

Review of long term cross border cooperation between the Netherlands and Lower Saxony (Germany) in the field of air quality monitoring



Niedersachsen



Staatliches Gewerbeaufsichtsamt Hildesheim

rivm

National Institute
for Public Health
and the Environment

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Summary

During a 10 year period (1998 - 2007) the Lufthygienisches Überwachungssystem Niedersachsen: LUEN (Lower Saxony/Germany) and the National Institute for Public Health and the Environment RIVM (Netherlands) have carried out a number of field inter comparisons as part of their ongoing quality assurance efforts to produce comparable air quality data in our neighbouring countries.

As a general conclusion, field inter comparisons are very useful to check inter comparability.

Basic requirements determining the quality of such field inter comparisons are amongst others collocated monitoring, comparable inlet sampling, adequate function control procedures (regarding both the monitoring and the calibration systems) and comparable treatment of the monitoring data. Also, proper documentation is of key importance.

Experience has shown once again the possibility of occasional measurement and/or calibration errors, despite intensive quality control. However due to periodic field comparisons such errors can be detected and taken care for.

These results do underline the extraordinary value of cross border inter comparisons to obtain comparable data at both sides of the border.

The cooperation led to a constructive improvement in the quality of the data produced by each institute and showed us how to improve the international comparability.

It also shows that mutual, personal contacts are important for an adequate exchange of air quality information as well as a high level quality notion.

Hence, it is considered as highly worthwhile to establish and maintain an appropriate platform to ensure a fruitful cooperation between our two countries.

Amongst others, a regular field inter comparison programme should be considered regarding notably EU regulatory air quality parameters.

Zusammenfassung

Über einen Zeitraum von 10 Jahren (1998 - 2007) haben das Lufthygienische Überwachungssystem Niedersachsen (LUEN) in Deutschland und das Reichsinstitut für Gesundheit und Umweltschutz der Niederlande (RIVM) eine Reihe von Feldvergleichsmessungen als Teil der Qualitätssicherung und zur Gewährleistung der Vergleichbarkeit der in den benachbarten Messnetzen gewonnenen Daten durchgeführt.

Die gewonnenen Erfahrungen haben gezeigt, dass trotz intensiven Qualitätsmanagements gelegentlich Mess- und Kalibrierfehler auftreten können.

Feldvergleichsmessungen sind geeignet, um solche Probleme festzustellen.

Die Resultate unterstreichen die Wichtigkeit solcher grenzüberschreitender Kooperationen um vergleichbare Ergebnisse auf beiden Seiten der Grenze zu erhalten.

Diese Zusammenarbeit führte zu einer konstruktiven Verbesserung in der Datenqualität der beiden Organisationen und zu Hinweisen für weitere Verbesserungen bei internationalen Vergleichen.

Samenvatting

In de periode 1998 – 2007 hebben het Duitse Lufthygienisches Überwachungssystem Niedersachsen (LUEN) uit Neder-Saksen en het RIVM een aantal vergelijkende meetcampagnes uitgevoerd. Doel was vergelijkbaarheid en kwaliteit van de wederzijdse metingen te verbeteren. De campagnes hebben waardevolle informatie opgeleverd op meerdere vlakken, vooral over de mogelijke gevolgen van de verschillende instellingen van technische aspecten, zoals kalibratie methoden, onderhoudsprocedures en data behandeling. Juist periodieke veldvergelijkingen dwingen ertoe om het eigen meetnetwerk kritisch te blijven bezien.

In dit licht worden internationale vergelijkingen dan ook gezien als zeer ondersteunend voor de kwaliteit van zowel nationale meetgegevens als internationale vergelijkbaarheid. Structurele wederzijdse persoonlijke contacten zijn hierbij van wezenlijk belang.

Het is daarom aan te bevelen om regelmatig vergelijkende meetcampagnes in 't veld uit te voeren, onder andere gericht op de EU componenten. Juist zulke periodieke veldvergelijkingen dwingen ertoe om het eigen monitoring netwerk kritisch te blijven bezien.

1 Introduction

The EU Directive 1996/62/EC and the recent one 2008/50/EC [1] on Ambient Air Quality define as objective, inter alia, “to assess the ambient air quality in Member States (MS) on the basis of common methods and criteria” (Article 1). This implies (among others) that the MS assessments of air quality should be harmonized in order to avoid discontinuities between MS, notably in view of:

- Unequivocal, comparable assessment of air quality concentrations, and
- Unequivocal and clear dissemination of air quality information to the general public and the (local) governments.

