



Air Quality Study in Relation to the
Environmental Impact Assessment (EIA)
for the Proposed Redevelopment of the
Ex-Jerma Palace

As per ERA requirements for PA/00437/23

Report



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 AIS Environment Ltd,
AIS House, 18, St. John Street,
Fgura, FGR 1447

 +356 21803374
 www.aisenvironment.mt
 info@ais.com.mt

VAT No: MT 1457-1625
Reg No: C18445

PART OF  AIS GROUP



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1 INTRODUCTION

This report outlines the outcomes from an air quality, to fulfil the Terms of Reference (ToRs) issued by ERA for PA/00437/23. The assessment focuses on the potential impacts on air quality from vehicular traffic caused by the operation of the proposed redevelopment of the ex-Jerma Palace hotel in Marsascala, henceforth referred to as the “Scheme”. It involves the demolition the existing dilapidated building, excavation the site to accommodate two subterranean levels and construction a new complex comprising of a new hotel, serviced apartments, commercial/retail outlets and a mixture of ancillary facilities.

The study made use of existing PM₁₀ and NO₂ data collected in 2019 as part of previous air quality studies carried out in the past for the same project. This update assessed the contribution of traffic from the revised plans and Traffic Impact Assessment.

1.1 OVERVIEW OF THE PROJECT AND SITE

The proposed facility incorporates the demolition of the ex-Jerma Palace Hotel, the excavation of the site and construction of a mixed-use resort.

The Jerma Palace Hotel started its operations in 1982 which ended abruptly in 2007 after the ownership of a Libyan Foreign Investment Company ended. The Hotel consisted of 345 rooms and was originally run by Corinthia Hotels International. Since 2008, the abandoned hotel has been vandalised, greatly damaged, littered and is currently considered an eyesore at Marsaskala’s coastline.

The Scheme is being proposed to add recreational and economic value to the area. The entire footprint of the site is 44,812m², but only around 17,570m² will be developed. The remainder of the site comprises of a coastal zone with natural bare rock, salt pans, derelict buildings, disturbed land and public streets.



FIGURE 1: SITE BOUNDARY OF THE PROPOSED EX-JERMA PALACE REDEVELOPMENT SITE

2 METHODOLOGY

The air quality study analysed the potential impacts from vehicular traffic arising from the Scheme's operational phase. The study adopted a methodology approach that has been shown to be appropriate and successful for such ambient air monitoring from studies carried out abroad and locally. The air quality study also incorporated the baseline monitoring readings of PM₁₀ and NO₂, the results of which were then used to determine the impact of the Scheme on air quality in the surrounding area.

2.1 BASELINE SAMPLING

Monitoring was carried out at one sampling point in close proximity to the proposed development in Marsascale. The exact location was accepted by the ERA in a Method Statement and is mapped in Figure 2.

The monitoring campaign lasted a minimum of six weeks (from January 23rd to 11th March 2019 for PM₁₀ and until 7th March 2019 for NO₂). Concentrations of both PM₁₀ and NO₂ were measured from the sampling station. Further details on the sampling protocols are available in Section 4.0.

The monitoring point was selected in line with the ERA ToRs, most notably requirement (k) of Section 2, and Annex I, which were in turn based on the relevant standards. In line with the relevant standards and the ERA ToRs, the instrument for PM₁₀ was placed around 2 m above ground level, and more than 0.5 m away from the nearest wall. The sampling head was not shielded by trees or vegetation. The analysers were placed less than 10 m away from the kerbside.

The sampling and analytical methods for PM₁₀ were carried out by Sunlab Group Ltd., which are an accredited and certified laboratory (ISO 17025:2015). The sampling for NO₂ was carried out by Passam ag, which are also an accredited and certified laboratory (ISO 17025:2015).



FIGURE 2: LOCATION OF SAMPLING POINT AND THE SCHEME SITE (SOURCE: GOOGLE EARTH)

2.1.1 PM_{10}

Baseline levels of PM_{10} were determined using the reference method (MSA EN 12341:2014), which describes both sampling and measurement methods for PM_{10} . Other specific details regarding the measurement of PM_{10} can be found in the Terms of Reference provided by ERA, which are presented in Appendix 1 of this report.

The monitoring of PM_{10} was carried out using a Sequential Automatic Sampler (Skypost). Since this sampler has to work with a constant flow rate of $2.3 \text{ m}^3/\text{h} \pm 2\%$ (EN 12341), the Skypost has a dry gas meter within 2% precision installed and it can electronically control the flow. Skypost is also equipped with a sensor to measure the atmospheric pressure and temperature and the pressure drop on filter. This sensor is installed on the suction tube and protected against adverse meteorological conditions.

The clean filter reservoir can contain up to 16 filter cassettes and this it can allow 16-days of monitoring without the need to go on the field and replace new filters. Unloaded filters were conditioned in the weighing room for a minimum of 48 h before weighing. Filters were weighed twice, with an interval of at least 12 hours, to confirm that the filter weight had stabilized. Loaded filters were placed in the weighing room for a minimum of 48 hours before weighing, and then weighed again after a further 24 to 72 hours, whilst retained in the appropriate conditions.

The monitoring phase lasted a total of 6 weeks (additional monitoring days were carried out to account for Saharan dust events), but a scale up factor provided by ERA was used to scale the 6-week values of PM_{10} to yearly values. The specific details on the methodology and instrumentation that were applied for the sampling and analysis of PM_{10} are listed in Table 1.

