field tests

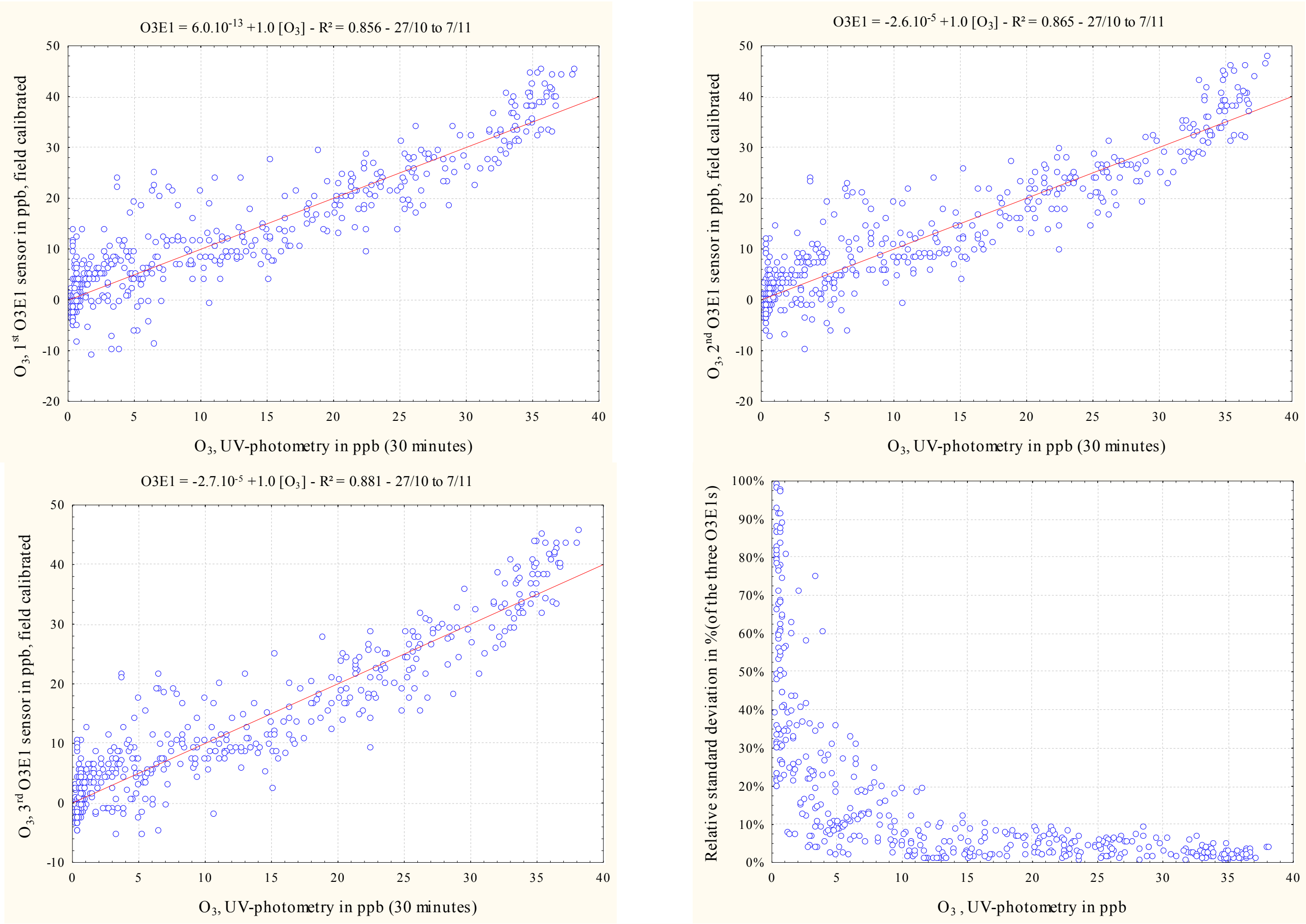

Figure 8: Responses of three O3E1 sensors versus UV photometry and reproducibility of the three sensors between 27/10 and 07/11/2006

The field tests were performed at the JRC Ispra EMEP[13]-GAW[14] Station for Atmospheric Research, Institute for the Environment and Sustainability, Climate Change Unit in Ispra (North of Italy). The EMEP station is a rural station nearby the Maggiore Lake where several atmospheric and meteorological parameters are monitored: NO, NOx, NO_2, SO_2, O_3, temperature, relative humidity, pressure, wind velocity and wind direction. The field tests were carried out in order to check the validity of the findings of the laboratory results. The field tests are necessary since the laboratory tests could only be carried out using synthetic mixtures, while under field conditions, real ambient air mixtures including all possible gaseous interference could be tested. In fact, complex ambient mixtures are nearly impossible to generate in laboratory. In particular mixtures of $NO/NO_2/O_3$ are difficult to artificially generate in laboratory due to the oxidation of NO with O_3.

One SENS3000, two OMC2s and three O3E1s micro-sensors were installed at the EMEP station. One NO_2 (44B-D05) and one NOx (12E-09) micro-sensors manufactured by UNITEC were also tested during the campaign. The monitoring station was equipped with a regularly calibrated UV photometer analyzer and other monitoring equipment. The measurements took place between 27 October and 7 November 2006 and from 7 to 22 of November. The SENS3000 and the OMC2 were used with the calibration given by the manufacturers. On the contrary, the O3E1 sensors were adjusted based on the O_3 values of the EMEP station given by the reference UV-photometer. The equations giving the O_3 according to the response of the

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[13] *Cooperative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP), Geneva, 1984*

[14] *Global Atmospheric Watch*

O3E1 sensors were $[O_3]_{ppb}$ = - 453 + 10982V_{Volt} (s/n 10665407), $[O_3]_{ppb}$ = -493 + 11982V_{Volt} (s/n 10665399) and $[O_3]_{ppb}$ = -418 + 10074V_{Volt} (s/n 10665408) where V is the response of the O3E1 in Volts. It is surprising that the slope and intercept of these equations under field conditions have opposite signs when compared to the equations under laboratory conditions (see 3.1.5). With these equations an increase of voltage corresponds to an increase of O_3.

The data acquisition system of the EMEP stations registered NOx/NO, SO_2, O_3, ambient temperature, ambient pressure and humidity every 10 minutes while ambient pressure and wind direction/velocity were registered every hour. The measurement of the SENS3000 and O3E1 sensors were registered 10 minutes while the ones of OMC2 were registered every 15 minutes. In order to normalize the data treatment, half-an-hour sensor responses versus the UV photometry values are plotted while one-hour averages of O_3 residuals are plotted versus wind, pressure and the other parameters.

Looking at the air pollution during the field tests, O_3 was strongly associated with humidity (r = -0.95) with wind velocity (r = 0.76), NOx (r = 0.58) and temperature (r = 0.54), see Figure 9. Moreover, in the presence of NO, O_3 decreases due to the oxidation of NO to NO_2 as expected.

3.2.1 O3E1 sensors

Figure 8 shows the response of O3E1 versus the O_3 measured by UV photometry between 17 October and 8 November. The correlations between UV-photometry and the response of sensors are rather strong with R^2 equal or more than 85 %. Figure 8 also shows that the relative standard deviation of the 3 sensors measurements is lower than 10 % for O_3 higher than 20 ppb.

By examining the correlation between ambient parameters {NO, NO_2, O_3 (UV and O3E1values), SO_2, temperature, humidity (relative and absolute), atmospheric pressure and wind (Direction and velocity)} and the differences of O_3 measured by UV photometry and by O3E1, it is possible to detect which parameters are associated with the bias of O3E1 sensor. Figure 9 shows these correlations for the 1st O3E1 in a matrix of scatter plots with hourly measurements. In the matrix of scatter plots, $[H_2O]$ is the absolute humidity in $g.m^{-3}$ calculated using temperature and relative humidity. The residuals are mainly correlated with NO_2 (r = -0.61), with SO_2 (r = -0.28), the O3E1 values themselves (r = -0.27) suggesting an autocorrelation and temperature (r = -0.23). The two different branches that can be observed in the scatter plot of the O_3 residuals versus O_3 (see Figure 9) could be explained by an effect of hysteresis of O3E1. In fact, the response of O3E1 generally decreases slower than the UV-photometry values do, as shows the time series given in Figure 10-a. However, it is more likely that this slow decrease of O3E1 is explained by an interference of NO_2 shown in Figure 9.

