



## CompAir: Field Inter-Comparison of Air Quality Measurements Between The Netherlands and North Rhine-Westphalia (Germany). **Materialien 71**



**CompAir: Field Inter-Comparison of Air Quality Measurements  
Between The Netherlands and North Rhine-Westphalia (Germany)**

Simultaneous Measurements of Ambient Air Levels of Air Pollution by the  
Landesumweltamt Nordrhein-Westfalen (LUA NRW, Germany) and the  
National Institute for Public Health and the Environment (RIVM, Netherlands)  
Dutch-German Working Group: Information Exchange on Implementation  
of European Air Quality Directives; Participants: RIVM (NL), LUA NRW (DE)

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## 1. Summary

In 2003 and 2004 a simultaneous measurement campaign was carried out between the national air quality monitoring networks of North Rhine-Westphalia, Germany (LUA NRW) and the Netherlands (RIVM).

The aim was to assess trans-border comparability, and thus quality of the measured results by each network within the framework of the pertinent EU Directives regarding ozone (O<sub>3</sub>), nitrogen oxides (NO/NO<sub>2</sub>), sulphur dioxide (SO<sub>2</sub>) and fine particles (PM<sub>10</sub>).

The campaign was carried out at an industrially dominated site in Bottrop in the northern part of the German Ruhr area. This site is part of the regular monitoring network of the German Land (state) North Rhine-Westphalia. A parallel campaign was carried out at the rural station Vredepeel in the south eastern part of the Netherlands with high ammonia levels. This site is part of the regular monitoring network of the Netherlands.

At these two sites, the ambient concentrations of PM<sub>10</sub>, NO, NO<sub>2</sub>, O<sub>3</sub> and SO<sub>2</sub> were independently measured by the two participating laboratories.

Assessment of measurement uncertainty demonstrates that the data quality objectives set by the European Directive are clearly met at both monitoring sites only for ozone with an expanded 95 %-uncertainty of 7 % or better. For sulphur dioxide expanded 95 %-uncertainty was found between 8 % at Bottrop and 18 % at Vredepeel, the latter exceeding the data quality objective of 15 %. For nitrogen dioxide expanded 95%-uncertainties between 9 % at Vredepeel and 18 % at Bottrop was found to be compared with a data quality objective of 15 %. It should be noted that according to the Directive the data quality objectives are applicable in the region of the appropriate limit value. Especially for sulphur dioxide most concentration values were far below the relevant limit values. Parts of the uncertainty budget may be attributed to this fact. For nitrogen dioxide a relatively high systematic difference (bias) was identified as a main source causing the uncertainty.

It was not surprising that the measurement of PM<sub>10</sub> showed the highest uncertainty values. The data quality objective of 25 % was met only at Bottrop both for FH62- as well as for TEOM-instrumentation. At Vredepeel both type of instruments failed to meet the data quality objective. These findings indicate that the correction factors applied were appropriate for a highly polluted monitoring site like Bottrop but not so much for rural site as Vredepeel.

These results of the joint study underline the extraordinary value of the performed inter-comparison between RIVM and LUA assessing data quality of ambient air measurements.

## 2. Legal Background

The Council Directive 96/62/EC of 27 September 1996 on ambient air quality assessment and management [1], the so-called Framework Directive (FWD), defines as one objective to '*assess the ambient air quality in Member States on the basis of common methods and criteria*' (art. 1). Article 3 of the FWD requires '*quality controls carried out in accordance, inter alia, with the requirements of European quality assurance standards*'. In the Annexes of the relevant Daughter Directives [2, 3], data quality objectives for measurement results are defined in terms of measurement uncertainty.

In order to comply with these data quality objectives, EU Member States should employ standard measurement techniques, the so-called EU reference methods standardized by CEN. But a Member State may use any other method which it can demonstrate gives results equivalent to the reference method, assuring the production of comparable air quality data.

This implies that an interregional comparison between the air quality monitoring networks of North Rhine-Westphalia (Germany) and the Netherlands could serve to test the compliance with the above mentioned data quality objectives.

## 3. Objectives

As part of quality assurance, a simultaneous measurement campaign was set up by the Dutch RIVM and the German LUA NRW at the Dutch site Vredepeel (131) and at the German site Bottrop (BOTT).

Main objective of this exercise is to compare measurement results in view of the data quality objectives (DQO) of the European Directives mentioned above.

Both sites were operated under routine conditions without any special 'tuning' for inter-comparison. Each laboratory applied its own operating procedures including maintenance, calibration, data acquisition, data transmission, and evaluation techniques.

Basic information about the network procedures is given in the following chapters.

A similar type of comparative exercise is taking place already between the Netherlands and Lower Saxony, Germany [4].

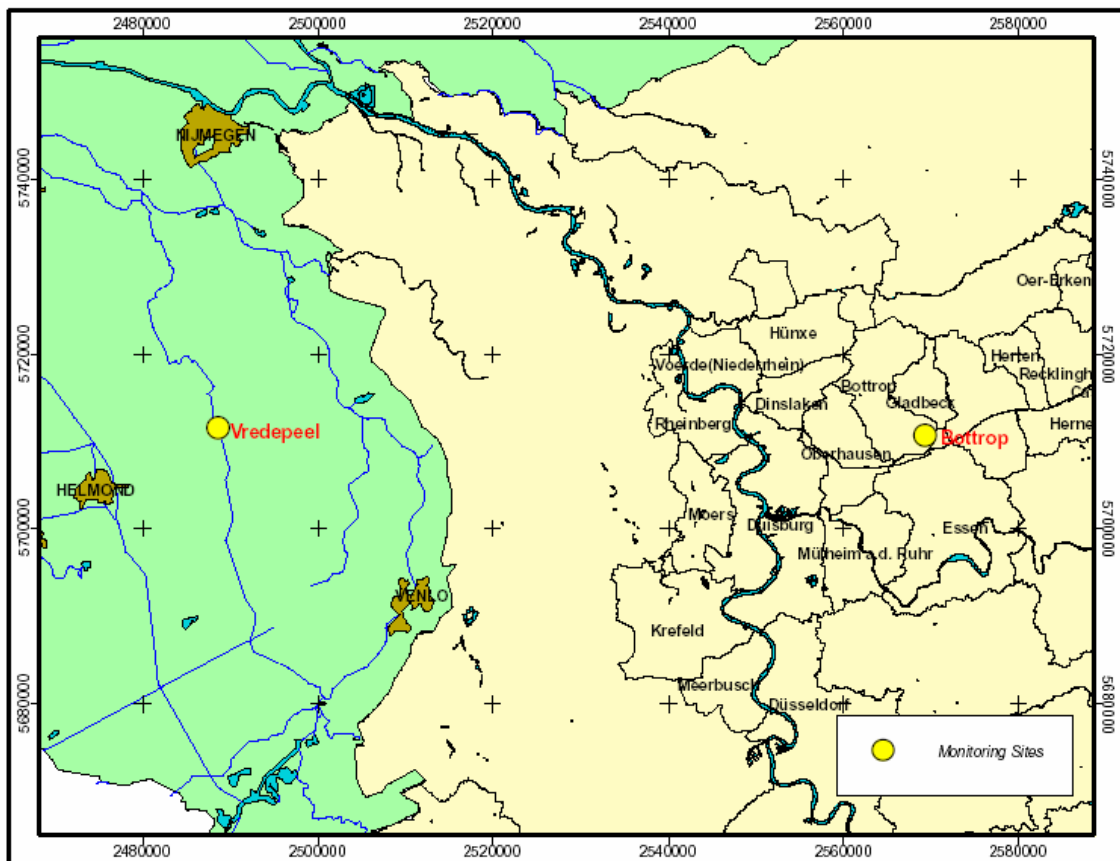
## 4. Strategy

In order to cover concentrations ranges as large as possible, a rural site in the Netherlands (Vredepeel, EU-code: 131; see [5]) and an industrial site in North Rhine-Westphalia (Bottrop, EU code: DENW021; see [5, 6]) were selected for the inter-comparisons. In addition, a different average composition of particles can be expected at these sites. Vredepeel,

characterized by agricultural use, is supposed to have higher shares of fine and secondary particles than Bottrop with various industrial installations in the vicinity.