Specifically this is important when it comes to comparison of air quality data from Air Quality Monitoring Networks in neighbouring countries like Lower Saxony/Germany and the Netherlands. Hence, during a 10 year period (1998 – 2007) the Lufthygienisches Überwachungssystem Niedersachsen: LUEN (Lower Saxony/Germany) and the National Institute for Public Health and the Environment: RIVM (Netherlands) have carried out a number of simultaneous measurement exercises as part of their quality assurance efforts to produce mutually comparable air quality data.

This report summarizes the experiences from these 10 years of comparative measurements in operational monitoring networks, as part of the continuous effort to improve data quality and comparability.

2 Harmonization of air quality measurements in EU

Article 1 of the Directives 96/62/EC respectively 2008/50/EC requires assessment of air quality on a consistent basis across the European Union. In this respect, key elements are:

- *Standard Measurement Methods*

EU Member States must employ standard measurement techniques, the so called EU reference methods. Harmonized methodologies from CEN standards are preferred, but also any other method equivalent to the reference method may be used.

- *QA/QC procedures*

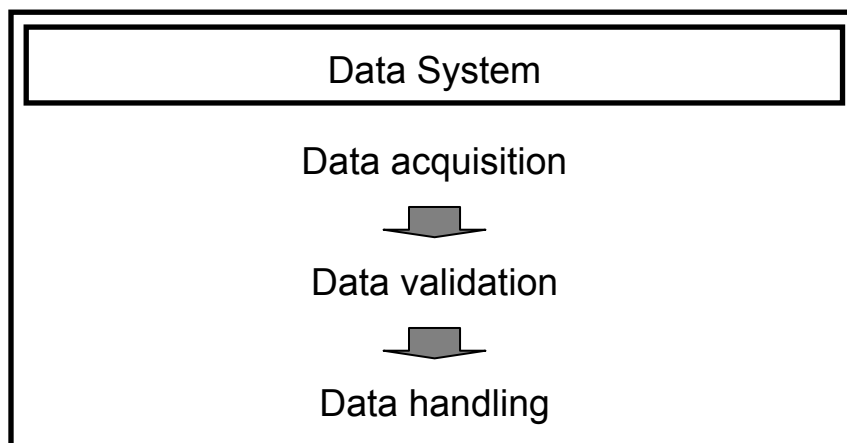
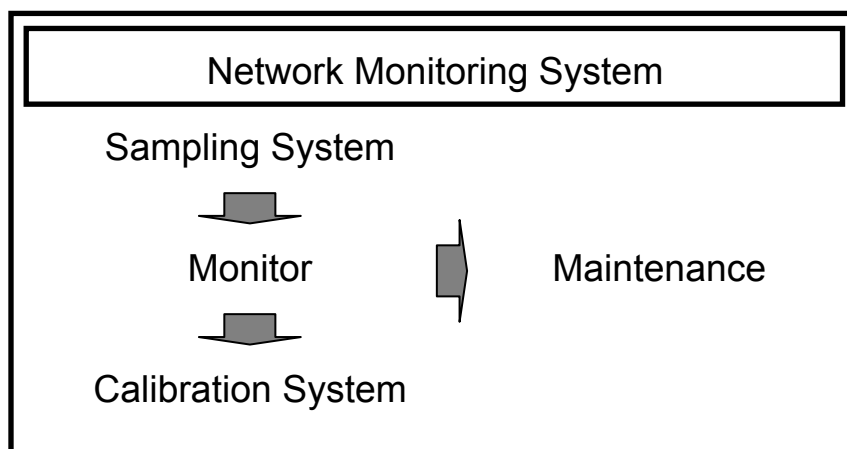
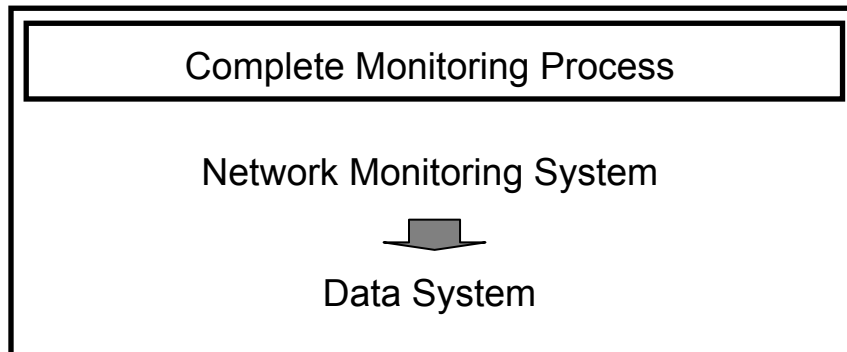
Article 3 of the aforementioned Directives 96/62/EC requires “quality controls carried out in accordance, inter alia, with the requirements of EU quality assurance standards”, in order to meet the pertinent quality objectives for measurement results. The recent Directive 2008/50/EC defines the responsibilities when it comes to ensuring the accuracy of the measurements. Note that QA/QC is nowadays a permanent part of CEN standard methods.