The O3E1 values can be corrected for the NO_2 interference using the equation given in Figure 10-b which shows the relationship between the O_3 residuals and NO_2 (O_3 - O3E1 = 4.0 - 0.41 NO_2). Indeed, it is expected that the oxydo-reduction reactions that take places in the sensor are affected by the presence of oxidizing gases like NO_2. The O3E1 values could have been corrected SO_2 as well since this is another gas able to affect O3E1. However, SO_2 was very low during the study, less than 2.5 ppb as it is generally observed in the majority of sites over Europe. The uncertainty involved into any correction with such low values would be too high.

After NO_2 correction, the O_3 residuals became highly correlated with wind velocity (Figure 10 c). From one side, the laboratory experiments showed a dependence of O3E1 on wind velocity but from another side, O_3 in ambient air at the EMEP station was associated with wind velocity. It is difficult to conclude if the relationship of the O_3 residuals with wind velocity is caused by a simple dependence of O_3 that is himself dependent to wind velocity or not.

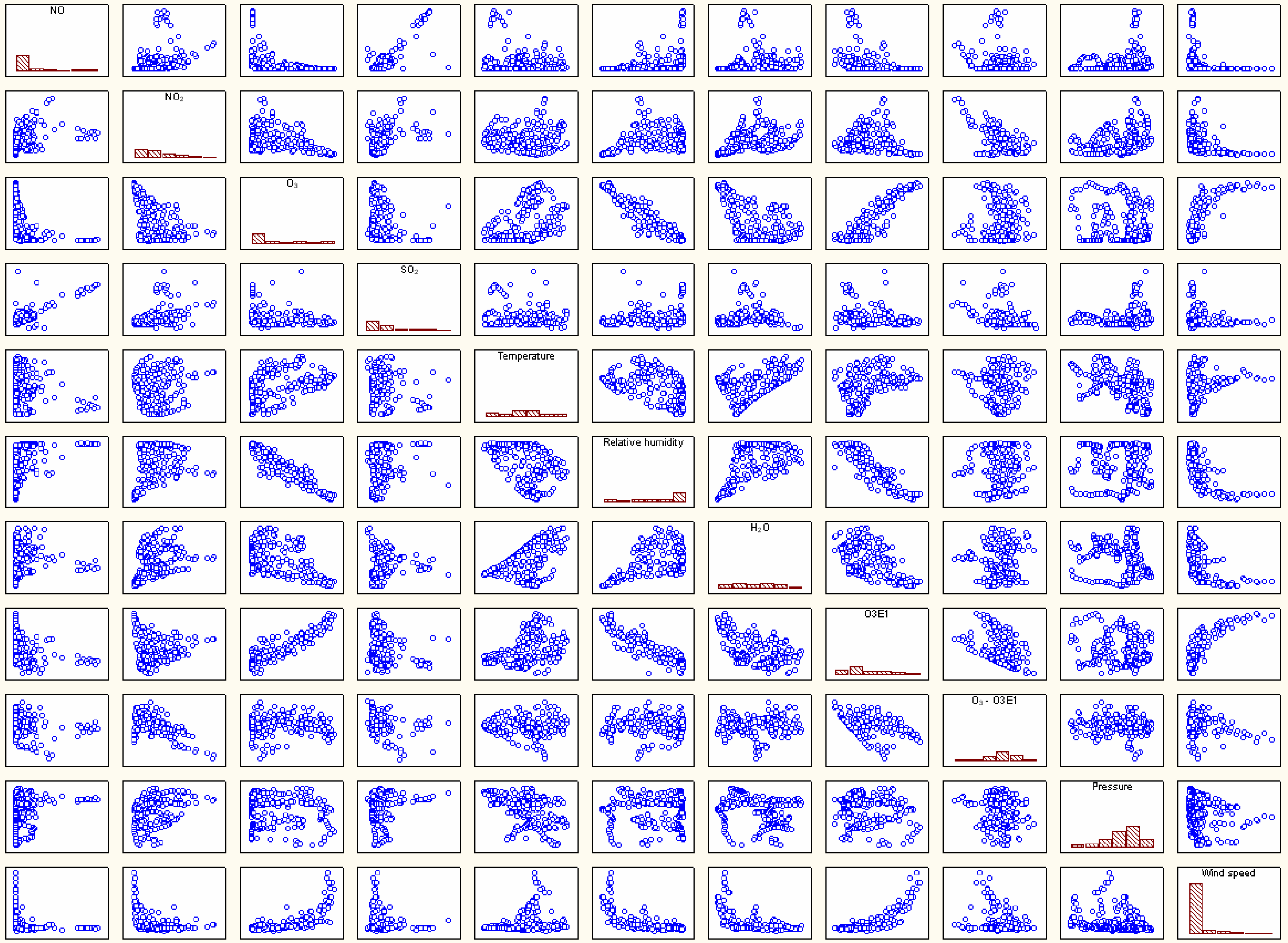

Figure 9: Matrix of scatter plots of hourly averages parameters measured at the EMEP station: NO, NO_2, O_3 (measured using UV photometry), Temperature (Temp), relative humidity and absolute humidity (H2O) including the 1st O3E1 values and the residuals O3 – O3E1 (UV photometry – O3E1)

Moreover, it is likely that the dependence of O3E1 on humidity and temperature that was observed in the laboratory experiments, has been hidden by the adjustment of the responses of O3E1 to ozone which is itself strongly correlated with humidity and temperature (see Figure 9). These difficulties can be solved using multiple regression analysis, finding the best linear relationship able to predict O_3 according to the O3E1 responses, NO2, relative humidity, temperature and wind speed. The regression analysis, performed between 27/10 and 07/11, showed that all the parameters were significant apart from temperature and the regression equation is:

$$O_{3\,[ppb]} = -269.9 - 0.471\ NO_{2\,[ppb]} + 7047\ O3E1_{[Volt]} - 0.154\ \text{Rel. Humidity}_{[\%]} - 1.8\ WS_{[m/s]} \quad (4)$$

The O_3 concentrations registered between 7 and 22 of November can be calculated first with the equation fitted between the UV photometry values and the sensor responses sampled between 27/10 and 07/11 (Figure 10 d), second using the NO_2 correction (Figure 10 e) and third with the multi regression equation 4 (see Figure 10 f). By applying these equations to the 2nd dataset, their application to a data set not used for fitting can be checked. In fact, Figure 10 d, e and f shows that compared to the simple UV photometry calibration, the NO_2 correction allows improvement of the slope (from 0.92 to 1.02), of the intercept (from 4.7 to 1.0) and of the squared coefficient of correlation (from 0.560 to 0.711). On the opposite by including wind velocity and relative humidity of equation 4, the agreement is only slightly improved: the squared coefficient of correlation only changes from 0.711 to 0.751 showing an increase of 4 % of the variability explained by the multi regression model. As O_3 was correlated with relative humidity and wind velocity, it is likely that adding theses parameters into the multi-regression equation does not improve significantly the agreement. We cannot thus conclude on the necessity to include these parameters into the prediction model of O3E1. One has to notice that the squared coefficient of correlations between O_3 measured by UV and O3E1 became very low on the measurements between 07/11 and 22/11 (R^2 from 0.560 to 0.751) compared to the period between 27/10 and 07/11 (R^2 from 0.865 and 0.970), the period used to fit the equations. This shows the limited applicability of the equations that have been produced.