In Vredepeel a LUQS container was installed besides the Dutch station, in Bottrop an RIVM container next to the LUQS station. A more detailed description of the measurement sites can be found in chapter 6.

Figure 1 shows a map with both monitoring sites.



**Figure 1:** Map of monitoring sites in Vredepeel and Bottrop

## 5. Financial Aspects

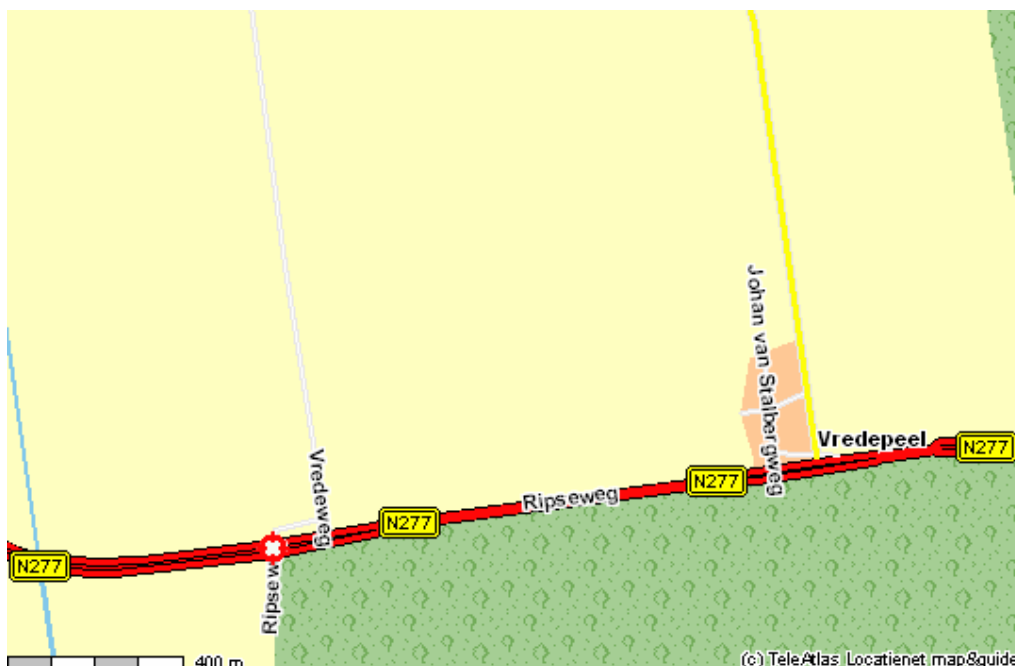
No specific arrangement was made. Both participants paid for the operation of their own measurement stations and equipment.



## 6. Measurement Sites

### 6.1 Vredepeel

The station is located in a rural area in the south eastern part of The Netherlands. On a macro scale in the very wide surroundings of the station there is intensive pig and poultry farming. On a micro scale, north easterly from the station there is a large pig farm. Apart from this farm, the local surroundings of the station is relatively even and flat. The flow around the inlet sampling probe is largely unrestricted.



**Figure 2:** Maps of RIVM-site in Vredepeel

## 6.2 Bottrop

The station is located at a secondary road in Bottrop-Welheim (school area), approximately 3.5 km east of the city centre (see Figure 3). The national road B224 passes about 1 km east of the station. On the other side of this street there is a waste incineration plant. 1.5 km south-east of the station are a power plant, some production facilities, and a coal liquefaction unit. The cokery Prosper II is situated about 800 m south-west. In the vicinity there are small houses with coal-fired stoves. The surrounding of the station is even and flat, the flow around the inlet sampling probe is largely unrestricted.

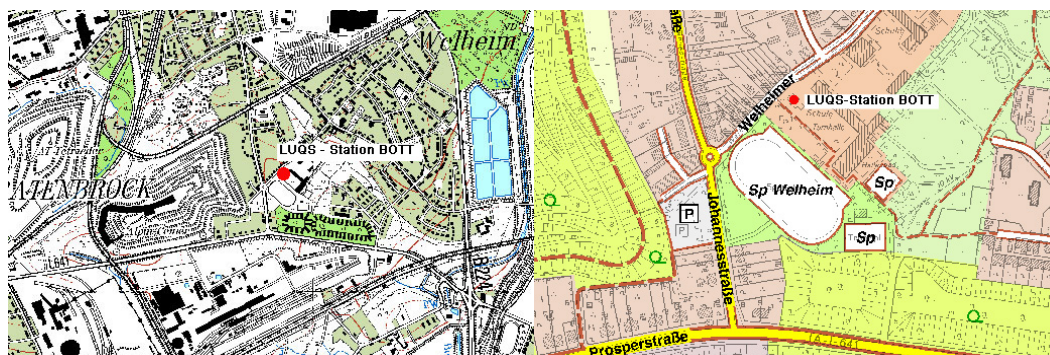


Figure 3: Map of LUA-site in Bottrop

## 7. Monitoring Equipment and Data Management

Both institutes carried out their measurements in their own container; both were completely independent systems, with separated inlets and data processing.

The following setup was agreed between RIVM and LUA (Table 1):

Table 1: Measurement periods and compounds

	Vredepeel, Netherlands	Bottrop, Germany
Period	November 2002 – March 2003	May 2003 - March 2004
Measured components	Sulphur dioxide (SO <sub>2</sub> ) Nitrogen Oxides (NO & NO <sub>2</sub> ) Ozone (O <sub>3</sub> ) Fine dust (PM10)	

Figures 4 and 5 give an impression of the monitoring equipment.



**Figure 4:** View of RIVM Set-up



**Figure 5:** LUA-site in Bottrop

## 7.1 Monitoring Methods

The LUA and RIVM do employ similar types of monitoring systems for the gaseous components NO, NO<sub>2</sub>, O<sub>3</sub>, SO<sub>2</sub> and fine dust PM<sub>10</sub>. The main measurement characteristics of the monitoring systems are given in Table 2.