TABLE 1: DETAILS ON THE METHODOLOGY AND INSTRUMENTATION OF THE PM₁₀ ANALYSISPM₁₀

Description of activity	Sampling was be carried out with a sampling constant flow set equal to 38.3 L/min using the appropriate sampling heads: LVS for PM₁₀. The filter sampled was delivered to the laboratory for analysis and then weighed with an analytical balance. The scale was positioned inside a room with controlled temperature and humidity. The flow was programmable under the conditions of temperature and pressure of the sampling point (Qa), or standard (Qs) at 101.3 kPa, 0°C.
Instrument used	Skypost PM was used for the monitoring; it had the following features: ● Flow Range: 0.5 to 50 L/min ● Autonomy: 16 filters ● Electronic measurement of flow ● Sensors measure of parameters: ○ Atmospheric Pressure ○ Pressure drop filter ○ Ambient temperature ○ Temperature volumetric ● Volumetric measurement meter with accuracy of $\pm 2\%$ As per specifications of the ISO standard, the room temperature and the relative humidity of the weighing room were continuously monitored and controlled to 20°C ± 1 K and 45% to 50% RH respectively. Unloaded filters were conditioned in the weighing room for a minimum of 48 h before weighing. Filters were weighed twice, with an interval of at least 12 h, to confirm weight stabilisation. Loaded filters were placed in the weighing room for at least 48 h before weighing, and then weighed again after a further 24-72 h, whilst retained in the appropriate conditions. The balance resolution was of 10 μg.



FIGURE 3: SKYPOST INSTALLED ON SITE

2.1.2 Nitrogen Dioxide (NO₂)

Baseline levels of NO₂ were determined with a method which is shown to be equivalent to the reference method (EN 14211:2012). This standard describes both sampling and measurement methods for NO₂. Other specific details regarding the measurement of NO₂ can be found in the Terms of Reference provided by ERA, which are attached to this report in Appendix 1.

The monitoring of NO₂ was carried out using a type of passive sampler known as Passam Tubes. The system of such diffusion samplers is based on that of Palmes. The devices are passive in that they do not require power for operation. NO₂ is collected by molecular diffusion along an inert tube to an absorbent, in this case triethanolamine. The tubes were replaced with fresh ones every four weeks. The monitoring phase lasted a total of six weeks, but a scale-up factor, provided by ERA, was used to scale the six-week values of NO₂ to yearly values.

The tubes used for the monitoring of NO₂ were then be sent to the laboratory, where they were treated to extract the pollutants and analysed. The analytical technique was divided into two distinct phases: sampling and analysis. The sampling was carried out by AIS. The analysis was be carried out by Passam ag, which is an ISO/IEC 17025:2015 accredited laboratory.

As requested by the ToRs, the Consultant provided at least one article in a peer-reviewed journal which showcases that the equivalence of these tubes has been demonstrated in at least 1 EU Member State. An article by Hafkenscheid et al. (2009) on the application of diffusive samplers in the European Union for the monitoring of nitrogen dioxide in ambient air was chosen. This article indicates that in France, Passam samplers were compared to the standard reference method in line with the Guidance to Demonstration of Equivalence (2010). The study found the Passam tubes to be equivalent to the reference method, with an uncertainty of 6.4% at a 95% confidence level, thus fulfilling the 15% uncertainty level for fixed NO₂ measurements. This value was based on 181 valid data pairs. The results are shown in Table 2.

TABLE 2: RESULTS FROM COMPARISON OF PASSAM TUBES TO REFERENCE METHOD (HAFKENSCHIED ET AL., 2009)

REGRESSION OUTPUT

slope, b	0.975
uncertainty of b	0.010
intercept, a	0.1
uncertainty of a	0.19
number of data pairs	181

EQUIVALENCE TEST RESULTS

random term	2.4	µg.m ⁻³
bias at LV	-0.9	µg.m ⁻³
combined uncertainty	2.6	µg.m ⁻³
relative uncertainty	6.4%	pass
reference uncertainty	1.0	µg.m ⁻³
limit value	40	µg.m ⁻³

The specific details on the methodology and instrumentation that were applied for the sampling and analysis of NO₂ can be seen in Table 3.

TABLE 3: DETAILS ON THE METHODOLOGY AND INSTRUMENTATION OF THE NO₂ ANALYSIS

NITROGEN DIOXIDE

Description of activity	The passive sampler that was used (type Passam) is equipped with an adsorbant (in this case triethanolamine) on which NO ₂ adsorbs.
-------------------------	--

NITROGEN DIOXIDE

Instruments used	The radially symmetrical diffusive body is fixed to a metal plate and is exposed to air between 1.5 and 4 meter above the ground level. The passive sampler was analyzed in the laboratory to determine the amount of NO₂. The uptake rate was calculated at 298.15K and then used to determine the average concentration of the pollutant during the exposure period. Further details on the analyser used are given below:	
	Principle of method	Passive sampler
	Instrumentation	Passam tube
	Lower detectable limit	0.3 µg/Nm ³



FIGURE 4: PASSAM TUBES WITHIN PROTECTIVE COVER ON SITE

2.1.3 Additional Data

Annual weather data, recorded as hourly averages in 2018 from the Malta International Airport was used to create the model. The consultants also made use of

annual concentrations of O₃, PM₁₀, NO and NO₂ in the form of hourly average 2017 data collected from the Zejtun air quality monitoring station operated by the ERA.

2.1.4 Traffic Studies

Traffic studies have been carried out by AIS Environment Ltd. In view of the magnitude of the number of vehicles that will be commuting to and from the proposed development, it is expected that the vehicular trips completion of the development will increase in the area. Thus, such an increase will also reflect on the existing network traffic.

A total of 5 modelling scenarios have been considered in the air quality study. The years considered in each scenario are indicated below:

- Scenario 1: Baseline year in 2018 (no development)
- Scenario 2: 1st year of Operation in 2030 (no development)
- Scenario 3: 1st year of Operation in 2030 (development fully operational)
- Scenario 4: 5th year of Operation in 2035 (no development)
- Scenario 5: 5th year of Operation in 2035 (development fully operational)

2.2 MODELLING WORK FOR IMPACT ASSESSMENT WITH BREEZE ROADS

Once the data was collected from the monitoring stations, the data was inputted into an air quality dispersion model using the software “Breeze Roads”. The model is an air dispersion modelling suite that predicts air quality impacts of a number of pollutants including Carbon monoxide (CO), Nitrogen Dioxide (NO₂) and Particular Matter (PM). It is specifically designed to model pollutant concentrations that are emitted from moving and idling motor vehicles at or alongside roadways and roadway intersections.