Time-series of the O_3 residuals (for O3E1 calculated with the multi regression equation) were plotted versus time. Any significant drift of the senor over time would have been detected by the slope of the regression line of the O_3 residuals versus time. However, the slope and intercept were not found significant. For the relative bias, the O_3 residuals divided by O_3, the slope was very slighted significant ($R^2 = 0.008$) with a drift of about -0.031 ± 0.013 % per day which is extremely small. Consequently, the lack of applicability of the equation fitted between 27/10 and 07/11 to the period of 07/11 to 22/11 was not caused by a drift of the O3E1 sensor.

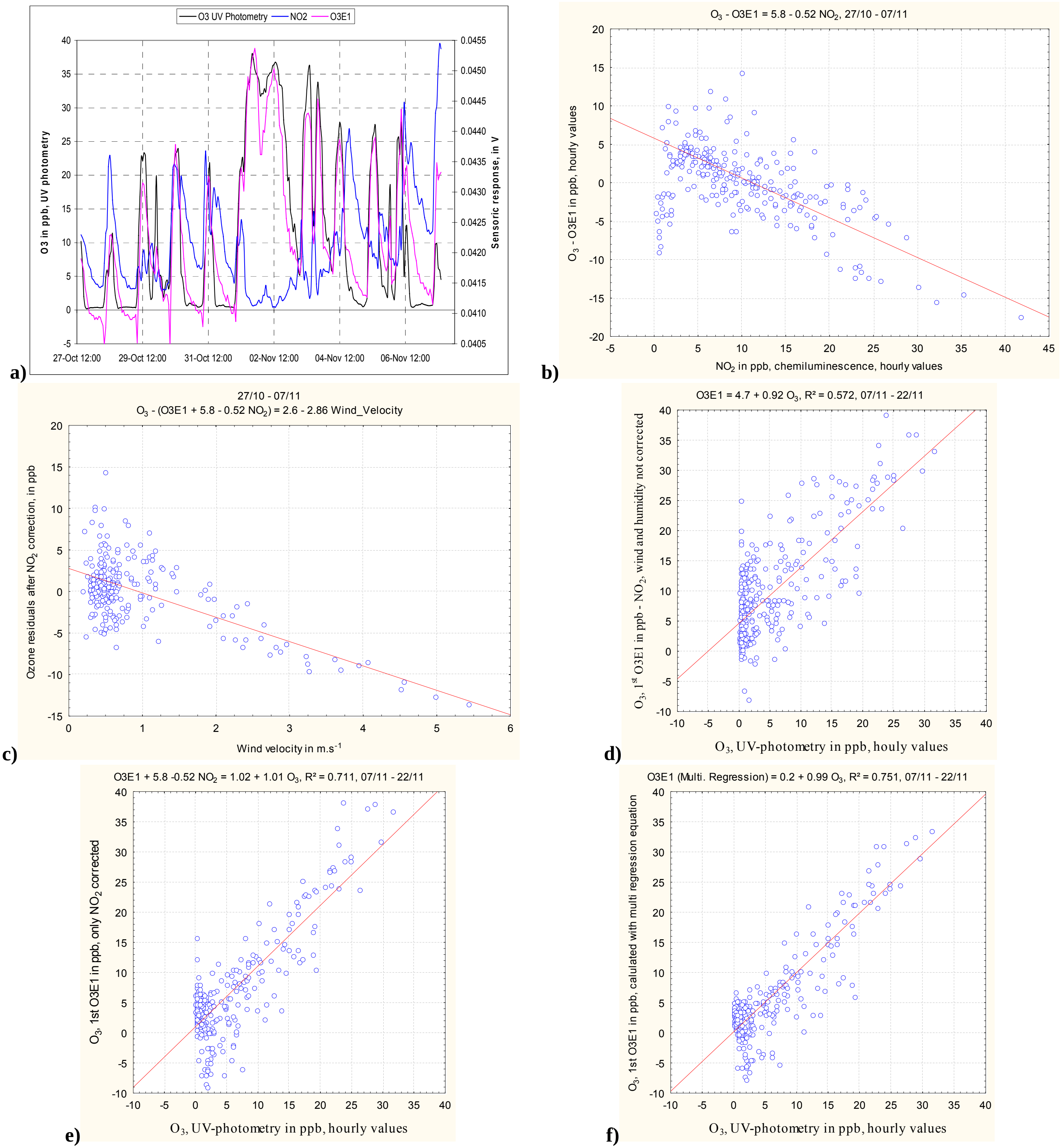

Figure 10: a) Time series of ozone measured by UV photometry and of the 1st O3E1; b) Relationship between the O_3 residuals and NO_2 with the correction equation; c) Relationship between wind velocity and the O_3 residuals after NO_2 correction; d) Response of O3E1 without correction with sampling between 07/1 and 22/11 (different sampling period); e) Response of O3E1 corrected for NO_2 with sampling between 07/11 and 22/11: f) Response of O3E1 calculated using a multi regression equation including O3E1 responses, NO_2, wind speed and humidity with sampling between 07/11 and 22/11

