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### Performance evaluation of five low-cost ozone sensors in the field

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# 2 VAQUUMS FIELD REPORT O<sub>3</sub> SENSORS

#### 2.1 General information

This report describes the field comparison of 5 types (Table 1) of low-cost O<sub>3</sub> sensors. Full details of the testing are provided in the test protocol (<u>https://vaquums.eu/sensor-db/tests/protocols/life-vaquums\_testprotocol\_final.pdf</u>).

Sensor units were co-located at the R801 urban background measurement site of VMM in Borgerhout, Antwerp (Belgium) for about 400 days (from February 23, 2019 until March 30 2020). The NO<sub>2</sub>-sensors were compared to the **reference method**, i.e. the UV photometric analyser Teledyne APIT400 measuring at a high time resolution (10 s) and operating according to the standard EN14625. Sensors usually reported data per second (Envea Cairclip per 15 minutes) but these were aggregated as minute, 5 minute, hourly and daily averages. The hourly level was chosen as the main aggregation level for most analyses.



Table 1:  $O_3$ -sensors that were tested in the VAQUUMS field campaign together with the abbreviation used in this report

For each sensor type we discuss the following points:

#### 2.1.1 Validation and data coverage

Specific issues with the validation of the sensors are mentioned here, in addition the number of available and not available minute and hourly data per validation code (0: valid, -1: suspicious, -2: invalid, 1: missing) are shown.

### 2.1.2 Uncalibrated data and sensor data calibrated with parameters from linear regression

#### 2.1.2.1 Calibration parameters

A calibration function was established by assuming linearity between the sensor data and the reference data. Orthogonal regression on the hourly data was used to establish the calibration function. The data from February 23, 2019 - March 31, 2019 were used to establish the calibration function.

The evaluation of the sensors was done on the the data in the remaining period from April 1, 2019 - March 30, 2020.

#### 2.1.2.2 Comparison of uncalibrated and calibrated sensor data with the reference data

The comparison is presented as time plots and scatter plots. The ratio of the sensor data versus the reference data was calculated and is presented as density plots.

#### 2.1.2.3 Influence of time temperature, relative humidity and O<sub>3</sub> on uncalibrated sensor data

The ratio sensor data versus reference data is plotted in function of time, temperature, relative humidity and NO<sub>2</sub>. Temperature, relative humidity and NO<sub>2</sub> are parameters with a known effect on (some)  $O_3$  sensors. The scatter plot in function of time is used to evaluate possible drift of the sensor.

#### 2.1.2.4 Descriptive parameters

 $R^2$ , mean bias and the between sampler uncertainty ( $u_{bs}$ ) are presented.

#### 2.1.2.5 Relative expanded uncertainty

Annex 1 of Directive 2008/50/EG gives data quality objectives for ambient air quality assessment. The maximum relative expanded uncertainty at the target value (TV) for indicative measurements is 30 %, for objective estimation 75 %. The TV for  $O_3$  for the maximum daily 8-hour mean is 120 µg/m<sup>3</sup>, not to be exceeded more than 25 days a year. As for NO<sub>2</sub>, we additionally evaluate the relative expanded uncertainty of the (calibrated) sensor data at lower concentrations, namely at 70 % and 50 % of the TV.

The table below summarizes the TV and the other test levels for  $O_3$ .

Averaging time	TV	70 % of TV	50 % of TV
8-hour	120 μg/m³	84 μg/m³	60 μg/m <sup>3</sup>

The relative expanded uncertainties of the (calibrated) sensor data are also calculated and plotted at  $O_3$  hourly concentrations of 10 to 200 µg/m<sup>3</sup> and at  $O_3$  8-hourly concentrations of 10 to 150 µg/m<sup>3</sup>.

The relative expanded uncertainty is calculated according to the 'Guide to the demonstration of equivalence of ambient air monitoring methods'. The calculation of the relative expanded uncertainty is based on the orthogonal regression of the sensor data versus the reference data. The parameters of the regression line are presented in a table.

#### 2.1.2.6 Conclusions

The conclusions are based on the tables and plots mentioned above.

#### 2.1.3 Sensor data calibrated with parameters from multiple linear regression (MLR)

#### 2.1.3.1 Calibration parameters

Besides linear regression, multiple linear regression (MLR) is a widely used technique to calibrate sensor data against reference data<sup>1</sup>. MLR includes the use of more than one independent variable to improve the quality of the calibration.

Two MLR calibration functions were calculated:

- a MLR function using reference O<sub>3</sub>, relative humidity and temperature as independent variables. This approach has the advantage that no reference data are needed for the calibration of the sensor data during the evaluation period,
- a MLR calibration function using reference O<sub>3</sub>, relative humidity, temperature and NO<sub>2</sub> as independent variables.

MLR makes several assumptions regarding the variables. One of the assumptions is a linear relation between the dependent variable (the uncalibrated sensor data) and the independent variables (reference  $O_3$ , relative humidity, temperature and  $NO_2$ ). In annex 1 correlation charts can be found for all sensors where this assumption can be checked. Another assumption of MLR is the independence of the independent variables. As expected correlation is noticed between the independent variables reference  $O_3$ , relative humidity, temperature and  $NO_2$ . The correlation coefficients are also shown in annex XX.

Several approaches can be followed to select the most significant variables to include in the MLR function but the further elaboration of the MLR functions is considered to be outside the objective of the project.

The same periods for calibration/evaluation are used for the multiple linear regression as for the linear regression.

#### 2.1.3.2 Comparison of the calibrated sensor data with the reference data

As for the sensor data calibrated with the parameters of the linear regression, the comparison is presented as time plots, scatter plots and density plots of the ratios of the calibrated sensor data versus reference data.

<sup>&</sup>lt;sup>1</sup> Karagulian, F., Gerboles, M., Barbiere, M., Kotsev, A., Lagler, F., Borowiak, A., *Review of sensors for air quality monitoring*, EUR 29826 EN, Publications Office of the European Union, Luxembourg, 2019, ISBN 978-92-76-09255-1, doi:10.2760/568261, JRC116534.



#### 2.1.3.3 Influence of time, temperature, relative humidity and NO<sub>2</sub>

As for the sensor data calibrated with the parameters of the linear regression, the ratio sensor/reference is plotted in function of time, temperature, relative humidity and NO<sub>2</sub>.

#### 2.1.3.4 Descriptive parameters

 $R^2,$  mean bias and the between sampler uncertainty  $(u_{\mbox{\tiny bs}})$  are presented for the calibrated sensor data.

#### 2.1.3.5 Relative expanded uncertainty

The calculation and the evaluation is done as described in the previous section.

#### 2.1.3.6 Conclusions

The conclusions are based on tables and plots mentioned above.

#### 2.2 Validation and calibration

#### 2.2.1 Validation

The two main processes involved in the sensor evaluation are validation and calibration. Data validation was done on 15-minutes values for the Envea Cairclip sensors and on minute values for the other sensors. Both invalid and suspicious data were left out and only valid data are used for the evaluation of several characteristics (information on validation, see technical manual). The evaluation of the sensor data is mainly done on hourly data.

#### 2.2.2 Calibration

The evaluation of the performance is done on:

-the uncalibrated sensor data O3\_s\_2

-the sensor data **O3\_s\_lab2:** sensor data after calibration with the linear regression parameters from the laboratory study. This evaluation is included in the annexes.

The calibration function is of the type:

 $O3_s_2 = a * O_3_ref + intercept$ 

The values for *a* and *intercept* can be found in the tables with the calibration parameters.

The resulting function applied to the sensor data from February 23 2019 - March 30 2020 is of the type:

O3\_s\_lab2 = (O3\_s\_2 - intercept) / a

-the sensor data **O3\_s\_1mLR2** after calibration with the linear regression parameters. The field campaign data from February 23, 2019 - March 31, 2019 were used to establish the calibration function.

The calibration function is of the type:

 $O3_s_2 = a * O_3_ref + intercept$ 

The values for *a* and *intercept* can be found in the tables with the calibration parameters.

The resulting measurement function applied to the sensor data during the evaluation period is of the type:

O3\_s\_1mLR2 = (O3\_s\_2 - intercept) / a

-the sensor data **O3\_s\_1mMLR2** after calibration with the parameters of the multiple linear regression (MLR) using reference  $O_3$ , relative humidity and temperature as variables. The field campaign data from February 23, 2019 - March 31, 2019 were used to establish the calibration function.

The calibration function is of the type:

 $O3_s_2 = a * O_3_ref + c*T + d*RH + intercept$ 

The values for *a*, *c*, *d* and *intercep*t can be found in the tables with the calibration parameters.

The resulting function applied to the sensor data during the evaluation period is of the type:

-the sensor data **O3\_s\_1mMLRext2** after calibration with the parameters of the multiple linear regression (MLR) using reference O<sub>3</sub>, relative humidity, temperature and NO<sub>2</sub> as variables. The field campaign data from February 23, 2019 - March 31, 2019 were used to establish the calibration function.

The calibration function is of the type:

 $O3_s_2 = a * O_3_ref + b * NO_2 + c * T + d * RH + intercept$ 

The values for *a*, *b*, *c*, *d* and *intercep*t can be found in the tables with the calibration parameters.

The resulting function applied to the sensor data during the measurement period is of the type:

O3\_s\_1mMLRext2 = (O3\_s\_2 - b\*NO2 - c\*T - d\*RH - intercept) / a



#### 2.3 Conditions during field campaign

Figure 1 and 2 show the time plots of the hourly and 8-hourly O<sub>3</sub> values measured with the reference instrument. Figure x and x show the histograms of the hourly and 8-hourly values. Most O<sub>3</sub> hourly and 8-hourly values are below 100  $\mu$ g/m<sup>3</sup>. No hourly values higher than 200  $\mu$ g/m<sup>3</sup> occur. A few negative values occur in the data of the reference O<sub>3</sub> values; according to standard EN14625 values  $\geq$  -(detection limit) are considered valid.

The data from February 23, 2019 - March 31, 2019 were used to establish the calibration function. The evalution of the sensors was done on the the data in the remaining period from April 1, 2019 - March 30, 2020. The average O<sub>3</sub>-concentration during the field campaign was 38.7  $\mu$ g/m<sup>3</sup>. During the calibration period and evaluation period the average O<sub>3</sub>-concentration was 41.6  $\mu$ g/m<sup>3</sup> and 38.4  $\mu$ g/m<sup>3</sup> respectively.



Figure 1: Time plot of hourly  $O_3$  values ( $\mu g/m^3$ ) measured with the reference instrument during the field campaign.



Figure 2: Time plot of 8-hourly  $O_3$  values ( $\mu g/m^3$ ) measured with the reference instrument during the field campaign.



Figure 3: Histogram of hourly  $O_3$  concentrations ( $\mu g/m^3$ ) measured with the reference instrument during the field campaign.



Figure 4: Histogram of 8-hourly  $O_3$  concentrations ( $\mu g/m^3$ ) measured with the reference instrument during the field campaign.

Figure 5 shows the variation in hourly values of temperature and relative humidity during the field campaign. Figure 3 and 4 show the histogram of the hourly relative humidity and temperature.

The average temperature and relative humidity in Borgerhout during the whole field campaign were 12.5 °C and 74% respectively. The average temperature and relative humidity were rather similar during the calibration period and validation period. During the calibration period the average temperature was 9.8 °C and the relative humidity was 72 %. During the evaluation period the average temperature was 12.8 °C and the relative humidity was 74 %. The winter 2019-2020 was warm: the minimum temperature was -1.2 °C in Borgerhout. During the calibration period the minimum temperature was 3.0 °C. As a consequence the sensors are not tested at extreme negative temperatures during this field campaign.



Figure 5: Time plot of hourly temperature (°C) and relative humidity (%) during the field campaign



Figure 6: Histogram of the hourly relative humidities (%) during the field campaign



Figure 7: Histogram of hourly temperatures (°C) during the field campaign

Figure 6 shows the time plot and figure 7 the histogram of the hourly NO<sub>2</sub> values measured with the reference instrument. Most NO<sub>2</sub> hourly values are below 100  $\mu$ g/m<sup>3</sup>. No hourly values higher than 200  $\mu$ g/m<sup>3</sup> occur.

The average NO<sub>2</sub>-concentration during the field campaign was 29.3  $\mu$ g/m<sup>3</sup>. During the calibration period the average NO<sub>2</sub>-concentration was somewhat higher (35.5  $\mu$ g/m<sup>3</sup>) than during the evaluation period (28.6  $\mu$ g/m<sup>3</sup>).



Figure 8: Time plot of hourly NO<sub>2</sub> values ( $\mu g/m^3$ ) measured with the reference instrument during the field campaign.



Figure 9: Histogram of hourly NO<sub>2</sub> concentrations ( $\mu$ g/m<sup>3</sup>) measured with the reference instrument during the field campaign.

Although the average temperature and  $O_3$  were rather similar during the calibration period and validation period, we hardly measured hourly temperatures higher than 20 °C or  $O_3$ concentrations higher than 100 µg/m<sup>3</sup> during the calibration period. In summertime these values are frequently exceeded. The choice of the calibration period from February 23, 2019 until March 31, 2019 compared to a calibration period of another length or in another season can affect the calibration functions. The investigation of the effect of the calibration period is considered outside the aim of the project.



### Field Evaluation Aeroqual SM50 O<sub>3</sub> sensor



Manufacturer: Aeroqual Link to website manufacturer Link to test protocol



### 3 Aeroqual SM50 O<sub>3</sub> sensor

#### 3.1 Validation and data coverage

Only a few peaks were seen in the sensor data. These peaks were marked as invalid or suspicious. The aeroqual  $O_3$  sensors don't give negative values. Sensor VQO3 didn't give any value between May 5, 2019 and June 18, 2019. Afterwards the values were much lower and marked as suspicious.

VQO5 was not included in the laboratory study.

Quite frequently, a lot of minute values are missing in an hour. In order not to lose too many hourly values, the criterium for aggregation was set to 70 % instead of 75 %.





Table 2: Aeroqual SM50  $O_3$  sensor: Number sensor minute values (-2: invalid, -1: suspicious, 0: valid, 1: missing) and percentage of available data

	-2	-1	0	1	%
					available
VQ01	1	0	388545	190334	67
VQO2	0	3	398796	180081	69
VQO3	0	287879	63749	227252	11
VQO5	0	7	390795	188078	68







Table 3: Aeroqual SM50  $O_3$  sensor: Number sensor hourly values (-2: invalid, -1: suspicious, 0: valid, 1: missing) and percentage of available data

	-2	-1	0	1	%
					available
VQ01	0	0	7112	2536	74
VQO2	0	0	7308	2340	76
VQO3	0	4742	1274	3632	13
VQO5	0	0	6961	2687	72

With the criterium for aggregation set to 75 % instead of 70 % the percentage of available hourly values would have been 60 %, 61 %, 11 % and 58 % for the sensors VQO1, VQO2, VQO3 and VQO5 respectively.



### 3.2 Uncalibrated sensor data and sensor data calibrated with parameters from linear regression

#### 3.2.1 Calibration parameters

Table 4: Aeroqual SM50 O<sub>3</sub> sensor: Parameters from linear regression against reference method - hourly field data from February 23 2019 - March 31 2019

sensor_internal_id	slope	intercept
VQO1	1.03	-1.2
VQO2	1.02	0.5
VQO3	1.01	1.7
VQO5	1.05	-1.6

#### 3.2.2 Comparison sensor versus reference

#### *3.2.2.1* Time plot and scatter plots of hourly values



Figure 12: Aeroqual SM50  $O_3$  sensor: Time plot uncalibrated sensor hourly values and reference values ( $\mu$ g/m<sup>3</sup>)





Figure 13: Aeroqual SM50  $O_3$  sensor: Time plot of sensor hourly values calibrated with the linear regression parameters and reference values ( $\mu g/m^3$ )



Figure 14: Aeroqual SM50  $O_3$  sensor: Scatter plot of uncalibrated sensor hourly values versus reference values ( $\mu g/m^3$ )





Figure 15: Aeroqual SM50  $O_3$  sensor: Scatter plot sensor hourly values calibrated with the linear regression parameters versus reference values ( $\mu g/m^3$ )



#### 3.2.2.2 Ratio of hourly sensor values versus reference values

Figure 16: Aeroqual SM50 O<sub>3</sub> sensor: Density plot of uncalibrated ratio sensor hourly values versus reference values





Figure 17: Aeroqual SM50  $O_3$  sensor: Density plot of ratio sensor hourly values calibrated with the linear regression parameters versus reference values

#### 3.2.3 Influence of time, temperature, relative humidity and NO<sub>2</sub>

There are some high ratios due to the fact that there are a considerable amount of data close to zero in the reference data . Therefore we chose to limit the y-as to -15 and +15.



Figure 18: Aeroqual SM50 O<sub>3</sub> sensor: Time plot ratio sensor hourly values versus reference values ( $\mu$ g/m<sup>3</sup>)





Figure 19: Aeroqual SM50  $O_3$  sensor: Scatter plot ratio sensor hourly values versus reference values in relation to relative humidity (%)

+Scatter plot ratio sensor hourly values versus reference values in relation to temperature (°C)



Figure 20: Aeroqual SM50  $O_3$  sensor: Scatter plot ratio sensor hourly values versus reference values in relation to temperature (°C)





Figure 21: Aeroqual SM50  $O_3$  sensor: Scatter plot ratio sensor hourly values versus reference values in relation to  $NO_2$  ( $\mu g/m^3$ )

#### 3.2.4 Descriptive parameters

Table 5: Aeroqual SM50  $O_3$  sensor: Descriptive parameters for uncalibrated sensors (O3\_S\_2) and sensors calibrated with the linear regression parameters (O3\_S\_1mLR2). ID: sensor idea, n: number of values,  $R^2$ : coefficient of determination,  $U_{bs}$ : between sampler uncertainty

		Calibr	ation			Evaluation		
	ID	n	R <sup>2</sup>	n	mean bias (μg/m³)	R <sup>2</sup>	u <sub>bs</sub> (µg/m³)	u <sub>bs</sub> (%)
03_s_2	VQ01			6595	3.54	0.92		
03_s_2	VQO2			6813	-0.74	0.96		
03_s_2	VQO3			1236	-3.64	0.97		
03_s_2	VQO5			6458	9.03	0.91		
03_s_2	all sensors			21102			16.68	38.37
O3_s_1mLR2	VQ01	699	0.99	5896	3.88	0.91		
O3_s_1mLR2	VQO2	723	0.98	6090	-2.39	0.97		
O3_s_1mLR2	VQO3	217	0.99	1019	-7.16	0.98		
O3_s_1mLR2	VQO5	723	0.99	5735	9.50	0.91		
O3_s_1mLR2	all sensors			18740			16.34	37.94







Figure 22: Aeroqual SM50 O<sub>3</sub> sensor: Relative expanded uncertainty (W (%)) for uncalibrated sensor values according to Guidance of Equivalence calculated at hourly O<sub>3</sub> reference concentrations of 10 to 200  $\mu$ g/m<sup>3</sup> in steps of 10  $\mu$ g/m<sup>3</sup>



Figure 23: Aeroqual SM50  $O_3$  sensor: Relative expanded uncertainty (W (%)) for sensor values calibrated with the linear regression parameters according to Guidance of Equivalence calculated at hourly  $O_3$  reference concentrations of 10 to 200  $\mu g/m^3$  in steps of 10  $\mu g/m^3$ 





Figure 24: Aeroqual SM50 O<sub>3</sub> sensor: Relative expanded uncertainty (W (%)) for uncalibrated sensor values according to Guidance of Equivalence calculated at 8-hourly O<sub>3</sub> reference concentrations of 10 to 150  $\mu$ g/m<sup>3</sup> in steps of 10  $\mu$ g/m<sup>3</sup>



Figure 25: Aeroqual SM50  $O_3$  sensor: Relative expanded uncertainty (W (%)) for sensor values calibrated with the linear regression parameters according to Guidance of Equivalence calculated at 8-hourly  $O_3$  reference concentrations of 10 to 150  $\mu$ g/m<sup>3</sup> in steps of 10  $\mu$ g/m<sup>3</sup>



Table 6: Aeroqual SM50 O<sub>3</sub> sensor: Relative expanded uncertainty for uncalibrated sensors (O3\_S\_2) and for sensors calibrated with the linear regression parameters (O3\_S\_1mLR2) according to Guidance of Equivalence calculated at O<sub>3</sub> 8-hourly reference concentrations of 60  $\mu$ g/m<sup>3</sup> (LAT), 84  $\mu$ g/m<sup>3</sup> (UAT) and 120  $\mu$ g/m<sup>3</sup> (LV)

	ID	O <sub>3</sub> _ref (µg/m³)	random term (μg/m³)	bias (µg/m³)	expanded uncertainty (%)
aighthaur 02 c 2	V001	60	2 21	2 5 6	20.19
eighthour O2 c 2	VQ01	60	1.64	2.20	15.62
eighthour_03_s_2	VQ02	60	1.04	-5.64	13.05
eighthour_03_s_2	VQ03	60	1.67	-4.36	17.27
eignthour_03_s_2	VQUS	60	2.32	9.61	36.74
eighthour_O3_s_1mLR2	VQ01	60	2.21	3.20	19.50
eighthour_O3_s_1mLR2	VQO2	60	1.56	-6.45	22.97
eighthour_O3_s_1mLR2	VQO3	60	1.46	-7.90	27.28
eighthour_O3_s_1mLR2	VQ05	60	2.23	8.98	34.18
eighthour_03_s_2	VQ01	84	2.21	3.61	14.49
eighthour_O3_s_2	VQO2	84	1.64	-7.40	18.74
eighthour_O3_s_2	VQO3	84	1.67	-6.37	16.57
eighthour_O3_s_2	VQ05	84	2.32	10.43	27.96
eighthour_O3_s_1mLR2	VQ01	84	2.21	2.40	12.98
eighthour_O3_s_1mLR2	VQ02	84	1.56	-11.05	26.93
eighthour O3 s 1mLR2	VQO3	84	1.46	-10.26	24.94
eighthour O3 s 1mLR2	VQ05	84	2.23	8.41	23.24
eighthour O3 s 2	VQ01	120	2.21	3.68	10.21
eighthour O3 s 2	VQO2	120	1.64	-12.73	21.68
eighthour_O3_s_2	VQO3	120	1.67	-9.39	16.32
eighthour O3 s 2	VQ05	120	2.32	11.66	21.42
eighthour O3 s 1mLR2	VQ01	120	2.21	1.20	8.40
eighthour O3 s 1mLR2	VQO2	120	1.56	-17.94	30.18
eighthour_O3_s_1mLR2	VQO3	120	1.46	-13.79	23.25
eighthour_O3_s_1mLR2	VQ05	120	2.23	7.56	15.06

Table 7: Aeroqual SM50  $O_3$  sensor: Parameters of orthogonal regression of 8-hourly sensor data versus reference  $O_3$  for uncalibrated sensors ( $O_3S_2$ ) and for sensors calibrated with the linear regression parameters ( $O_3S_1mLR_2$ )

	ID	slope	intercept (μg/m³)
eighthour_03_s_2	VQ01	1.00	3.45
eighthour_03_s_2	VQO2	0.85	5.04
eighthour_03_s_2	VQO3	0.92	0.66
eighthour_03_s_2	VQO5	1.03	7.55
eighthour_O3_s_1mLR2	VQ01	0.97	5.20
eighthour_O3_s_1mLR2	VQO2	0.81	5.05
eighthour_O3_s_1mLR2	VQO3	0.90	-2.02
eighthour_03_s_1mLR2	VQ05	0.98	10.40



#### 3.2.6 Conclusions

In wintertime the ratios versus the reference method seem higher. We also see higher ratios with lower temperatures, higher relative humidity and higher NO<sub>2</sub> concentrations. The low  $O_3$  concentrations when these conditions occur together with the fact that the sensor data are all positive, are most likely the cause of these patterns in the ratios.