The diffusion of pollutants from linear sources (roads) is calculated using algorithms. The data inputted into the model was:

- Area of the Scheme (use of sensitive receptors);
- Geometry of the road segments (length, width etc.);
- Dislocation of the receptors;
- Weather conditions; and
- Vehicular emission factors.

2.2.1 Area of the Scheme

The model was created by using two types of planimetries. In line with the ToRs, numerous sensitive receptors were identified around the Scheme site. These sensitive receptors were plotted using Google Earth. **Error! Reference source not found.** maps

the geographical location of the selected receptors, whilst



FIGURE 5: AREA OF STUDY MODELLED USING BREEZE ROADS WITH RECEPTORS

Table 4 lists the coordinates of each receptor.



FIGURE 5: AREA OF STUDY MODELLED USING BREEZE ROADS WITH RECEPTORS

TABLE 4: SENSITIVE RECEPTOR COORDINATES

RECEPTOR	UTM COORDINATES	
	NORTH	EAST
R1	460213.6 N	3968784.7 E
R2	460494.1 N	3968845.5 E
R3	461031.9 N	3969011.8 E
R4	460538.3 N	3968674.5 E
R5	460887.4 N	3968818.4 E
R6	461155.3 N	3968704.9 E
R7	461183.7 N	3968568.3 E
R8	461326.9 N	3968855.4 E
R9	461014.7 N	3968219.2 E
R10	460824.7 N	3968399.3 E
R11	460481.5 N	3968345.2 E
R12	460709.2 N	3968019.2 E
JERMA MS	459980.0 N	3968789.9 E
JERMA SITE	461362.6 N	3968641.3 E

2.2.2 Selected Roads (Links)

The model identifies the road network as the source of pollution. The key input information regarding the road network in the model includes:

- Length of the road section;
- Width of the road section;
- Vehicular traffic (vehicles /hour);
- Emission Factor (g /vehicle x Km);
- Type of road (acts grade, depressed, fill, bridge);
- Type of links (free flow, queue).

The roads considered in the model are mapped in **Error! Reference source not found..**



FIGURE 6: ROADS INCLUDED IN THE MODELLING

The traffic data used for the model was provided by the traffic consultant. Traffic data is expressed as average annual daily traffic (AADT), shown in Appendix 2. Therefore, considering that the template allows the user to enter a single data traffic for each road, it was decided to use total traffic (vehicle entry and exit) for each road. The model allows the user to enter a value expressed in vehicles per hour. The roads which were considered in the model were:

- Triq Sant Antnin
- Triq il-Qaliet (upper part)
- Triq il-Qaliet (lower part)
- Triq tal-Gardiel
- Triq is-Salini

For the Breeze roads model, all roads were considered as roads without traffic lights, ie "free flow links".

2.2.3 Emission Factor

Emission factors (EF) for "Free Flow Links" were obtained from HBEFA (Handbook Emission Factors for Road Transport). The emission factors, expressed in g/veh*km, were derived from HBEFA 4.1 processing software.

Since the Maltese vehicular EF is not present in the HBEFA database, the vehicular composition in Germany is similar to that of Malta and considering that the average age of the German fleet is 5-6 years lower, then the emission coefficients were corrected by a multiplication factor [PM_{10} (x1.10) / PM_{10} non-exhaust (x1.10) / NO_2 (x1.3)].

The roads included in the study are classed as "Free Flow Links" which are characterised by straight sections, access and local roads with low-speed limits and roads within residential areas. The average EF used for each of the scenarios are listed in Table 5.

TABLE 5: EMISSION FACTORS FOR "FREE FLOW LINKS"

POLLUTANT	SCENARIO	BALANCE AVERAGE EMISSION FACTOR
PM ₁₀	Scenario 1: 2018 Baseline (No development)	0.05175
	Scenario 2: 2030 (No development)	0.04439
	Scenario 3: 2030 (Development in full operation)	
	Scenario 4: 2035 (No development)	0.04380
	Scenario 5: 2035 (Development in full operation)	
Nitrogen Dioxide (NO ₂)	Scenario 1: 2025 Baseline (No development)	0.18010
	Scenario 2: 2030 (No development)	0.10104
	Scenario 3: 2030 (Development in full operation)	
	Scenario 4: 2035 (No development)	0.09023
	Scenario 5: 2035 (Development in full operation)	

The PM₁₀ emission coefficient includes PM (non-exhaust), i.e. emissions from the wear of motor vehicle brake pads, tires, and resuspension particles on the road.

A single weighted emission factor was included for each Scenario. This was obtained from the average emission factor of light vehicles (PC - Passenger Car), heavy vehicles (HGV), light commercial vehicles (LCV) and Bus considering that an average 15% of HGV- BUS, 10% LGV and 75% PC.

2.2.4 Meteorological Data

The weather data used for the transaction modelling were recorded by a weather sensor installed on an atmospheric monitoring station in Luqa, Malta. The weather data used in the model was compiled from this station in 2024:

- Wind direction (°N)
- Wind speed (m/s)
- Temperature (°K)

- Global Solar Radiation (W/m²)
- Precipitation (mm)

2.2.5 Urban Background

Emissions from an urban background site were required since Breeze Roads only estimates emissions attributed to traffic. The traffic emissions then need to be added to background air quality levels to predict the overall level of emissions (for example a construction site, domestic heating, industries etc.). The data used was taken from scientific studies or from atmospheric monitoring stations operated by the ERA.