**Table 2:** Main measurement characteristics of the monitoring systems

	<b>RIVM</b>	<b>LUA NRW</b>
<b>Nitrogen oxides</b>	NO & NO <sub>2</sub>	NO & NO <sub>2</sub>
Measuring instrument	Thermo Environmental 42	Environment AC31M
Measuring Principle	Chemiluminescence	Chemiluminescence
<b>Ozone</b>	O <sub>3</sub>	O <sub>3</sub>
Measuring instrument	Thermo Electron 49	Environment O <sub>3</sub> 41M
Measuring Principle	Ultraviolet absorption	Ultraviolet absorption
<b>Sulphur dioxide</b>	SO <sub>2</sub>	SO <sub>2</sub>
Measuring instrument	Thermo Electron 43	Environment AF21M
Measuring Principle	Ultraviolet fluorescence	Ultraviolet fluorescence
<b>Fine Dust</b>	PM <sub>10</sub>	PM <sub>10</sub>
Measuring instrument	ESM FH 62 I-R Inlet tubing (350 cm) heated at +10 °C with respect to ambient temperature	TEOM 1400a with SES Adjusted according to technical note number 4 of Rupprecht & Patashnik, means temperature T <sub>case</sub> 30°C T <sub>cap</sub> 0°C T <sub>air</sub> 30°C
Measuring Principle	Attenuation of β-radiation	Oscillating microbalance technology with tapered element (R&P)
Remark	Due to underestimation of particulate concentration in comparison to the reference method EN 12341 a default correction factor is applied. Commonly employed automated dust monitoring systems such as β-attenuation (or oscillating mass balance method TEOM) systematically underestimate particulate concentrations in comparison with the reference method EN12341. To provide for this underestimation an average multiplicative correction factor is employed: RIVM factor for FH62: 1.3	Due to underestimation of particulate concentration in comparison to the reference method EN 12341 a correction factor is applied. This factor was evaluated by parallel measurements with the reference method at a large number of stations over one year.  LUA factor for TEOM: 1.28

## 7.2 Zero and span check

By way of on-site quality control during regular operation, the LUA and RIVM monitors were periodically subjected to a so called function control; the pertinent procedures are shortly listed below (Tables 3 and 4).

**Table 3:** Zero and span check – RIVM

Component	Method	Frequency
NO & NO <sub>2</sub>	Combination of a multi-gas calibrator and calibration gas of 600 ppb and zero check. Gas bottle is diluted 500 times from a 300 ppm NO bottle.	Every 24 <sup>th</sup> hour at midnight
O <sub>3</sub>	Zero check with ambient humidity, span check with ozone source from multi-gas calibrator by gas titration.	Every 24 <sup>th</sup> hour at midnight
SO <sub>2</sub>	Calibration gas of 400 ppb; Zero check	Every day at midnight; Every 4 <sup>th</sup> day at midnight
PM10	Zero foil and span check by calibration foils	Every 3 months

**Table 4:** Zero and span check – LUA NRW

Component	Method	Frequency
NO & NO <sub>2</sub>	Dilution system (50 ppm NO gas cylinder) for span NO, two values possible about 200 and 400 ppb);  GPT (gas phase titration) for span NO <sub>2</sub> , two values possible about 150 and 300 ppb; zero check with ambient air and charcoal; For adjustment only NO about 700 ppb	Automatic check every 25 <sup>th</sup> hour;  recalibration with transfer standard every 3 months
O <sub>3</sub>	Dilution system with ozone generator; span check, two values possible about 80 and 120 ppb; zero check with ambient air and charcoal scrubber	Automatic check between 22:00 and 6:00;  recalibration with transfer standard every 3 months
SO <sub>2</sub>	Dilution system (20 ppm SO <sub>2</sub> gas cylinder); span check, two values possible about 150 and 300 ppb; zero check with ambient air and charcoal scrubber	Automatic check every 25 <sup>th</sup> hour;  recalibration with transfer standard every 3 months
PM10	TEOM: calibration (reference filter); check and adjustment of massflow controller and internal set points, done by dealer (in Germany MLU Corporation)	Once a year

### 7.3 Network data treatment

In RIVM and LUA all measured concentration values are retained always, also small positive or negative concentration values. Only negative values smaller than “minus EL” (evaluation limit) are disapproved, hence discarded, based on operational experiences. Details are stated in Table 5.

**Table 5:** Data treatment by RIVM and LUA on measurements around zero

Component	EL [ $\mu\text{g}/\text{m}^3$ ] RIVM	EL [ $\mu\text{g}/\text{m}^3$ ] LUA	MV [ $\mu\text{g}/\text{m}^3$ ]	Value taken
NO & NO <sub>2</sub>	5	7 & 10	< - EL > - EL	None; measurement disapproved MV
O <sub>3</sub>	5	4	< - EL > - EL	None; measurement disapproved MV
PM10	5	10	< - EL > - EL	None; measurement disapproved MV
SO <sub>2</sub>	3	10	< - EL > - EL	None; measurement disapproved MV

EL = Evaluation limit      MV = Monitor value

## 8 Basic results

Tables 6 and 7 comprise mean and maximum values of the parallel measurements performed at Vredepeel and Bottrop.

**Table 6:** Basic statistics of parallel measurements performed at **Vredepeel** within the time period 01.11.2002 to 31.03.2003

Pollutant	Sampling interval	RIVM Mean value in $\mu\text{g}/\text{m}^3$	LUA Mean value in $\mu\text{g}/\text{m}^3$	RIVM Maximum in $\mu\text{g}/\text{m}^3$	LUA Maximum in $\mu\text{g}/\text{m}^3$
Ozone	1h	27.3	26.9	109	113
Nitrogen dioxide	1h	27.6	25.3	100	85
Sulphur dioxide	1h	3.2	3.8	29	36
PM10-FH62	24h	39.2	-	101	-
PM10-TEOM	24h	-	29.0	-	87
PM10-HVS	24h	-	33.6	-	88

**Table 7:** Basic statistics of parallel measurements performed at **Bottrop** within the time period 01.05.2003 to 31.03.2004

Pollutant	Sampling interval	RIVM Mean value in $\mu\text{g}/\text{m}^3$	LUA Mean value in $\mu\text{g}/\text{m}^3$	RIVM Maximum in $\mu\text{g}/\text{m}^3$	LUA Maximum in $\mu\text{g}/\text{m}^3$
Ozone	1h	33.4	35.2	283	297
Nitrogen dioxide	1h	41.5	34.7	199	180
Sulphur dioxide	1h	15.8	16.3	273	268
PM10-FH62	24h	33,0	-	135,4	-
PM10-TEOM	24h	-	35.1	-	120
PM10-HVS	24h	-	32.9	-	87

## 9 Measurement uncertainty

### 9.1 General aspects

The parallel measurements of RIVM and LUA executed at Bottrop and at Vredepeel offered excellent opportunities to evaluate measurement uncertainty of the participating measuring systems in line with the statistical concept of GUM [7] and ISO/DIS 20988 [8]. Evaluation of measurement uncertainty was performed for values exceeding the applicable higher evaluation limit as used by LUA:

- hourly values of sulphur dioxide exceeding  $10 \mu\text{g}/\text{m}^3$ ,
- hourly values of nitrogen dioxide exceeding  $10 \mu\text{g}/\text{m}^3$ ,
- hourly values of ozone exceeding  $4 \mu\text{g}/\text{m}^3$ ,
- daily mean values of PM10 exceeding  $10 \mu\text{g}/\text{m}^3$  provided by a gravimetric Digital DHA-80 High-Volume-Sampler (HVS) as operated by LUA,
- daily mean values of PM10 exceeding  $10 \mu\text{g}/\text{m}^3$  provided by automatic FH62-instrument as operated by RIVM using a correction factor of 1.3,
- daily mean values of PM10 exceeding  $10 \mu\text{g}/\text{m}^3$  provided by automatic TEOM-instrument as operated by LUA using a correction factor of 1.28.

The obtained estimates of measurement uncertainty were compared to data quality objectives of the applicable EU-directives.

For the gaseous pollutants sulphur dioxide, nitrogen dioxide and ozone, hourly values were provided by the applied measuring instruments which were considered to exhibit the same measurement uncertainty.