The R<sup>2</sup> varies between 0.91 and 0.97 for the uncalibrated sensor data ( $O3\_s\_2$ ). The between sensor uncertainty is 38 %. The mean biases vary between -4 and 9 µg/m<sup>3</sup>.

The expanded uncertainty for the 8-hourly values is smaller than 30 % at the test concentrations of 60  $\mu$ g/m<sup>3</sup>, 80  $\mu$ g/m<sup>3</sup> and 120  $\mu$ g/m<sup>3</sup> (TV), with the exception of VQO5 at 60  $\mu$ g/m<sup>3</sup>.

Calibration of the sensors with the linear regression parameters ( $O3\_s\_1mLR2$ ) does not improve the between sensor uncertainty in comparison with the uncalibrated sensor data ( $O3\_s\_2$ ). The mean biases of the sensors VQO2 and VQO3 are more negative after calibration and the relative expanded uncertainty at the test concentrations ( $60 \ \mu g/m^3$ ,  $80 \ \mu g/m^3$  and  $120 \ \mu g/m^3$  (TV)) increases for some sensors.



#### 3.3 Sensor data calibrated with parameters from multiple linear regression

#### 3.3.1 Calibration parameters

Table 8: Aeroqual SM50  $O_3$  sensor: Parameters from multiple linear regression (including  $O_3$  reference measurements ( $O_3$ \_ref), temperature (T), relative humidity (RH)) - hourly field data from February 23 2019- March 31 2019

sensor_internal_id	intercept	O <sub>3</sub> _ref	Т	RH
VQO1	-3.4	1.02	0.29	0.00*
VQO2	-4.1	1.01	0.30	0.03
VQO3	13.6	0.99	-0.36	-0.10
VQO5	-0.7*	1.04	0.12	-0.02

\*:Variable not significant at 0.05 significance level

Table 9: Aeroqual SM50 O<sub>3</sub> sensor: Parameters from extended multiple linear regression (including ozone reference measurements ( $O_3$ \_ref),  $NO_2$  reference measurements ( $NO_2$ \_ref), temperature (T), relative humidity (RH)) - hourly field data from February 23 2019- March 31 2019

sensor_internal_id	intercept	O <sub>3</sub> _ref	NO <sub>2</sub> _ref	Т	RH
VQ01	-0.9*	1.00	-0.02	0.29	-0.02*
VQO2	-5.6	1.02	0.01*	0.31	0.04
VQO3	9.5	1.01	0.02*	-0.30	-0.07
VQO5	-0.2*	1.03	-0.01*	0.13	-0.03

\*:Variable not significant at 0.05 significance level

The variable reference NO<sub>2</sub> is not significant in the MLR function for three of the four sensors. We will not discuss the sensor data *O3\_s\_1mMLRext* further on. We also see that the effect of relative humidity is small (with parameters varying between -0.10 and 0.04).



3.3.2 Comparison sensor versus reference

*3.3.2.1* Time plot and scatter plots of hourly values



Figure 26: Aeroqual SM50 O<sub>3</sub> sensor: Time plot of sensor hourly values calibrated with multiple linear regression model and reference values ( $\mu g/m^3$ )



Figure 27: Aeroqual SM50  $O_3$  sensor: Scatter plot of sensor hourly values calibrated with multiple linear regression model and reference values ( $\mu g/m^3$ )







Figure 28: Aeroqual SM50 O<sub>3</sub> sensor: Density plot of ratio sensor hourly values calibrated with multiple linear regression versus reference values



#### 3.3.3 Influence of time, temperature, relative humidity and NO<sub>2</sub>

Figure 29: Aeroqual SM50 O<sub>3</sub> sensor: Time plot of ratio sensor hourly values calibrated with multiple linear regression versus reference values ( $\mu g/m^3$ )





Figure 30: Aeroqual SM50  $O_3$  sensor: Scatter plot ratio sensor hourly values calibrated with multiple linear regression versus reference values in relation to relative humidity (%)



Figure 31: Aeroqual SM50  $O_3$  sensor: Scatter plot ratio sensor hourly values calibrated with multiple linear regression versus reference values in relation to temperature (°C)





Figure 32: Aeroqual SM50  $O_3$  sensor: Scatter plot ratio sensor hourly values calibrated with multiple linear regression versus reference values in relation to nitrogen dioxide ( $\mu g/m^3$ )

#### 3.3.4 Descriptive parameters

Table 10: Aeroqual SM50  $O_3$  sensor: Descriptive parameters for sensors calibrated with multiple linear regression. ID: sensor idea, n: number of values,  $R^2$ : coefficient of determination,  $U_{bs}$ : between sampler uncertainty

		Calibration		Evaluation				
	ID	n	R <sup>2</sup>	n	mean bias (μg/m³)	R <sup>2</sup>	u <sub>bs</sub> (µg/m³)	u <sub>bs</sub> (%)
O3_s_1mMLR2	VQ01	699	0.99	5864	3.06	0.90		
O3_s_1mMLR2	VQO2	723	0.99	6059	-3.40	0.96		
O3_s_1mMLR2	VQO3	217	0.99	1019	-6.72	0.98		
O3_s_1mMLR2	VQO5	723	0.99	5704	9.22	0.91		
O3_s_1mMLR2	all sensors	2362		18646			16.20	38.06







Figure 33: Aeroqual SM50  $O_3$  sensor: Relative expanded uncertainty (W (%)) of sensor calibrated with multiple linear regression according to Guidance of Equivalence calculated at hourly  $O_3$  reference concentrations of 10 to 200 µg/m<sup>3</sup> in steps of 10 µg/m<sup>3</sup>. The relative expanded uncertainties are presented on a logarithmic scale



Figure 34: Aeroqual SM50  $O_3$  sensor: Relative expanded uncertainty (W (%)) of sensor calibrated with multiple linear regression according to Guidance of Equivalence calculated at 8-hourly  $O_3$  reference concentrations of 10 to 150 µg/m<sup>3</sup> in steps of 10 µg/m<sup>3</sup>. The relative expanded uncertainties are presented on a logarithmic scale


Table 11: Aeroqual SM50  $O_3$  sensor: Relative expanded uncertainty of sensors calibrated with multiple linear regression ( $O3\_S\_1mMLR2$ ) according to Guidance of Equivalence calculated at  $O_3$  8- hourly reference concentrations of 60 µg/m<sup>3</sup> (LAT), 84 µg/m<sup>3</sup> (UAT) and 120 µg/m<sup>3</sup> (LV)

	ID	NO <sub>2</sub> _ref (μg/m³)	random term (μg/m³)	bias (μg/m³)	expanded uncertainty (%)
eighthour_O3_s_1mMLR2	VQ01	60	2.29	1.95	18.61
eighthour_O3_s_1mMLR2	VQO2	60	1.64	-7.74	27.30
eighthour_03_s_1mMLR2	VQO3	60	1.46	-7.33	25.44
eighthour_O3_s_1mMLR2	VQ05	60	2.24	8.33	32.41
eighthour_O3_s_1mMLR2	VQ01	84	2.29	0.63	12.55
eighthour_O3_s_1mMLR2	VQO2	84	1.64	-12.65	30.80
eighthour_O3_s_1mMLR2	VQO3	84	1.46	-9.37	22.87
eighthour_O3_s_1mMLR2	VQ05	84	2.24	7.30	21.09
eighthour_O3_s_1mMLR2	VQ01	120	2.29	-1.35	9.01
eighthour_O3_s_1mMLR2	VQO2	120	1.64	-20.03	33.68
eighthour_03_s_1mMLR2	VQO3	120	1.46	-12.42	21.00
eighthour_O3_s_1mMLR2	VQ05	120	2.24	5.76	12.72

Table 12: Aeroqual SM50  $O_3$  sensor: Parameters of orthogonal regression of 8-hourly sensor data calibrated with multiple linear regression ( $O3_5_1mMLR2$ ) versus reference  $O_3$ 

	ID	slope	intercept (μg/m³)
eighthour_O3_s_1mMLR2	VQ01	0.95	5.25
eighthour_O3_s_1mMLR2	VQO2	0.80	4.56
eighthour_O3_s_1mMLR2	VQO3	0.92	-2.24
eighthour_O3_s_1mMLR2	VQ05	0.96	10.91

#### 3.3.6 Conclusions

Reference NO<sub>2</sub> was not significant in the MLR function for three of the 4 four sensors.

The R<sup>2</sup> for the sensor data calibrated with the MLR parameters without NO<sub>2</sub> (*O3\_s\_1mMLR2*) are comparable to the uncalibrated sensor data (*O3\_s\_2*). The between sensor uncertainty is also very comparable. The mean biases for the sensors VQO2 and VQO3 become larger after calibration with parameters from the MLR without NO<sub>2</sub>. The relative expanded uncertainty for the 8-hourly calibrated sensor data at the test concentrations (60 µg/m<sup>3</sup>, 80 µg/m<sup>3</sup> and 120 µg/m<sup>3</sup> (TV)) becomes only smaller for the sensors VQO1 and VQO5. The effect of relative humidity in the MLR calibration function is small.





#### Field Evaluation Citytech 3E1F O<sub>3</sub> sensor



Manufacturer: Citytech Link to website manufacturer Link to test protocol



#### 4 Citytech 3E1F O<sub>3</sub> sensor

#### 4.1 Validation and data coverage

Both positive and negative peaks are occasionally present in the raw sensor data. These were marked as suspicious when they were remarkable lower or higher than the values of the other sensors.

VQJ1 constantly gave high values and is not included in the further analysis. VQJ2 only started measuring in August 2019 and is also not included in the further analysis since there are no data for this sensor in the calibration period.

During the field testing the Citytech 3E1F sensors where not oriented according to the supplied manual. They were oriented with the membrane sideways instead of downwards. It is unknown to what extend this orientation affected the data.



Figure 35: Citytech 3E1F O<sub>3</sub> sensor: Number sensor minute values (-2: invalid, -1: suspicious, 0: valid, 1: missing)

Table 13: Citytech 3E1F O <sub>3</sub> sensor: Number sensor minute value	es (-2: invalid, -1: suspicious, 0: valid, 1: missing) ar	۱d
percentage of available data		

	-2	-1	0	1	%
					available
VQJ3	0	1059	505131	72690	87
VQJ4	0	690	523540	54650	90
VQJ5	0	263	504496	74121	87





Figure 36: Citytech 3E1F O<sub>3</sub> sensor: Number sensor hourly values (-2: invalid, -1: suspicious, 0: valid, 1: missing)

Table 14: Citytech 3E1F  $O_3$  sensor: Number sensor hourly values (-2: invalid, -1: suspicious, 0: valid, 1: missing) and percentage of available data

	-2	-1	0	1	%
					available
VQJ3	0	23	8405	1220	87
VQJ4	0	15	8711	922	90
VQJ5	0	5	8398	1245	87

#### 4.2 Uncalibrated sensor data and sensor data calibrated with parameters from linear regression

#### 4.2.1 Calibration parameters

Table 15: Citytech 3E1F O₃ sensor: Parameters from linear regression against reference method - hourly field data from February 23 2019 - March 31 2019

sensor_internal_id	slope	intercept
VQJ3	1.35	49.0
VQJ4	1.42	45.1
VQJ5	1.24	42.3





4.2.2 Comparison sensor versus reference

4.2.2.1 Time plot and scatter plots of hourly values



Figure 37: Citytech 3E1F O<sub>3</sub> sensor: Time plot uncalibrated sensor hourly values and reference values ( $\mu$ g/m<sup>3</sup>)



Figure 38: Citytech 3E1F O<sub>3</sub> sensor: Time plot of sensor hourly values calibrated with the linear regression parameters and reference values ( $\mu g/m^3$ )





Figure 39: Citytech 3E1F O<sub>3</sub> sensor: Scatter plot of uncalibrated sensor hourly values versus reference values ( $\mu g/m^3$ )



Figure 40: Citytech 3E1F O<sub>3</sub> sensor: Scatter plot sensor hourly values calibrated with the linear regression parameters versus reference values ( $\mu g/m^3$ )





Figure 41: Citytech 3E1F O<sub>3</sub> sensor: Density plot of uncalibrated ratio sensor hourly values versus reference values



Figure 42: Citytech 3E1F  $O_3$  sensor: Density plot of ratio sensor hourly values calibrated with the linear regression parameters versus reference values



4.2.3 Influence of time, temperature, relative humidity and NO<sub>2</sub>

There are some high ratios due to the fact that there are a considerable amount of data close to zero in the reference data . Therefore we chose to limit the y-as to -15 and +15.



Figure 43: Citytech 3E1F O<sub>3</sub> sensor: Time plot ratio sensor hourly values versus reference values ( $\mu g/m^3$ )



Figure 44: Citytech 3E1F  $O_3$  sensor: Scatter plot ratio sensor hourly values versus reference values in relation to relative humidity (%)





Figure 45: Citytech 3E1F  $O_3$  sensor: Scatter plot ratio sensor hourly values versus reference values in relation to temperature (°C)



Figure 46: Citytech 3E1F  $O_3$  sensor: Scatter plot ratio sensor hourly values versus reference values in relation to  $NO_2$  ( $\mu$ g/m<sup>3</sup>)



#### 4.2.4 Descriptive parameters

Table 16: Citytech 3E1F O<sub>3</sub> sensor: Descriptive parameters for uncalibrated sensors (O3\_S\_2) and sensors calibrated with the linear regression parameters (O3\_S\_1mLR2). ID: sensor idea, n: number of values,  $R^2$ : coefficient of determination,  $U_{bs}$ : between sampler uncertainty

		Calibi	ration			Evaluation		
	ID	n	R <sup>2</sup>	n	mean bias (μg/m³)	R <sup>2</sup>	u <sub>bs</sub> (µg/m³)	u <sub>bs</sub> (%)
03_s_2	VQJ3			7780	71.97	0.85		
03_s_2	VQJ4			8077	74.99	0.80		
03_s_2	VQJ5			7771	59.90	0.84		
03_s_2	all sensors			23628			35.37	33.44
O3_s_1mLR2	VQJ3	770	0.65	7010	7.73	0.88		
O3_s_1mLR2	VQJ4	772	0.60	7305	10.71	0.83		
O3_s_1mLR2	VQJ5	772	0.67	6999	7.64	0.87		
O3_s_1mLR2	all sensors	2314		21314			26.67	58.70



Figure 47: Citytech 3E1F  $O_3$  sensor: Relative expanded uncertainty (W (%)) for uncalibrated sensor values according to Guidance of Equivalence calculated at hourly  $O_3$  reference concentrations of 10 to 200  $\mu$ g/m<sup>3</sup> in steps of 10  $\mu$ g/m<sup>3</sup>





Figure 48: Citytech 3E1F  $O_3$  sensor: Relative expanded uncertainty (W (%)) for sensor values calibrated with the linear regression parameters according to Guidance of Equivalence calculated at hourly  $O_3$  reference concentrations of 10 to 200  $\mu$ g/m<sup>3</sup> in steps of 10  $\mu$ g/m<sup>3</sup>



Figure 49: Citytech 3E1F O<sub>3</sub> sensor: Relative expanded uncertainty (W (%)) for uncalibrated sensor values according to Guidance of Equivalence calculated at 8-hourly O<sub>3</sub> reference concentrations of 10 to 150  $\mu$ g/m<sup>3</sup> in steps of 10  $\mu$ g/m<sup>3</sup>





Figure 50: Citytech 3E1F  $O_3$  sensor: Relative expanded uncertainty (W (%)) for sensor values calibrated with the linear regression parameters according to Guidance of Equivalence calculated at 8-hourly  $O_3$  reference concentrations of 10 to 150  $\mu$ g/m<sup>3</sup> in steps of 10  $\mu$ g/m<sup>3</sup>

Table 17: Citytech 3E1F O <sub>3</sub> sensor: Relative expanded uncertainty for uncalibrated sensors (O3_S_2) and for sensors
calibrated with the linear regression parameters (O3_S_1mLR2) according to Guidance of Equivalence calculated at O $_3$ 8-
hourly reference concentrations of 60 $\mu$ g/m³ (LAT), 84 $\mu$ g/m³ (UAT) and 120 $\mu$ g/m³ (LV)

	ID	O <sub>3</sub> _ref (µg/m <sup>3</sup> )	random term	bias (µg/m³)	expanded
			(µg/m³)		uncertainty (%)
eighthour_03_s_2	VQJ3	60	10.70	99.06	332.13
eighthour_O3_s_2	VQJ4	60	14.40	109.18	367.10
eighthour_O3_s_2	VQJ5	60	10.91	87.57	294.17
eighthour_O3_s_1mLR2	VQJ3	60	7.04	22.66	79.11
eighthour_O3_s_1mLR2	VQJ4	60	9.19	28.52	99.88
eighthour_O3_s_1mLR2	VQJ5	60	7.97	26.57	92.46
eighthour_O3_s_2	VQJ3	84	10.70	129.10	308.43
eighthour_O3_s_2	VQJ4	84	14.40	146.70	350.97
eighthour_O3_s_2	VQJ5	84	10.91	117.23	280.31
eighthour_O3_s_1mLR2	VQJ3	84	7.04	38.93	94.20
eighthour_O3_s_1mLR2	VQJ4	84	9.19	47.70	115.67
eighthour_O3_s_1mLR2	VQJ5	84	7.97	46.45	112.21
eighthour_O3_s_2	VQJ3	120	10.70	174.15	290.80
eighthour_O3_s_2	VQJ4	120	14.40	202.98	339.15
eighthour_O3_s_2	VQJ5	120	10.91	161.70	270.12
eighthour_O3_s_1mLR2	VQJ3	120	7.04	63.34	106.21
eighthour_O3_s_1mLR2	VQJ4	120	9.19	76.48	128.38
eighthour_O3_s_1mLR2	VQJ5	120	7.97	76.26	127.80





Table 18: Citytech 3E1F  $O_3$  sensor: Parameters of orthogonal regression of 8-hourly sensor data versus reference  $O_3$  for uncalibrated sensors ( $O_3S_2$ ) and for sensors calibrated with the linear regression parameters ( $O_3S_1mLR2$ )

	ID	slope	intercept (μg/m³)
eighthour_O3_s_2	VQJ3	2.25	23.97
eighthour_O3_s_2	VQJ4	2.56	15.39
eighthour_03_s_2	VQJ5	2.24	13.44
eighthour_O3_s_1mLR2	VQJ3	1.68	-18.01
eighthour_O3_s_1mLR2	VQJ4	1.80	-19.44
eighthour_O3_s_1mLR2	VQJ5	1.83	-23.13

#### 4.2.6 Conclusions

No clear drift in the uncalibrated sensor data  $(O3\_s\_2)$  is observed. In wintertime the ratios versus the reference method seem higher. We also see higher ratios with lower temperatures, higher relative humidity and higher NO<sub>2</sub> concentrations. The low O<sub>3</sub> concentrations when these conditions occur together with the fact that the sensor data are mostly positive make it difficult to determine the effect of temperature, relative humidity and NO<sub>2</sub> on the sensor data.