- *Inter comparison programs*

Inter comparison campaigns between monitoring networks under full operational field conditions are a *conditio-sine-qua-non*. For, data quality of monitoring networks can only be determined when all favourable and unfavourable conditions during network operation are being dealt with.

Next to such field comparisons, also periodic ring exercises in the laboratory regarding calibration and/or transfer standards are essential. Basically, the technical monitor performance is assessed under ideal laboratory conditions. However, such dedicated laboratory inter comparisons do not necessarily reflect the normal operating conditions during field monitoring.

Ideally, field inter comparisons should cover the complete monitoring process, i.e. from sampling to data acquisition and data storage. Such a complete monitoring process can be considered as a two step process, consisting of a Network Monitoring System followed by a Data System, as shown in the following scheme:



3 Field inter comparisons: General procedures

To check the comparability of cross border air quality data, field inter comparisons are an important tool. Basic elements in such inter comparisons are:

- Multi parallel measurements of the air quality components upon consideration
- Monitoring is carried out on site and under field conditions
- Monitoring processes are done institute specific and independent from each other.

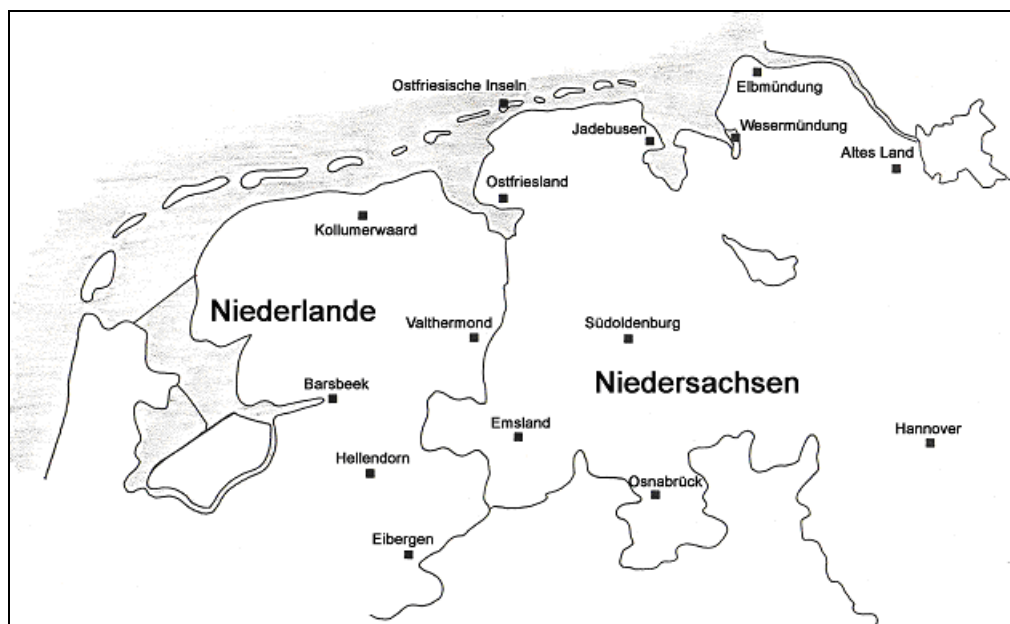
As mentioned above, a field inter comparison ideally should cover the complete monitoring process. However, quite often calibration is limited to the monitor itself, and does not include inlet sampling and the connecting tubing.

4 Field inter comparisons campaigns: Set up

In the period 1998 – 2007 Lower Saxony/Germany and the Netherlands have carried out a number of field inter comparison campaigns, regarding:

- Ozone, during summer 1998 at the Dutch monitoring network site Kollumerwaard in the north of the country [2].
- A complete set of EU FWD components, in 2001 at the Lower Saxony monitoring network site Osnabrück [3].
- A complete set of EU FWD components, in the period 2004 - 2007 at the Dutch monitoring network site Valthermond in the north-eastern part of the Netherlands, about 15 kilometres from the Dutch-German border [4].

Figure 1: Map of NL and Lower Saxony showing some monitoring locations that are used by RIVM and LUEN



4.1 Ozone comparison, 1998

During summer 1998 an ozone field comparison was carried out because of suspicious high ozone values were observed in the north-western part of Lower Saxony as compared to levels in the neighbouring regions in the Netherlands and Lower Saxony itself. The campaign was carried out at the remote background site Kollumerwaard in the very northern part of the Netherlands, far away from various local and regional influences. Appendix 1 gives a detailed overview of the employed Ozone monitoring systems and procedures Appendix 2 gives an overview of the Kollumerwaard measurement site.