Since the compared measuring systems of gaseous pollutants are not expected to exhibit a common systematic deviation (bias), a reference value  $x_R(j)$  for the time interval  $j$  was constructed as arithmetic mean of value  $x_1(j)$  observed by the RIVM-instrument and value  $x_2(j)$  observed in parallel by the LUA-instrument operated at the same site.

$$x_R(j) = [x_1(j) + x_2(j)]/2 \quad \text{for } j = 1 \text{ to } N. \quad (1)$$

For particulate matter PM10, the performed inter-comparison study provided parallel measurements  $x_1(j)$  and  $x_2(j)$  of daily mean values obtained with a FH62 instrument operated by RIVM and a TEOM instrument operated by LUA. The FH62 results have been corrected for bias by multiplying with a factor 1.3. The TEOM results have been corrected for bias by multiplying with a factor 1.28.

For particulate matter PM10, a reference value  $x_R(j)$  for day  $j$  is provided by the result of the HVS-instrument  $x_{\text{HVS}}(j)$  operated by LUA.



Equation (2) provides a mathematical model to describe variations of the observed results  $x_1(j)$  about the reference value  $x_R(j)$ . The following equations apply as well, if  $x_1(j)$  is replaced by  $x_2(j)$ .

$$x_1(j) = b \cdot x_R(j) + e(j) \quad \text{for } j = 1 \text{ to } N. \quad (2)$$

Here,  $N$  designates the number of valid data pairs  $x_1(j)$ ,  $x_R(j)$ . The slope  $b$  is calculated by equation (3).

$$b = \frac{\sum_{j=1}^N x_1(j)}{\sum_{j=1}^N x_R(j)} = \frac{\overline{x_1}}{\overline{x_R}} \quad (3)$$

Since the expected value of  $b$  is one, a bias term  $d(j) = (b-1) \cdot x_R(j)$  has to be taken into account in uncertainty estimation.

Residual deviation  $e(j) = x_1(j) - b \cdot x_R(j)$  is treated as a random variable of expected value zero exhibiting a standard deviation  $s(e)$  not depending on the reference value  $x_R(j)$  as described by equation (4a).

$$s(e) = \sqrt{\sum_{j=1}^N [x_1(j) - b \cdot x_R(j)]^2 / [N-1]} \quad (4a)$$

The standard uncertainty of slope estimate  $b = \frac{\overline{x_1}}{\overline{x_R}}$  is given by equation (4b).

$$u(b) = \frac{s(e)}{\overline{x_R} \sqrt{N}} \quad (4b)$$

Application of the rules of uncertainty propagation to model equation (2) provides the wanted variance equation (5).

$$u^2(x_1(j)) = [(b-1)^2 + u^2(b)] \cdot x_R^2(j) + s^2(e) \quad (5)$$

The contributions to the uncertainty budget of  $x_1(j)$  taken into account by equation (5) are

- bias term  $[(b-1)^2 + u^2(b)] \cdot x_R^2(j)$ , and
- residual variance  $s^2(e)$

Equation (5) provides a standard approach to uncertainty estimation well known from zero-intercept regression. In cases of  $N > 100$ , the uncertainty contribution of  $u(b)$  can be neglected.

In a first step, relationship (5) was used to evaluate separately data sets of parallel measurements provided at Bottrop (BOTT) and at Vredepeel (NLVR). Finally, a pooled estimate of measurement uncertainty for a considered method of measurement was obtained as described in equation (6) using evaluation results provided separately.

$$u(x) = \sqrt{\frac{N_{BOTT}}{N} u^2(x_{BOTT}) + \frac{N_{NLVR}}{N} u^2(x_{NLVR})} \quad (6)$$

Here,  $N = N_{BOTT} + N_{NLVR}$  describes the total number of parallel measurements provided within the evaluated inter-comparison study for a considered measuring technique.

Due to daily offset control (at least for the LUA-instruments) the number of degrees of freedom  $\nu$  may be estimated by the number of days that provided valid results exceeding the detection limits. In conclusion, it is  $\nu > 19$ .

Since the number of degrees of freedom  $\nu$  exceeds 19, the expanded 95 %-uncertainty  $U_{95}(x)$  is provided by equation  $U_{95}(x) = 2 \cdot u(x)$ . For a large concentration level  $x$ , the relative 95 %-uncertainty is estimated in good approximation by  $U_{95}(x) / x \cong 2 \cdot u(b)$ .

## 9.2 Estimates of measurement uncertainty

Best estimates of measurement uncertainty provided by evaluation of the inter-comparison study between RIVM and LUA at Bottrop and Vredepeel are summarized in Table 8.

For hourly values of ozone, Table 8 indicates an expanded 95 %-uncertainty of 6,6 % for Vredepeel (NLVR) respectively 1,8 % for Bottrop (BOTT) close to the EU-information value of  $180 \mu\text{g}/\text{m}^3$ . This demonstrates compliance with the data quality objective of 15 % of the applicable EU-directive at Vredepeel and Bottrop. Figures A.1 to A.4 demonstrate that the pooled estimate of 4 % for expanded 95 %-uncertainty is well suited to describe the properties of ozone measurements performed at Vredepeel and Bottrop.

For hourly values of nitrogen dioxide, Table 8 indicates an expanded 95 %-uncertainty of 9,5 % for Vredepeel (NLVR) and 17,7 % for Bottrop close to the EU-limit value of  $200 \mu\text{g}/\text{m}^3$ . This indicates a problem with meeting the data quality objective of 15 % of the applicable EU-directive at the measuring site Bottrop. As main source causing the increased uncertainty in Bottrop, the bias term was identified. Figures A.1 to A.4 demonstrate that the pooled estimate of 4 % for expanded 95 %-uncertainty is well suited to describe the properties of ozone measurements performed at Vredepeel and Bottrop. Figures B.1 to B.4 demonstrate that the pooled estimate of 16 % for expanded 95 %-uncertainty is well suited to describe the properties of nitrogen dioxide measurements performed at Vredepeel and Bottrop.

For hourly values of sulphur dioxide, Table 8 indicates an expanded 95 %-uncertainty of 18,4 % at Vredepeel (NLVR) and 8,1 % at Bottrop close to the EU-limit value of  $350 \mu\text{g}/\text{m}^3$ . This indicates a problem with meeting the data quality objective of 15 % of the applicable EU-directive at Vredepeel. As main source causing this uncertainty, the bias term was identified. Figures C.1 to C.4 demonstrate that the pooled estimate of 9 % for expanded 95 %-uncertainty is well suited to describe the properties of sulphur dioxide measurements performed at Vredepeel and Bottrop.

**Table 8:** Results of uncertainty estimation

Pollutant	Method	Site	b	u(b)	s(e) in $\mu\text{g}/\text{m}^3$	u(LV) in $\mu\text{g}/\text{m}^3$	$U_{95}(\text{LV})$ in %	LV in $\mu\text{g}/\text{m}^3$	N
Ozone	UV-absorption	NLVR	0,967	0,0005	0,8	5,9*	6,6*	180	2390
Ozone	UV-absorption	BOTT	0,998	0,001	1,6	1,6	1,8	180	5294
Ozone	UV-absorption	pooled			1,4	3,6	4,0	180	7684
Nitrogen dioxide	Chemilumin.	NLVR	1,047	0,001	1,4	9,5*	9,5*	200	2170
Nitrogen dioxide	Chemilumin.	BOTT	0,912	0,001	1,8	17,7	17,7	200	6802
Nitrogen dioxide	Chemilumin.	pooled			1,7	16,1	16,1	200	8972
Sulphur dioxide	UV-fluorescence	NLVR	0,916	0,038	0,8	32,3*	18,4*	350	236
Sulphur dioxide	UV-fluorescence	BOTT	1,034	0,020	2,5	14,2	8,1	350	3208
Sulphur dioxide	UV-fluorescence	pooled			2,4	16,1	9,2	350	3444
PM10	TEOM	NLVR	0,898	0,022	5,6	7,6	30,6	50	61
PM10	TEOM	BOTT	1,066	0,013	5,4	6,4	25,5	50	152
PM10	TEOM	pooled			5,5	6,8	27,1	50	213
PM10	FH62	NLVR	1,177	0,018	4,8	10,1	40,5	50	61
PM10	FH62	BOTT	1,017	0,015	6,2	6,3	25,1	50	154
PM10	FH62	pooled			5,8	7,6	30,4	50	213

\* : extrapolation based on evaluated data set.