The R<sup>2</sup> of the uncalibrated sensor data  $O3_s_2$  varies between 0.80 and 0.85. The sensors largely overestimate the O<sub>3</sub> concentrations: the mean biases vary between 60 – 75 µg/m<sup>3</sup>. At higher O<sub>3</sub> concentrations the uncalibrated sensor data  $O3_s_2$  deviate from the linear trendline.

Application of the LR parameters ( $O3\_s\_1mLR2$ ) improves the sensor data leading to smaller mean biases, a smaller absolute between sensor uncertainty and smaller relative expanded uncertainties. However, the expanded uncertainty for the 8-hourly calibrated sensor data at the test concentrations ( $60 \mu g/m^3$ ,  $80 \mu g/m^3$  and  $120 \mu g/m^3$  (TV)) remains higher than 75 %.



#### 4.3 Sensor data calibrated with parameters from multiple linear regression

#### 4.3.1 Calibration parameters

Table 19: Citytech 3E1F  $O_3$  sensor: Parameters from multiple linear regression (including  $O_3$  reference measurements ( $O_3$ \_ref), temperature (T), relative humidity (RH)) - hourly field data from February 23 2019- March 31 2019

sensor_internal_id	intercept	O₃_ref	Т	RH
VQJ3	46.24	0.99	2.72	-0.13
VQJ4	47.71	0.98	2.63	-0.14
VQJ5	57.68	0.95	1.70	-0.28

Table 20: Citytech 3E1F O<sub>3</sub> sensor: Parameters from extended multiple linear regression (including ozone reference measurements ( $O_3$ \_ref),  $NO_2$  reference measurements ( $NO_2$ \_ref), temperature (T), relative humidity (RH)) - hourly field data from February 23 2019- March 31 2019

sensor_internal_id	intercept	O <sub>3</sub> _ref	NO <sub>2</sub>	Т	RH
VQJ3	-57.2	1.76	0.89	3.37	0.37
VQJ4	-65.1	1.82	0.97	3.37	0.39
VQJ5	-56.8	1.79	0.98	2.44	0.27

#### 4.3.2 Comparison sensor versus reference

#### 4.3.2.1 Time plot and scatter plots of hourly values



Figure 51: Citytech 3E1F O<sub>3</sub> sensor: Time plot of sensor hourly values calibrated with multiple linear regression model and reference values ( $\mu g/m^3$ )





Figure 52: Citytech 3E1F  $O_3$  sensor: Time plot of sensor hourly values calibrated with extended multiple linear regression model and reference values ( $\mu$ g/m<sup>3</sup>)



Figure 53: Citytech 3E1F O<sub>3</sub> sensor: Scatter plot of sensor hourly values calibrated with multiple linear regression model and reference values ( $\mu g/m^3$ )





Figure 54: Citytech 3E1F  $O_3$  sensor: Scatter plot of sensor hourly values calibrated with extended multiple linear regression model and reference values ( $\mu g/m^3$ )



#### 4.3.2.2 Ratio of hourly sensor values versus reference values

Figure 55: Citytech 3E1F  $O_3$  sensor: Density plot of ratio sensor hourly values calibrated with multiple linear regression versus reference values





Figure 56: Citytech 3E1F  $O_3$  sensor: Density plot of ratio sensor hourly values calibrated with extended multiple linear regression versus reference values



#### 4.3.3 Influence of time, temperature, relative humidity and NO<sub>2</sub>

Figure 57: Citytech 3E1F O<sub>3</sub> sensor: Time plot of ratio sensor hourly values calibrated with multiple linear regression versus reference values ( $\mu g/m^3$ )





Figure 58: Citytech 3E1F  $O_3$  sensor: Time plot of ratio sensor hourly values calibrated with extended multiple linear regression versus reference values ( $\mu g/m^3$ )



Figure 59: Citytech 3E1F  $O_3$  sensor: Scatter plot ratio sensor hourly values calibrated with multiple linear regression versus reference values in relation to relative humidity (%)





Figure 60: Citytech 3E1F  $O_3$  sensor: Scatter plot ratio sensor hourly values calibrated with extended multiple linear regression versus reference values in relation to relative humidity (%)



Figure 61: Citytech 3E1F  $O_3$  sensor: Scatter plot ratio sensor hourly values calibrated with multiple linear regression versus reference values in relation to temperature (°C)







Figure 62: Citytech 3E1F  $O_3$  sensor: Scatter plot ratio sensor hourly values calibrated with extended multiple linear regression versus reference values in relation to temperature (°C)



Figure 63: Citytech 3E1F O<sub>3</sub> sensor: Scatter plot ratio sensor hourly values calibrated with multiple linear regression versus reference values in relation to nitrogen dioxide ( $\mu g/m^3$ )





Figure 64: Citytech 3E1F O<sub>3</sub> sensor: Scatter plot ratio sensor hourly values calibrated with extended multiple linear regression versus reference values in relation to nitrogen dioxide ( $\mu g/m^3$ )

#### 4.3.4 Descriptive parameters

Table 21: Citytech 3E1F O<sub>3</sub> sensor: Descriptive parameters for sensors calibrated with multiple linear regression (O3\_S\_mMLR2) and extended multiple linear regression(O3\_S\_mMLRext2). ID: sensor idea, n: number of values,  $R^2$ : coefficient of determination,  $U_{bs}$ : between sampler uncertainty

		Calibi	ration	Evaluation				
	ID	n	R <sup>2</sup>	n	mean bias (μg/m³)	R <sup>2</sup>	u <sub>bs</sub> (µg/m³)	u <sub>bs</sub> (%)
O3_s_1mMLR2	VQJ3	770	0.73	6965	1.60	0.80		
O3_s_1mMLR2	VQJ4	772	0.67	7258	6.25	0.76		
O3_s_1mMLR2	VQJ5	772	0.74	6952	5.00	0.82		
O3_s_1mMLR2	all sensors			21175			31.01	75.29
O3_s_1mMLRext2	VQJ3	735	0.93	6621	3.37	0.89		
O3_s_1mMLRext2	VQJ4	737	0.91	6884	5.91	0.87		
O3_s_1mMLRext2	VQJ5	737	0.96	6587	5.49	0.92		
O3_s_1mMLRext2	all sensors			20092			21.51	50.99









Figure 65: Citytech 3E1F  $O_3$  sensor: Relative expanded uncertainty (W (%)) of sensor calibrated with multiple linear regression according to Guidance of Equivalence calculated at hourly  $O_3$  reference concentrations of 10 to 200 µg/m<sup>3</sup> in steps of 10 µg/m<sup>3</sup>. The relative expanded uncertainties are presented on a logarithmic scale



Figure 66: Citytech 3E1F O<sub>3</sub> sensor: Relative expanded uncertainty (W (%)) of sensor calibrated with extended multiple linear regression according to Guidance of Equivalence calculated at hourly O<sub>3</sub> reference concentrations of 10 to 200  $\mu$ g/m<sup>3</sup> in steps of 10  $\mu$ g/m<sup>3</sup>. The relative expanded uncertainties are presented on a logarithmic scale





Figure 67: Citytech 3E1F  $O_3$  sensor: Relative expanded uncertainty (W (%)) of sensors calibrated with multiple linear regression according to Guidance of Equivalence calculated at 8-hourly  $O_3$  reference concentrations of 10 to 150 µg/m<sup>3</sup> in steps of 10 µg/m<sup>3</sup>. The relative expanded uncertainties are presented on a logaritmic scale.



Figure 68: Citytech 3E1F  $O_3$  sensor: Relative expanded uncertainty (W (%)) of sensors calibrated with extended multiple linear regression according to Guidance of Equivalence calculated at 8-hourly  $O_3$  reference concentrations of 10 to 150  $\mu$ g/m<sup>3</sup> in steps of 10  $\mu$ g/m<sup>3</sup>. The relative expanded uncertainties are presented on a logarithmic scale.



Table 22: Citytech 3E1F O<sub>3</sub> sensor: Relative expanded uncertainty of sensors calibrated with multiple linear regression (O3\_S\_1mMLR2) and extended multiple linear regression (O3\_S\_1mMLRext2) according to Guidance of Equivalence calculated at O<sub>3</sub> 8- hourly reference concentrations of 60  $\mu$ g/m<sup>3</sup> (LAT), 84  $\mu$ g/m<sup>3</sup> (UAT) and 120  $\mu$ g/m<sup>3</sup> (LV)

	ID	O <sub>3</sub> _ref (µg/m <sup>3</sup> )	random term	bias (µg/m³)	expanded
			(µg/m³)		uncertainty (%)
eighthour_O3_s_1mMLR2	VQJ3	60	11.58	22.89	85.49
eighthour_O3_s_1mMLR2	VQJ4	60	13.98	33.86	122.10
eighthour_O3_s_1mMLR2	VQJ5	60	11.02	29.47	104.88
eighthour_O3_s_1mMLRext2	VQJ3	60	5.93	9.59	37.58
eighthour_O3_s_1mMLRext2	VQJ4	60	6.54	14.06	51.69
eighthour_O3_s_1mMLRext2	VQJ5	60	5.04	12.52	44.98
eighthour_O3_s_1mMLR2	VQJ3	84	11.58	46.17	113.34
eighthour_O3_s_1mMLR2	VQJ4	84	13.98	63.77	155.43
eighthour_O3_s_1mMLR2	VQJ5	84	11.02	55.26	134.17
eighthour_O3_s_1mMLRext2	VQJ3	84	5.93	16.55	41.87
eighthour_O3_s_1mMLRext2	VQJ4	84	6.54	23.07	57.10
eighthour_O3_s_1mMLRext2	VQJ5	84	5.04	20.06	49.26
eighthour_O3_s_1mMLR2	VQJ3	120	11.58	81.11	136.55
eighthour_O3_s_1mMLR2	VQJ4	120	13.98	108.63	182.55
eighthour_O3_s_1mMLR2	VQJ5	120	11.02	93.95	157.65
eighthour_O3_s_1mMLRext2	VQJ3	120	5.93	27.00	46.08
eighthour_O3_s_1mMLRext2	VQJ4	120	6.54	36.59	61.95
eighthour_O3_s_1mMLRext2	VQJ5	120	5.04	31.38	52.98

Table 23: Citytech 3E1F  $O_3$  sensor: Parameters of orthogonal regression of 8-hourly sensor data calibrated with multiple linear regression ( $O_3_1$ mMLR2) and extended multiple linear regression ( $O_3_1$ mMLRext2) versus reference  $O_3$ 

	ID	slope	intercept (μg/m³)
eighthour_O3_s_1mMLR2	VQJ3	1.97	-35.34
eighthour_O3_s_1mMLR2	VQJ4	2.25	-40.92
eighthour_O3_s_1mMLR2	VQJ5	2.07	-35.00
eighthour_O3_s_1mMLRext2	VQJ3	1.29	-7.83
eighthour_O3_s_1mMLRext2	VQJ4	1.38	-8.47
eighthour O3 s 1mMLRext2	VQJ5	1.31	-6.35

#### 4.3.6 Conclusions

No clear drift in the calibrated sensor data is observed. In wintertime we see higher positive and negative ratios. We also see a larger range in ratios with lower temperatures, higher relative humidity and higher NO<sub>2</sub> concentrations. The low O<sub>3</sub> concentrations when these conditions occur make it difficult to determine the effect of temperature, relative humidity and NO<sub>2</sub> on the calibrated sensor data.

When we look at the scatter plots in relation to temperature, relative humidity and NO<sub>2</sub>, we see that there is less scatter after calibration with the parameters of the MLR with NO<sub>2</sub> ( $O3\_s\_1mMLRext2$ ) in comparison with the calibration with the parameters of the MLR



without NO<sub>2</sub> ( $O3\_s\_1mMLR2$ ). The sensor data  $O3\_s\_1mMLRext2$  deviate less from the linear trendline at higher concentrations.

The sensor data calibrated with the parameters from the MLR without NO<sub>2</sub> ( $O3\_s\_1mMLR2$ ) are not improved in comparison to the sensor data calibrated with the LR parameters ( $O3\_s\_1mLR2$ ): calibration leads to smaller R<sup>2</sup>, a higher between sensor uncertainty and higher relative expanded uncertainties.

The sensor data calibrated with the parameters from MLR with NO<sub>2</sub> ( $O3\_s\_1mMLRext2$ ) shows better performance characteristics compared to the sensor data calibrated with the LR parameters ( $O3\_s\_1mLR2$ ). The R<sup>2</sup> varies between 0.87 and 0.92, the mean biases vary between 3 and 6 µg/m<sup>3</sup> and the expanded uncertainty at the test concentrations (60 µg/m<sup>3</sup>, 80 µg/m<sup>3</sup> and 120 µg/m<sup>3</sup> (TV)) is for all three sensors  $\leq$  75 % (but > than 30 %). The between sensor uncertainty is 51 %.





Field Evaluation Membrapor C-5 O<sub>3</sub> sensor



Manufacturer: Membrapor Link to website manufacturer Link to test protocol



#### 5 Membrapor C-5 O<sub>3</sub> sensor

#### 5.1 Validation

A lot of negative and positive peaks occurred in the raw data. It was not possible to remove these peaks manually, so the peaks were marked suspicious automatically when higher than 200  $\mu$ g/m<sup>3</sup> and lower than -50  $\mu$ g/m<sup>3</sup>.

VQM2 was tested in the laboratory, but was not included in the evaluation of the laboratory testing due to malfunctioning.

When looking at the time plots, we noticed diverging ata for VQM2 from January 2020 on. We also saw more peaks and aberrant data for the other sensors at the end of the measurement campaign. Therefore the data from January 1, 2020 until March 30, 2020 were considered suspicious for all sensors and left out of the further data analysis.



Figure 69: Membrapor C-5 O<sub>3</sub> sensor: Number sensor minute values (-2: invalid, -1: suspicious, 0: valid, 1: missing)

Table 24: Membrapor C-5  $O_3$  sensor: Number sensor minute values (-2: invalid, -1: suspicious, 0: valid, 1: missing) and percentage of available data

	-2	-1	0	1	% available
VQM1	0	121390	285060	172430	49
VQM2	0	88686	361576	128618	62
VQM3	0	80311	382831	115738	66
VQM4	0	123279	365373	90228	63
VQM5	0	78450	317692	182738	55







Table 25: Membrapor C-5  $O_3$  sensor: Number sensor hourly values (-2: invalid, -1: suspicious, 0: valid, 1: missing) and percentage of available data

	-2	-1	0	1	%
					available
VQM1	0	457	6305	2886	49
VQM2	0	14	7476	2158	62
VQM3	0	7	7706	1935	66
VQM4	0	109	8025	1514	63
VQM5	0	58	6535	3055	55



#### 5.2 Uncalibrated sensor data and sensor data calibrated with parameters from linear regression

#### 5.2.1 Calibration parameters

Table 26: Membrapor C-5 O<sub>3</sub> sensor: Parameters from linear regression against reference method - hourly field data from February 23 2019 - March 31 2019

sensor_internal_id	slope	intercept
VQM1	0.19	52.3
VQM2	0.06	2.7
VQM3	0.20	8.9
VQM4	0.18	33.2
VQM5	0.16	57.8

#### 5.2.2 Comparison sensor versus reference





Figure 71: Membrapor C-5  $O_3$  sensor: Time plot uncalibrated sensor hourly values and reference values ( $\mu$ g/m<sup>3</sup>)





Figure 72: Membrapor C-5  $O_3$  sensor: Time plot of sensor hourly values calibrated with the linear regression parameters and reference values ( $\mu g/m^3$ )



Figure 73: Membrapor C-5  $O_3$  sensor: Scatter plot of uncalibrated sensor hourly values versus reference values ( $\mu g/m^3$ )





Figure 74: Membrapor C-5  $O_3$  sensor: Scatter plot sensor hourly values calibrated with the linear regression parameters versus reference values ( $\mu g/m^3$ )



#### 5.2.2.2 Ratio of hourly sensor values versus reference values

Figure 75: Membrapor C-5 O<sub>3</sub> sensor: Density plot of uncalibrated ratio sensor hourly values versus reference values





Figure 76: Membrapor C-5  $O_3$  sensor: Density plot of ratio sensor hourly values calibrated with the linear regression parameters versus reference values

#### 5.2.3 Influence of time, temperature, relative humidity and NO<sub>2</sub>

There are some high ratios due to the fact that there are a considerable amount of data close to zero in the reference data . Therefore we chose to limit the y-as to -15 and +15.



Figure 77: Membrapor C-5  $O_3$  sensor: Time plot ratio sensor hourly values versus reference values ( $\mu$ g/m<sup>3</sup>)





Figure 78: Membrapor C-5  $O_3$  sensor: Scatter plot ratio sensor hourly values versus reference values in relation to relative humidity (%)



Figure 79: Membrapor C-5  $O_3$  sensor: Scatter plot ratio sensor hourly values versus reference values in relation to temperature (°C)





Figure 80: Membrapor C-5  $O_3$  sensor: Scatter plot ratio sensor hourly values versus reference values in relation to  $NO_2$  ( $\mu g/m^3$ )

#### 5.2.4 Descriptive parameters

Table 27: Membrapor C-5  $O_3$  sensor: Descriptive parameters for uncalibrated sensors (O3\_S\_2) and sensors calibrated with the linear regression parameters (O3\_S\_1mLR2). ID: sensor idea, n: number of values,  $R^2$ : coefficient of determination,  $U_{bs}$ : between sampler uncertainty

		Calibration		Evalua				
	ID	n	R <sup>2</sup>	n	mean bias (μg/m³)	R <sup>2</sup>	u <sub>bs</sub> (µg/m³)	u <sub>bs</sub> (%)
03_s_2	VQM1			4525	14.29	0.35		
03_s_2	VQM2			5607	-35.03	0.27		
03_s_2	VQM3			5960	-21.99	0.43		
03_s_2	VQM4			5819	-3.31	0.24		
03_s_2	VQM5			4878	26.20	0.06		
03_s_2	all sensors			26789			24.31	74.01
O3_s_1mLR2	VQM1	772	0.11	3753	-40.82	0.40		
O3_s_1mLR2	VQM2	522	0.28	5085	-30.01	0.26		
O3_s_1mLR2	VQM3	772	0.20	5188	-3.88	0.46		
O3_s_1mLR2	VQM4	772	0.14	5047	-35.52	0.25		
O3_s_1mLR2	VQM5	739	0.10	4139	18.11	0.06		
O3_s_1mLR2	all sensors			23212			64.60	325.06





5.2.5 Relative expanded uncertainty



Figure 81: Membrapor C-5  $O_3$  sensor: Relative expanded uncertainty (W (%)) for uncalibrated sensor values according to Guidance of Equivalence calculated at hourly  $O_3$  reference concentrations of 10 to 200  $\mu$ g/m<sup>3</sup> in steps of 10  $\mu$ g/m<sup>3</sup>



Figure 82: Membrapor C-5  $O_3$  sensor: Relative expanded uncertainty (W (%)) for sensor values calibrated with the linear regression parameters according to Guidance of Equivalence calculated at hourly  $O_3$  reference concentrations of 10 to 200  $\mu$ g/m<sup>3</sup> in steps of 10  $\mu$ g/m<sup>3</sup>





Figure 83: Membrapor C-5  $O_3$  sensor: Relative expanded uncertainty (W (%)) for uncalibrated sensor values according to Guidance of Equivalence calculated at 8-hourly  $O_3$  reference concentrations of 10 to 150  $\mu$ g/m<sup>3</sup> in steps of 10  $\mu$ g/m<sup>3</sup>



Figure 84: Membrapor C-5  $O_3$  sensor: Relative expanded uncertainty (W (%)) for sensor values calibrated with the linear regression parameters according to Guidance of Equivalence calculated at 8-hourly  $O_3$  reference concentrations of 10 to 150  $\mu$ g/m<sup>3</sup> in steps of 10  $\mu$ g/m<sup>3</sup>