As a result of this cooperation both monitoring networks were able to better harmonize their respective ozone calibration procedures.

4.2 Field comparison Osnabrück, 2001

In 2001 a full year campaign was carried out in the south-western suburban part of Osnabrück. The site can be characterised as urban background with the German highway E30 about 1 km south, and an urban street with heavy traffic about 500 m in east direction. The air quality components involved were the EU FWD components, namely the gaseous ones sulphur dioxide, nitrogen oxides, ozone and carbon monoxide, and Fine Dust PM₁₀. Both institutes carried out the measurements in their own separate measurement cabins, completely independent from each other.

Appendix 1 gives a detailed overview of the employed monitoring systems and procedures; Appendix 3 details the Osnabrück measurement site.

4.3 Field comparison Valthermond, 2004 - 2007

During the period 2004 - 2007 a permanent campaign was carried out at the rural site Valthermond of the Dutch monitoring network.

The monitoring equipment of both institutes was installed in the same cabin, but with completely independent systems with separate sampling inlets and data processing. The air quality components involved were as before the EU FWD components, namely the gaseous ones sulphur dioxide, nitrogen oxides, ozone and carbon monoxide and Fine Dust PM₁₀, and also Ammonia.

As before, Appendix 1 gives a detailed overview of the employed monitoring systems and procedures, and Appendix 4 details the Valthermond measurement site.

4.4 Concentrations

Appendix 5 gives an overview of the measured concentration values, i.e. yearly averages.

For the detailed concentration values see the respective internet sites: <http://www.luen-ni.de> and <http://www.lml.rivm.nl> regarding the Lower Saxony or Netherlands monitoring results.

5 Field inter comparisons campaigns: Lessons Learned

As main observation, the monitors itself do perform correctly. But the following peripheral issues are of prime importance when judging inter comparability:

- Calibration
- Maintenance
- Data treatment of small concentration values, i.e. small positive values (< Lower Detection Limit LDL) and (even) negative ones.

5.1 Calibration

It goes without saying that differences in the calibration and/or transfer standards employed in the monitoring networks will result in concomitant systematic differences between observed concentration values. As a consequence, also systematic differences will be found in statistical parameters like e.g. average values or percentile ones.

When determining each others calibration and/or transfer standards in the field, it shows:

- NO_x (NO₂) calibration gases are within a few %
- O₃: a systematic difference was observed between the Gas Phase Titration procedure used in NL and UV-photometry employed by Lower Saxony.

However, it has to be pointed out that this difference is (probably) not due to differences in the transfer standards (less then some 3 %), but for a greater part to lacking maintenance.

- PM₁₀ calibration foils are within few %.

In terms of monitoring uncertainty, this implies a so called B-type contribution (based on a model equation describing the measurement process), on the order of 1 – 2 % at most. This can be considered as very satisfactory.

5.2 Maintenance

Maintenance shall follow the prescriptions from the pertinent SOPs, especially when it comes to the periodic cleaning of the connecting tubing of the complete monitoring system. If not, differences on the order of 10 % are easily possible; such differences have been observed indeed. An easy check is by comparing each others transfer standards as mentioned before.

The following example serves to illustrate this.

For Ozone, a systematic difference was observed between the GPT procedure used in NL and the UV-photometry employed by Lower Saxony. RIVM did underestimate the Lower Saxony standard by some 16 %, on the same order as the observed difference between the pertinent annual O₃ averages. Upon close inspection of the RIVM calibration procedure, it showed that the calibration did not include the inlet sampling and the connecting tubing, hence limiting the calibration *only to the monitor itself*. Due to lacking maintenance of the connecting tubing, it is thought that ambient sampled Ozone will be partly removed, giving rise to lower observed O₃ values.

Again it shows that one should stick to FEP prescribed instead of PTFE tubing (although it seems tempting to use PTFE when FEP is not at hand). PTFE tubing could give rise to some 3 % loss of Ozone.

The dust filter to protect the monitor should be as close as possible to the inlet, and not just in front of the monitor. Although in the latter situation it is possible to calibrate the effect of the filter together with the monitor, a prohibitive deterioration of the inlet tubing will result.

5.3 Data treatment at low concentrations

The monitoring data are collected and treated by each institute according to its own standard procedures. It shows that our different monitoring networks are applying different acceptance rules for low or negative concentration values.

Basically, three ranges are distinguished, viz. Monitoring Value MV “positive”, “negative” or “in between”; see Table 1.