Daily mean values of particulate matter PM10 were observed by RIVM using a FH62-instrument with a correction factor of 1.3. For this type of instrument, Table 8 indicates an expanded 95 %-uncertainty of 25,1 % at Bottrop respectively 40,5 % at Vredepeel close to the applicable EU-limit value of  $50 \mu\text{g}/\text{m}^3$ . As main source of the expanded 95 %-uncertainty of 40,5 % assigned to the Vredepeel data, the bias term was identified indicating a non-optimum correction factor. This indicates a problem with meeting the data quality objective of 25 % of the applicable EU-directive at Vredepeel.

Daily mean values of particulate matter PM10 were observed by LUA using TEOM with a correction factor of 1.28. For this type of instrument, Table 8 indicates an expanded 95 %-uncertainty of 25,5 % at Bottrop respectively 30,6 % at Vredepeel close to the applicable EU-limit value of  $50 \mu\text{g}/\text{m}^3$ . As a major source of this uncertainty, the bias term was identified. This indicates a problem with meeting the data quality objective of 25 % of the applicable EU-directive at Vredepeel.

The pooled estimates of measurement uncertainty summarized in Table 8 were used to construct 95 %-prediction ranges, briefly called 95 %-ranges, about the reference values  $x_R$  displayed in Figures A.1 to D.2 of the Annex. Furthermore, Figures A.1 to D.2 comprise Linear-Regression lines with intercept zero and the corresponding coefficients of determination  $R^2$ .

## 10 Conclusions

The results evaluated in the present inter-comparison between RIVM and LUA NRW are – in a general way – in harmony with those found during the parallel measurement between RIVM and Lower Saxony [4]. But it should be noted that the technical procedures used were not completely comparable and that the statistical methods applied for uncertainty assessment were different.

As a result of the present study, the data quality objective of 15 % for ozone was safely fulfilled at Vredepeel within the interval of observed values between 10 and 120  $\mu\text{g}/\text{m}^3$  by an expanded 95 %-uncertainty of 7 %. At Bottrop, an expanded uncertainty of 1,8 % was found within the concentration range between 10 and 250  $\mu\text{g}/\text{m}^3$ .

For nitrogen dioxide, the data quality objective of 15 % was fulfilled within the interval between 10 and 90  $\mu\text{g}/\text{m}^3$  by an expanded 95 %-uncertainty of 10 % at Vredepeel. At Bottrop, an expanded uncertainty of 18 % was evaluated for nitrogen dioxide within the concentration range between 10 and 190  $\mu\text{g}/\text{m}^3$ . This underlines that especially in the case of nitrogen dioxide all measurements should be checked very attentively.

For sulphur dioxide, the data quality objective of 15 % was safely met at Bottrop with an expanded uncertainty of 8 % within a concentration range between 10 and 200  $\mu\text{g}/\text{m}^3$ . At Vredepeel an expanded 95 %-uncertainty of 18 % was found within the interval between 10 and 35  $\mu\text{g}/\text{m}^3$ , which can partly be attributed to the low concentrations compared with the limit value. For the pooled data set 9 % were estimated.

For particulate matter PM10, the data quality objective of 25 % was fulfilled at Bottrop both for FH62 and TEOM instrumentation. At Vredepeel, the data quality objective of 25 % was exceeded for FH62 by an expanded 95 %-uncertainty of 40,5 % and for TEOM by an expanded 95 %-uncertainty of 30,6 %. At this site, the signal-proportional deviation (bias) provided a considerable contribution to measurement uncertainty.

These results indicate that for FH62 and TEOM instruments an expanded 95 %-uncertainty of about 25 % can be achieved, even when using a general correction factor.

These results for PM are generally consistent with those of a comprehensive experiment performed in Wiesbaden by the German Länder (states) in 2003 [9, 10]. This study already underpinned that the application of correction factors for automated PM10 measurement methods is mandatory but does not necessarily ensure that the data quality objectives are met .

First results with newly developed PM10-measurement equipment, e. g. TEOM-FDMS or modified beta gauge techniques gained in various European countries, indicate that significantly smaller uncertainties may be achievable in the future.

These results of the joint study underline the extraordinary value of the performed inter-comparison between RIVM and LUA assessing data quality of ambient air measurements.

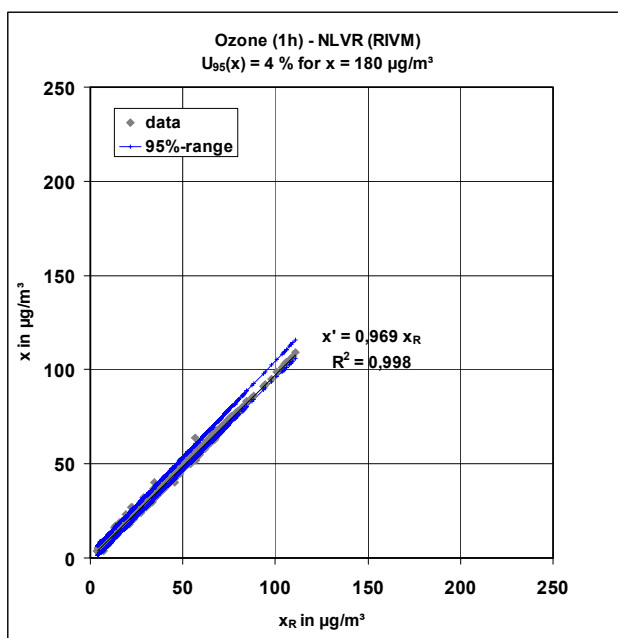
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- [2] Council Directive 1999/30/EC of 22 April 1999 relating to limit values for sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter and lead in ambient air, Official Journal of the European Communities No L 163/41-60
- [3] Directive 2002/3/EC of 12 February 2002 relating to ozone in ambient air, Official Journal of the European Communities No L 67/14-30
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- [6] [www.lua.nrw.de](http://www.lua.nrw.de)
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KRdL-Experten-Forum Staub und Staubinhaltsstoffe 10./11. November 2004, KRdL-Schriftenreihe 33, S. 171-186 (2004)
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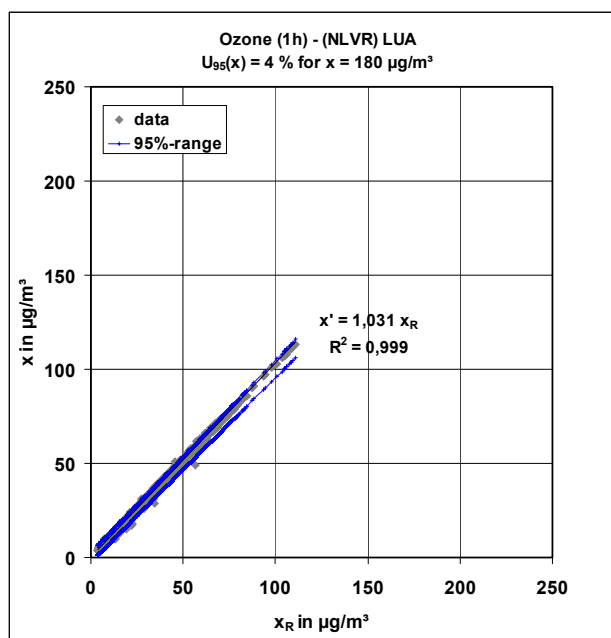
## 12 Annex