Table 28: Membrapor C-5 O<sub>3</sub> sensor: Relative expanded uncertainty for uncalibrated sensors (O3\_S\_2) and for sensors calibrated with the linear regression parameters (O3\_S\_1mLR2) according to Guidance of Equivalence calculated at O<sub>3</sub> 8-hourly reference concentrations of 60  $\mu$ g/m<sup>3</sup> (LAT), 84  $\mu$ g/m<sup>3</sup> (UAT) and 120  $\mu$ g/m<sup>3</sup> (LV)

	ID	O <sub>3</sub> _ref (µg/m <sup>3</sup> )	random term	bias (µg/m³)	expanded
			(µg/m³)		uncertainty (%)
eighthour_O3_s_2	VQM1	60	10.36	1.40	34.84
eighthour_03_s_2	VQM2	60	2.49	-55.05	183.68
eighthour_O3_s_2	VQM3	60	8.55	-35.97	123.23
eighthour_03_s_2	VQM4	60	13.35	-15.50	68.19
eighthour_03_s_2	VQM5	60	14.38	11.42	61.22
eighthour_O3_s_1mLR2	VQM1	60	73.90	18.90	254.28
eighthour_O3_s_1mLR2	VQM2	60	63.91	19.60	222.81
eighthour_O3_s_1mLR2	VQM3	60	59.19	53.04	264.92
eighthour_O3_s_1mLR2	VQM4	60	134.36	92.33	543.42
eighthour_O3_s_1mLR2	VQM5	60	396.29	338.79	1737.88
eighthour_03_s_2	VQM1	84	10.36	-13.32	40.18
eighthour_03_s_2	VQM2	84	2.49	-77.37	184.30
eighthour_03_s_2	VQM3	84	8.55	-50.89	122.86
eighthour_03_s_2	VQM4	84	13.35	-28.63	75.20
eighthour_O3_s_2	VQM5	84	14.38	-6.83	37.91
eighthour_O3_s_1mLR2	VQM1	84	73.90	85.40	268.89
eighthour_O3_s_1mLR2	VQM2	84	63.91	72.66	230.39
eighthour_O3_s_1mLR2	VQM3	84	59.19	112.40	302.46
eighthour_O3_s_1mLR2	VQM4	84	134.36	226.62	627.27
eighthour_O3_s_1mLR2	VQM5	84	396.29	737.64	1993.69
eighthour_03_s_2	VQM1	120	10.36	-35.40	61.48
eighthour_03_s_2	VQM2	120	2.49	-110.85	184.79
eighthour_O3_s_2	VQM3	120	8.55	-73.27	122.94
eighthour_03_s_2	VQM4	120	13.35	-48.31	83.53
eighthour_03_s_2	VQM5	120	14.38	-34.21	61.85
eighthour_O3_s_1mLR2	VQM1	120	73.90	185.14	332.24
eighthour_O3_s_1mLR2	VQM2	120	63.91	152.25	275.20
eighthour_O3_s_1mLR2	VQM3	120	59.19	201.44	349.93
eighthour_03_s_1mLR2	VQM4	120	134.36	428.04	747.73
eighthour_O3_s_1mLR2	VQM5	120	396.29	1335.91	2322.42

Table 29: Membrapor C-5  $O_3$  sensor: Parameters of orthogonal regression of 8-hourly sensor data versus reference  $O_3$  for uncalibrated sensors ( $O_3S_2$ ) and for sensors calibrated with the linear regression parameters ( $O_3S_1$ mLR2)

	ID	slope	intercept (μg/m³)
eighthour_O3_s_2	VQM1	0.39	38.20
eighthour_O3_s_2	VQM2	0.07	0.75
eighthour_O3_s_2	VQM3	0.38	1.33
eighthour_O3_s_2	VQM4	0.45	17.31
eighthour_O3_s_2	VQM5	0.24	57.05
eighthour_O3_s_1mLR2	VQM1	3.77	-147.33
eighthour_O3_s_1mLR2	VQM2	3.21	-113.05
eighthour_O3_s_1mLR2	VQM3	3.47	-95.37
eighthour_O3_s_1mLR2	VQM4	6.60	-243.38
eighthour_O3_s_1mLR2	VQM5	17.62	-658.33



#### 5.2.6 Conclusions

No clear drift in the uncalibrated sensor data  $(O3\_s\_2)$  is observed. In wintertime we see more positive and negative ratios. We also see higher ratios with lower temperatures, higher relative humidity and higher NO<sub>2</sub> concentrations. The low O<sub>3</sub> concentrations when these conditions occur together with the fact that the sensor data are mostly positive make it difficult to determine the effect of temperature, relative humidity and NO<sub>2</sub> on the sensor data.

The R<sup>2</sup> of the uncalibrated sensor data varies between 0.24 and 0.43, except for one sensor (VQM5) with a R<sup>2</sup> of 0.06. Some sensors overestimate the O<sub>3</sub> concentrations, while others underestimate the O<sub>3</sub> concentrations: the mean biases vary between -35 and 26  $\mu$ g/m<sup>3</sup>.

The expanded uncertainty of the 8-hourly values of some of the uncalibrated sensors is  $\leq$  75 % at the test concentrations (60 µg/m<sup>3</sup>, 80 µg/m<sup>3</sup> and 120 µg/m<sup>3</sup> (TV)). This is due to the fact that the slope of the orthogonal regression of the uncalibrated sensor data versus the reference data is small for the uncalibrated sensors (< 0.5) with a small contribution from random errors to the uncertainty as a result.

Calibration of the sensor data with the parameters from LR leads to biases between -41 and 18  $\mu$ g/m<sup>3</sup>. The between uncertainty is 64.4  $\mu$ g/m<sup>3</sup> and the expanded uncertainty of the 8-hourly values is for all sensors and for all concentrations (between 10 and 200  $\mu$ g/m<sup>3</sup>) higher than 200 %.





### 5.3 Sensor data calibrated with parameters from multiple linear regression

#### 5.3.1 Calibration parameters

Table 30: Membrapor C-5  $O_3$  sensor: Parameters from multiple linear regression (including  $O_3$  reference measurements ( $O_3$ \_ref), temperature (T), relative humidity (RH)) - hourly field data from February 23 2019- March 31 2019

sensor_internal_id	intercept	O₃_ref	Т	RH
VQM1	53.7	0.16	-0.25*	0.03*
VQM2	15.8	0.04	-0.31	-0.12
VQM3	35.7	0.17	-0.24	-0.33
VQM4	59.1	0.16	-0.55	-0.27
VQM5	78.6	0.13	-0.27	-0.24

\*:Variable not significant at 0.05 significance level

Table 31: Membrapor C-5  $O_3$  sensor: Parameters from extended multiple linear regression (including ozone reference measurements ( $O_3$ \_ref),  $NO_2$  reference measurements ( $NO_2$ \_ref), temperature (T), relative humidity (RH)) - hourly field data from February 23 2019- March 31 2019

sensor_internal_id	intercept	O <sub>3</sub> _ref	NO <sub>2</sub> _ref	Т	RH
VQM1	-22.2	0.73	0.65	0.20*	0.39
VQM2	-0.1*	0.16	0.14	-0.21	-0.05
VQM3	-34.5	0.69	0.60	0.16	0.01*
VQM4	-28.3	0.81	0.75	-0.06*	0.15
VQM5	2.6*	0.69	0.64	0.18*	0.13

\*:Variable not significant at 0.05 significance level





5.3.2 Comparison sensor versus reference

*5.3.2.1 Time plot and scatter plots of hourly values* 



Figure 85: Membrapor C-5  $O_3$  sensor: Time plot of sensor hourly values calibrated with multiple linear regression model and reference values ( $\mu g/m^3$ )



Figure 86: Membrapor C-5  $O_3$  sensor: Time plot of sensor hourly values calibrated with extended multiple linear regression model and reference values ( $\mu g/m^3$ )





Figure 87: Membrapor C-5  $O_3$  sensor: Scatter plot of sensor hourly values calibrated with multiple linear regression model and reference values ( $\mu g/m^3$ )



Figure 88: Membrapor C-5  $O_3$  sensor: Scatter plot of sensor hourly values calibrated with extended multiple linear regression model and reference values ( $\mu g/m^3$ )



### OUUMS 5.3.2.2 Ratio of hourly sensor values versus reference values 0.3 sensor\_internal\_id 0.2 VQM1 density VQM2 VQM3 VQM4 VQM5 0.1 -0.0 -1 0 1 O3\_s\_1mMLR2\_ratio 2 -3 -2 3

Figure 89: Membrapor C-5  $O_3$  sensor: Density plot of ratio sensor hourly values calibrated with multiple linear regression versus reference values



Figure 90: Membrapor C-5 O<sub>3</sub> sensor: Density plot of ratio sensor hourly values calibrated with extended multiple linear regression versus reference values



### Influence of time, temperature, relative humidity and NO<sub>2</sub> 5.3.3 10 sensor\_internal\_id 03\_s\_1mMLR2\_ratio VQM1 VQM2 0-VQM3 VQM4 VQM5 -10 apr 2019 jul 2019 jan 2020 apr 2020 okt 2019 date

Figure 91: Membrapor C-5  $O_3$  sensor: Time plot of ratio sensor hourly values calibrated with multiple linear regression versus reference values ( $\mu g/m^3$ )



Figure 92: Membrapor C-5  $O_3$  sensor: Time plot of ratio sensor hourly values calibrated with extended multiple linear regression versus reference values ( $\mu g/m^3$ )





Figure 93: Membrapor C-5  $O_3$  sensor: Scatter plot ratio sensor hourly values calibrated with multiple linear regression versus reference values in relation to relative humidity (%)



Figure 94: Membrapor C-5  $O_3$  sensor: Scatter plot ratio sensor hourly values calibrated with extended multiple linear regression versus reference values in relation to relative humidity (%)





Figure 95: Membrapor C-5  $O_3$  sensor: Scatter plot ratio sensor hourly values calibrated with multiple linear regression versus reference values in relation to temperature (°C)



Figure 96: Membrapor C-5  $O_3$  sensor: Scatter plot ratio sensor hourly values calibrated with extended multiple linear regression versus reference values in relation to temperature (°C)





Figure 97: Membrapor C-5  $O_3$  sensor: Scatter plot ratio sensor hourly values calibrated with multiple linear regression versus reference values in relation to nitrogen dioxide ( $\mu g/m^3$ )



Figure 98: Membrapor C-5  $O_3$  sensor: Scatter plot ratio sensor hourly values calibrated with extended multiple linear regression versus reference values in relation to nitrogen dioxide ( $\mu g/m^3$ )



#### 5.3.4 Descriptive parameters

Table 32: Membrapor C-5  $O_3$  sensor: Descriptive parameters for sensors calibrated with multiple linear regression (O3\_S\_mMLR2) and extended multiple linear regression(O3\_S\_mMLRext2). ID: sensor idea, n: number of values,  $R^2$ : coefficient of determination,  $U_{bs}$ : between sampler uncertainty

		Calibi	ration	Evaluation				
	ID	n	R <sup>2</sup>	n	mean bias (μg/m³)	R <sup>2</sup>	u <sub>bs</sub> (µg/m³)	u <sub>bs</sub> (%)
O3_s_1mMLR2	VQM1	772	0.12	3720	-44.12	0.49		
O3_s_1mMLR2	VQM2	522	0.19	5054	-15.51	0.21		
O3_s_1mMLR2	VQM3	772	0.26	5148	4.75	0.29		
O3_s_1mMLR2	VQM4	772	0.15	5008	-23.46	0.24		
O3_s_1mMLR2	VQM5	739	0.11	4118	33.24	0.02		
O3_s_1mMLR2	all sensors			23048			76.32	255.18
O3_s_1mMLRext2	VQM1	737	0.82	3506	-7.56	0.86		
O3_s_1mMLRext2	VQM2	499	0.86	4790	0.88	0.75		
O3_s_1mMLRext2	VQM3	737	0.96	4865	5.49	0.85		
O3_s_1mMLRext2	VQM4	737	0.95	4732	-0.34	0.73		
O3_s_1mMLRext2	VQM5	706	0.86	3903	9.48	0.30		
O3_s_1mMLRext2	all sensors			21796			20.54	51.37

#### 5.3.5 Relative expanded uncertainty



Figure 99: Membrapor C-5  $O_3$  sensor: Relative expanded uncertainty (W (%)) of sensor calibrated with multiple linear regression according to Guidance of Equivalence calculated at hourly  $O_3$  reference concentrations of 10 to 200  $\mu$ g/m<sup>3</sup> in steps of 10  $\mu$ g/m<sup>3</sup>. The relative expanded uncertainties are presented on a logarithmic scale





Figure 100: Membrapor C-5  $O_3$  sensor: Relative expanded uncertainty (W (%)) of sensor calibrated with extended multiple linear regression according to Guidance of Equivalence calculated at hourly  $O_3$  reference concentrations of 10 to 200  $\mu$ g/m<sup>3</sup> in steps of 10  $\mu$ g/m<sup>3</sup>. The relative expanded uncertainties are presented on a logarithmic scale



Figure 101: Membrapor C-5  $O_3$  sensor: Relative expanded uncertainty (W (%)) of sensors calibrated with multiple linear regression according to Guidance of Equivalence calculated at 8-hourly  $O_3$  reference concentrations of 10 to 150 µg/m<sup>3</sup> in steps of 10 µg/m<sup>3</sup>. The relative expanded uncertainties are presented on a logaritmic scale.





Figure 102: Membrapor C-5  $O_3$  sensor: Relative expanded uncertainty (W (%)) of sensors calibrated with extended multiple linear regression according to Guidance of Equivalence calculated at 8-hourly  $O_3$  reference concentrations of 10 to 150  $\mu$ g/m<sup>3</sup> in steps of 10  $\mu$ g/m<sup>3</sup>. The relative expanded uncertainties are presented on a logaritmic scale.



Table 33: Membrapor C-5 O<sub>3</sub> sensor: Relative expanded uncertainty of sensors calibrated with multiple linear regression (O3\_S\_1mMLR2) and extended multiple linear regression (O3\_S\_1mMLRext2) according to Guidance of Equivalence calculated at O<sub>3</sub> 8- hourly reference concentrations of 60  $\mu$ g/m<sup>3</sup> (LAT), 84  $\mu$ g/m<sup>3</sup> (UAT) and 120  $\mu$ g/m<sup>3</sup> (LV)

	ID	O <sub>3</sub> _ref (µg/m³)	random term	bias (µg/m³)	expanded
			(µg/m³)		uncertainty (%)
eighthour_O3_s_1mMLR2	VQM1	60	80.66	30.98	288.02
eighthour_O3_s_1mMLR2	VQM2	60	110.63	83.76	462.55
eighthour_O3_s_1mMLR2	VQM3	60	81.05	76.16	370.73
eighthour_O3_s_1mMLR2	VQM4	60	149.20	119.47	637.11
eighthour_O3_s_1mMLR2	VQM5	60	1152.99	982.76	5049.96
eighthour_O3_s_1mMLRext	VQM1	60	10.02	-7.70	42.12
eighthour_O3_s_1mMLRext	VQM2	60	10.89	-2.23	37.06
eighthour_O3_s_1mMLRext	VQM3	60	8.05	1.19	27.13
eighthour_O3_s_1mMLRext	VQM4	60	12.72	-1.38	42.66
eighthour_O3_s_1mMLRext	VQM5	60	25.30	11.33	92.41
eighthour_O3_s_1mMLR2	VQM1	84	80.66	115.08	334.61
eighthour_O3_s_1mMLR2	VQM2	84	110.63	189.73	522.92
eighthour_O3_s_1mMLR2	VQM3	84	81.05	150.80	407.63
eighthour_O3_s_1mMLR2	VQM4	84	149.20	269.90	734.27
eighthour_O3_s_1mMLR2	VQM5	84	1152.99	2163.67	5837.38
eighthour_O3_s_1mMLRext	VQM1	84	10.02	-7.62	29.98
eighthour_O3_s_1mMLRext	VQM2	84	10.89	-5.49	29.04
eighthour_O3_s_1mMLRext	VQM3	84	8.05	-3.25	20.67
eighthour_O3_s_1mMLRext	VQM4	84	12.72	-2.55	30.90
eighthour_O3_s_1mMLRext	VQM5	84	25.30	14.01	68.86
eighthour_O3_s_1mMLR2	VQM1	120	80.66	241.23	423.93
eighthour_O3_s_1mMLR2	VQM2	120	110.63	348.68	609.68
eighthour_O3_s_1mMLR2	VQM3	120	81.05	262.77	458.32
eighthour_O3_s_1mMLR2	VQM4	120	149.20	495.56	862.55
eighthour_O3_s_1mMLR2	VQM5	120	1152.99	3935.04	6834.13
eighthour_O3_s_1mMLRext	VQM1	120	10.02	-7.51	20.87
eighthour_O3_s_1mMLRext	VQM2	120	10.89	-10.37	25.07
eighthour_O3_s_1mMLRext	VQM3	120	8.05	-9.91	21.28
eighthour_O3_s_1mMLRext	VQM4	120	12.72	-4.31	22.39
eighthour_O3_s_1mMLRext	VQM5	120	25.30	18.03	51.78

Table 34: Membrapor C-5  $O_3$  sensor: Parameters of orthogonal regression of 8-hourly sensor data calibrated with multiple linear regression ( $O_3_5_1mMLR2$ ) and extended multiple linear regression ( $O_3_5_1mMLR2$ ) versus reference  $O_3$ 

	ID	slope	intercept (μg/m³)
eighthour_O3_s_1mMLR2	VQM1	4.50	-179.27
eighthour_O3_s_1mMLR2	VQM2	5.42	-181.15
eighthour_O3_s_1mMLR2	VQM3	4.11	-110.46
eighthour_O3_s_1mMLR2	VQM4	7.27	-256.63
eighthour_O3_s_1mMLR2	VQM5	50.20	-1969.53
eighthour_O3_s_1mMLRext2	VQM1	1.00	-7.90
eighthour_O3_s_1mMLRext2	VQM2	0.86	5.91
eighthour_O3_s_1mMLRext2	VQM3	0.81	12.30
eighthour_O3_s_1mMLRext2	VQM4	0.95	1.56
eighthour_O3_s_1mMLRext2	VQM5	1.11	4.64



#### 5.3.6 Conclusions

No clear drift in the calibrated sensor data is observed. In wintertime we see higher positive and negative ratios. We also see a larger range in ratios with lower temperatures, higher relative humidity and higher NO<sub>2</sub> concentrations. The low O<sub>3</sub> concentrations when these conditions occur make it difficult to determine the effect of temperature, relative humidity and NO<sub>2</sub> on the calibrated sensor data.

When we look at the scatter plots in relation to temperature, relative humidity and NO<sub>2</sub>, we see that there is less scatter after calibration with the parameters of the MLR with NO<sub>2</sub> ( $O3\_s\_1mMLRext2$ ) in comparison with the calibration with the parameters of the MLR without NO<sub>2</sub> ( $O3\_s\_1mMLR2$ ).

Calibration of the sensor data with the parameters from the MLR regression without NO<sub>2</sub> ( $O3\_s\_1mMLR2$ ) results in R<sup>2</sup> between 0.02 and 0.49, a between sensor uncertainty of 76  $\mu$ g/m<sup>3</sup> and an expanded uncertainty for all sensors higher than 200 % at concentrations between 10 and 200  $\mu$ g/m<sup>3</sup>.

After calibration with the parameters from the MLR with NO<sub>2</sub> (*O3\_s\_1mMLRext2*), we see higher R<sup>2</sup>, smaller mean biases, a smaller between sensor uncertainty and smaller relative expanded uncertainties. The R<sup>2</sup> varies between 0.73 and 0.86, except for one sensor (VQM5) with a R<sup>2</sup> of 0.3. The between sensor uncertainty is 21 µg/m<sup>3</sup> (51 %). At the TV of 120 µg/m<sup>3</sup> the expanded uncertainty of the 8-hourly values is  $\leq$  30 % for all sensors, except for VQM5. At 84 µg/m<sup>3</sup> the expanded uncertainty is  $\leq$  30 % for three of the five sensors and at 60 µg/m<sup>3</sup> for one of the five sensors.





### Field Evaluation Envea Cairclip NO<sub>2</sub>/O<sub>3</sub> sensor



Manufacturer: Envea Link to website manufacturer

Link to test protocol



### 6 Envea Cairclip NO<sub>2</sub>/O<sub>3</sub> sensor

### 6.1 Validation and data coverage

The time resolution configured for this sensors was fifteen minutes. The sensors don't give negative values.

These sensors needed to be read manually. Data were marked as invalid on the moments when the data were read out. No data were marked suspicious. VQT1 and VQT3 lost their time indication in June and VQT2, VQT4 and VQT5 in August. After reconfiguration the sensors gave the indication that the lifetime was exceeded. The lifetime of this sensor type is one year.