The average background PM₁₀ concentration at the Zejtun Station in the baseline year is 26.0 µg/m³. This value was validated with the average concentration detected at the 6-week monitoring point.

The average background of NO₂, was corrected with a multiplicative factor and validated so that the annual average NO₂ concentration in the baseline scenario is equal to the average concentration detected at the 6-week monitoring point. The average annual value of NO₂ is equal to 13.2 µg/m³.

2.3 IMPACT SIGNIFICANCE

The analysis of the significance of the potential impact of both PM₁₀ and NO₂ (positive or negative) includes:

- Description of impact;
- Policy importance of impact (Local, National, International);
- Extent of effect;
- Duration of impact (temporary / permanent);
- Adverse or beneficial impact;
- Reversible / irreversible impact;
- Sensitivity of receptors;
- Probability of impact occurring (certain, likely, uncertain, unlikely, remote); and
- Scope for mitigation / enhancement (very good, good, none).

The above criteria enabled the determination of the significance of each impact in respect of the studies described above. The impacts are described as negligible, slightly adverse, moderate adverse and substantial adverse, as shown in Table 6 and Table 7. A significance criteria tool provided by the ERA was used to determine the significance of the impact on all sensitive receptors. To determine the impact, the tool considers the following inputs:

- The annual limit value (µg/m³) as established by local legislation (S.L. 549.59).
- The baseline concentration (µg/m³) – the baseline concentration value considered was the average daily value
- The change (µg/m³) – the worst-case emissions reported from the air dispersion model was considered for the determination of the exchange rate

TABLE 6: SIGNIFICANCE CRITERIA FOR ANNUAL LEVELS OF NO₂/PM₁₀ IN µG/M³ (SOURCE: ERA TORs)

BASELINE ANNUAL LEVELS CAA OF NO ₂ /PM ₁₀ (µG/M ³)	CHANGE IN ANNUAL NO ₂ /PM ₁₀ (DAA) LEVELS DUE TO SCHEME (µG/M ³)			
	DAA ≤ 0.4 µG/M ³	0.8 ≤ DAA ≤ 2.0 µG/M ³	2.4 ≤ DAA ≤ 4.0 µG/M ³	DAA ≥ 4.0 µG/M ³
CAA ≥ 44 µg/m ³	Moderate	Substantial	Substantial	Substantial
43.6 ≤ CAA ≤ 41.2 µg/m ³	Moderate	Moderate	Substantial	Substantial
40.8 ≤ CAA ≤ 38.0 µg/m ³	Slight	Moderate	Moderate	Substantial
37.6 ≤ CAA ≤ 30.4 µg/m ³	Negligible	Slight	Moderate	Moderate
CAA ≤ 30 µg/m ³	Negligible	Negligible	Slight	Moderate

TABLE 7: SIGNIFICANCE CRITERIA FOR ANNUAL LEVELS OF 90.4TH PERCENTILE CRITERION FOR PM₁₀ (SOURCE: ERA TORs)

BASELINE ANNUAL LEVELS PCT OF PM ₁₀ (µG/M ³)	CHANGE IN THE PCT (DPCT) LEVELS DUE TO SCHEME (µG/M ³)			
	DPCT ≤ 0.5 µG/M ³	1.0 ≤ DPCT ≤ 2.5 µG/M ³	3.0 ≤ DPCT ≤ 5.0 µG/M ³	DPCT ≥ 5.0 µG/M ³
PCT ≥ 55 µg/m ³	Moderate	Substantial	Substantial	Substantial
54.5 ≤ PCT ≤ 51.5 µg/m ³	Moderate	Moderate	Substantial	Substantial
51.0 ≤ PCT ≤ 47.5 µg/m ³	Slight	Moderate	Moderate	Substantial
47.0 ≤ PCT ≤ 38.0 µg/m ³	Negligible	Slight	Moderate	Moderate
PCT ≤ 37.5 µg/m ³	Negligible	Negligible	Slight	Moderate

2.4 MITIGATION MEASURES AND MONITORING

This report also contains recommendations and mitigation measures that can be implemented by the applicant to prevent and minimise as much as possible, any significant adverse impacts resulting from the operational phase of the scheme. A monitoring programme has also been developed.

3 RESULTS

3.1 BASELINE CONDITIONS

3.1.1 PM₁₀

The monitoring results for PM₁₀ concentrations returned an average concentration in 42 days equal to 41.1 µg/m³ (discarding days from Sahara dust). This result was scaled up to one year through the use of a corresponding multiplicative coefficient of 0.82 provided by ERA (Environment & Resources Authority), and it is 33.7 µg/m³. Appendix 3 shows the daily particulate matter PM₁₀.

3.1.2 NO₂

The monitoring results for NO₂ concentrations over the 42-day sampling period are summarized hereunder.

TABLE 8: SUMMARY OF NO₂ RESULTS

SAMPLER	START	END	NO ₂ (µG/M ³)
3	24/01/2019 at 13:40	14/02/2019 at 14:00	18.5
5	24/01/2019 at 13:40	14/02/2019 at 14:00	19.4
10	24/01/2019 at 13:40	14/02/2019 at 14:00	18.0
4	14/02/2019 at 14:00	07/03/2019 at 14:30	24.3
6	14/02/2019 at 14:00	07/03/2019 at 14:30	22.5
8	14/02/2019 at 14:00	07/03/2019 at 14:30	23.4
Average			21.0

The average result was scaled up to one year through the use of a corresponding multiplicative coefficient of 0.94+0.325 provided by ERA (Environment & Resources Authority), to obtain a figure of 20.1 µg/m³.

3.2 SCENARIO MODELLING

The Breeze Roads software produces contour maps as output, which allow the user to view the diffusion of pollutants into the atmosphere. The sources of such pollutants originate from the different road sections concerned. Contour maps for four different forecast scenarios and additional one for the baseline conditions were modelled and are described in the following subsections.