### A Ozone

#### A.1 Vredepeel

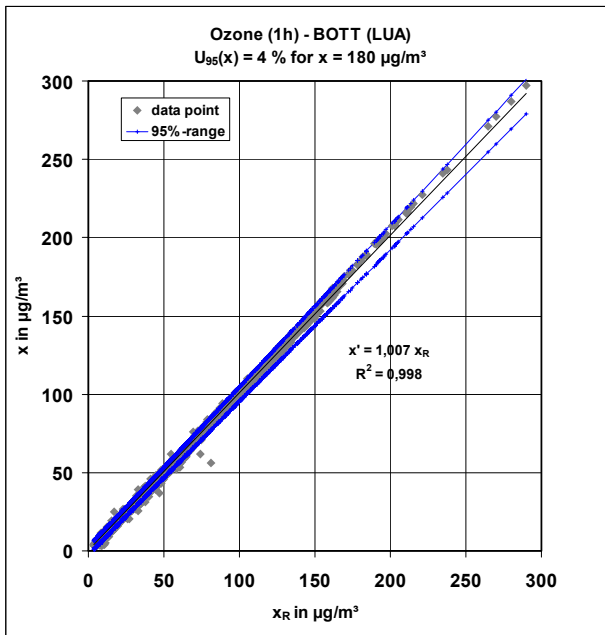


**Figure A.1:** Distribution of hourly values  $x$  of ozone observed by RIVM at Vredepeel (NLVR) about reference value  $x_R = (x_1 + x_2)/2$  obtained as mean value of RIVM and LUA instruments.

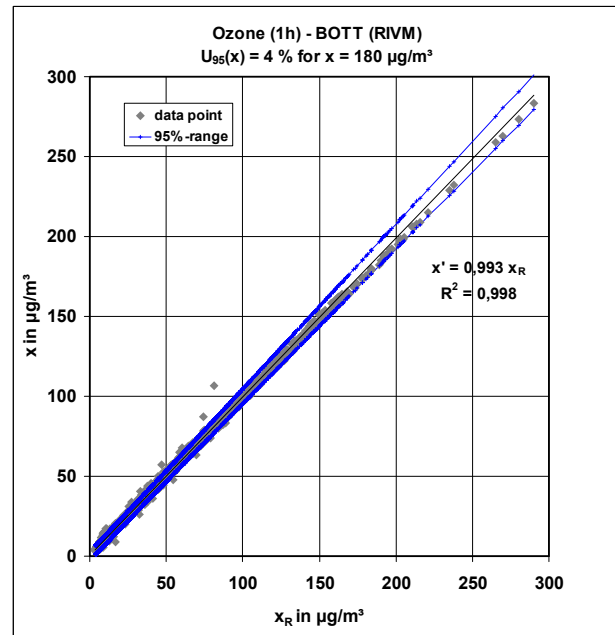


**Figure A.2:** Distribution of hourly values  $x$  of ozone observed by LUA at Vredepeel (NLVR) about reference value  $x_R = (x_1 + x_2)/2$  obtained as mean value of RIVM and LUA instruments.

## A.2 Bottrop



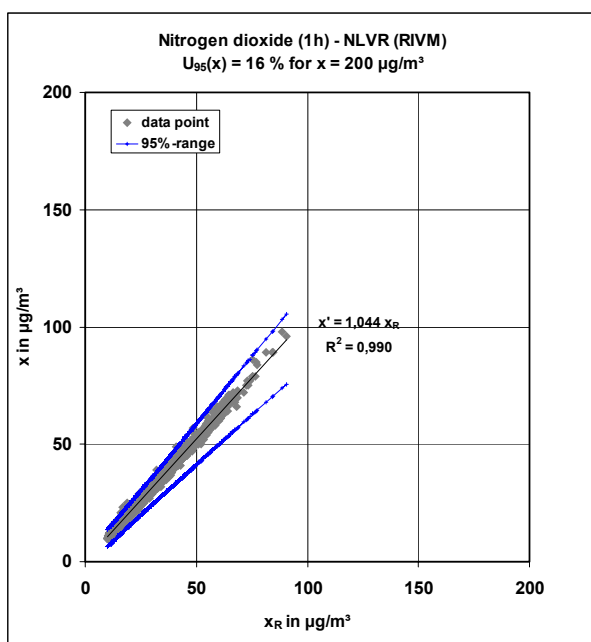
**Figure A.3:** Distribution of hourly values  $x$  of ozone observed by RIVM at Bottrop (BOTT) about reference value  $x_R = (x_1 + x_2)/2$  obtained as mean value of RIVM and LUA instruments.



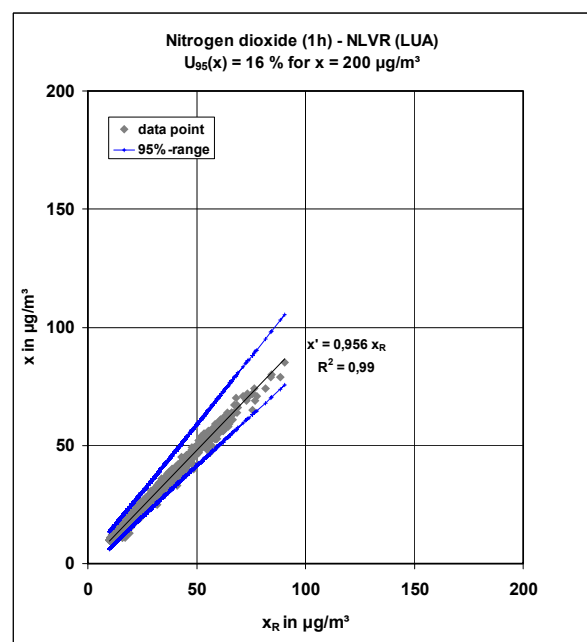
**Figure A.4:** Distribution of hourly values  $x$  of ozone observed by LUA at Bottrop (BOTT) about reference value  $x_R = (x_1 + x_2)/2$  obtained as mean value of RIVM and LUA instruments.

## B Nitrogen dioxide

### B.1 Vredepeel



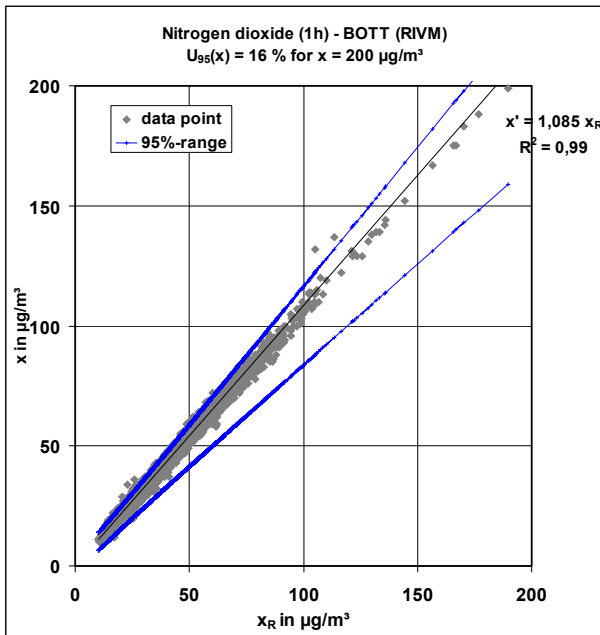
**Figure B.1:** Distribution of hourly values  $x$  of nitrogen dioxide observed by RIVM at Vredepeel (NLVR) about reference value  $x_R = (x_1 + x_2)/2$  obtained as mean value of RIVM and LUA instruments.