Table 1: Acceptance rules of concentration values zero

MV (µg/m ³)	RIVM	LUEN
MV > + LDL	MV	MV
- LDL < MV < + LDL	MV	+ 0.5 x LDL
MV < - LDL	Data disapproved	Data disapproved

The detailed acceptance rules of both institutes are given in Appendix 1.3.

The effects of the differences in data treatment are shown in the following example for the year 2004 at Valthermond: see Table 2.

Firstly, the results are shown using the standard data treatment procedures per institute. As quite low concentrations are observed, these different acceptance rules exert a relatively high influence on the averages (on the order of 10 %).

Next, the results are shown using similar data treatment. For that purpose only the so called “positive values” were used; all data from the so called “negative” and “in between” ranges were deleted (for NO and NO₂, below 3.0 µg/m³, for O₃ below 2.0 µg/m³, for PM₁₀ below 5.0 µg/m³ and for NH₃ below 2.0 µg/m³).

It goes without saying that averaging was only done if the data from both monitors were simultaneously available.

Table 2: 2004 Annual averages for LUEN and RIVM with institute specific and with similar data treatment (based on preliminary data)

Component	Specific data treatment			Similar data treatment		
	LUEN	RIVM	Diff.	LUEN	RIVM	Diff.
	µg/m ³	µg/m ³	%	µg/m ³	µg/m ³	%
NO	3.0	2.7	10.7	10.4	10.5	1.7
NO ₂	14.2	13.3	6.3	14.3	13.9	2.8
O ₃	48.4	41.5	12.2	52.0	43.7	16.0
PM ₁₀	21.7	18.8	13.4	27.7	27.6	0.4
<i>Revalidation & Recalibration</i>		24.2	11.5		26.9	2.8
NH ₃	3.56	3.17	11.2	5.06	3.84	24.1

Note that the figures under “similar data treatment” do not represent the real average values, since all low values have been deleted. This implies a significant influence when it comes to lower averages, like NO and to a lesser extent PM₁₀. For ever increasing annual averages, the influence obviously will be decreasing; see e.g. O₃.

It is seen that for the greater part the differences between LUEN and RIVM averages do disappear for NO, NO₂ and PM₁₀. In other words, institute specific data treatment plays an important role in explaining the observed differences between average values, notably for NO, NO₂ and PM₁₀.

For O₃, the differences did increase using similar data treatment. It is thought that this increase might be explained from the lacking RIVM inlet tubing maintenance, afore mentioned.

Note regarding PM₁₀.

In 2006 a thorough check has been carried out in the Netherlands on the operating procedures, the monitoring devices and the various settings in the Netherlands National Air Quality Monitoring Network. Subsequently, a revalidation of measurement results had to be carried out, however with only very minor consequences [5].

In the report of reference 4 the 2004 PM₁₀ raw data from RIVM were multiplied using the interim EU default calibration factor of 1,3.

Also in 2006, an equivalence study has been carried out to determine the equivalence between the automatic PM₁₀ monitors in NL and the EU reference method. Based on this study, the automatic PM₁₀ measurements in the Netherlands have been recalibrated, starting from monitoring type dedicated calibration functions for regional and urban situations (instead of applying one calibration factor of 1,3) [5].

The thus recalculated PM₁₀ results are shown in table 2 as *italics*. It is concluded that the basic findings do not differ materially from the original conclusions in ref. 4.

As to the yearly air quality averages we conclude that they are:

- Gases: to within $\pm 5\%$, and
- PM₁₀: to within some $2\ \mu\text{g}/\text{m}^3$.

Compared to the annual PM₁₀ limit value of $40\ \mu\text{g}/\text{m}^3$ the agreement is to within some 5% , i.e. already some 10% extended uncertainty out of the pertinent EU Data Quality Objective of 25% . This is a relatively important difference given the societal impact of PM₁₀ where “every $\mu\text{g}/\text{m}^3$ counts”!

Especially in low level background areas (like in the Valthermond area between NL and Lower Saxony) with yearly PM₁₀ averages of ca. $20\ \mu\text{g}/\text{m}^3$, the difference is even more important (ca 10%).

As to NH₃, the following does apply.