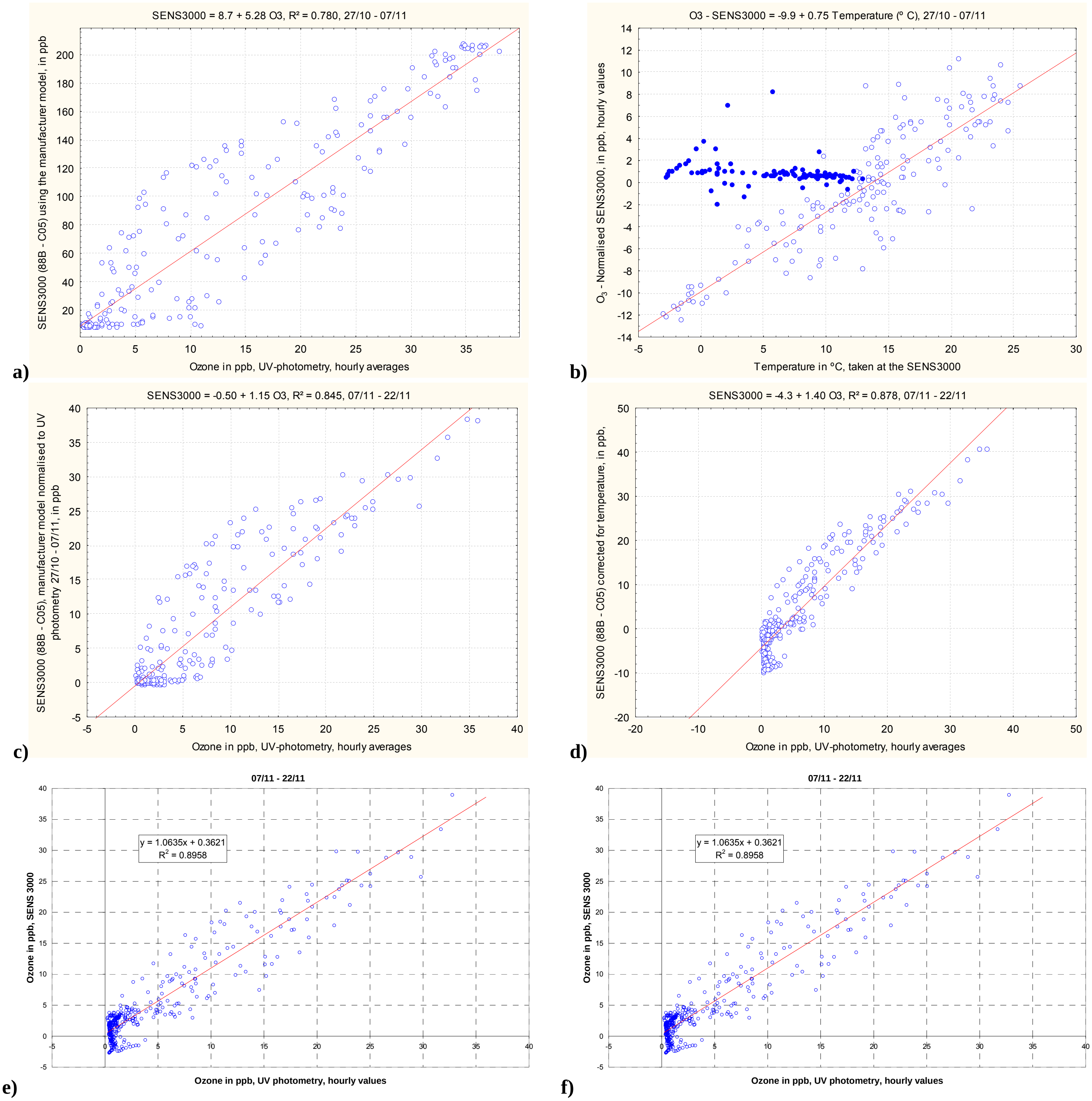

Figure 11: a) SENS3000 versus UV photometry; b) Normalised residuals between O_3 measured by UV photometry and SENS3000 versus ambient temperature; c) SENS3000 (normalized with equation in a) versus UV photometry, sampling between 07/11 and 22/11; d) Normalized SENS3000 corrected for the temperature dependence versus UV photometry, sampling between 07/11 and 22/11; e) SENS3000 versus UV photometry after optimization of the coefficients of the manufacturer model equation, sampling between 27/10 and 07/11 e) SENS3000 versus UV photometry after optimization of the coefficients of the manufacturer model equation, sampling between 07/11 and 22/11

3.2.2 SENS3000 sensors

Figure 11 shows the SENS3000 responses versus the O_3 measured by UV photometry. The SENS3000 values were transformed in ppb using the temperature given by a probe placed nearby the SENS 3000. The correlation between UV-photometry and the response of sensors is rather strong with R^2 about 0.867. The scatter plot giving the response sensor versus O_3 measured by UV photometry is curved as in Figure 4 when the sensor was submitted to linearity test under several conditions of temperature and humidity. The sensor responses using the model equation established by the manufacturer gave too high O_3 values with a slope of about 5.

As for the O3E1 sensors, the correlation between ambient parameters {NO, NO2, O_3 (UV and SENS3000 values), SO_2, temperature, humidity (relative and absolute), atmospheric pressure and wind (Direction and velocity)} and the differences of O_3 measured by UV photometry and by SENS 3000 are examined to detect which parameters are associated with the bias of SENS3000. However, the SENS3000 values needed correction (SENS3000 – 9.0/5.25) to normalize the sensor response to a slope of 1 and a 0 intercept. This is to avoid biased conclusions caused by the high values given by the SENS3000 . Figure 14 shows these correlations in a matrix of scatter plots. Measurements are all averaged over one hour since this was the minimum time resolution of pressure and wind velocity. The residuals are mainly correlated with temperature (r = 0.56), with NO_2 (r = 0.40), the SENS3000 itself (r = -0.38) suggesting an autocorrelation and wind direction (r = 0.33) which does not make any physical sense. The SENS3000 values are corrected for temperature using the equation (O_3 – SENS3000 = -9.9 + 0.75 TºC) given in Figure 11-b which shows the relationship between the O_3 residuals and temperature. This figure shows some outliers in a horizontal branch corresponding to low O_3 (between 0 and 2 ppb) measured during night time by both sensors at whatever temperature. These night time values were not included into the regression equation giving the O_3 bias according to temperature. After temperature correction, the O_3 bias dependence on NO_2 disappears and the one on wind direction decreases to r = 0.23. The O_3 residuals were still slightly correlated with SENS 3000 (r = -0.25) itself.

The temperature correction was also applied to the measurement registered between 7 and 22 of November. In fact, Figure 10-c and d shows that by correcting for temperature, the slope and intercept worsened (from 1.15 to 1.40 and from 0.5 to -0.4, respectively) and the squared coefficient of correlation improved (from 0.845 to 0.878). The higher value of the slope with the temperature correction is a shortcoming for the application of this equation to a dataset other than the modelled data set. Consequently, we have instead of the sole temperature correction optimized the constants proposed by the manufacturer in his model equation still keeping the temperature correction. Applying a minimization algorithm to the orthogonal sum of square residuals of SENS3000 responses and UV-photometry values (with the following constraints: slope =1 and intercept = 0) to the minimisation process, the new model equation became:

$$O_3 = -7.39 + 1.02T + 5330.9\,V^{-1.0302} \quad (5)$$

Where V is the SENS3000 response in mV and O_3 is in µg/m³. Applying this equation to the data of 27/10 to 07/11, this model is successful in extrapolation using the dataset between 07/11 and 22/11, it keeps an intercept around 0, a slope near of 1 and a R^2 of about 90 % as when applied to the period 27/10 to 07/11 used for fitting the model equation.

Applying regression analysis to the relationship between time and the relative ozone bias, the rate of sensor daily drift was not found significant.

3.2.3 *OMC2 sensors*

Figure 12 a and c show the response of the OMC2 (3A126) versus O_3 measured by UV photometry. Both graphs appear curved. In order to remove the curved dependence of OMC2 on O_3, the coefficients (x_3, x_2, x_1 , x_0 K is the coefficient of the temperature correction) of the model equation were optimized in order to minimize the orthogonal sum of square residuals of both the OMC2 responses and UV-photometry values (error on x and on y with constraints of slope and intercept equals to 1 and 0, respectively). The changes of coefficient were for x_0 from -1.71 to -3.51, x_1 from -0.678 to -0.247, x_2 from -1.82 10^{-3} to -1.77 10^{-4}, x_3 from -4.69 10^{-6} to -2.29 10^{-6} while K kept the same value. Figure 12-d shows that the model can be used for extrapolating on another sampling period with success comparing to the original model supplied by the manufacturer, see Figure 12-c.

The same data treatment was applied to the second OMC2 (1C195). Figure 13 shows the results. For the 2nd OMC2, the data were curved as well and the same optimization of coefficients of the model was performed. . The changes of coefficient were for x_0 from -4.97 to -5.20, x_1 from -0.122 to -0.340, x_2 from -6.15 10^{-4} to 1.36 10^{-2}, x_3 from -2.44 10^{-7} to -6.57 10^{-5} while K changed from 0.05 to 0.0231. The same conclusion as for the 1st OMC2 is valid for the second one: the model can be used in extrapolation with different data set over time even though the square coefficient of correlation is not as good as for the first one (R^2 of 0.902 instead of 0.971).