The prediction from the model exercise was compared and validated with the data from the 6-week monitoring. To verify calibration of the model, were used. Since the monitoring period covered 42 days, the multiplicative coefficients below were used for scaling up to one year provided by the Environment & Resources Authority (ERA):

- PM_{10} : 0.82
- NO_2 : 0.94 + 0.325

TABLE 9: PREDICTION EVALUATION

PARAMETER	RESULT OF THE MONITORING	ANNUALISATION/ SCALE FACTORS	RESULT OF THE MONITORING CORRECT TO FACTOR ERA	MODEL RESULTS AT THE SAME POINT	RESULTS
PM_{10}	41.1	0.82	33.7	33.7	Positive
NO_2	21	0.94 + 0.325	20.1	20.1	Positive

3.2.1 Scenario 1: Baseline 2018



FIGURE 7: SCENARIO 1 (2018, NO DEVELOPMENT): BASELINE CONTOUR MAP FOR PM₁₀



FIGURE 8: SCENARIO 1 (2018, NO DEVELOPMENT): BASELINE CONTOUR MAP FOR DAILY PM_{10} PCT 90.4TH

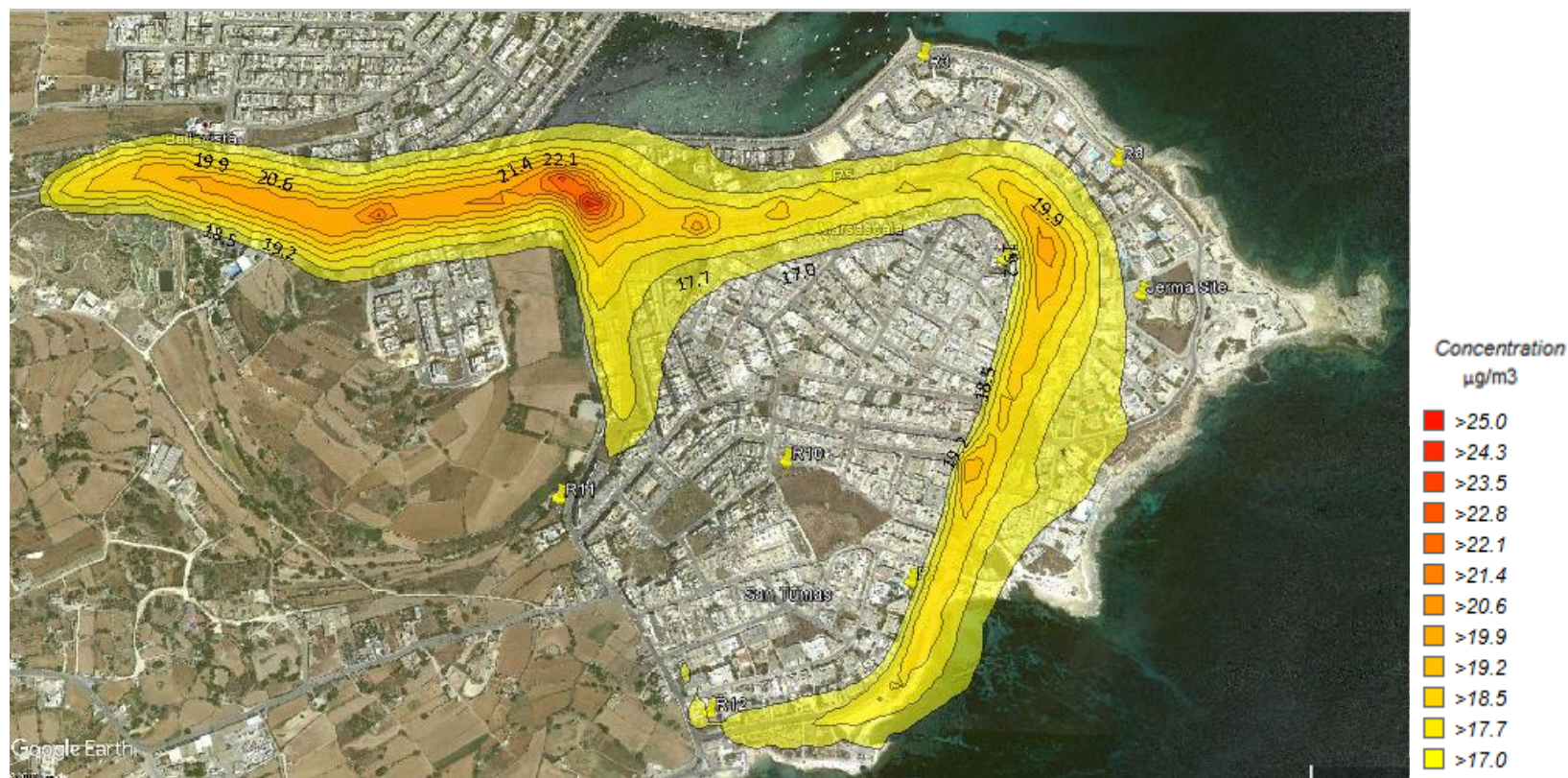


FIGURE 9: SCENARIO 1 (2018, NO DEVELOPMENT): BASELINE CONTOUR MAP FOR NO₂

The values obtained at each sensitive receptor location are expressed in annual averages in the emission contour maps. These average annual values have been extracted and presented in Table 10.