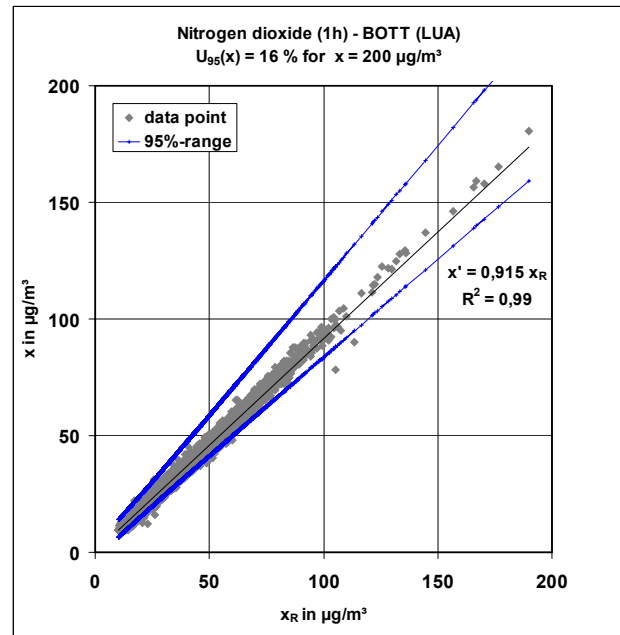
**Figure B.2:** Distribution of hourly values  $x$  of nitrogen dioxide observed by LUA at Vredepeel (NLVR) about reference value  $x_R = (x_1 + x_2)/2$  obtained as mean value of RIVM and LUA instruments.



## B.2 Bottrop



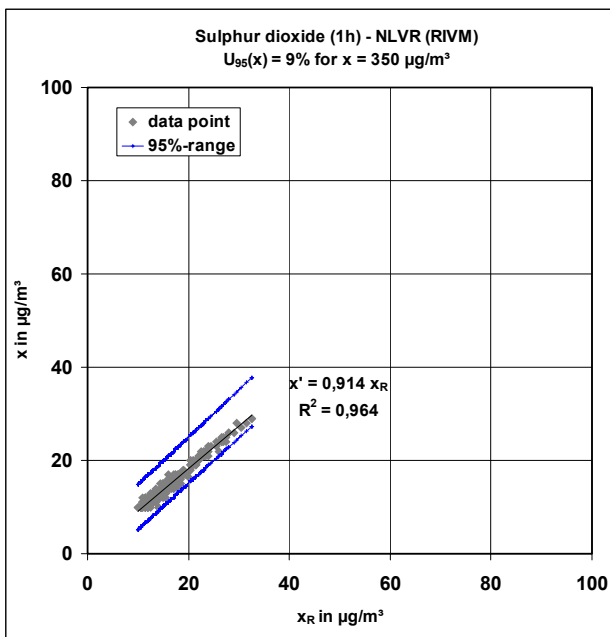
**Figure B.3:** Distribution of hourly values  $x$  of nitrogen oxide observed by RIVM at Bottrop (BOTT) about reference value  $x_R = (x_1 + x_2)/2$  obtained as mean value of RIVM and LUA instruments.



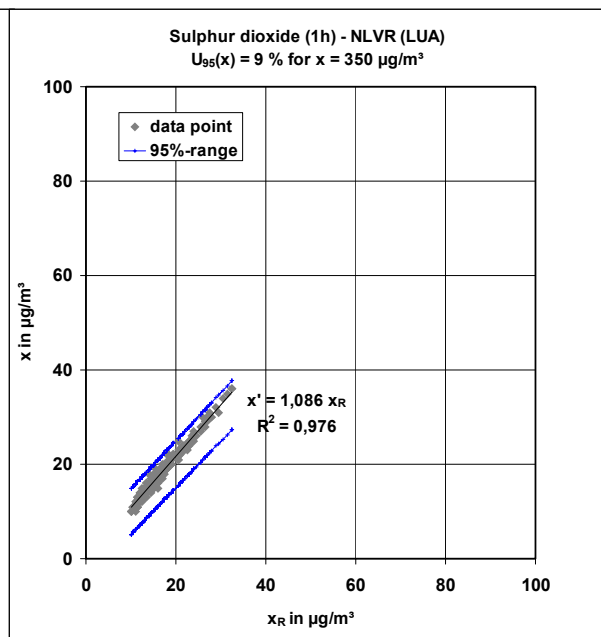
**Figure B.4:** Distribution of hourly values  $x$  of nitrogen oxide observed by LUA at Bottrop (BOTT) about reference value  $x_R = (x_1 + x_2)/2$  obtained as mean value of RIVM and LUA instruments.

## C Sulphur dioxide

### C.1 Vredepeel

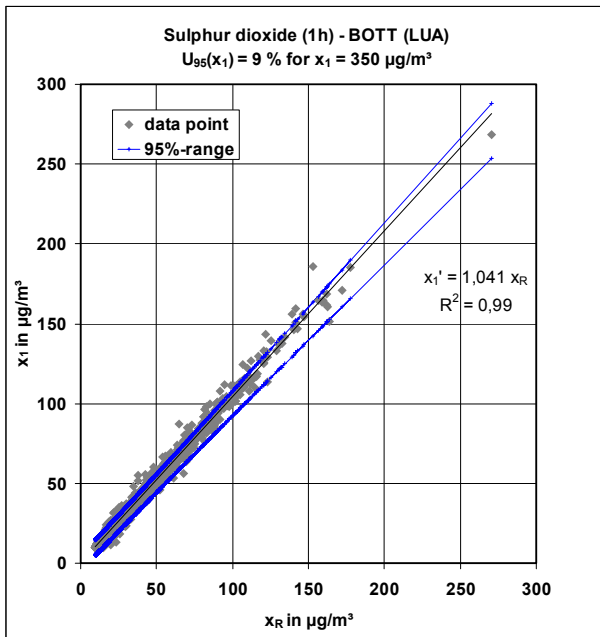


**Figure C.1:** Distribution of hourly values  $x$  of sulphur dioxide observed by RIVM at Vredepeel (NLVR) about reference value  $x_R = (x_1 + x_2)/2$  obtained as mean value of RIVM and LUA instruments.