The NH₃-NO_y TE42 monitor used by LUEN to detect NH₃ is based on thermal conversion at circa $850\ ^\circ\text{C}$ to convert total-N to NO_x, followed by chemiluminescent detection of NO_x. In this way not only NH₃ is converted into NO_x, but also other gaseous components like nitric acid and (nitrate-, sulphate-) ammonium aerosol. This results in over reading of NH₃, especially at low concentrations. The NH₃ levels are rather low (circa $4\ \mu\text{g}/\text{m}^3$), whereas the ammonium aerosol is on the order of $1\ \mu\text{g}/\text{m}^3$. And by that, and taking into account the different LDL's (LUEN 1,5 vs. RIVM 0,12 $\mu\text{g}/\text{m}^3$) the difference between LUEN and RIVM (LUEN reading somewhat higher than RIVM, viz. some $5\ \mu\text{g}/\text{m}^3$ vs. $4\ \mu\text{g}/\text{m}^3$) seems plausible.

Apparently, the differences (both in absolute and in relative sense) between LUEN and RIVM are steadily decreasing throughout the years. See Table 3.

Table 3: Ammonia yearly concentration levels

Year	LUEN	RIVM	Difference LUEN – RIVM	
	Yearly average ($\mu\text{g}/\text{m}^3$)		Absolute ($\mu\text{g}/\text{m}^3$)	Relative to RIVM (%)
2004	3.88	2.85	1.03	36.1
2005	4.68	4.29	0.39	9.1
2006	5.16	4.73	0.43	9,1
2007	3.69	3.49	0.20	5.7

From this comparison it is thought that the automatic thermo catalytic system can be used as indicative total ammonium / NH_3 monitor with a high time resolution.

Recently, a detailed study under field and laboratory conditions has been carried out to test the performance of a number of ambient ammonia monitors. The monitoring techniques involved were sampling ones (Denuder, Laser Cavity Ring Down LCRD, Photo Acoustics and Thermal Conversion) and the non sampling in-situ long path Differential Optical Absorption Spectroscopy DOAS technique. The final report regarding this study is foreseen by the end of this year 2008 [6].

6 Conclusions

During 10 years a field comparison of standard air pollutants has been carried out by Lower Saxony-Germany and RIVM-NL. The main aim was to investigate the comparability of the mutual cross border Air Quality Monitoring Networks under full field operating conditions.

Main aspects determining the validity of such inter comparison campaigns are:

- collocated measurements at the same location
- comparable inlet sampling conditions
- adequate function control procedures and handling of calibration / transfer standards
- comparable data treatment and validation procedures
- complete documentation.

Key findings playing an important role in determining inter comparability are (amongst others):

- Inter comparisons of transfer standards are very useful for revealing:
 - systematic differences between these transfer standards,
 - internal drift, and
 - lacking maintenance.For, differences in calibration will result in systematic differences between observed concentration values, hence corresponding statistical parameters like e.g. average values.
Hence, it is very useful to perform periodic evaluations of the mutual (calibration) results, to adequately deal in time with notably internal drifts and / or maintenance problems
- Similar data treatment procedures:
if not, comparability is obscured by mutual different data treatment.
- Maintenance: follow the prescriptions!

As a general conclusion, field inter comparisons are very useful to check inter comparability. Bitter experience has shown once again the possibility of occasional measurement and/or calibration errors, despite intensive quality control. However due to periodic field comparisons such errors can be detected and taken care for.

These results do underline the extraordinary value of such cross border inter comparisons to obtain comparable data at both sides of the border.

The cooperation led to a constructive improvement in the quality of the data produced by each institute and showed us how to improve the international comparability. Additional benefits of such cross border cooperation's are amongst others:

- Personal contacts between the co-workers
 facilitating direct contacts, and overcoming language problems.
- Improved communication between our monitoring networks
- Exchange of mutual monitoring experience and know-how

7 Outlook

The permanent inter comparison of RIVM and Lower Saxony at the border site Valthermond has been terminated per January 2008. The objective was to improve the comparability, and thus the quality, of the measurements. International comparisons turned out to be highly supportive of the quality of national measurements. It shows that mutual, personal contacts are important to establish and to maintain an adequate exchange of air quality information as well as a high level quality notion.

Hence, to ensure a fruitful cooperation between our two countries, the following is proposed:

- Periodic meetings to keep each other informed.
- Periodic field inter comparisons, regarding the pertinent EU air quality components. Such comparisons should take place alternately in the Netherlands and Lower Saxony in mutual characteristic situations.

As a first step, an inter comparison for PM_{2.5} monitors should be on top of the list. Such a inter comparison should include not only automatic PM_{2.5} monitors but also PM_{2.5} reference instruments.

In the Northwest of Lower Saxony near the Dutch border there is a considerable increase of plants for intensive mass animal farming, serving as an important source of ammonia. Therefore, a common interest could be an assessment based on a combination of modelling and measurements.

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Appendix 1: Monitoring Systems

This appendix successively describes the monitoring methods (1.1), calibration (1.2) and data treatment (1.3).