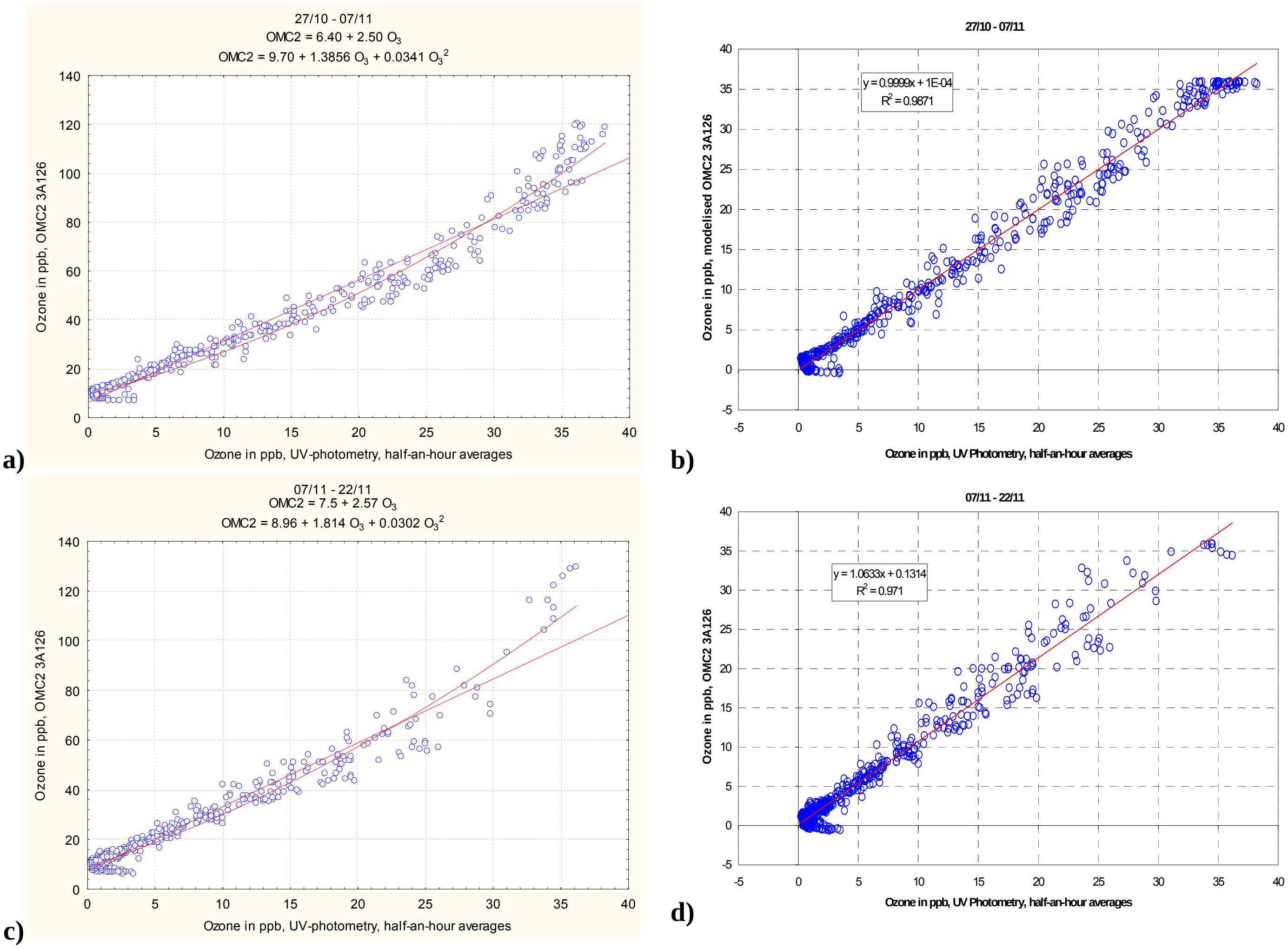

Figure 12: a) Half-an-hour averages of OMC2 versus UV photometry, sampling between 27/10- 07/11; (b) Normalised OMC2 versus UV photometry with X_0, X_1, X_2 and X_3 optimised to minimize the O_3 residuals, sampling between 27/10- 07/11; c) OMC2 versus UV photometry, sampling between 07/11- 22/11; d) Normalised OMC2 versus UV photometry, sampling between 07/11- 22/11.

For OMC2, Figure 15 shows the correlations in a matrix of scatter plots where the OMC2 values are the ones calculated with the optimized models. The O_3 bias of the OMC2 was not found correlated to any of the parameters measured so that further corrections are not needed. In fact, once O_3 is used to adjust the model equation, it is no more possible to evidence an effect of temperature, humidity and wind velocity that are strongly correlated with O_3.

Applying regression analysis to the relationship between time and the relative ozone bias, the rate of sensor daily drift was not found significant.

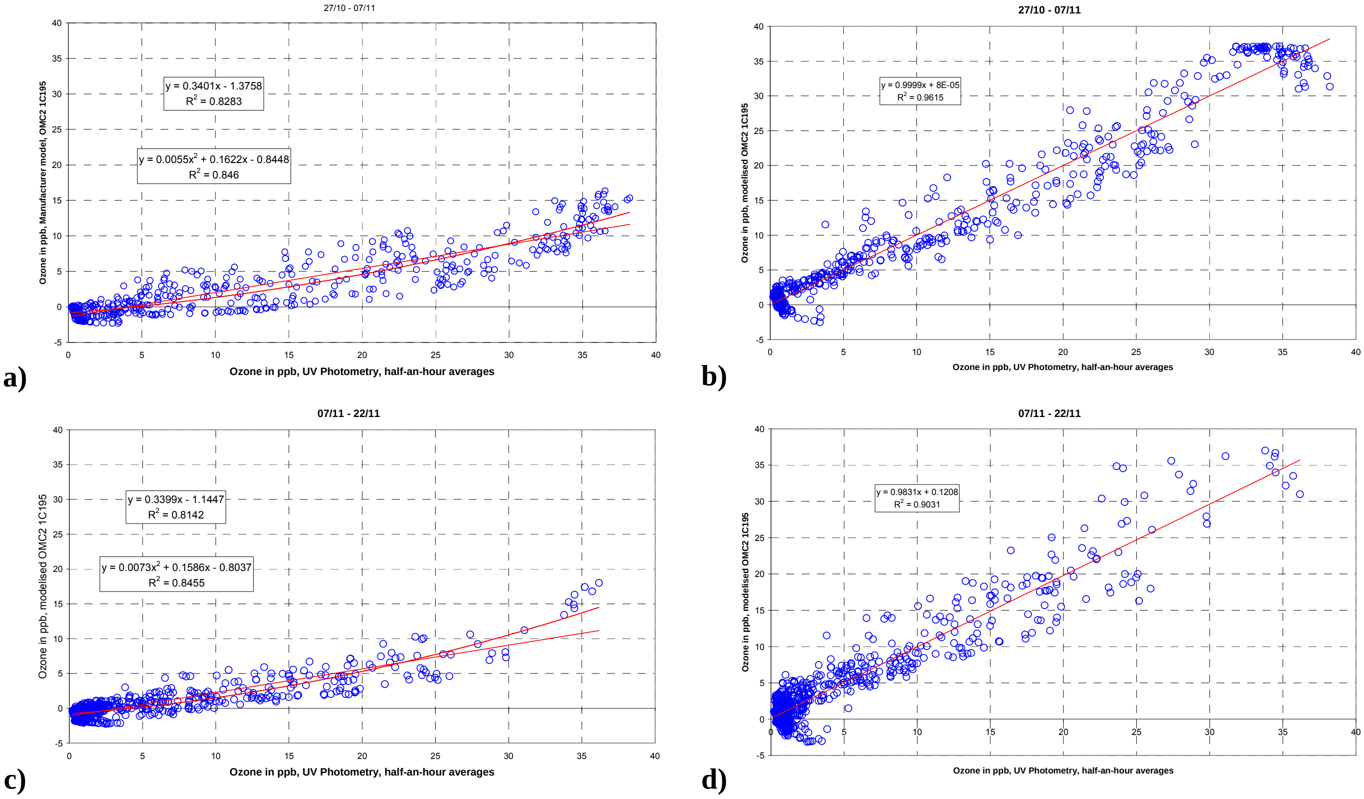

Figure 13: a) Half-an-hour averages of OMC2 versus UV photometry, sampling between 27/10- 07/11; (b) Normalised OMC2 versus UV photometry with X_0, X_1, X_2 and X_3 optimised to minimize the O_3 residuals, sampling between 27/10- 07/11; c) OMC2 versus UV photometry, sampling between 07/11- 22/11; d) Normalised OMC2 versus UV photometry, sampling between 07/11- 22/11.