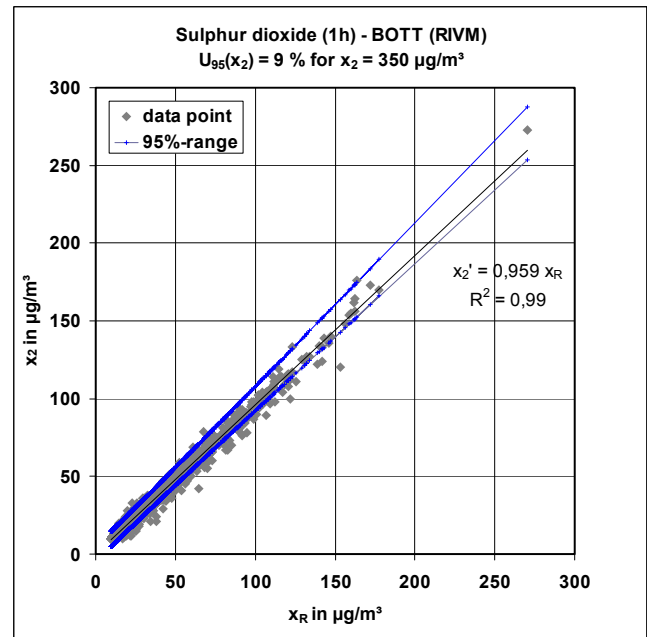


**Figure C.2:** Distribution of hourly values  $x$  of sulphur dioxide observed by LUA at Vredepeel (NLVR) about reference value  $x_R = (x_1 + x_2)/2$  obtained as mean value of RIVM and LUA instruments.

## C.2 Bottrop



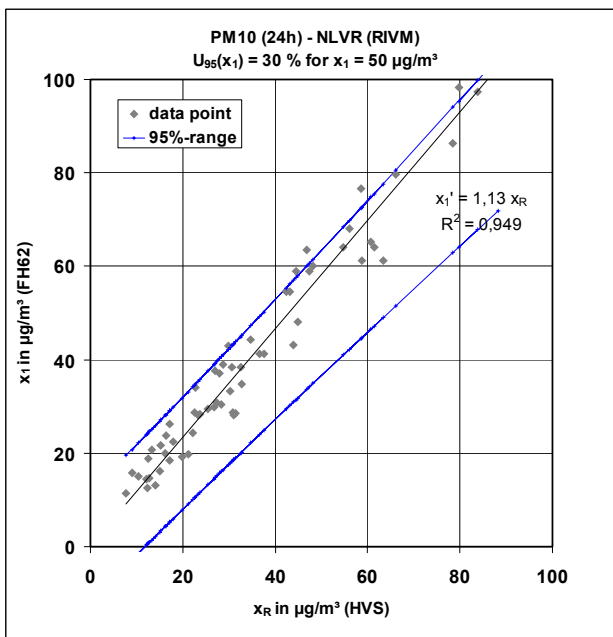
**Figure C.3:** Distribution of hourly values  $x$  of sulphur dioxide observed by RIVM at Bottrop (BOTT) about reference value  $x_R = (x_1 + x_2)/2$  obtained as mean value of RIVM and LUA instruments.



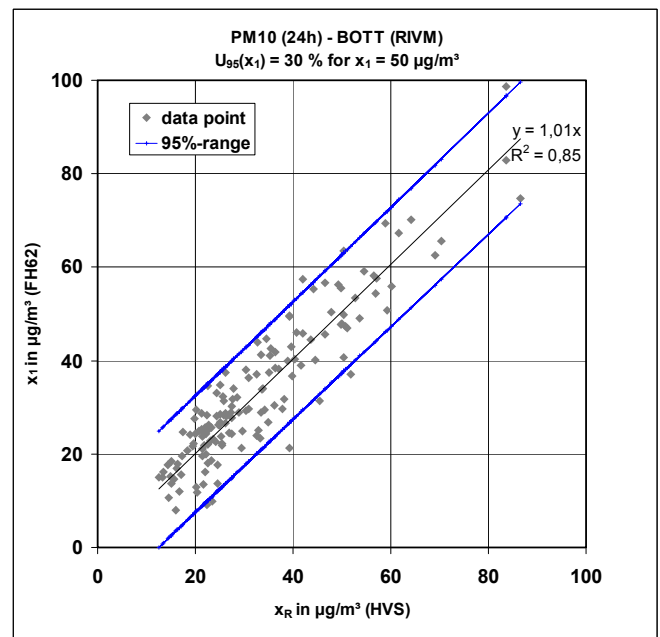
**Figure C.4:** Distribution of hourly values  $x$  of sulphur dioxide observed by LUA at Bottrop (BOTT) about reference value  $x_R = (x_1 + x_2)/2$  obtained as mean value of RIVM and LUA instruments.

## D Particulate matter PM10

### D.1 Measuring system FH 62

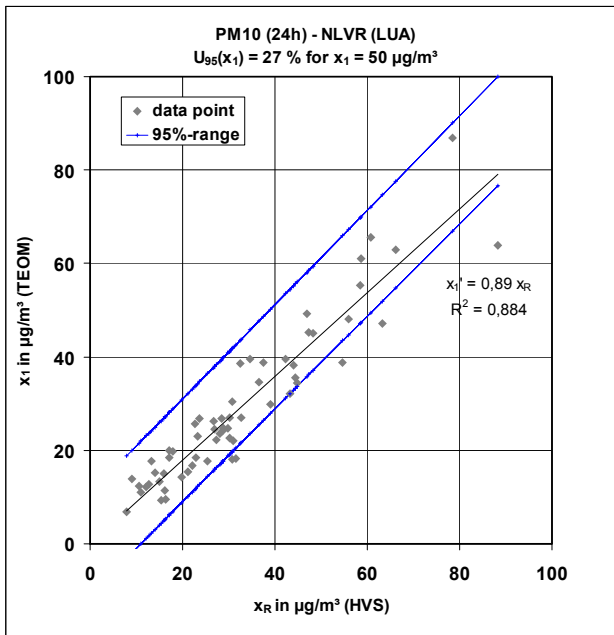


**Figure D.1:** Distribution of daily mean values  $x$  of PM10 provided by FH62 operated by RIVM at Vredepeel (NLVR) about reference value  $x_R = x_{\text{HVS}}$ .

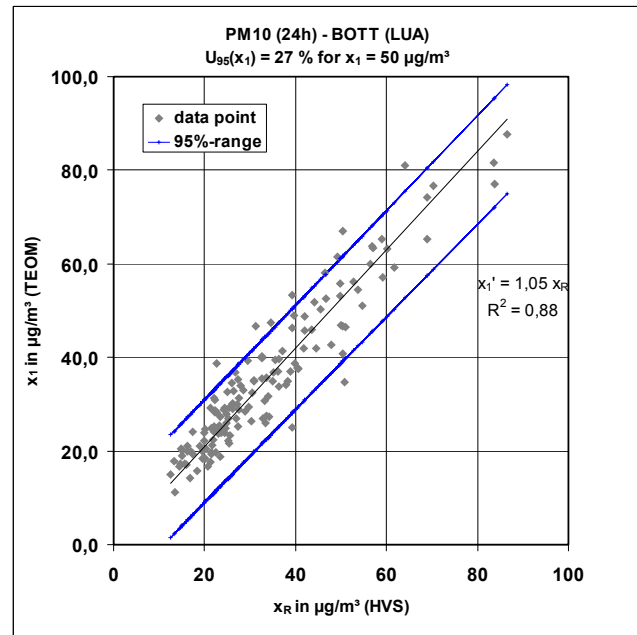


**Figure D.2:** Distribution of daily mean values  $x$  of PM10 provided by FH62 operated by RIVM at Bottrop (BOTT) about reference value  $x_R = x_{\text{HVS}}$ .

## D.2 Measuring system TEOM



**Figure D.3:** Distribution of daily mean values  $x$  of PM10 provided by TEOM operated by LUA at Vredepeel (NLVR) about reference value  $x_R = x_{\text{HVS}}$ .



**Figure D.4:** Distribution of daily mean values  $x$  of PM10 provided by TEOM operated by LUA at Bottrop (BOTT) about reference value  $x_R = x_{\text{HVS}}$ .