Figure 103: Envea Cairclip NO<sub>2</sub>/O<sub>3</sub> sensor: Number sensor hourly values (-2: invalid, -1: suspicious, 0: valid, 1: missing)

Table 35: Envea Cairclip  $NO_2/O_3$  sensor: Number sensor hourly values (-2: invalid, -1: suspicious, 0: valid, 1: missing) and percentage of available data

	-2	-1	0	1	%
					available
VQT1	0	0	2651	6997	27
VQT2	0	0	4279	5369	44
VQT3	0	0	2824	6824	29
VQT4	1	0	4452	5195	46
VQT5	0	0	4358	5290	45



### 6.2 Uncalibrated sensor data and sensor data calibrated with parameters from linear regression

This sensor measures  $O_3 + NO_2$ . Before analyzing the sensor data, the mean of the fifteen minutes values of all Envea Cairclip  $NO_2$  sensors are substracted from the Envea Cairclip  $NO_2/O_3$  fifteen minutes values.

#### 6.2.1 Calibration parameters

Table 36: Envea Cairclip NO<sub>2</sub>/O<sub>3</sub> sensor: Parameters from linear regression against reference method - hourly field data from February 23 2019 - March 31 2019

sensor_internal_id	slope	intercept
VQT1	0.65	-12.99
VQT2	0.73	-4.00
VQT3	0.77	-4.54
VQT4	0.65	-9.34
VQT5	0.70	-10.25

### 6.2.2 Comparison sensor versus reference

### 6.2.2.1 Time plot and scatter plots of hourly values



Figure 104: Envea Cairclip  $NO_2/O_3$  sensor: Time plot uncalibrated sensor hourly values and reference values ( $\mu g/m^3$ )





Figure 105: Envea Cairclip  $NO_2/O_3$  sensor: Time plot of sensor hourly values calibrated with the linear regression parameters and reference values ( $\mu g/m^3$ )



Figure 106: Envea Cairclip  $NO_2/O_3$  sensor: Scatter plot of uncalibrated sensor hourly values versus reference values ( $\mu g/m^3$ )





Figure 107: Envea Cairclip  $NO_2/O_3$  sensor: Scatter plot sensor hourly values calibrated with the linear regression parameters versus reference values ( $\mu g/m^3$ )



### 6.2.2.2 Ratio of hourly sensor values versus reference values

Figure 108: Envea Cairclip NO<sub>2</sub>/O<sub>3</sub> sensor: Density plot of uncalibrated ratio sensor hourly values versus reference values





Figure 109: Envea Cairclip  $NO_2/O_3$  sensor: Density plot of ratio sensor hourly values calibrated with the linear regression parameters versus reference values

#### 6.2.3 Influence of time, temperature, relative humidity and NO<sub>2</sub>

There are some high ratios due to the fact that there are a considerable amount of data close to zero in the reference data . Therefore we chose to limit the y-as to -15 and +15.



Figure 110: Envea Cairclip NO<sub>2</sub>/O<sub>3</sub> sensor: Time plot ratio sensor hourly values versus reference values ( $\mu$ g/m<sup>3</sup>)





Figure 111: Envea Cairclip  $NO_2/O_3$  sensor:  $NO_2$  sensor: Scatter plot ratio sensor hourly values versus reference values in relation to relative humidity (%)



Figure 112: Envea Cairclip  $NO_2/O_3$  sensor: Scatter plot ratio sensor hourly values versus reference values in relation to temperature (°C)





Figure 113: Envea Cairclip  $NO_2/O_3$  sensor: Scatter plot ratio sensor hourly values versus reference values in relation to  $NO_2$  ( $\mu g/m^3$ )

#### 6.2.4 Descriptive parameters

Table 37: Envea Cairclip  $NO_2/O_3$  sensor: Descriptive parameters for uncalibrated sensors ( $O3\_S\_2$ ) and sensors calibrated with the linear regression parameters ( $O3\_S\_1mLR2$ ). ID: sensor idea, n: number of values,  $R^2$ : coefficient of determination,  $U_{bs}$ : between sampler uncertainty

		Calibi	ration			Evaluation		
	ID	n	R <sup>2</sup>	n	mean bias (µg/m³)	R <sup>2</sup>	u <sub>bs</sub> (µg/m³)	u <sub>bs</sub> (%)
03_s_2	VQT1			2465	-31.58	0.76		
03_s_2	VQT2			4032	-16.75	0.77		
03_s_2	VQT3			2603	-17.97	0.76		
03_s_2	VQT4			4192	-27.05	0.82		
03_s_2	VQT5			4102	-26.03	0.70		
03_s_2	all sensors			17394			15.43	64.95
O3_s_1mLR2	VQT1	772	0.90	1693	-5.55	0.72		
O3_s_1mLR2	VQT2	704	0.89	3328	0.91	0.76		
O3_s_1mLR2	VQT3	772	0.90	1831	-4.91	0.72		
O3_s_1mLR2	VQT4	772	0.89	3420	-1.17	0.83		
O3_s_1mLR2	VQT5	706	0.89	3396	-2.25	0.67		
O3_s_1mLR2	all sensors			13668	-		21.79	46.03



6.2.5 Relative expanded uncertainty



Figure 114: Envea Cairclip  $NO_2/O_3$  sensor: Relative expanded uncertainty (W (%)) for uncalibrated sensor values according to Guidance of Equivalence calculated at hourly  $O_3$  reference concentrations of 10 to 200 µg/m<sup>3</sup> in steps of 10 µg/m<sup>3</sup>



Figure 115: Envea Cairclip  $NO_2/O_3$  sensor: Relative expanded uncertainty (W (%)) for sensor values calibrated with the linear regression parameters according to Guidance of Equivalence calculated at hourly  $O_3$  reference concentrations of 10 to 200  $\mu g/m^3$  in steps of 10  $\mu g/m^3$ 





Figure 116: Envea Cairclip  $NO_2/O_3$  sensor: Relative expanded uncertainty (W (%)) for uncalibrated sensor values according to Guidance of Equivalence calculated at 8-hourly  $O_3$  reference concentrations of 10 to 150  $\mu$ g/m<sup>3</sup> in steps of 10  $\mu$ g/m<sup>3</sup>



Figure 117: Envea Cairclip  $NO_2/O_3$  sensor: Relative expanded uncertainty (W (%)) for sensor values calibrated with the linear regression parameters according to Guidance of Equivalence calculated at 8-hourly  $O_3$  reference concentrations of 10 to 150  $\mu$ g/m<sup>3</sup> in steps of 10  $\mu$ g/m<sup>3</sup>



Table 38: Envea Cairclip  $NO_2/O_3$  sensor: Relative expanded uncertainty for uncalibrated sensors (O3\_S\_2) and for sensors calibrated with the linear regression parameters (O3\_S\_1mLR2) according to Guidance of Equivalence calculated at  $O_3$  8-hourly reference concentrations of 60  $\mu$ g/m<sup>3</sup> (LAT), 84  $\mu$ g/m<sup>3</sup> (UAT) and 120  $\mu$ g/m<sup>3</sup> (LV)

	ID	O <sub>3</sub> _ref (μg/m <sup>3</sup> )	random term	bias (µg/m <sup>3</sup> )	expanded
			(µg/m³)		uncertainty (%)
eighthour_O3_s_2	VQT1	60	5.68	-37.10	125.13
eighthour_O3_s_2	VQT2	60	7.75	-18.73	67.57
eighthour_O3_s_2	VQT3	60	6.75	-21.59	75.41
eighthour_O3_s_2	VQT4	60	5.72	-30.71	104.11
eighthour_O3_s_2	VQT5	60	7.53	-30.23	103.83
eighthour_O3_s_1mLR2	VQT1	60	9.42	-6.53	38.21
eighthour_O3_s_1mLR2	VQT2	60	11.65	2.83	39.96
eighthour_O3_s_1mLR2	VQT3	60	9.68	-5.06	36.41
eighthour_O3_s_1mLR2	VQT4	60	9.52	0.11	31.74
eighthour_O3_s_1mLR2	VQT5	60	11.65	-2.84	39.96
eighthour_O3_s_2	VQT1	84	5.68	-47.00	112.73
eighthour_O3_s_2	VQT2	84	7.75	-23.14	58.11
eighthour_O3_s_2	VQT3	84	6.75	-27.89	68.31
eighthour_O3_s_2	VQT4	84	5.72	-38.07	91.66
eighthour_O3_s_2	VQT5	84	7.53	-39.01	94.60
eighthour_O3_s_1mLR2	VQT1	84	9.42	-8.71	30.55
eighthour_O3_s_1mLR2	VQT2	84	11.65	7.18	32.58
eighthour_O3_s_1mLR2	VQT3	84	9.68	-5.27	26.24
eighthour_O3_s_1mLR2	VQT4	84	9.52	3.14	23.87
eighthour_O3_s_1mLR2	VQT5	84	11.65	-4.32	29.58
eighthour_O3_s_2	VQT1	120	5.68	-61.85	103.52
eighthour_O3_s_2	VQT2	120	7.75	-29.76	51.26
eighthour_O3_s_2	VQT3	120	6.75	-37.32	63.22
eighthour_O3_s_2	VQT4	120	5.72	-49.12	82.41
eighthour_O3_s_2	VQT5	120	7.53	-52.19	87.89
eighthour_O3_s_1mLR2	VQT1	120	9.42	-11.99	25.41
eighthour_O3_s_1mLR2	VQT2	120	11.65	13.71	29.98
eighthour_O3_s_1mLR2	VQT3	120	9.68	-5.58	18.63
eighthour_O3_s_1mLR2	VQT4	120	9.52	7.68	20.39
eighthour_O3_s_1mLR2	VQT5	120	11.65	-6.54	22.26

Table 39: Envea Cairclip  $NO_2/O_3$  sensor: Parameters of orthogonal regression of 8-hourly sensor data versus reference  $O_3$  for uncalibrated sensors ( $O3_5_2$ ) and for sensors calibrated with the linear regression parameters ( $O3_5_1mLR2$ )

	ID	slope	intercept (μg/m³)
eighthour_O3_s_2	VQT1	0.59	-12.36
eighthour_O3_s_2	VQT2	0.82	-7.70
eighthour_O3_s_2	VQT3	0.74	-5.86
eighthour_O3_s_2	VQT4	0.69	-12.30
eighthour_O3_s_2	VQT5	0.63	-8.26
eighthour_O3_s_1mLR2	VQT1	0.91	-1.08
eighthour_O3_s_1mLR2	VQT2	1.18	-8.04
eighthour_O3_s_1mLR2	VQT3	0.99	-4.53
eighthour_O3_s_1mLR2	VQT4	1.13	-7.45
eighthour_O3_s_1mLR2	VQT5	0.94	0.85





#### 6.2.6 Conclusions

The time plot with the ratios of the sensor data against the reference method shows no occurrence of drift. We see no clear pattern in the ratio plots in relation to temperature, relative humidity and  $NO_2$  concentrations.

The sensors largely underestimate the O<sub>3</sub> concentrations. The mean biases of the uncalibrated sensor data ( $O3\_s\_2$ ) versus the reference data are negative for all sensors (between -32 µg/m<sup>3</sup> and -17 µg/m<sup>3</sup>). The R<sup>2</sup> varies between 0.70 and 0.82. The between sensor uncertainty is 65 %. De expanded uncertainty for the 8-hourly values is  $\leq$  75 % for two of the five sensors at 120 µg/m<sup>3</sup> (TV) , 84 µg/m<sup>3</sup> and 60 µg/m<sup>3</sup>.

Calibration with the LR regression parameters (NO<sub>2</sub>\_2\_1mLR) leads to mean biases between -6 and 1  $\mu$ g/m<sup>3</sup>. The between sensor uncertainty is 46 %. De expanded uncertainty for the 8-hourly values is  $\leq$  30% for all five sensors at 120  $\mu$ g/m<sup>3</sup> (TV) and for 3 sensors at 84  $\mu$ g/m<sup>3</sup>. At 60  $\mu$ g/m<sup>3</sup> the expanded uncertainty is for all five sensors  $\leq$  40  $\mu$ g/m<sup>3</sup>.



### 6.3 Sensor data calibrated with parameters from multiple linear regression –without reference NO<sub>2</sub>

This sensor measures  $O_3 + NO_2$ . Before analyzing the sensor data, the mean of the fifteen minutes values of all Envea Cairclip  $NO_2$  sensors are substracted from the Envea Cairclip  $NO_2/O_3$  fifteen minutes values. Next, the corrected sensor data are calibrated with the parameters from the MLR function with temperature and relative humidity (but without reference  $NO_2$ ).

#### 6.3.1 Calibration parameters

Table 40: Envea Cairclip  $NO_2/O_3$  sensor: Parameters from multiple linear regression (including  $O_3$  reference measurements ( $O_3$ \_ref), temperature (T), relative humidity (RH)) - hourly field data from February 23 2019- March 31 2019

sensor_internal_id	intercept	O <sub>3</sub> _ref	Т	RH
VQT1	-15.16	0.64	-0.16	0.06
VQT2	-9.64	0.70	0.01*	0.09
VQT3	-8.74	0.74	0.15*	0.06
VQT4	-14.49	0.63	-0.04	0.09
VQT5	-15.85	0.68	-0.16*	0.11

\*:Variable not significant at 0.05 significance level

### 6.3.2 Comparison sensor versus reference

### 6.3.2.1 Time plot and scatter plots of hourly values



Figure 118: Envea Cairclip  $NO_2/O_3$  sensor: Time plot of sensor hourly values calibrated with multiple linear regression model and reference values ( $\mu g/m^3$ )





Figure 119: Envea Cairclip  $NO_2/O_3$  sensor: Scatter plot of sensor hourly values calibrated with multiple linear regression model and reference values ( $\mu g/m^3$ )



6.3.2.2 Ratio of hourly sensor values versus reference values

Figure 120: Envea Cairclip  $NO_2/O_3$  sensor: Density plot of ratio sensor hourly values calibrated with multiple linear regression versus reference values



6.3.3 Influence of time, temperature, relative humidity and NO<sub>2</sub>



Figure 121: Envea Cairclip  $NO_2/O_3$  sensor: Time plot of ratio sensor hourly values calibrated with multiple linear regression versus reference values ( $\mu g/m^3$ )



Figure 122: Envea Cairclip  $NO_2/O_3$  sensor: Scatter plot ratio sensor hourly values calibrated with multiple linear regression versus reference values in relation to relative humidity (%)





Figure 123: Envea Cairclip  $NO_2/O_3$  sensor: Scatter plot ratio sensor hourly values calibrated with multiple linear regression versus reference values in relation to temperature (°C)



Figure 124: Envea Cairclip  $NO_2/O_3$  sensor: Scatter plot ratio sensor hourly values calibrated with multiple linear regression versus reference values in relation to nitrogen dioxide ( $\mu g/m^3$ )





#### 6.3.4 Descriptive parameters

Table 41: Envea Cairclip  $NO_2/O_3$  sensor: Descriptive parameters for sensors calibrated with multiple linear regression ( $O3_S_mMLR2$ ). ID: sensor idea, n: number of values,  $R^2$ : coefficient of determination,  $U_{bs}$ : between sampler uncertainty

		Calibi	alibration		Evaluation			
	ID	n	R <sup>2</sup>	n	mean bias (μg/m³)	R <sup>2</sup>	u <sub>bs</sub> (µg/m³)	u <sub>bs</sub> (%)
O3_s_1mMLR2	VQT1	772	0.91	1693	-4.01	0.76		
O3_s_1mMLR2	VQT2	704	0.90	3327	1.82	0.78		
O3_s_1mMLR2	VQT3	772	0.90	1831	-5.32	0.74		
O3_s_1mMLR2	VQT4	772	0.90	3419	0.35	0.85		
O3_s_1mMLR2	VQT5	706	0.91	3395	0.59	0.72		
O3_s_1mMLR2	all sensors	3726		13665			23.76	48.33

#### 6.3.5 Relative expanded uncertainty



Figure 125: Envea Cairclip  $NO_2/O_3$  sensor: Relative expanded uncertainty (W (%)) of sensor calibrated with multiple linear regression according to Guidance of Equivalence calculated at hourly  $O_3$  reference concentrations of 10 to 200 µg/m<sup>3</sup> in steps of 10 µg/m<sup>3</sup>. The relative expanded uncertainties are presented on a logarithmic scale





Figure 126: Envea Cairclip  $NO_2/O_3$  sensor: Relative expanded uncertainty (W (%)) of sensors calibrated with multiple linear regression according to Guidance of Equivalence calculated at 8-hourly  $O_3$  reference concentrations of 10 to 150 µg/m<sup>3</sup> in steps of 10 µg/m<sup>3</sup>. The relative expanded uncertainties are presented on a logaritmic scale.

Table 42: Envea Cairclip NO <sub>2</sub> /O <sub>3</sub> sensor: Relative expanded uncertainty of sensors calibrated with multiple linear regression
(O3_S_1mMLR2) according to Guidance of Equivalence calculated at O <sub>3</sub> 8- hourly reference concentrations of 60 $\mu$ g/m <sup>3</sup>
(LAT), 84 μg/m³ (UAT) and 120 μg/m³ (LV)

	ID	O <sub>3</sub> _ref (μg/m <sup>3</sup> )	random term (μg/m³)	bias (µg/m³)	expanded uncertainty (%)
eighthour_O3_s_1mMLR2	VQT1	60	9.37	-3.95	33.89
eighthour_O3_s_1mMLR2	VQT2	60	11.93	4.79	42.84
eighthour_O3_s_1mMLR2	VQT3	60	9.83	-4.80	36.46
eighthour_O3_s_1mMLR2	VQT4	60	9.83	2.78	34.04
eighthour_O3_s_1mMLR2	VQT5	60	11.93	1.43	40.04
eighthour_O3_s_1mMLR2	VQT1	84	9.37	-3.84	24.11
eighthour_O3_s_1mMLR2	VQT2	84	11.93	11.70	39.77
eighthour_O3_s_1mMLR2	VQT3	84	9.83	-3.56	24.89
eighthour_O3_s_1mMLR2	VQT4	84	9.83	8.54	30.99
eighthour_O3_s_1mMLR2	VQT5	84	11.93	3.39	29.53
eighthour_O3_s_1mMLR2	VQT1	120	9.37	-3.67	16.77
eighthour_O3_s_1mMLR2	VQT2	120	11.93	22.06	41.79
eighthour_O3_s_1mMLR2	VQT3	120	9.83	-1.70	16.62
eighthour_O3_s_1mMLR2	VQT4	120	9.83	17.17	32.97
eighthour_O3_s_1mMLR2	VQT5	120	11.93	6.34	22.51





Table 43: Envea Cairclip  $NO_2/O_3$  sensor: Parameters of orthogonal regression of 8-hourly sensor data calibrated with multiple linear regression (O3\_S\_1mMLR2) versus reference  $O_3$ 

	ID	slope	intercept (μg/m³)
eighthour_O3_s_1mMLR2	VQT1	1.00	-4.24
eighthour_O3_s_1mMLR2	VQT2	1.29	-12.48
eighthour_O3_s_1mMLR2	VQT3	1.05	-7.90
eighthour_O3_s_1mMLR2	VQT4	1.24	-11.60
eighthour_O3_s_1mMLR2	VQT5	1.08	-3.48

#### 6.3.6 Conclusions

The plot with the ratios of the sensor data against the reference method in function of time shows no occurrence of drift. We see no clear pattern in the ratio plots in relation to temperature, relative humidity and NO<sub>2</sub> concentrations.

After calibration of the sensors data -corrected with sensors NO<sub>2</sub> data- with regression parameters from MLR without NO<sub>2</sub> (*O3\_s\_1mMLR2*), we see less scatter in the ratio plots of the sensor data versus the reference data in relation to temperature, relative humidity and NO<sub>2</sub>. When we look at the regression parameters we see that the effect of temperature and relative humidity is small.

The  $R^2$  is slightly higher for all sensors (between 0.72 and 0.85) in comparison with the sensor data calibrated with the LR parameters ( $O3_s_1mLR2$ ). The relative expanded uncertainties become smaller for some sensors, but higher for others. The between sensor uncertainty is slightly higher (48 %).



### 6.4 Sensor data calibrated with parameters from multiple linear regression –with reference NO<sub>2</sub>

This sensor measures  $O_3 + NO_2$ . In this section the sensor data are not corrected with sensor  $NO_2$  data but calibrated with the parameters of the MLR with reference  $NO_2$ .