TABLE 10: MODELING RESULTS FOR SCENARIO 1: 2018 BASELINE

RECEPTOR	PM ₁₀ μG/M ³	NO ₂ μG/M ³	PCT 90.4 TH PM ₁₀ μG/M ³
R1	32.5	19.9	55.8
R2	33.0	20.3	60.4
R3	27.5	15.8	41.8
R4	30.8	18.7	48.6
R5	31.4	19.0	54.4
R6	27.5	16.4	41.5
R7	31.7	19.4	51.1
R8	27.6	16.5	42.1
R9	27.5	16.1	42.2
R10	27.0	15.6	40.5
R11	26.5	14.3	39.5
R12	29.7	17.1	46.1
Jerma MS	33.7	20.1	54.6
Jerma site	27.6	16.8	42.0

3.2.2 Scenario 2: 2030 (No Development)



FIGURE 10: SCENARIO 2 (2030, NO DEVELOPMENT): CONTOUR MAP FOR PM_{10}



FIGURE 11: SCENARIO 2 (2030, NO DEVELOPMENT): CONTOUR MAP FOR DAILY PM_{10} PCT 90.4TH



FIGURE 12: SCENARIO 2 (2030, NO DEVELOPMENT): CONTOUR MAP FOR NO_2

The values obtained at each sensitive receptor location are expressed in annual averages in the emission contour maps. These average annual values have been extracted and presented in Table 11.

TABLE 11: MODELING RESULTS FOR SCENARIO 2: 2030 (NO DEVELOPMENT)

RECEPTOR	PM ₁₀ μG/M ³	NO ₂ μG/M ³	PCT 90.4 TH PM ₁₀ μG/M ³
R1	32.3	18.0	55.1
R2	32.8	18	59.6
R3	27.4	15.3	41.7
R4	30.6	17.0	48.2
R5	31.2	17.2	53.8
R6	27.4	15.5	41.4
R7	31.5	17.6	50.6
R8	27.5	15.6	41.9
R9	27.5	15.3	42.1
R10	27.0	15.0	40.4
R11	26.5	14.1	39.4
R12	29.6	15.8	45.9
Jerma MS	33.4	18.0	54.0
Jerma site	27.5	15.7	41.9

3.2.3 Scenario 3: 2030 (With Development)



FIGURE 13: SCENARIO 3 (2030, WITH DEVELOPMENT): CONTOUR MAP FOR PM_{10}



FIGURE 14: SCENARIO 3 (2030, WITH DEVELOPMENT): CONTOUR MAP FOR DAILY PM₁₀ PCT 90.4TH



FIGURE 15: SCENARIO 3 (2030, WITH DEVELOPMENT): CONTOUR MAP FOR NO₂

The values obtained at each sensitive receptor location are expressed in annual averages in the emission contour maps. These average annual values have been extracted and presented in Table 12.

TABLE 12: MODELING RESULTS FOR SCENARIO 3: 2030 (WITH DEVELOPMENT)

RECEPTOR	PM ₁₀ μG/M ³	NO ₂ μG/M ³	PCT 90.4 TH PM ₁₀ μG/M ³
R1	32.6	18.2	55.9
R2	33.1	18.5	60.6
R3	27.8	15.4	42.5
R4	31.2	17.4	49.6
R5	31.4	17.4	54.3
R6	27.5	15.6	41.6
R7	31.7	17.8	50.9
R8	27.7	15.8	42.2
R9	27.5	15.4	42.1
R10	27.1	15.1	40.6
R11	26.5	14.1	39.5
R12	30	16.1	46.6
Jerma MS	33.7	18.2	54.7
Jerma site	27.6	15.9	42.1

3.2.4 Scenario 4: 2035 (No Development)



FIGURE 16: SCENARIO 4 (2035, NO DEVELOPMENT): CONTOUR MAP FOR PM_{10}



FIGURE 17: SCENARIO 4 (2035, NO DEVELOPMENT): CONTOUR MAP FOR DAILY PM₁₀ PCT 90.4TH



FIGURE 18: SCENARIO 4 (2035, NO DEVELOPMENT): CONTOUR MAP FOR NO_2

The values obtained at each sensitive receptor location are expressed in annual averages in the emission contour maps. These average annual values have been extracted and presented in Table 13.

TABLE 13: MODELING RESULTS FOR SCENARIO 4: 2035 (NO DEVELOPMENT)

RECEPTOR	PM ₁₀ μG/M ³	NO ₂ μG/M ³	PCT 90.4 TH PM ₁₀ μG/M ³
R1	32.5	17.8	55.8
R2	33.0	18.1	60.4
R3	27.5	15.0	41.8
R4	30.8	16.6	48.6
R5	31.4	17.0	54.4
R6	27.5	15.4	41.5
R7	31.7	17.4	51.0
R8	27.6	15.4	42.1
R9	27.5	15.2	42.2
R10	27.0	14.9	40.5
R11	26.5	14.0	39.5
R12	29.7	15.7	46.1
Jerma MS	33.7	17.8	54.6
Jerma site	27.6	15.6	42.0

3.2.5 Scenario 5: 2035 (With Development)



FIGURE 19: SCENARIO 5 (2035, WITH DEVELOPMENT): CONTOUR MAP FOR PM_{10}



FIGURE 20: SCENARIO 5 (2035, WITH DEVELOPMENT): CONTOUR MAP FOR DAILY PM_{10} PCT 90.4TH



FIGURE 21: SCENARIO 5 (2035, WITH DEVELOPMENT): CONTOUR MAP FOR NO₂

The values obtained at each sensitive receptor location are expressed in annual averages in the emission contour maps. These average annual values have been extracted and presented in Table 14.

TABLE 14: MODELING RESULTS FOR SCENARIO 5: 2030 (WITH DEVELOPMENT)

RECEPTOR	PM ₁₀ μG/M ³	NO ₂ μG/M ³	PCT 90.4 TH PM ₁₀ μG/M ³
R1	32.8	18.0	56.5
R2	33.3	18.3	61.4
R3	27.8	15.3	42.6
R4	31.3	17.1	49.9
R5	31.6	17.2	54.8
R6	27.6	15.5	41.7
R7	31.9	17.5	51.4
R8	27.8	15.6	42.4
R9	27.6	15.2	42.3
R10	27.1	15.0	40.7
R11	26.5	14.1	39.5
R12	30.1	15.9	46.9
Jerma MS	34.0	18.0	55.3
Jerma site	27.7	15.8	42.2

3.2.6 Comparison Between Scenarios

For ease of comparison, the results obtained from the different modelling scenarios have been combined in the tables hereunder. Values highlighted in red indicate an increase in pollutant level, and those in grey indicate no change in levels from the no development scenario.