1.1 Monitoring methods

LUEN and RIVM use the same type of monitoring systems from the same manufacturer for the gaseous components NO, NO₂ and O₃ and particulate matter (PM₁₀). The NH₃ monitors are from different manufacturers and employ different measuring principles.

The main measurement characteristics of the monitoring systems are given in Table 1.1.1.

Table 1.1.1: The main measurement characteristics of the monitoring systems

Sulphur dioxide [SO₂]	
Measuring instrument	Thermo Electron 43 C
Measuring principle	Chemiluminescence
Detection limit	2.0 µg/m ³
Nitrogen oxides [NO & NO₂]	
Measuring instrument	Thermo Electron 42
Measuring principle	Chemiluminescence
Detection limit	2.0 µg/m ³
Ozone [O₃]	
Measuring instrument	Thermo Electron 49
Measuring principle	Ultraviolet absorption
Detection limit	1.0 µg/m ³
Carbon monoxide [CO]	
Measuring instrument	Thermo Electron 48 C
Measuring principle	Ultraviolet absorption
Detection limit	600 µg/m ³
Calibration unit	
RIVM	SO ₂ , NO, NO ₂ , O ₃ , and CO
LUEN	SO ₂ , NO, NO ₂ , CO and NH ₃ O ₃ : internal function control

Table 1.1.1 (continued)

Particulate matter [PM₁₀]	
LUEN	
Measuring instrument	EMS FH 62 I-R with TRS-system heated at + 3 to + 8 °C over ambient temperature Inlet housing: 350 cm
RIVM	
Measuring instrument	EMS FH 62 I-R heated at + 10 °C over ambient temperature Inlet housing: 350 cm
Measuring principle	Attenuation of β radiation
Detection limit	4 µg/m ³
Remark	Due to underestimation of the particulate concentration in comparison to the reference method EN12341, a default correction factor is applied: - LUEN : 1.33 - RIVM : 1.3
Ammonia [NH₃]	
LUEN	
Measuring instrument	NH ₃ -NO _y Thermo Electron 42
Measuring principle	Chemiluminescence + Thermal conversion of total-N
Detection limit	1.5 µg/m ³
RIVM	
Measuring instrument	AMOR, ECN fabricate
Measuring principle	Absorption of NH ₃ in an acid solution followed by membrane separation and detection through conductance.
Detection limit	0.12 µg/m ³
Data Acquisition	
LUEN	By digital RS232 connection from monitors to PC
RIVM	By analogue connection from monitors to PC. Connection by telephone to database

1.2 Calibration and verification procedure

All monitors (from both institutes) are set such as to frequently check their own quality status (automatically on a daily basis). Although this is often referred to as “calibration”, it actually serves as “verification” of the monitor. The calibration is performed manually, as a rule during maintenance.

The difference between verification and calibration is roughly as follows:

- Verification results in a report of the monitor’s status to check whether the monitor responds within certain limits.
- Calibration involves adjusting the monitor’s hardware to meet certain criteria.

The verification and calibration methods for PM (calibration foils for PM₁₀) and NO_x (calibration gases) are similar for both institutes, but the verification methods for O₃ and NH₃ are different. Tables 1.2.1 and 1.2.2 give the details of the verification methods used.

Table 1.2.1: The verification methods used by LUEN

Component	Verification and calibration method	Frequency
SO₂	Span check: 300 µg/m ³ calibration gas from internal permeation tube Zero check: dry zero air	Every 25 th hour
	Permeation tube is checked with transfer standard	Every 4 months
NO & NO₂	Span check: 300 ppb calibration gas from NO gas bottle. Gas bottle is diluted 300 times from a 100 ppm NO calibration gas bottle. Zero check: dry zero air from permeation dryer	Every 25 th hour
	Calibration unit is checked with transfer standard (LN Industries 3012).	Every 4 months
O₃	Span check: internal UV lamp Zero check: dry zero air from permeation dryer	Every 25 th hour
	Lamp checked by transfer standard (TE 49PC).	Every 4 months
CO	Span check: 20 ppm calibration gas from CO gas bottle Zero check: dry zero air	Every 25 th hour
	Calibration unit is checked with transfer standard (LN Industries 3012).	Every 4 months

Table 1.2.1 (continued)

Component	Verification and calibration method	Frequency
PM₁₀	Filter change	At specific load of filter.
	Span and Zero check with calibration foils.	Every 4 months
NH₃	Continuous calibration with test gas from permeation tube.	Every 73 rd hour
	Calibration unit is checked with transfer standard (LN Industries 3014).	Every 4 months