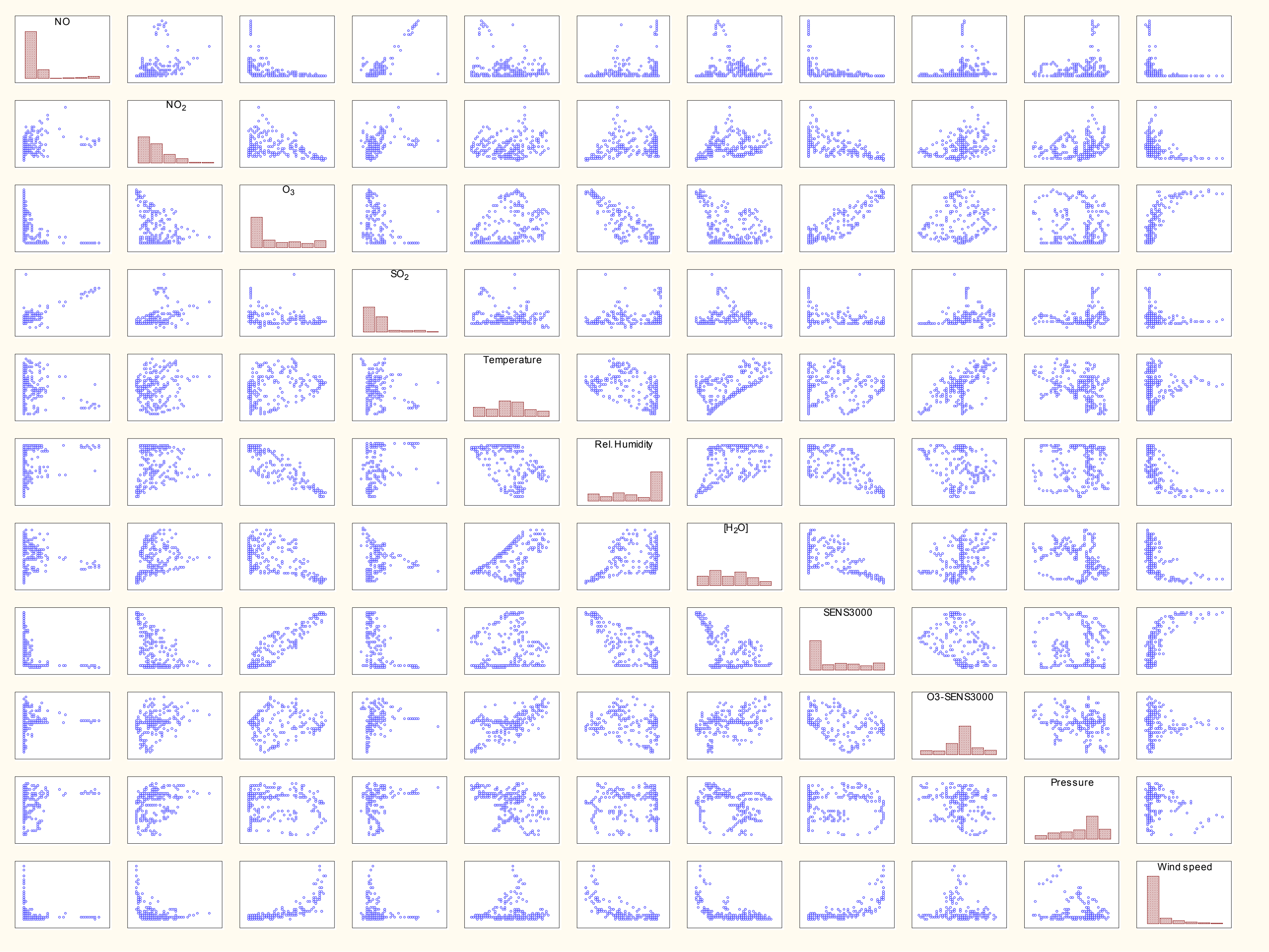

Figure 14: Relationship between the parameters measured at the EMEP station (27/10 – 07/11): NO, NO_2, O_3, Temperature (Temp), relative humidity (RH), absolute humidity ([H2O]) and the difference between ozone measured at the station by UV photometry and by SENS3000 (O3-SENS3000)

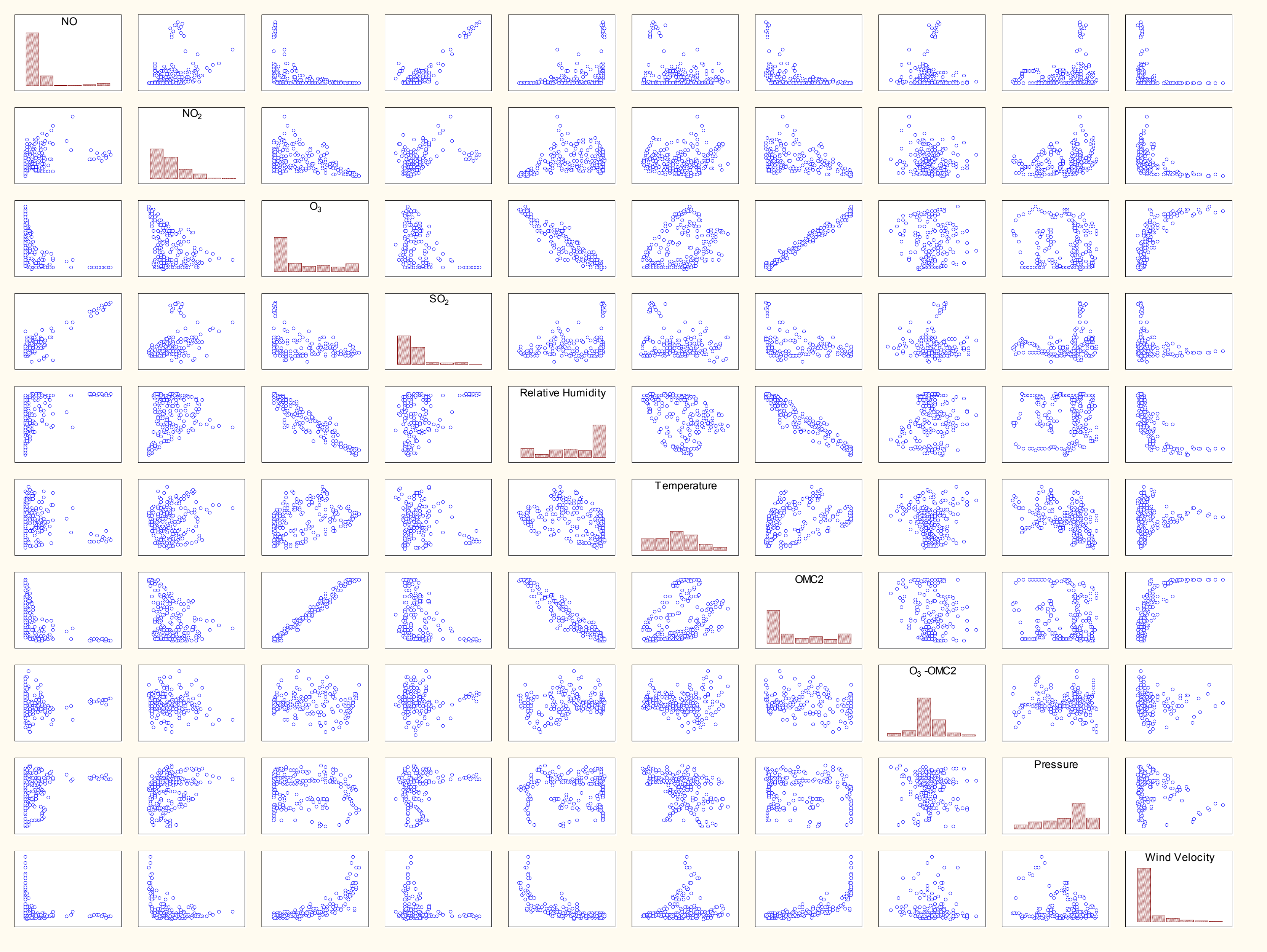

Figure 15: Relationship between the parameters measured at the EMEP station: NO, NO_2, O_3, Temperature (Temp), relative humidity (RH), absolute humidity ([H2O]), pressure and wind velocity and the difference between ozone measured at the station by UV photometry and by OMC2 (O3- OMC2)

4 Discussion and conclusions

The electrochemical cells (O3E1) did not need a long warming time after a cold start. They reached 99 % of their final value after about 2 hours. On the opposite the semi conductor based sensors needed a long warming time. One day was more than enough with the exception of one of the SENS3000. Once the sensors were warm enough their response time to a square signal was less than 20 minutes (slightly more for OMC2), here also with the exception of one of the SENS3000.