TABLE 15: COMPARISON OF PM₁₀ VALUE ACROSS THE DIFFERENT SCENARIOS

RECEPTOR	SCENARIO 1 BASELINE ($\mu\text{G}/\text{M}^3$)	SCENARIO 2 2030 NO DEVELOPMENT ($\mu\text{G}/\text{M}^3$)	SCENARIO 3 2030 WITH DEVELOPMENT ($\mu\text{G}/\text{M}^3$)	SCENARIO 4 2035 NO DEVELOPMENT ($\mu\text{G}/\text{M}^3$)	SCENARIO 5 2035 WITH DEVELOPMENT ($\mu\text{G}/\text{M}^3$)
R1	32.5	32.3	32.6	32.5	32.8
R2	33.0	32.8	33.1	33.0	33.3
R3	27.5	27.4	27.8	27.5	27.8
R4	30.8	30.6	31.2	30.8	31.3
R5	31.4	31.2	31.4	31.4	31.6
R6	27.5	27.4	27.5	27.5	27.6
R7	31.7	31.5	31.7	31.7	31.9
R8	27.6	27.5	27.7	27.6	27.8
R9	27.5	27.5	27.5	27.5	27.6
R10	27.0	27.0	27.1	27.0	27.1
R11	26.5	26.5	26.5	26.5	26.5
R12	29.7	29.6	30.0	29.7	30.1
Jerma MS	33.7	33.4	33.7	33.7	34.0
Jerma site	27.6	27.5	27.6	27.6	27.7

At R11 the model predicts no increase in PM₁₀ values across all scenarios considered. At R9 no change is predicted in 2030. Increases in PM₁₀ values above the No Development Scenarios, ranging between 0.1 to 0.6 $\mu\text{g}/\text{m}^3$ are predicted at the other receptors in 2030 and 2035.

TABLE 16: COMPARISON OF DAILY PM₁₀ PCT 90.4TH ACROSS THE DIFFERENT SCENARIOS

RECEPTOR	SCENARIO 1 BASELINE ($\mu\text{G}/\text{M}^3$)	SCENARIO 2 2030 NO DEVELOPMENT ($\mu\text{G}/\text{M}^3$)	SCENARIO 3 2030 WITH DEVELOPMENT ($\mu\text{G}/\text{M}^3$)	SCENARIO 4 2035 NO DEVELOPMENT ($\mu\text{G}/\text{M}^3$)	SCENARIO 5 2035 WITH DEVELOPMENT ($\mu\text{G}/\text{M}^3$)
R1	55.8	55.1	55.9	55.8	56.5
R2	60.4	59.6	60.6	60.4	61.4

RECEPTOR	SCENARIO 1 BASELINE ($\mu\text{G}/\text{M}^3$)	SCENARIO 2 2030 NO DEVELOPMENT ($\mu\text{G}/\text{M}^3$)	SCENARIO 3 2030 WITH DEVELOPMENT ($\mu\text{G}/\text{M}^3$)	SCENARIO 4 2035 NO DEVELOPMENT ($\mu\text{G}/\text{M}^3$)	SCENARIO 5 2035 WITH DEVELOPMENT ($\mu\text{G}/\text{M}^3$)
R3	41.8	41.7	42.5	41.8	42.6
R4	48.6	48.2	49.6	48.6	49.9
R5	54.4	53.8	54.3	54.4	54.8
R6	41.5	41.4	41.6	41.5	41.7
R7	51.1	50.6	50.9	51.0	51.4
R8	42.1	41.9	42.2	42.1	42.4
R9	42.2	42.1	42.1	42.2	42.3
R10	40.5	40.4	40.6	40.5	40.7
R11	39.5	39.4	39.5	39.5	39.5
R12	46.1	45.9	46.6	46.1	46.9
Jerma MS	54.6	54.0	54.7	54.6	55.3
Jerma site	42.0	41.9	42.1	42.0	42.2

At R9 and R11, the model predicts no increase in PM_{10} PCT values across the 2030 and 2035 scenarios respectively. Increases in PM_{10} PCT values above the No Development Scenarios, ranging between 0.1 to $1.4\mu\text{g}/\text{m}^3$ are predicted at the other receptors in 2030 and 2035.

TABLE 17: COMPARISON OF NO_2 VALUES ACROSS DIFFERENT SCENARIOS

RECEPTOR	SCENARIO 1 BASELINE ($\mu\text{G}/\text{M}^3$)	SCENARIO 2 2030 NO DEVELOPMENT ($\mu\text{G}/\text{M}^3$)	SCENARIO 3 2030 WITH DEVELOPMENT ($\mu\text{G}/\text{M}^3$)	SCENARIO 4 2035 NO DEVELOPMENT ($\mu\text{G}/\text{M}^3$)	SCENARIO 5 2035 WITH DEVELOPMENT ($\mu\text{G}/\text{M}^3$)
R1	19.9	18.0	18.2	17.8	18.0
R2	20.3	18.0	18.5	18.1	18.3
R3	15.8	15.3	15.4	15.0	15.3
R4	18.7	17.0	17.4	16.6	17.1
R5	19.0	17.2	17.4	17.0	17.2
R6	16.4	15.5	15.6	15.4	15.5
R7	19.4	17.6	17.8	17.4	17.5
R8	16.5	15.6	15.8	15.4	15.6
R9	16.1	15.3	15.4	15.2	15.2
R10	15.6	15.0	15.1	14.9	15.0
R11	14.3	14.1	14.1	14.0	14.1
R12	17.1	15.8	16.1	15.7	15.9