#### 6.4.1 Calibration parameters

Table 44: Envea Cairclip  $NO_2/O_3$  sensor: Parameters from extended multiple linear regression (including ozone reference measurements ( $O_3$ \_ref),  $NO_2$  reference measurements ( $NO_2$ \_ref), temperature (T), relative humidity (RH)) - hourly field data from February 23 2019- March 31 2019

sensor_internal_id	intercept	O₃_ref	NO <sub>2</sub> _ref	Т	RH
VQT1	-14.8	0.59	0.23	0.12*	0.02*
VQT2	-14.0	0.70	0.28	0.29	0.07
VQT3	-9.5	0.70	0.24	0.43	0.02*
VQT4	-15.2	0.59	0.24	0.24	0.05
VQT5	-17.4	0.65	0.25	0.13*	0.08

\*:Variable not significant at 0.05 significance level

### 6.4.2 Comparison sensor versus reference

### 6.4.2.1 Time plot and scatter plots of hourly values



Figure 127: Envea Cairclip  $NO_2/O_3$  sensor: Time plot of sensor hourly values calibrated with extended multiple linear regression model and reference values ( $\mu g/m^3$ )



+ Scatter plot sensor hourly values versus reference values (µg/m<sup>3</sup>)



Figure 128: Envea Cairclip  $NO_2/O_3$  sensor: Scatter plot of sensor hourly values calibrated with extended multiple linear regression model and reference values ( $\mu g/m^3$ )



6.4.2.2 Ratio of hourly sensor values versus reference values

Figure 129: Envea Cairclip  $NO_2/O_3$  sensor: Density plot of ratio sensor hourly values calibrated with extended multiple linear regression versus reference values


6.4.3 Influence of time, temperature, relative humidity and NO<sub>2</sub>



Figure 130: Envea Cairclip  $NO_2/O_3$  sensor: Time plot of ratio sensor hourly values calibrated with extended multiple linear regression versus reference values ( $\mu g/m^3$ )



Figure 131: Envea Cairclip  $NO_2/O_3$  sensor: Scatter plot ratio sensor hourly values calibrated with extended multiple linear regression versus reference values in relation to relative humidity (%)





Figure 132: Envea Cairclip  $NO_2/O_3$  sensor: Scatter plot ratio sensor hourly values calibrated with extended multiple linear regression versus reference values in relation to temperature (°C)



Figure 133: Envea Cairclip  $NO_2/O_3$  sensor: Scatter plot ratio sensor hourly values calibrated with extended multiple linear regression versus reference values in relation to nitrogen dioxide ( $\mu g/m^3$ )



#### 6.4.4 Descriptive parameters

Table 45: Envea Cairclip  $NO_2/O_3$  sensor: Descriptive parameters for sensors calibrated with extended multiple linear regression (O3\_S\_mMLRext2). ID: sensor idea, n: number of values,  $R^2$ : coefficient of determination,  $U_{bs}$ : between sampler uncertainty

		Calibi	ration			Evaluation		
	ID	n	R <sup>2</sup>	n	mean bias (μg/m³)	R <sup>2</sup>	u <sub>bs</sub> (µg/m³)	u <sub>bs</sub> (%)
O3_s_1mMLRext2	VQT1	737	0.92	1606	-5.85	0.72		
O3_s_1mMLRext2	VQT2	674	0.91	3165	0.15	0.76		
O3_s_1mMLRext2	VQT3	737	0.90	1738	-6.51	0.71		
O3_s_1mMLRext2	VQT4	737	0.90	3253	-1.77	0.82		
O3_s_1mMLRext2	VQT5	673	0.92	3231	-1.48	0.70		
O3_s_1mMLRext2	all sensors			12993			24.54	51.89

#### 6.4.5 Relative expanded uncertainty



Figure 134: Envea Cairclip  $NO_2/O_3$  sensor: Relative expanded uncertainty (W (%)) of sensor calibrated with extended multiple linear regression according to Guidance of Equivalence calculated at hourly  $O_3$  reference concentrations of 10 to 200 µg/m<sup>3</sup> in steps of 10 µg/m<sup>3</sup>. The relative expanded uncertainties are presented on a logarithmic scale





Figure 135: Envea Cairclip  $NO_2/O_3$  sensor: Relative expanded uncertainty (W (%)) of sensors calibrated with extended multiple linear regression according to Guidance of Equivalence calculated at 8-hourly  $O_3$  reference concentrations of 10 to 150 µg/m<sup>3</sup> in steps of 10 µg/m<sup>3</sup>. The relative expanded uncertainties are presented on a logaritmic scale.

Table 46: Envea Cairclip  $NO_2/O_3$  sensor: Relative expanded uncertainty of sensors calibrated with extended multiple linear regression ( $O3_5_1mMLRext_2$ ) according to Guidance of Equivalence calculated at  $O_3$  8- hourly reference concentrations of 60  $\mu$ g/m<sup>3</sup> (LAT), 84  $\mu$ g/m<sup>3</sup> (UAT) and 120  $\mu$ g/m<sup>3</sup> (LV)

	ID	O <sub>3</sub> _ref (µg/m <sup>3</sup> )	random term (μg/m³)	bias (µg/m³)	expanded uncertainty (%)
eighthour_O3_s_1mMLRext2	VQT1	60	11.07	-5.60	41.36
eighthour_O3_s_1mMLRext2	VQT2	60	12.96	3.19	44.49
eighthour_O3_s_1mMLRext2	VQT3	60	11.49	-5.81	42.92
eighthour_O3_s_1mMLRext2	VQT4	60	11.41	1.14	38.23
eighthour_O3_s_1mMLRext2	VQT5	60	13.01	-0.29	43.37
eighthour_O3_s_1mMLRext2	VQT1	84	11.07	-4.44	28.40
eighthour_O3_s_1mMLRext2	VQT2	84	12.96	10.59	39.85
eighthour_O3_s_1mMLRext2	VQT3	84	11.49	-3.49	28.59
eighthour_O3_s_1mMLRext2	VQT4	84	11.41	8.63	34.07
eighthour_O3_s_1mMLRext2	VQT5	84	13.01	2.76	31.66
eighthour_O3_s_1mMLRext2	VQT1	120	11.07	-2.69	18.99
eighthour_O3_s_1mMLRext2	VQT2	120	12.96	21.69	42.11
eighthour_O3_s_1mMLRext2	VQT3	120	11.49	0.00	19.15
eighthour_O3_s_1mMLRext2	VQT4	120	11.41	19.87	38.18
eighthour_O3_s_1mMLRext2	VQT5	120	13.01	7.33	24.88





Table 47: Envea Cairclip  $NO_2/O_3$  sensor: Parameters of orthogonal regression of 8-hourly sensor data calibrated with extended multiple linear regression ( $O3_5_1mMLRext2$ ) versus reference  $O_3$ 

	ID	slope	intercept (μg/m³)
eighthour_O3_s_1mMLRext2	VQT1	1.05	-8.51
eighthour_O3_s_1mMLRext2	VQT2	1.31	-15.31
eighthour_O3_s_1mMLRext2	VQT3	1.10	-11.63
eighthour_O3_s_1mMLRext2	VQT4	1.31	-17.58
eighthour_O3_s_1mMLRext2	VQT5	1.13	-7.90

### 6.4.6 Conclusions

After calibration of the sensor data– not corrected with the sensor  $NO_2$  data- with the parameters based from MLR with relative humidity, temperature and reference  $NO_2$  ( $O3_s\_mMLRext2$ ) we see no drift in the data. We see less scatter in the ratios in relation to temperature, relative humidity and  $NO_2$ .

In comparison with the sensor data  $O3\_s\_1mMLR2$  (sensor data corrected with sensor NO<sub>2</sub> and calibrated with parameters from MLR with relative humidity and temperature (but without NO<sub>2</sub>), the R<sup>2</sup> are slightly smaller (between 0.70 and 0.82) and the between sensor uncertainty (52 %) and the relative expanded uncertainties are slightly higher.

In comparison with the sensor data  $O3_s_1mLR2$  (sensor data calibrated with LR parameters) The R<sup>2</sup> are very comparable, but the between sensor uncertainty is higher and also the expanded uncertainty is higher for all sensors at most concentrations.





## Field Evaluation Alphasense OX-B431 O<sub>3</sub> sensor



Manufacturer: Alphasense Link to website manufacturer

Link to test protocol



### 7 Alphasense OX-B431 O<sub>3</sub> sensor

### 7.1 Validation and data coverage

Positive peaks occur in the raw sensor data. When these peaks occurred after a restart of the measurements, they were marked as invalid. Other peaks were marked as suspicious when they were remarkable higher or lower than the values of the other sensors.

VQG1 was tested in the laboratory but was not included in the evaluation of the laboratory testing due malfunctioning.



Figure 136: Alphasense OX-B431 O<sub>3</sub> sensor: Number sensor minute values (-2: invalid, -1: suspicious, 0: valid, 1: missing)

-2 -1 % available VQG0 VQG1 VQG2 VQG3 VQG6 

Table 48: Alphasense OX-B431  $O_3$  sensor: Number sensor minute values (-2: invalid, -1: suspicious, 0: valid, 1: missing) and percentage of available data





Figure 137: Alphasense OX-B431 O<sub>3</sub> sensor: Number sensor hourly values (-2: invalid, -1: suspicious, 0: valid, 1: missing)

	-2	-1	0	1	%
					available
VQG0	3	1	8050	1594	83
VQG1	3	0	7875	1770	82
VQG2	3	0	8214	1431	85
VQG3	4	1	8032	1611	83
VQG6	8	9	7776	1855	81

Table 49: Alphasense OX-B431  $O_3$  sensor: Number sensor hourly values (-2: invalid, -1: suspicious, 0: valid, 1: missing) and percentage of available data

### 7.2 Uncalibrated sensor data and sensor data calibrated with parameters from linear regression

This sensor measures  $O_3 + NO_2$ . Before analyzing the sensor data, the mean of the minutes values of the Alphasense B43F NO<sub>2</sub> sensors are substracted from the Alphasense OX-B431 minutes values. Alphasense B43F NO<sub>2</sub> sensor VQH6 is not included, because this sensor has a remarkable smaller correlation with reference NO<sub>2</sub> than the other sensors.



### 7.2.1 Calibration parameters

Table 50: Alphasense OX-B431 O<sub>3</sub> sensor: Parameters from linear regression against reference method - hourly field data from February 23 2019 - March 31 2019

sensor_internal_id	slope	intercept
VQG0	1.2	14.63
VQG1	1.1	12.04
VQG2	1.3	4.83
VQG3	1.1	11.30
VQG6	1.2	-0.65

### 7.2.2 Comparison sensor versus reference





Figure 138: Alphasense OX-B431 O<sub>3</sub> sensor: Time plot uncalibrated sensor hourly values and reference values ( $\mu$ g/m<sup>3</sup>)





Figure 139: Alphasense OX-B431  $O_3$  sensor: Time plot of sensor hourly values calibrated with the linear regression parameters and reference values ( $\mu g/m^3$ )



Figure 140: Alphasense OX-B431  $O_3$  sensor: Scatter plot of uncalibrated sensor hourly values versus reference values ( $\mu g/m^3$ )





Figure 141: Alphasense OX-B431 O<sub>3</sub> sensor: Scatter plot sensor hourly values calibrated with the linear regression parameters versus reference values ( $\mu g/m^3$ )



7.2.2.2 Ratio of hourly sensor values versus reference values

Figure 142: Alphasense OX-B431 O<sub>3</sub> sensor: Density plot of uncalibrated ratio sensor hourly values versus reference values





Figure 143: Alphasense OX-B431  $O_3$  sensor: Density plot of ratio sensor hourly values calibrated with the linear regression parameters versus reference values

### 7.2.3 Influence of time, temperature, relative humidity and NO<sub>2</sub>

There are some high ratios due to the fact that there are a considerable amount of data close to zero in the reference data . Therefore we chose to limit the y-as to -15 and +15.



Figure 144: Alphasense OX-B431  $O_3$  sensor: Time plot ratio sensor hourly values versus reference values ( $\mu$ g/m<sup>3</sup>)





Figure 145: Alphasense OX-B431  $O_3$  sensor: Scatter plot ratio sensor hourly values versus reference values in relation to relative humidity (%)



Figure 146: Alphasense OX-B431  $O_3$  sensor: Scatter plot ratio sensor hourly values versus reference values in relation to temperature (°C)





Figure 147: Alphasense OX-B431 O<sub>3</sub> sensor: Scatter plot ratio sensor hourly values versus reference values in relation to  $NO_2$  ( $\mu g/m^3$ )

#### 7.2.4 Descriptive parameters

Table 51: Alphasense OX-B431 O<sub>3</sub> sensor: Descriptive parameters for uncalibrated sensors (O3\_S\_2) and sensors calibrated with the linear regression parameters (O3\_S\_1mLR2). ID: sensor idea, n: number of values,  $R^2$ : coefficient of determination,  $U_{bs}$ : between sampler uncertainty

		Calib	ration			Evaluation		
	ID	n	R <sup>2</sup>	n	mean bias (µg/m³)	R <sup>2</sup>	u <sub>bs</sub> (µg/m³)	u <sub>bs</sub> (%)
03_s_2	VQG0			7433	14.46	0.87		
03_s_2	VQG1			7261	9.63	0.88		
03_s_2	VQG2			7705	11.88	0.88		
03_s_2	VQG3			7498	5.55	0.88		
03_s_2	VQG6			7170	2.20	0.87		
03_s_2	all sensors			37067			21.64	47.34
O3_s_1mLR2	VQG0	772	0.96	6661	-6.93	0.87		
O3_s_1mLR2	VQG1	772	0.95	6489	-7.51	0.88		
O3_s_1mLR2	VQG2	772	0.93	6933	-3.34	0.88		
O3_s_1mLR2	VQG3	772	0.93	6726	-10.86	0.89		
O3_s_1mLR2	VQG6	734	0.92	6436	-4.93	0.87		
O3_s_1mLR2	all sensors			33245			17.83	59.46



7.2.5 Relative expanded uncertainty



Figure 148: Alphasense OX-B431  $O_3$  sensor: Relative expanded uncertainty (W (%)) for uncalibrated sensor values according to Guidance of Equivalence calculated at hourly  $O_3$  reference concentrations of 10 to 200  $\mu$ g/m<sup>3</sup> in steps of 10  $\mu$ g/m<sup>3</sup>



Figure 149: Alphasense OX-B431  $O_3$  sensor: Relative expanded uncertainty (W (%)) for sensor values calibrated with the linear regression parameters according to Guidance of Equivalence calculated at hourly  $O_3$  reference concentrations of 10 to 200  $\mu$ g/m<sup>3</sup> in steps of 10  $\mu$ g/m<sup>3</sup>





Figure 150: Alphasense OX-B431 O<sub>3</sub> sensor: Relative expanded uncertainty (W (%)) for uncalibrated sensor values according to Guidance of Equivalence calculated at 8-hourly O<sub>3</sub> reference concentrations of 10 to 150  $\mu$ g/m<sup>3</sup> in steps of 10  $\mu$ g/m<sup>3</sup>



Figure 151: Alphasense OX-B431  $O_3$  sensor: Relative expanded uncertainty (W (%)) for sensor values calibrated with the linear regression parameters according to Guidance of Equivalence calculated at 8-hourly  $O_3$  reference concentrations of 10 to 150  $\mu$ g/m<sup>3</sup> in steps of 10  $\mu$ g/m



Table 52: Alphasense OX-B431 O<sub>3</sub> sensor: Relative expanded uncertainty for uncalibrated sensors (O3\_S\_2) and for sensors calibrated with the linear regression parameters (O3\_S\_1mLR2) according to Guidance of Equivalence calculated at O<sub>3</sub> 8-hourly reference concentrations of 60  $\mu$ g/m<sup>3</sup> (LAT), 84  $\mu$ g/m<sup>3</sup> (UAT) and 120  $\mu$ g/m<sup>3</sup> (LV)

	ID	O <sub>3</sub> _ref (µg/m <sup>3</sup> )	random term	bias (µg/m³)	expanded
			(µg/m³)		uncertainty (%)
eighthour_03_s_2	VQG0	60	10.87	22.03	81.90
eighthour_O3_s_2	VQG1	60	11.24	16.93	67.73
eighthour_O3_s_2	VQG2	60	12.01	22.70	85.62
eighthour_O3_s_2	VQG3	60	10.67	13.33	56.92
eighthour_O3_s_2	VQG6	60	10.50	8.88	45.84
eighthour_O3_s_1mLR2	VQG0	60	9.18	-4.32	33.81
eighthour_O3_s_1mLR2	VQG1	60	9.98	-3.47	35.22
eighthour_O3_s_1mLR2	VQG2	60	9.46	-0.11	31.55
eighthour_O3_s_1mLR2	VQG3	60	8.94	-6.97	37.78
eighthour_O3_s_1mLR2	VQG6	60	8.62	-4.18	31.92
eighthour_O3_s_2	VQG0	84	10.87	30.30	76.64
eighthour_O3_s_2	VQG1	84	11.24	25.33	65.97
eighthour_O3_s_2	VQG2	84	12.01	34.32	86.58
eighthour_O3_s_2	VQG3	84	10.67	21.82	57.84
eighthour_O3_s_2	VQG6	84	10.50	15.76	45.09
eighthour_O3_s_1mLR2	VQG0	84	9.18	-1.50	22.14
eighthour_O3_s_1mLR2	VQG1	84	9.98	1.12	23.91
eighthour_O3_s_1mLR2	VQG2	84	9.46	3.29	23.86
eighthour_O3_s_1mLR2	VQG3	84	8.94	-2.79	22.29
eighthour_O3_s_1mLR2	VQG6	84	8.62	-3.40	22.06
eighthour_O3_s_2	VQG0	120	10.87	42.70	73.43
eighthour_O3_s_2	VQG1	120	11.24	37.92	65.92
eighthour_O3_s_2	VQG2	120	12.01	51.75	88.54
eighthour_O3_s_2	VQG3	120	10.67	34.56	60.28
eighthour_03_s_2	VQG6	120	10.50	26.08	46.86
eighthour_O3_s_1mLR2	VQG0	120	9.18	2.73	15.96
eighthour_O3_s_1mLR2	VQG1	120	9.98	8.00	21.31
eighthour_O3_s_1mLR2	VQG2	120	9.46	8.39	21.08
eighthour_O3_s_1mLR2	VQG3	120	8.94	3.49	15.99
eighthour_O3_s_1mLR2	VQG6	120	8.62	-2.24	14.84

Table 53: Alphasense OX-B431  $O_3$  sensor: Parameters of orthogonal regression of 8-hourly sensor data versus reference  $O_3$  for uncalibrated sensors ( $O_3S_2$ ) and for sensors calibrated with the linear regression parameters ( $O_3S_1mLR_2$ )

	ID	slope	intercept (μg/m³)
eighthour_O3_s_2	VQG0	1.34	1.37
eighthour_O3_s_2	VQG1	1.35	-4.06
eighthour_O3_s_2	VQG2	1.48	-6.34
eighthour_O3_s_2	VQG3	1.35	-7.89
eighthour_O3_s_2	VQG6	1.29	-8.32
eighthour_O3_s_1mLR2	VQG0	1.12	-11.37
eighthour_O3_s_1mLR2	VQG1	1.19	-14.94
eighthour_O3_s_1mLR2	VQG2	1.14	-8.61
eighthour_O3_s_1mLR2	VQG3	1.17	-17.42
eighthour_O3_s_1mLR2	VQG6	1.03	-6.11



### 7.2.6 Conclusions

No clear drift in the calibrated sensor data is observed. In wintertime we see more higher positive and negative ratios. We also see a larger range in ratios with lower temperatures, higher relative humidity and higher  $NO_2$  concentrations. The low  $O_3$  concentrations when these conditions occur are most likely the cause of these patterns in the ratios.

The sensors overestimate the O<sub>3</sub> concentrations. The mean biases of the uncalibrated sensor data ( $O3\_s\_2$ ) vary between 2 and 14 µg/m<sup>3</sup>. The R<sup>2</sup> varies between 0.87 and 0.88. The between sensor uncertainty is 47 %.

The expanded uncertainty for the 8-hourly values is  $\leq$  75 % for four of the five sensors at 120  $\mu$ g/m<sup>3</sup> (TV) and for three of the five sensors at 84  $\mu$ g/m<sup>3</sup> and at 60  $\mu$ g/m<sup>3</sup>. The expanded uncertainty does not drop below 30 %.

Calibration of the sensors with the LR parameters (O3\_s\_1mLR2) leads to mean biases between -11 and -3  $\mu$ g/m<sup>3</sup>. The between sensor uncertainty is 59 %. The expanded uncertainty for the 8-hourly values is smaller at the test concentrations of 120  $\mu$ g/m<sup>3</sup> (TV), at 84  $\mu$ g/m<sup>3</sup> and at 60  $\mu$ g/m<sup>3</sup>. The expanded uncertainty is  $\leq$  30 % for all sensors at 120  $\mu$ g/m<sup>3</sup> (TV) and at 84  $\mu$ g/m<sup>3</sup>. At 60  $\mu$ g/m<sup>3</sup> the expanded uncertainty is  $\leq$  40 %.



### 7.3 Sensor data calibrated with parameters from multiple linear regression –without reference NO<sub>2</sub>

This sensor measures  $O_3 + NO_2$ . Before analyzing the sensor data, the mean of the minutes values of the Alphasense B43F NO<sub>2</sub> sensors are substracted from the Alphasense OX-B431 minutes values. Alphasense B43F NO<sub>2</sub> sensor VQH6 is not included, because this sensor has a remarkable smaller correlation with reference NO<sub>2</sub> than the other sensors. Next, the corrected sensor data are calibrated with the parameters from the MLR function with temperature and relative humidity (but without reference NO<sub>2</sub>).