The precision of the semi-conductor based sensors (OMC2 and SENS 3000) expressed in terms of relative standard deviation (RSD) was constant and better than 2 % for minute average with O_3 ranging between 0 and 90 ppb. However, for O3E1, the relative standard deviation was higher than 5 %. These RSDs were used to estimate the limit of quantifications that were found to be less than 0.5 ppb for OMC2, 2 ppb for SENS3000 and about 30 ppb for O3E1. These figures decrease strongly if half an hour averages are considered, for example the limit of quantification of O3E1 goes down to about 5.5 ppb. However, during the field tests it was observed that the semi conductors showed high bias at small O_3 values that do not match the limit of quantification estimated in laboratories.

Under laboratory conditions, the linearity of sensors was quite questionable: the OMC2 was found linear but the slopes and intercepts of the regression lines were found completely different according to temperature and humidity of the measured O_3 mixtures. For example the slope was found three times higher at 22.5 ºC and 31 % of relative humidity than at 14 ºC and 80 % of relative humidity. Moreover for O3E1 and SENS3000, the slopes and intercepts of the regression lines were still varying to the same extent but the responses were also often curved instead of being linear. In particular, all sensors were found extremely dependent on the relative humidity when O_3 and temperature were kept constant with their responses decreasing with an increase relative humidity.

Apart from temperature and humidity, the results of the laboratory experiments showed that the electrochemical cells (O3E1) were found to be sensitive to NO_2 and to wind velocity. SENS3000 had a little effect on only wind velocity while OMC2 was not influenced by both parameters.

However, the results of the field tests are in contradiction with some of these findings. Unfortunately, the field test took place at the same time as the laboratory tests and we could not use the sensors for which we acquired the results of the laboratory tests under field conditions.

For O3E1, the main interferences were NO_2 and wind velocity as was observed under laboratory conditions. However, it was not possible to conclude on the influence of temperature and humidity. In fact, as from one side O_3 in ambient air was strongly correlated with humidity and temperature and on the other side O3E1 was calibrated using O_3 in ambient air, it is likely that any potential influence of temperature and relative humidity on O3E1 was already accounted for calibrating O3E1 with O_3. This remark remains valid also for OMC2 and SENS300. The simple calibration of O3E1 with O_3 did not give good results when applied to another time series of O3E1/ O_3 data. By using a NO_2 correction the agreement between O3E1 and O_3 improved. An attempt to use multi-regression analysis did not bring much improvement while increasing the quantity of needed input data to wind velocity and humidity. A rapid estimation of the uncertainty of O3E1 for hourly averages based on the lack of fit of the multi-regression model versus O_3 (of the extrapolated dataset), on the repeatability of the sensor and on the bias of the multi-regression would give at 30 ppb an expanded uncertainty of 7.4 ppb (about 25 %).

For SENS300, using the manufacturer model yielded some curved responses with huge difference compared to O_3 measured by UV photometry. A first attempt to normalize SENS3000 to O_3 and to correct for temperature was carried out. These corrections were successful with the dataset used for modelling but did not give satisfaction when applied to the dataset used for validation. Better results were obtained by fitting the coefficients of the model equation proposed by the manufacturer to O_3. Similar and good agreements were observed both with the modelling dataset and the dataset used for validation. The need of modification of the coefficients of the model could be due to a mistake of calibration but it is more likely that it is caused by the different conditions of temperature, humidity observed under field conditions and when the manufacturer calibrated the SENS3000 sensor. In fact, the solution that is proposed here may require that the model is fitted to the exposure conditions of any new field site where the sensor would be used. It should also be checked if the coefficients of the model remain the same over a full year at the same sampling site. These points need further investigation. As for O3E1, a rapid estimation of the uncertainty of SENS3000 would give at 30 ppb an expanded uncertainty of 6.8 ppb (about 23 %).

For OMC2, using the manufacturer model also produced some slightly curved responses with high values compared to O_3 measured by UV photometry. As for SENS3000, best results were obtained by fitting the coefficients of the model equation proposed by the manufacturer. Similar and good agreements were observed both with the modelling dataset and the dataset used for validation. The same conclusion as for SENS300 applies for OMC2 as well: the new coefficients of the model are likely to be valid at the studied field site and it may be required to fit new coefficients at each sampling site or for different sampling periods over the year. A rapid estimation of the uncertainty of OMC2 for hourly averages would give at 30 ppb an expanded uncertainty of 4.8 ppb (about 16 %).

Looking at what has been done so far, the laboratory experiments gave some useful information about the parameters that influence the sensors. However, this information was not directly usable during the field experiments. From another side, it was possible to fit the coefficients of the model equations of each sensor just using O_3 measured by UV photometry. However this method is less universal and it is feared that for each exposure conditions the coefficients will have to be fitted again. In the future, laboratory experiments should be continued. However, instead of using the model equations proposed by the manufacturer, the responses of the sensors (directly in mV or in resistance) should be modelled according to the parameters of influence.

In parallel, some field tests should still be carried out but using the sensors included in the laboratory experiments. For the field experiments two routes are possible: either a multiplication of sampling sites with different conditions of exposure where the sensors should be compared to UV photometry to fit the coefficients of the manufacturer models or to check the applicability of the laboratory model under field conditions without any correction.

Moreover, some information is still needed about the behaviour of the sensors:

- the extent of possible saturation of the sensor with high concentration of O_3, NO_2 and H_2O … and possible poisoning of the sensitive layer of the sensors;
- the temperature effect: using a constant O_3 and humidity, look at the responses of sensor with temperature varying;
- the drift of the sensors over a long period;
- field tests with high O_3 concentrations over 40 ppb as in this study;
- the reproducibility of sensors of the same brand on field tests;
- the effect of a rapid change of humidity like heavy rain
- the influence of stability of voltage on the sensor responses
- to increase the list of tested gaseous interference
- to evaluate the hysteresis of sensors

Finally, we were recently informed that Sensoric now produces the O3E1 F sensor measuring in the range 0-300 ppb instead of 0-1000 ppb. This sensor could be a solution for the difficulty of sensitivity of the O3E1 sensor in this study.