Table 1.2.2: The verification methods used by RIVM

Component	Verification and calibration method	Frequency
SO ₂	Span check: 400 ppb calibration gas from SO ₂ calibration gas bottle Zero check: ambient humidity zero air	Every 25 th hour
	The calibration gas bottle is cross-checked with certified reference standard	Every year
NO & NO ₂	Span check: 600 ppb calibration gas from NO gas bottle. Gas bottle is diluted 500 times from a 300 ppm NO calibration gas bottle. Zero check: ambient humidity zero air	Every 24 th hour
	The calibration gas bottle is cross-checked with certified reference standard.	Every year
O ₃	Span check: ozone source from multigas calibrator by NO gas phase titration. Zero check: ambient humidity zero air	Every 24 th hour at midnight
	Multi gas calibrator is checked with transfer standard.	Every year
CO	Span check: 20 ppm calibration gas from CO calibration gas bottle Zero check: ambient humidity zero air	Every 25 th hour
	The calibration gas bottle is cross-checked with certified reference standard	Every 2 nd year
PM ₁₀	Filter change and deleting next hour.	Every 25 th hour
	Span and Zero check with calibration foils.	Every 3 months
NH ₃	Zero with absorption liquid and span check 2000 ppb NH ₄ ⁺ .	Every 80 th hour

1.3 Data treatment

Tables 1.3.1 and 1.3.2 give the details of the LUEN and RIVM validation procedures, as described in section 5.3.

Table 1.3.1: Validation procedure for LUEN on measurements near zero

Component	LDL [$\mu\text{g}/\text{m}^3$]	MV [$\mu\text{g}/\text{m}^3$]	Value taken
SO ₂	2	< - LDL - LDL < MV < + LDL > LDL	None; data disapproved 1 $\mu\text{g}/\text{m}^3$ MV
NO & NO ₂	2	< - LDL - LDL < MV < + LDL > LDL	None; data disapproved 1 $\mu\text{g}/\text{m}^3$ MV
O ₃	1	< - LDL - LDL < MV < + LDL > LDL	None; data disapproved 0.5 $\mu\text{g}/\text{m}^3$ MV
CO	600	< - LDL - LDL < MV < + LDL > LDL	None; data disapproved 300 $\mu\text{g}/\text{m}^3$ MV
PM ₁₀	4	< - LDL - LDL < MV < + LDL > LDL	None; data disapproved 2.0 $\mu\text{g}/\text{m}^3$ MV
NH ₃	1.5	< - LDL - LDL < MV < + LDL > LDL	None; data disapproved 0.75 $\mu\text{g}/\text{m}^3$ MV

LDL = Lower detection limit MV = Monitor value

Table 1.3.2: Validation procedure for RIVM on measurements near zero

Component	LDL [$\mu\text{g}/\text{m}^3$]	MV [$\mu\text{g}/\text{m}^3$]	Value taken
SO ₂	2	< - LDL > - LDL	None; data disapproved MV
NO & NO ₂	2	< - LDL > - LDL	None; data disapproved MV
O ₃	1	< - LDL > - LDL	None; data disapproved MV
CO	600	< - LDL > - LDL	None; data disapproved MV
PM ₁₀	4	< - LDL > - LDL	None; data disapproved MV
NH ₃	0.12	< - LDL > - LDL	None; data disapproved MV

LDL = Lower detection limit MV = Monitor value

**Appendix 2: Overview of the Kollumerwaard (NL)
measurement site**



**Appendix 3: Overview of the Osnabrück (Lower Saxony)
measurement site**



Appendix 4: Overview of the Valthermond (NL) measurement site



Appendix 5: Yearly concentration averages (final data)

Year	RIVM		LUEN
NO [$\mu\text{g}/\text{m}^3$]			
2004	2,6		2,9
2005	1,6		2,0
2006	1,6		2,0
2007	1,2		--
NO₂ [$\mu\text{g}/\text{m}^3$]			
2004	13,6		12,1
2005	13,3		10,2
2006	13,3		11,0
2007	11,1		--
NO_x [$\mu\text{g}/\text{m}^3$]			
2004	17,5		14,5
2005	15,6		12,2
2006	15,6		13,1
2007	12,9		--
O₃ [$\mu\text{g}/\text{m}^3$]			
2004	41,9		48,5
2005	39,7		48,4
2006	43,4		49,4
2007	38,7		47,9
PM₁₀ [$\mu\text{g}/\text{m}^3$]			
2004	24,6		21,7
2005	25,5		23,0
2006	27,2		25,0
2007	23,8		20,5
NH₃ [$\mu\text{g}/\text{m}^3$]			
2004	2,9		3,9
2005	4,3		4,7
2006	4,7		5,2
2007	3,5		3,7