### 7.3.1 Calibration parameters

Table 54: Alphasense OX-B431  $O_3$  sensor: Parameters from multiple linear regression (including  $O_3$  reference measurements ( $O_3$ \_ref), temperature (T), relative humidity (RH)) - hourly field data from February 23 2019- March 31 2019

sensor_internal_id	intercept	O <sub>3</sub> _ref	Т	RH
VQG0	-1.3*	1.14	1.25	0.08
VQG1	-7.0	1.08	1.46	0.09
VQG2	-25.5	1.21	2.01	0.19
VQG3	-2.2	1.08	1.50	0.02
VQG6	-24.1	1.14	1.73	0.14

\*:Variable not significant at 0.05 significance level



7.3.2 Comparison sensor versus reference7.3.2.1 Time plot and scatter plots of hourly values



Figure 152: Alphasense OX-B431 O<sub>3</sub> sensor: Time plot of sensor hourly values calibrated with multiple linear regression model and reference values ( $\mu$ g/m<sup>3</sup>)



Figure 153: Alphasense OX-B431 O<sub>3</sub> sensor: Scatter plot of sensor hourly values calibrated with multiple linear regression model and reference values ( $\mu g/m^3$ )







Figure 154: Alphasense OX-B431  $O_3$  sensor: Density plot of ratio sensor hourly values calibrated with multiple linear regression versus reference values



### 7.3.3 Influence of time, temperature, relative humidity and NO<sub>2</sub>

Figure 155: Alphasense OX-B431  $O_3$  sensor: Time plot of ratio sensor hourly values calibrated with multiple linear regression versus reference values ( $\mu g/m^3$ )





Figure 156: Alphasense OX-B431  $O_3$  sensor: Scatter plot ratio sensor hourly values calibrated with multiple linear regression versus reference values in relation to relative humidity (%)



Figure 157: Alphasense OX-B431  $O_3$  sensor: Scatter plot ratio sensor hourly values calibrated with multiple linear regression versus reference values in relation to temperature (°C)





Figure 158: Alphasense OX-B431 O<sub>3</sub> sensor: Scatter plot ratio sensor hourly values calibrated with multiple linear regression versus reference values in relation to nitrogen dioxide ( $\mu g/m^3$ )

### 7.3.4 Descriptive parameters

Table 55: Alphasense OX-B431 O<sub>3</sub> sensor: Descriptive parameters for sensors calibrated with multiple linear regression (O3\_S\_mMLR2). ID: sensor idea, n: number of values,  $R^2$ : coefficient of determination,  $U_{bs}$ : between sampler uncertainty

		Calibration		Evaluation				
	ID	n	R <sup>2</sup>	n	mean bias (μg/m³)	R <sup>2</sup>	u <sub>bs</sub> (µg/m³)	u <sub>bs</sub> (%)
O3_s_1mMLR2	VQG0	772	0.97	6614	-10.46	0.92		
O3_s_1mMLR2	VQG1	772	0.97	6442	-11.66	0.93		
O3_s_1mMLR2	VQG2	772	0.96	6893	-9.50	0.94		
O3_s_1mMLR2	VQG3	772	0.97	6682	-15.28	0.91		
O3_s_1mMLR2	VQG6	734	0.95	6390	-9.57	0.93		
O3_s_1mMLR2	all sensors			33021			16.61	64.86



7.3.5 Relative expanded uncertainty



Figure 159: Alphasense OX-B431  $O_3$  sensor: Relative expanded uncertainty (W (%)) of sensor calibrated with multiple linear regression according to Guidance of Equivalence calculated at hourly  $O_3$  reference concentrations of 10 to 200  $\mu$ g/m<sup>3</sup> in steps of 10  $\mu$ g/m<sup>3</sup>. The relative expanded uncertainties are presented on a logarithmic scale



Figure 160: Alphasense OX-B431  $O_3$  sensor: Relative expanded uncertainty (W (%)) of sensors calibrated with multiple linear regression according to Guidance of Equivalence calculated at 8-hourly  $O_3$  reference concentrations of 10 to 150  $\mu$ g/m<sup>3</sup> in steps of 10  $\mu$ g/m<sup>3</sup>. The relative expanded uncertainties are presented on a logaritmic scale.



Table 56: Alphasense OX-B431 O<sub>3</sub> sensor: Relative expanded uncertainty of sensors calibrated with multiple linear regression (O3\_S\_1mMLR2) acording to Guidance of Equivalence calculated at O<sub>3</sub> 8- hourly reference concentrations of 60  $\mu$ g/m<sup>3</sup> (LAT), 84  $\mu$ g/m<sup>3</sup> (UAT) and 120  $\mu$ g/m<sup>3</sup> (LV)

	ID	O <sub>3</sub> _ref (μg/m³)	random term (μg/m³)	bias (µg/m³)	expanded uncertainty (%)
eighthour_O3_s_1mMLR2	VQG0	60	6.27	-10.47	40.68
eighthour_O3_s_1mMLR2	VQG1	60	6.32	-11.42	43.50
eighthour_O3_s_1mMLR2	VQG2	60	5.33	-10.11	38.09
eighthour_O3_s_1mMLR2	VQG3	60	6.85	-15.06	55.14
eighthour_O3_s_1mMLR2	VQG6	60	5.01	-12.25	44.12
eighthour_O3_s_1mMLR2	VQG0	84	6.27	-10.43	28.97
eighthour_O3_s_1mMLR2	VQG1	84	6.32	-11.10	30.40
eighthour_O3_s_1mMLR2	VQG2	84	5.33	-10.73	28.53
eighthour_O3_s_1mMLR2	VQG3	84	6.85	-14.78	38.78
eighthour_O3_s_1mMLR2	VQG6	84	5.01	-14.89	37.40
eighthour_O3_s_1mMLR2	VQG0	120	6.27	-10.36	20.18
eighthour_O3_s_1mMLR2	VQG1	120	6.32	-10.61	20.58
eighthour_O3_s_1mMLR2	VQG2	120	5.33	-11.67	21.38
eighthour_O3_s_1mMLR2	VQG3	120	6.85	-14.35	26.50
eighthour_O3_s_1mMLR2	VQG6	120	5.01	-18.85	32.50

### + parameters of orthogonal regression of 8-hourly sensor data versus reference O3

Table 57: Alphasense OX-B431  $O_3$  sensor: Parameters of orthogonal regression of 8-hourly sensor data calibrated with multiple linear regression ( $O3_5_1mMLR2$ ) versus reference  $O_3$ 

	ID	slope	intercept (μg/m³)
eighthour_O3_s_1mMLR2	VQG0	1.00	-10.58
eighthour_O3_s_1mMLR2	VQG1	1.01	-12.23
eighthour_O3_s_1mMLR2	VQG2	0.97	-8.55
eighthour_O3_s_1mMLR2	VQG3	1.01	-15.77
eighthour_O3_s_1mMLR2	VQG6	0.89	-5.66

### 7.3.6 Conclusions

No clear drift in the calibrated sensor data is observed. In wintertime we see more higher positive and negative ratios. We also see a larger range in ratios with lower temperatures, higher relative humidity and higher  $NO_2$  concentrations. The low  $O_3$  concentrations when these conditions occur are most likely the cause of these patterns in the ratios.

The R<sup>2</sup> is for all sensors higher (between 0.91 and 0.94) in comparison with the sensor data calibrated with the LR parameters ( $O3\_s\_1mLR2$ ), but the between sensor uncertainty is slightly higher (65 %) and the relative expanded uncertainties are also higher higher. The expanded uncertainty for the 8-hourly values is  $\leq$  30 % for four of the five sensors at 120 µg/m<sup>3</sup> (TV), and for three of the five sensors at 84 µg/m<sup>3</sup>. At 60 µg/m<sup>3</sup> the expanded uncertainty is  $\leq$  55 %. The mean biases are very negative (between -10 and -15 µg/m<sup>3</sup>)



### 7.4 Sensor data calibrated with parameters from multiple linear regression –with reference NO<sub>2</sub>

This sensor measures  $O_3 + NO_2$ . In this section the sensor data are not corrected with sensor  $NO_2$  data but calibrated with the parameters of the MLR with reference  $NO_2$ .

### 7.4.1 Calibration parameters

Table 58: Alphasense OX-B431  $O_3$  sensor: Parameters from extended multiple linear regression (including ozone reference measurements ( $O_3$ \_ref),  $NO_2$  reference measurements ( $NO_2$ \_ref), temperature (T), relative humidity (RH)) - hourly field data from February 23 2019- March 31 2019

sensor_internal_id	intercept	O₃_ref	$NO_2_ref$	Т	RH
VQG0	-50.1	1.34	1.23	-0.28	0.60
VQG1	-48.7	1.23	1.17	-0.10*	0.59
VQG2	-69.5	1.37	1.19	0.47	0.70
VQG3	-46.5	1.24	1.19	-0.05*	0.53
VQG6	-56.9	1.23	1.09	0.06*	0.59

\*:Variable not significant at 0.05 significance level

### 7.4.2 Comparison sensor versus reference7.4.2.1 Time plot and scatter plots of hourly values



Figure 161: Alphasense OX-B431 O<sub>3</sub> sensor: Time plot of sensor hourly values calibrated with extended multiple linear regression model and reference values ( $\mu$ g/m<sup>3</sup>)





Figure 162: Alphasense OX-B431 O<sub>3</sub> sensor: Scatter plot of sensor hourly values calibrated with extended multiple linear regression model and reference values ( $\mu g/m^3$ )



7.4.2.2 Ratio of hourly sensor values versus reference values

Figure 163: Alphasense OX-B431  $O_3$  sensor: Density plot of ratio sensor hourly values calibrated with extended multiple linear regression versus reference values



7.4.3 Influence of time, temperature, relative humidity and NO<sub>2</sub>



Figure 164: Alphasense OX-B431 O<sub>3</sub> sensor: Time plot of ratio sensor hourly values calibrated with extended multiple linear regression versus reference values ( $\mu g/m^3$ )



Figure 165: Alphasense OX-B431  $O_3$  sensor: Scatter plot ratio sensor hourly values calibrated with extended multiple linear regression versus reference values in relation to relative humidity (%)





Figure 166: Alphasense OX-B431  $O_3$  sensor: Scatter plot ratio sensor hourly values calibrated with extended multiple linear regression versus reference values in relation to temperature (°C)



Figure 167: Alphasense OX-B431  $O_3$  sensor: Scatter plot ratio sensor hourly values calibrated with extended multiple linear regression versus reference values in relation to nitrogen dioxide ( $\mu g/m^3$ )



#### 7.4.4 Descriptive parameters

Table 59: Alphasense OX-B431  $O_3$  sensor: Descriptive parameters for sensors calibrated with extended multiple linear regression (O3\_S\_mMLRext2). ID: sensor idea, n: number of values,  $R^2$ : coefficient of determination,  $U_{bs}$ : between sampler uncertainty

		Calibration		Evaluation				
	ID	n	R <sup>2</sup>	n	mean bias (μg/m³)	R <sup>2</sup>	u <sub>bs</sub> (µg/m³)	u <sub>bs</sub> (%)
O3_s_1mMLRext2	VQG0	737	0.96	6302	-1.61	0.93		
O3_s_1mMLRext2	VQG1	737	0.96	6100	-3.37	0.91		
O3_s_1mMLRext2	VQG2	737	0.95	6552	-2.46	0.91		
O3_s_1mMLRext2	VQG3	737	0.97	6328	-6.02	0.93		
O3_s_1mMLRext2	VQG6	700	0.95	6053	-1.63	0.90		
O3_s_1mMLRext2	all sensors			31335			15.93	46.71

### 7.4.5 Relative expanded uncertainty



Figure 168: Alphasense OX-B431  $O_3$  sensor: Relative expanded uncertainty (W (%)) of sensor calibrated with extended multiple linear regression according to Guidance of Equivalence calculated at hourly  $O_3$  reference concentrations of 10 to 200  $\mu$ g/m<sup>3</sup> in steps of 10  $\mu$ g/m<sup>3</sup>. The relative expanded uncertainties are presented on a logarithmic scale





Figure 169: Alphasense OX-B431  $O_3$  sensor: Relative expanded uncertainty (W (%)) of sensors calibrated with extended multiple linear regression according to Guidance of Equivalence calculated at 8-hourly  $O_3$  reference concentrations of 10 to 150 µg/m<sup>3</sup> in steps of 10 µg/m<sup>3</sup>. The relative expanded uncertainties are presented on a logaritmic scale.

Table 60: Alphasense OX-B431 O<sub>3</sub> sensor: Relative expanded uncertainty of sensors calibrated with extended multiple linear regression (O3\_S\_1mMLRext2) according to Guidance of Equivalence calculated at O<sub>3</sub> 8- hourly reference concentrations of 60  $\mu$ g/m<sup>3</sup> (LAT), 84  $\mu$ g/m<sup>3</sup> (UAT) and 120  $\mu$ g/m<sup>3</sup> (LV)

	ID	O <sub>3</sub> _ref (μg/m³)	random term (μg/m³)	bias (μg/m³)	expanded uncertainty (%)
eighthour_O3_s_1mMLRext2	VQG0	60	5.72	-0.44	19.12
eighthour_O3_s_1mMLRext2	VQG1	60	6.79	-1.48	23.15
eighthour_O3_s_1mMLRext2	VQG2	60	6.53	-1.85	22.61
eighthour_O3_s_1mMLRext2	VQG3	60	5.93	-4.34	24.49
eighthour_O3_s_1mMLRext2	VQG6	60	6.85	-0.74	22.96
eighthour_O3_s_1mMLRext2	VQG0	84	5.72	0.83	13.76
eighthour_O3_s_1mMLRext2	VQG1	84	6.79	0.71	16.24
eighthour_O3_s_1mMLRext2	VQG2	84	6.53	-1.25	15.82
eighthour_O3_s_1mMLRext2	VQG3	84	5.93	-2.52	15.34
eighthour_O3_s_1mMLRext2	VQG6	84	6.85	0.10	16.31
eighthour_O3_s_1mMLRext2	VQG0	120	5.72	2.73	10.56
eighthour_O3_s_1mMLRext2	VQG1	120	6.79	3.99	13.12
eighthour_O3_s_1mMLRext2	VQG2	120	6.53	-0.34	10.89
eighthour_O3_s_1mMLRext2	VQG3	120	5.93	0.20	9.89
eighthour_O3_s_1mMLRext2	VQG6	120	6.85	1.37	11.64





Table 61: Alphasense OX-B431  $O_3$  sensor: Parameters of orthogonal regression of 8-hourly sensor data calibrated with extended multiple linear regression ( $O_3S_1mMLRext2$ ) versus reference  $O_3$ 

	ID	slope	intercept (μg/m³)
eighthour_O3_s_1mMLRext2	VQG0	1.05	-3.61
eighthour_O3_s_1mMLRext2	VQG1	1.09	-6.95
eighthour_O3_s_1mMLRext2	VQG2	1.03	-3.37
eighthour_O3_s_1mMLRext2	VQG3	1.08	-8.88
eighthour_O3_s_1mMLRext2	VQG6	1.04	-2.86

### 7.4.6 Conclusions

After calibration of the sensor data – not corrected with sensor NO<sub>2</sub> data - with the regression parameters based on MLR with reference NO<sub>2</sub> ( $O3\_s\_1mMLRext2$ ), we see more negative ratios in winter. We also see negative ratios with lower temperatures, higher relative humidity and higher NO<sub>2</sub> concentrations. The low O<sub>3</sub> concentrations together with the sensor data that are often negative when these conditions occur are most likely the cause of these patterns in the ratios.

The scatter plot of the calibrated sensor data versus the reference data no longer shows a lineair relationship with the reference  $O_3$ .

The R<sup>2</sup> is for all sensors higher (between 0.90 and 0.93) in comparison with the sensor data calibrated with the LR parameters ( $O3\_s\_1mLR2$ ), the between sensor uncertainty is smaller (47 %) and the relative expanded uncertainties are also higher lower. The mean biases vary between between -6 and -2 µg/m<sup>3</sup>. The expanded uncertainty for the 8-hourly values is  $\leq$  30 % for all sensors at 120 µg/m<sup>3</sup> (TV), 84 µg/m<sup>3</sup> and 60 µg/m<sup>3</sup>.





### Field Evaluation O<sub>3</sub> sensors

**General conclusions** 





### 8 General conclusions

The raw data of the different sensors were manually validated. Both positive and negative peaks are occasionally present in the raw sensor data. When these peaks occurred after a restart of the measurements or a technical intervention, they were marked as invalid. Other peaks were marked as suspicious when they were remarkable higher or lower than the values of the other sensors.

A lot of negative and positive peaks occurred in the raw data of the sensors **Membrapor C-5**. It was not possible to remove these peaks manually, so they were marked suspicious automatically when higher than 200  $\mu$ g/m<sup>3</sup> or lower than -50  $\mu$ g/m<sup>3</sup>. We noticed diverging data for one sensor Membrapor C-5 from January 2020 on. We also saw more aberrant data for the other Membrapor C-5 sensors at the end of the measurement campaign. Therefore the data from January 1, 2020 until March 30, 2020 were left out in the further data analysis for this sensor type. T

The **Envea Cairclip** sensors have limited data (until June- August 2019) due to technical issues and a life time of only one year.

The sensors **Envea Cairclip** and **Alphasense OX-B431** measure  $O_3 + NO_2$ . Before analyzing the sensor data, the mean of the data of the Envea Cairclip and the Alphasense B43F NO<sub>2</sub> sensors are substracted from the Envea Cairclip  $NO_2/O_3$  and Alphasense OX-B431 sensors respectively. Two approaches are followed for MLR calibration. In the first approach the corrected sensor data are calibrated with the parameters from the MLR function with temperature and relative humidity (but without reference  $NO_2$ ). In a second approach the sensor data are not corrected with sensor  $NO_2$  data but calibrated with the parameters of the MLR with reference  $NO_2$ .

The uncalibrated **Aeroqual SM50** sensor data shows very good correlation with the reference method: the R<sup>2</sup> varies between 0.91 and 0.97. The between sensor uncertainty is 38 %. The mean biases vary between -4 and 9  $\mu$ g/m<sup>3</sup>. The expanded uncertainty for the 8-hourly values is smaller than 30 % for all sensors at the target value of 120  $\mu$ g/m<sup>3</sup>.

Calibration of the sensors with the linear regression parameters does not improve the between sensor uncertainty in comparison with the uncalibrated sensor data. The mean bias of some sensors are more negative after calibration and for some sensors the relative expanded uncertainty at 120  $\mu$ g/m<sup>3</sup> increases. Similar observations can be made for the sensor data calibrated with the parameters of the MLR function that includes temperature and relative humidity. The sensors appear not to be influenced by NO<sub>2</sub> so they were not calibrated with the MLR function that besides temperature and relative humidity also includes NO<sub>2</sub>.

For all other sensors, calibration leads to better performance characteristics. The field campaign data from February 23, 2019 - March 31, 2019 were used to establish the calibration functions.



The uncalibrated **Envea Cairclip** sensors show a moderate correlation with the reference method but largely underestimate the O<sub>3</sub> concentrations. The mean biases are negative for all the sensors (between -32  $\mu$ g/m<sup>3</sup> and -17  $\mu$ g/m<sup>3</sup>). The R<sup>2</sup> varies between 0.70 and 0.82. The between sensor uncertainty is 65 %. De expanded uncertainty for the 8-hourly values is  $\leq$  75 % for only two of the five sensors at the target value of 120  $\mu$ g/m<sup>3</sup>.

Calibration of the sensors with the LR parameters reduces the mean bias to between -6 and  $1 \mu g/m^3$ . The between sensor uncertainty is 46 %. De expanded uncertainty for the 8-hourly values is smaller than 30% for all five sensors at 120  $\mu g/m^3$ .

Calibration of the sensor data (corrected with sensor NO<sub>2</sub> data) with the MLR regression parameters based on the function with temperature and relative humidity but without NO<sub>2</sub> leads to mixed results: R<sup>2</sup> become slightly higher in comparison to the data calibrated with the LR parameters, but the between sensor uncertainty is slighly higher and the relative expanded uncertainties for the 8-hourly values at 120  $\mu$ g/m<sup>3</sup> are smaller for some sensor, but higher for others.

Another aproach is the calibration of the non corrected sensor data with the parameters of the MLR function that also includes reference NO<sub>2</sub>. This also leads to mixed results. R<sup>2</sup> is comparable with the sensor data calibrated with the LR parameters. The between sensor uncertainty is higher and the expanded uncertainty for the 8-hourly values at 120  $\mu$ g/m<sup>3</sup> is higher for four of the five sensors.