Annex 1: Additional figures

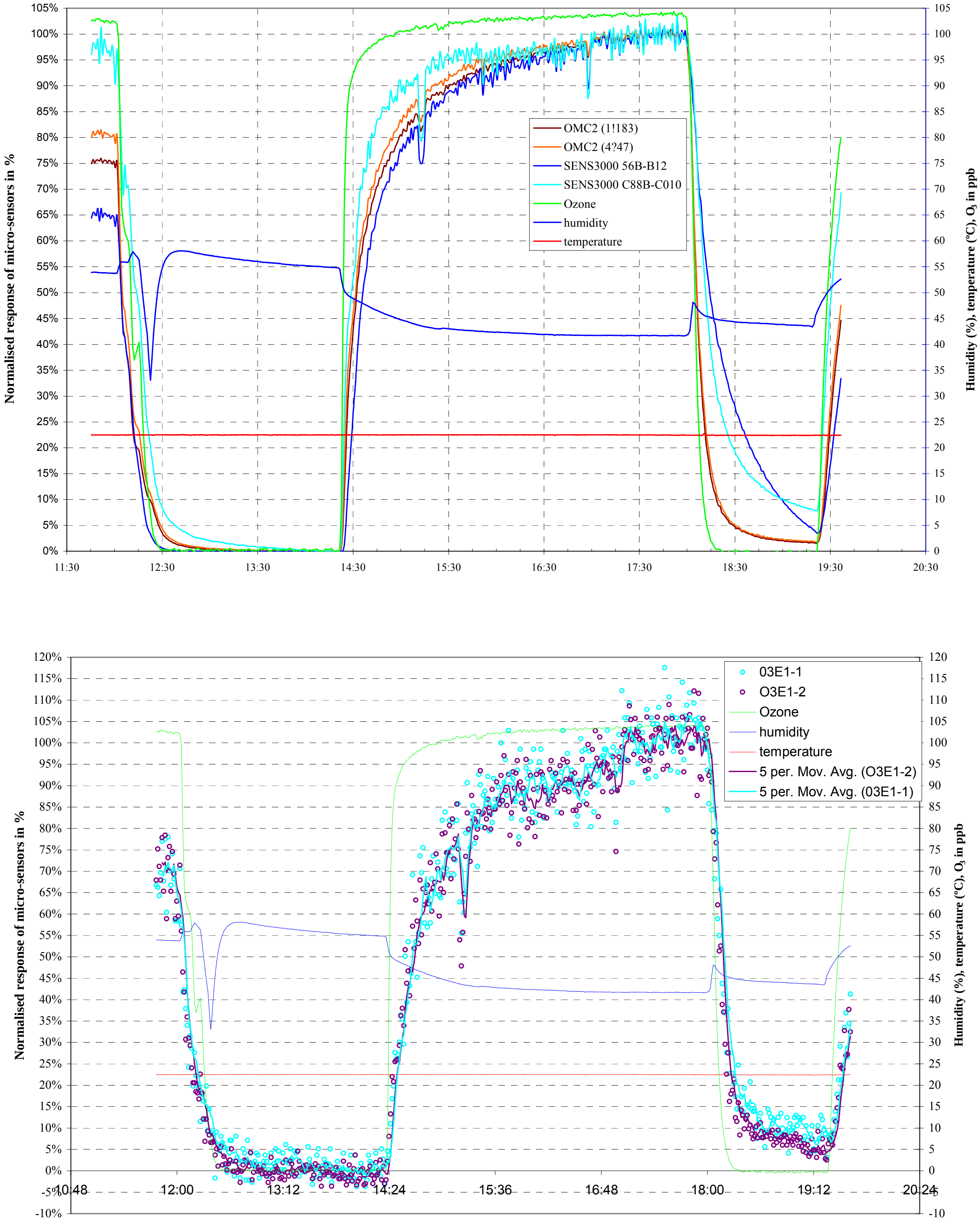

Figure 16: First experiment for evaluating the response time of the micro-sensors

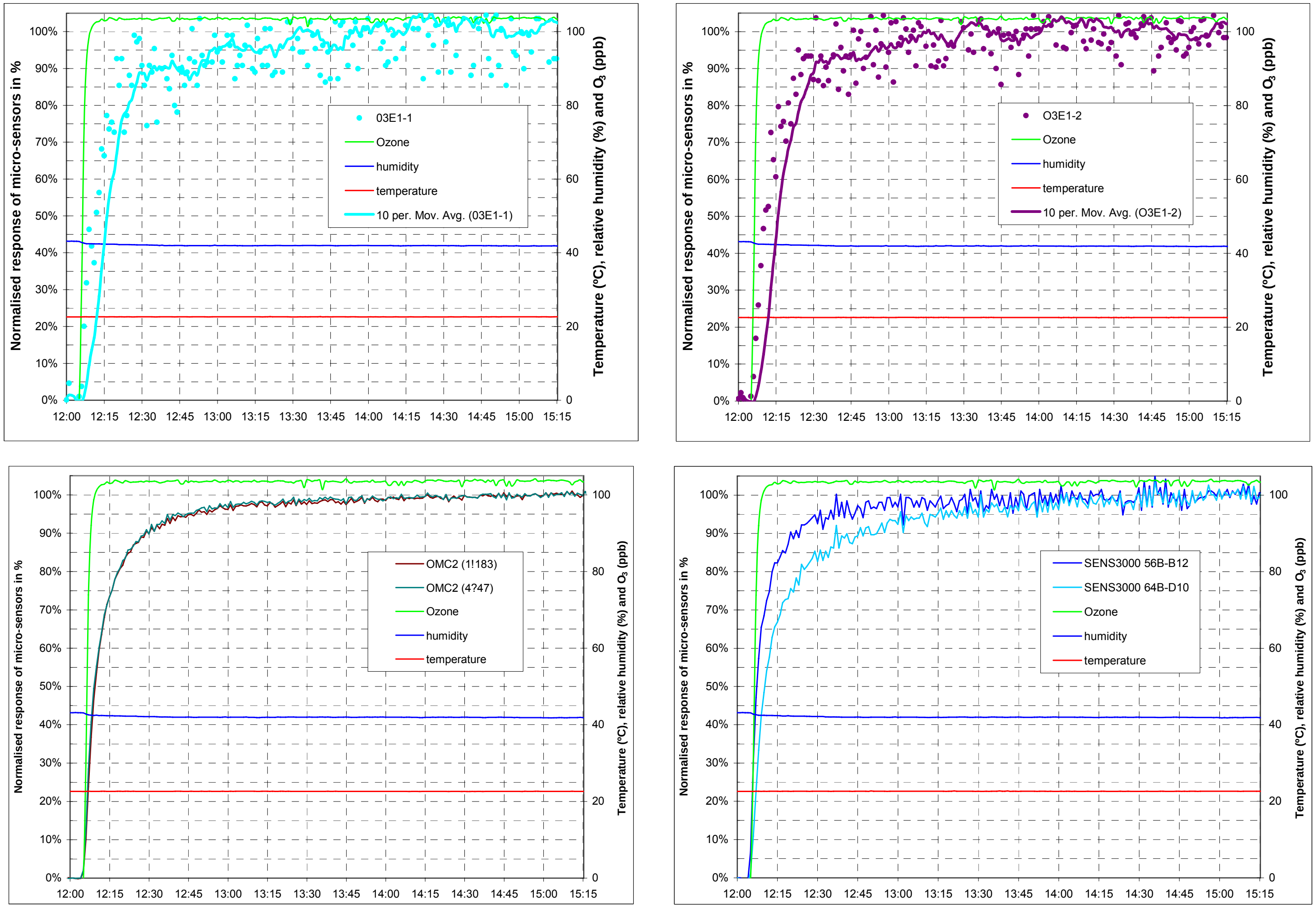

Figure 17: Time response of micro-sensors, data acquisition every minute. The line of the O3E1 shows the moving average (every 20 measurements)

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Abstract

Micro-sensors are very small sensors with physical dimensions in the sub-micrometer to millimetre range that are used to monitor ozone (O_3) in ambient air. They are either based on the variation of the resistance of a semi-conductor or on miniaturized electrochemical cells able to deliver a current varying with the level of the pollutant of interest. In the last years, some technological progress took place and a few commercial sensors are now available in the market. In fact, micro-sensors represent a promising technology in several fields like: monitoring of O_3 in ambient air to survey of the limit/target values of the Air Quality Directive, rapid mapping of air pollution over small area, validation of dispersion models, evaluation of exposure of population, emissions monitoring and forest monitoring.

However, due to reliability problems there is a hesitancy to apply these sensors for air pollution monitoring. The suitability of these sensors is evaluated in this report. In this study, the response time of micro-sensors is investigated. Moreover, warming time after a cold start, linearity, drift over time and the effect of NO_2 interference, wind velocity, temperature and humidity on the response of sensors are presented. The comparison of the response of these samplers versus UV photometry is investigated both under controlled conditions using exposure chamber and under field conditions. All sensors used in the study are commercially available. O_3 is determined according to the specifications of the manufacturers, without modification of the model equation proposed by the manufacturers.

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