The uncalibrated data of the **Citytech 3E1F** sensors show good correlation but with a clear positive bias: the R<sup>2</sup> varies between 0.80 and 0.85 and the mean biases vary between 60 and 75  $\mu$ g/m<sup>3</sup>. At higher O<sub>3</sub> concentrations the uncalibrated sensor data deviate from the linear trendline. The expanded uncertainty for the 8-hourly values at 120  $\mu$ g/m<sup>3</sup> is higher than 250 % for the three sensors. The performance characteristics are therefore not shown on the figures below.

Calibration with the LR calibration parameters improves the results: smaller mean biases, smaller between sensor uncertainty and smaller expanded uncertainties. However, the relative expanded uncertainty for the 8-hourly calibrated sensor data at the target value of 120  $\mu$ g/m<sup>3</sup> remains higher than 100 %.

Calibration with the MLR parameters based on the function without NO<sub>2</sub> are not improved in comparison to the sensor data calibrated with the LR parameters: smaller  $R^2$ , a higher between sensor uncertainty and higher relative expanded uncertainties.

After calibrating with the MLR parameters with NO<sub>2</sub> the expanded uncertainty at 120  $\mu$ g/m<sup>3</sup> is still higher than 30 % but smaller than 75 % for all three sensors. The R<sup>2</sup> varies between 0.87 and 0.92, the mean biases vary between 3 and 6  $\mu$ g/m<sup>3</sup>. The between sensor uncertainty is 51 %.

The uncalibrated **Membrapor C-5 O<sub>3</sub>** sensors shows poor correlation with the reference  $O_3$ . The R<sup>2</sup> varies between 0.24 and 0.43, except for one sensor (VQM5) which has an even



worse  $R^2$  of 0.06. Some sensors overestimate the O<sub>3</sub> concentrations, others underestimate the O<sub>3</sub> concentrations: the mean biases vary between -35 and 26 µg/m<sup>3</sup>. The expanded uncertainty of the 8-hourly values of some of the uncalibrated sensors is smaller than 75 %. This is due to the fact that the slope of the orthogonal regression of the uncalibrated sensor data versus the reference data is small for all sensors (< 0.5) with a small contribution from random errors to the uncertainty as a result. The performance characteristics of the uncalibrated sensor data are not shown on the figures below.

Calibration with the LR parameters or with the parameters from the MLR function without NO<sub>2</sub> does not improve the sensor data: we observe higher mean biases for some sensors, a higher between sensor uncertainty and expanded uncertainties higher than 250 % for the 8-hourly values at 120  $\mu$ g/m<sup>3</sup>. The performance characteristics of the sensor data calibrated with the LR parameters or with the parameters from the MLR function are therefore not shown on the figures below.

After calibration with the parameters based on the MLR regression function with reference NO<sub>2</sub> we see higher R<sup>2</sup>, smaller mean biases, a smaller between sensor uncertainty and smaller relative expanded uncertainties. The R<sup>2</sup> varies between 0.73 and 0.86, except for one sensor (VQM5 with a R<sup>2</sup> of 0.30). The between sensor uncertainty is 51 %. At 120  $\mu$ g/m<sup>3</sup> the expanded uncertainty of the 8-hourly values is  $\leq$  30 % for four of the five sensors.

The **Alphasense OX-B431** sensors – after correction with the NO<sub>2</sub> sensor values - show good correlation with the reference method but overestimate the O<sub>3</sub> concentrations. The mean biases of the uncalibrated sensor data vary between 2 and 14  $\mu$ g/m<sup>3</sup>. The R<sup>2</sup> varies between 0.87 and 0.88. The between sensor uncertainty is 47 %. The expanded uncertainty for the 8-hourly values is  $\leq$  75 % for four of the five sensors at 120  $\mu$ g/m<sup>3</sup>. The expanded uncertainty does not drop below 30 %.

Calibration of the sensors with the LR parameters leads to expanded uncertainties smaller than 30 % for the 8-hourly values at the test concentrations of 120  $\mu$ g/m<sup>3</sup>. The mean biases are negative, they vary between -11 and -3  $\mu$ g/m<sup>3</sup>.

Calibration of the the sensor data with the parameters from MLR with temperature and humidity but without reference NO<sub>2</sub> leads to R<sup>2</sup> that are slightly higher. The expanded uncertainty for the 8-hourly values is  $\leq$  30 % for four of five the five sensors at 120 µg/m<sup>3</sup>. However the mean biases become more negative: between -10 and -15 µg/m<sup>3</sup>.

After calibration of the sensor data – not corrected with the NO<sub>2</sub> sensor data - with the parameters of the MLR function that also includes reference NO<sub>2</sub>, the mean biases vary between -6 and -2  $\mu$ g/m<sup>3</sup>. The R<sup>2</sup> varies between 0.90 and 0.93. The expanded uncertainty for the 8-hourly values is smaller than 30 % for all five sensors at 120  $\mu$ g/m<sup>3</sup>. At high concentrations the deviations of the sensor data from the reference concentration remain high.

All studied sensor types, with the exception of the **Aeroqual SM50** sensors, need a calibration in the field in order to obtain the best performance. The Aeroqual SM50 can be used without any calibration. For the **Envea Cairclip NO<sub>2</sub>/O<sub>3</sub>** sensors a LR regression


calibration based on a month of colocation with the reference method gives as good results as a MLR calibration based on the same month of colocation. Sensor data from the Envea Cairclip NO<sub>2</sub> sensors need to be available for correcting the Envea Cairclip NO<sub>2</sub>/O<sub>3</sub> sensor.

For the **Citytech 3E1F** sensors, the **Membrapor C-5 O<sub>3</sub>** sensors and the **Alpahsense OX-B431** sensors, calibration with parameters from a MLR function with temperature, relative humidity and reference NO<sub>2</sub> give the best results. These reference NO<sub>2</sub> data can possibly be replaced by sensor NO<sub>2</sub> data or modelled NO<sub>2</sub> data.

The calibration functions were determined for every single sensor of a sensor type. For most sensor types there is some degree of variability in the parameters of the LR and MLR calibration functions between the sensors. This makes it unlikely that one calibration function for the different sensors of a sensor types can be used in future. The **Citytech 3E1F** sensors show the best reproducibility of the parameters of the MLR calibration function.

An important final remark is that the calibration and the evaluation of these sensors was performed at the same measurement site in Borgerhout. We therefore have no information on how the sensors - calibrated with the calibration functions established at the measurement site of Borgerhout - would have performed at other locations.





Figure 170: Summary:  $R^2$  for the hourly sensor data for different sensor types and different calibrations. Uncalibrated (O3\_S\_2), Calibrated with linear regression parameters (O3\_S\_1mLR2), calibrated with multiple linear regression (O3\_S\_1mMLR2) and calibrated with extended multiple linear regression (O3\_S\_1mMLR2)





Figure 171: Summary: Mean bias ( $\mu$ g/m<sup>3</sup>) for the hourly sensor data for different sensor types and different calibrations. Uncalibrated (O3\_S\_2), Calibrated with linear regression parameters (O3\_S\_1mLR2), calibrated with multiple linear regression (O3\_S\_1mMLR2) and calibrated with extended multiple linear regression (O3\_S\_1mMLR2)





Figure 172: Summary: Between sensor uncertainty ( $\mu$ g/m<sup>3</sup> and %) for the hourly sensor data for different sensor types and different calibrations. Uncalibrated (O3\_S\_2), Calibrated with linear regression parameters (O3\_S\_1mLR2), calibrated with multiple linear regression (O3\_S\_1mMLR2) and calibrated with extended multiple linear regression (O3\_S\_1mMLR2)





Figure 173: Summary: Relative expanded uncertainty (%) for the 8-hourly uncalibrated and calibrated sensor data at 120  $\mu$ g/m<sup>3</sup> for different sensor types and different calibrations. Uncalibrated (O3\_S\_2), Calibrated with linear regression parameters (O3\_S\_1mLR2), calibrated with multiple linear regression (O3\_S\_1mMLR2) and calibrated with extended multiple linear regression (O3\_S\_1mMLR2)





### **Appendices**

## Performance evaluation of five low-cost ozone sensors in the field

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### 9 Appendices

### 9.1 Appendix 1: Correlation charts for the field campaign February 23, 2019 - March 30, 2020

The charts show :

- The distribution of each variable is on the diagonal.
- On the bottom of the diagonal : the bivariate scatter plots with a fitted line
- On the top of the diagonal : the value of the correlation plus the significance level as stars
- Each significance level is associated to a symbol : p-values(0, 0.001, 0.01, 0.05, 0.1, 1) <=> symbols("\*\*\*", "\*\*", "\*", ".", "")



### 9.1.1 Aeroqual SM50 O<sub>3</sub> sensor

Figure 174: Correlation chart of Aeroqual SM50  $O_3$  sensor VQO1. R = pearson correlation coefficient



Figure 175: Correlation chart of Aeroqual SM50  $O_3$  sensor VQO2. R = pearson correlation coefficient







Figure 176: Correlation chart of Aeroqual SM50  $O_3$  sensor VQO3. R = pearson correlation coefficient



Figure 177: Correlation chart of Aeroqual SM50  $O_3$  sensor VQO5. R = pearson correlation coefficient

### 9.1.2 Citytech 3E1F O<sub>3</sub> sensor



Figure 178: Correlation chart of Citytech 3E1F  $O_3$  sensor VQJ3. R = pearson correlation coefficient







Figure 179: Correlation chart of Citytech 3E1F  $O_3$  sensor VQJ4. R = pearson correlation coefficient



Figure 180: Correlation chart of Citytech 3E1F O<sub>3</sub> sensor VQJ5. R = pearson correlation coefficient

#### 9.1.3 Membrapor C-5 O<sub>3</sub> sensor



Figure 181: Correlation chart of Membrapor C-5  $O_3$  sensor VQM1. R = pearson correlation coefficient







Figure 182: Correlation chart of Membrapor C-5  $O_3$  sensor VQM2. R = pearson correlation coefficient



Figure 183: Correlation chart of Membrapor C-5  $O_3$  sensor VQM3. R = pearson correlation coefficient



Figure 184: Correlation chart of Membrapor C-5  $O_3$  sensor VQM4. R = pearson correlation coefficient





Figure 185: Correlation chart of Membrapor C-5  $O_3$  sensor VQM5. R = pearson correlation coefficient





Figure 186: Correlation chart of Envea Cairclip  $NO_2/O_3$  sensor VQT1 without reference  $NO_2$ . R = pearson correlation coefficient



Figure 187: Correlation chart of Envea Cairclip  $NO_2/O_3$  sensor VQT2 without reference  $NO_2$ . R = pearson correlation coefficient







Figure 188: Correlation chart of Envea Cairclip  $NO_2/O_3$  sensor VQT3 without reference  $NO_2$ . R = pearson correlation coefficient



Figure 189: Correlation chart of Envea Cairclip  $NO_2/O_3$  sensor VQT4 without reference  $NO_2$ . R = pearson correlation coefficient



Figure 190: Correlation chart of Envea Cairclip  $NO_2/O_3$  sensor VQT5 without reference  $NO_2$ . R = pearson correlation coefficient





9.1.5 Envea Cairclip NO<sub>2</sub>/O<sub>3</sub> sensor



Figure 191: Correlation chart of Envea Cairclip  $NO_2/O_3$  sensor VQT1 with reference  $NO_2$ . R = pearson correlation coefficient



Figure 192: Correlation chart of Envea Cairclip  $NO_2/O_3$  sensor VQT2 with reference  $NO_2$ . R = pearson correlation coefficien



Figure 193: Correlation chart of Envea Cairclip  $NO_2/O_3$  sensor VQT3 with reference  $NO_2$ . R = pearson correlation coefficient







Figure 194: Correlation chart of Envea Cairclip  $NO_2/O_3$  sensor VQT4 with reference  $NO_2$ . R = pearson correlation coefficient



Figure 195: Correlation chart of Envea Cairclip  $NO_2/O_3$  sensor VQT4 with reference  $NO_2$ . R = pearson correlation coefficient

9.1.6 Alphasense OX-B431 O<sub>3</sub> sensor –minus sensor NO<sub>2</sub>



Figure 196: Correlation chart of Alphasense OX-B431  $NO_2/O_3$  sensor VQH0 without reference  $NO_2$ . R = pearson correlation coefficient







Figure 197: Correlation chart of Alphasense OX-B431  $NO_2/O_3$  sensor VQH1 without reference  $NO_2$ . R = pearson correlation coefficient



Figure 198: Correlation chart of Alphasense OX-B431  $NO_2/O_3$  sensor VQH2 without reference  $NO_2$ . R = pearson correlation coefficient



Figure 199: Correlation chart of Alphasense OX-B431  $NO_2/O_3$  sensor VQH3 without reference  $NO_2$ . R = pearson correlation coefficient







Figure 200: Correlation chart of Alphasense OX-B431  $NO_2/O_3$  sensor VQH6 without reference  $NO_2$ . R = pearson correlation coefficient



#### 9.1.7 Alphasense OX-B431 O<sub>3</sub> sensor

Figure 201: Correlation chart of Alphasense OX-B431  $NO_2/O_3$  sensor VQH0 with reference  $NO_2$ . R = pearson correlation coefficient



Figure 202: Correlation chart of Alphasense OX-B431  $NO_2/O_3$  sensor VQH1 with reference  $NO_2$ . R = pearson correlation coefficient







Figure 203: Correlation chart of Alphasense OX-B431  $NO_2/O_3$  sensor VQH2 with reference  $NO_2$ . R = pearson correlation coefficient



Figure 204: Correlation chart of Alphasense OX-B431  $NO_2/O_3$  sensor VQH3 with reference  $NO_2$ . R = pearson correlation coefficient



Figure 205: Correlation chart of Alphasense OX-B431  $NO_2/O_3$  sensor VQH5 with reference  $NO_2$ . R = pearson correlation coefficient



### 9.2 Appendix 2: Calibration parameters from laboratory study

Based on the sensor data of the ramping experiment during the laboratory study, a linear regression function against the reference instrument was calculated

The table 62 below gives the parameters of this calibration function for the different sensors. The parameters of the Citytech 3E1F are not included due to the fact that during the laboratory study, these sensors were not oriented according to the supplied manual.

VQM2 and VQG1 were tested in the laboratory, but were not included in the evaluation of the laboratory testing due to malfunctioning. VQO5 was not included in the laboratory study.

During the field campaign a linear calibration function was established based on the data from February 23, 2019 - March 31, 2019.

The intercepts calculated during the laboratory study and the field test are quite different. There is however some relation between the slopes of the different sensor types calculated during the laboratory study and the field test : when we found lower slopes during the laboratory study, we also found lower slopes during the field test.

Table 63 gives some performance characteristics of the uncalibrated sensor data  $(O3_s_2)$  and of the data calibrated with the calibration parameters established during the laboratory study  $(O3_s_lab_2)$ .

Application of the lab calibration parameters on the Membrapor C-5 O3 sensor data does not improve the results. The mean biases and the relative expanded uncertainty of the 8-hourly values at the target value become larger.

Application of the lab calibration parameters on the Aeroqual SM50 sensor and on the Alphasense OX-B431 sensors data leads to higher mean biases at all or some sensors. The relative expanded uncertainty of the 8-hourly values at the target value decreases only for some sensors.

Application of the lab calibration parameters on the Envea Cairclip sensor data decreases the the mean biases and leads to a lower relative expanded uncertainty for all sensors.

So application of the lab calibration parameters does not improve the sensor data of most of the sensor types. This is not surprising, since e.g. temperature, relative humidity and NO<sub>2</sub> are known to have an effect on  $O_3$  sensors. The conditions during the laboratory test with constant temperature and relative humidity and the absence of NO<sub>2</sub> are quite different from the conditions during the field test. Different sensors of one sensor type also seem to react differently to variations in temperature, relative humidity and NO<sub>2</sub>.

Application of the lab calibration parameters only improves the sensor data of the Envea Cairclip sensors. The effect of temperature and relative humidity on this sensor type is small.





Table 62: Calibration parameters based on the laboratory study and field campaign

	Laboratory study		Field campaign					
sensor_internal_id	slope	intercept	slope	intercept				
		(µg/m³)		(µg/m³)				
Aeroqual SM50								
VQ01	0.94	-4.2	1.03	-1.2				
VQO2	0.95	-11.3	1.02	0.5				
VQO3	0.96	-11.6	1.01	1.7				
VQO5	-	-	1.05	-1.6				
Membrapor C-5								
VQM1	0.52	4.1	0.19	52.3				
VQM2	0.11	-7.0	0.06	2.7				
VQM3	0.38	-20.5	0.20	8.9				
VQM4	0.38	-9.2	0.18	33.2				
VQM5	0.44	17.7	0.16	57.8				
VQT1	0.70	-7.9	0.65	-12.99				
Envea Cairclip								
VQT2	0.72	-0.5	0.73	-4.00				
VQT3	0.60	-3.4	0.77	-4.54				
VQT4	0.68	-1.4	0.65	-9.34				
VQT5	0.72	-4.0	0.70	-10.25				
VQG0	1.06	4.2	1.2	14.63				
Alpahsense OX-B431								
VQG1	0.96	-8.8	1.1	12.04				
VQG2	1.09	-4.8	1.3	4.83				
VQG3	1.06	4.1	1.1	11.30				
VQG6	0.99	-4.6	1.2	-0.65				



Table 63: Performance characteristics of the uncalibrated sensor data (O3\_s\_2) and of the sensor data calibrated with the calibration parameters established during the laboratory study (O3\_S\_lab2). Mean bias,  $R^2$ ,  $u_{bs}$  (between sampler uncertainty) and W (expanded uncertainty) at 120  $\mu$ g/m<sup>3</sup> on 8-hourly values.

	ID	n	mean	R <sup>2</sup>	W at 120	ubs	u <sub>bs</sub> (%)			
			μg/m <sup>3</sup> )		hourly)	(µg/m²)				
Aeroqual SM50										
03 5 2	V001	6595	3.54	0.92	10.21					
03 5 2	V002	6813	-0.74	0.96	21.68					
03 \$ 2	V003	1236	-3.64	0.97	16.32					
03 \$ 2	V005	6458	9.03	0.91	21 / 2					
03 5 2	all sensors	21102	5.05	0.51	21.42	16.68	38 37			
$03_{2}$	VOO1	6595	10.82	0.92	20 72	10.00	50.57			
$O3_s lab2$	V002	6813	12.02	0.92	20.72					
03_5_1052	VQ02	1226	10.7	0.50	14 11					
	VQ05	1230	10.7	0.97	14.11					
		1/6//	-	_	-	16.4	21 59			
Mombraner C E	an sensors	14044				10.4	51.56			
	VOM1	4525	1/ 20	0.25	61 49	1	I			
03_3_2		4J2J 5607	-25.02	0.33	194 70					
03_3_2		5007	-33.03	0.27	184.79					
03_5_2	VQIVIS	5900	-21.99	0.45	122.94					
03_5_2	VQIVI4	1070	-5.51	0.24	63.33 61.95					
03_3_2		26780	20.20	0.00	01.05	2/1 21	74.01			
03_3_2		4525	EC 12	0.25	104.07	24.31	74.01			
		4J2J 5607	50.45 60.45	0.33	104.97					
		5060	59.21	0.27	170.05					
	VQMA	5900	38.31 77 E	0.43	170.95					
		2019	77.5	0.24	359.1					
		4878	72.01	0.06	500.36	70.27	27.22			
	all sensors	20789				20.57	27.52			
	VOT1	2465	21.62	0.76	102 52		T			
03_5_2		4022	-51.02	0.70	105.52 E1 2E7					
03_5_2	VQT2	2603	-18.01	0.76	63 216					
03_3_2		4102	-10.01	0.70	92 /12					
03_3_2	VQ14	4192	-27.12	0.84	97 990					
03_3_2		1720/	-20.03	0.70	07.005	15 22	64.64			
$03_3_2$		2465	12.05	0.76	42.02	15.55	04.04			
		4022	-15.95	0.70	42.05					
		4052	-5.07	0.76	23.00					
		4102	-15 20	0.70	25.09					
	VQT4	4102	-11.5	0.04	22.00					
		1720/	-11.5	0.70	32.91	22.20	57.01			
Alnahsense OX-R431										
03 5 2	VOG0	7433	14.46	0.87	73.43					
03 s 2	VOG1	7261	9.63	0.88	65.92					
03 s 2	VOG2	7705	11.88	0.88	88.54					
03 s 2	VOG3	7498	5.55	0.88	60.28					
03 s 2	VOG6	7170	2.20	0.87	46.86					
03 s 2	all sensors	37067	-			21.64	47.34			
03 s lab2	VQG0	7433	3.54	7.49	51.15		-			
03 s lab2	VQG1	7261	29.92	20.8	92.08					
03 s lab2	VQG2	7705	16.88	12.42	72.5					
 O3_s_lab2	VQG3	7498	-4.56	-0.66	40.43					
O3_s_lab2	VQG6	7170	12.00	7.37	57.52	1	1			
O3_s_lab2	all sensors	37067		ĺ		21.56	46.47			