RECEPTOR	SCENARIO 1 BASELINE ($\mu\text{G}/\text{M}^3$)	SCENARIO 2 2030 NO DEVELOPMENT ($\mu\text{G}/\text{M}^3$)	SCENARIO 3 2030 WITH DEVELOPMENT ($\mu\text{G}/\text{M}^3$)	SCENARIO 4 2035 NO DEVELOPMENT ($\mu\text{G}/\text{M}^3$)	SCENARIO 5 2035 WITH DEVELOPMENT ($\mu\text{G}/\text{M}^3$)
Jerma MS	20.1	18.0	18.2	17.8	18.0
Jerma site	16.8	15.7	15.9	15.6	15.8

At R9 and R11, the model predicts no increase in NO_2 values across the 2030 and 2035 scenarios, respectively. Increases in NO_2 values above the No Development Scenarios, ranging between 0.1 to $0.5\mu\text{g}/\text{m}^3$ are predicted at the other receptors in 2030 and 2035.

4 IMPACT ASSESSMENT

As specified in the ERA Terms of References, the cumulative impact of all developments taking place and/or which are planned for the site in question should be considered, irrespective of the number of separate Planning Applications involved.

The results of the monitoring of NO₂, PM₁₀ and traffic counts, together with the use of data from other baseline surveys, were integrated to enable prediction of potential impacts on the concentrations of these airborne pollutants. The dispersion model software Breeze Roads was used to determine the impact of the Scheme on the air quality of the area. The impact significance criteria which were used for the assessment are described in Section 2.3 of this report.

Table 18 and Table 19 show the computation of the impact assessment on each of the sensitive receptors for both pollutants. The concentration of the baseline level was compared with the results obtained from the model for the two future scenarios. This comparison enabled the calculation of the difference in the concentration of the pollutant and the annual exceedances, which in turn led to the identification of the significance of the impact. As can be seen from the impact assessment tables, the increase in traffic created by the proposed Scheme will lead to a mixture of adverse impacts ranging from negligible to substantial impacts. For NO₂, the impacts across all scenarios are expected to be negligible adverse. For PM₁₀, the impact is also expected to be negligible across all scenarios, except at R4 in 2030, where a slight adverse impact is predicted. The impacts predicted for PCT PM₁₀ are more significant, with a variety of negligible, slight, moderate and substantial impacts predicted at different locations and in different scenarios.

The values calculated in the model have also been compared to the thresholds stipulated in the AMBIENT AIR QUALITY REGULATIONS (S.L.549.59). In terms of PM₁₀, the aforementioned regulations set the annual threshold at 40 µg/m³. In all scenarios considered, this threshold is not surpassed at any of the receptors considered.

The AMBIENT AIR QUALITY REGULATIONS (S.L.549.59) threshold for PCT PM₁₀ is established at 50 µg/m³. This value is exceeded at some of the receptors and across all the Scenarios considered.

The annual threshold for NO₂ in accordance with the AMBIENT AIR QUALITY REGULATIONS (S.L.549.59) is 40 µg/m³. The baseline readings and predicted concentrations at all sensitive receptors fall below the threshold limit.

TABLE 18: IMPACT ASSESSMENT FOR SCENARIOS 2 & 3 IN 2030

RECEPTOR	SCENARIO 1 2018 BASELINE (µG/M³)	PREDICTED CAA PM ₁₀ (µG/M³)				PREDICTED PCT PM ₁₀ (µG/M³)				
		SCENARIO 2 2030 NO DEVELOPMENT (µG/M³)	SCENARIO 3 2030 WITH DEVELOPMENT (µG/M³)	DIFFERENCE (DCAA) (µG/M³)	IMPACT	SCENARIO 1 2018 BASELINE (µG/M³)	SCENARIO 2 2030 NO DEVELOPMENT (µG/M³)	SCENARIO 3 2030 WITH DEVELOPMENT (µG/M³)	DIFFERENCE (DPCT) (µG/M³)	IMPACT
R1	32.5	32.3	32.6	0.3	Negligible	55.8	55.1	55.9	0.8	Substantial
R2	33.0	32.8	33.1	0.3	Negligible	60.4	59.6	60.6	1.0	Substantial
R3	27.5	27.4	27.8	0.4	Negligible	41.8	41.7	42.5	0.8	Slight
R4	30.8	30.6	31.2	0.6	Slight	48.6	48.2	49.6	1.4	Moderate
R5	31.4	31.2	31.4	0.2	Negligible	54.4	53.8	54.3	0.5	Moderate
R6	27.5	27.4	27.5	0.1	Negligible	41.5	41.4	41.6	0.2	Negligible
R7	31.7	31.5	31.7	0.2	Negligible	51.1	50.6	50.9	0.3	Slight
R8	27.6	27.5	27.7	0.2	Negligible	42.1	41.9	42.2	0.3	Negligible
R9	27.5	27.5	27.5	0	Negligible	42.2	42.1	42.1	0	Negligible
R10	27.0	27.0	27.1	0.1	Negligible	40.5	40.4	40.6	0.2	Negligible
R11	26.5	26.5	26.5	0	Negligible	39.5	39.4	39.5	0.1	Negligible
R12	29.7	29.6	30	0.4	Negligible	46.1	45.9	46.6	0.7	Negligible
Jerma MS	33.7	33.4	33.7	0.3	Negligible	54.6	54.0	54.7	0.7	Moderate
Jerma site	27.6	27.5	27.6	0.1	Negligible	42.0	41.9	42.1	0.2	Negligible

RECEPTOR	SCENARIO 1 2018 BASELINE (µG/M³)	PREDICTED CAA NO ₂ (µG/M³)			
		SCENARIO 2 2030 NO DEVELOPMENT (µG/M³)	SCENARIO 3 2030 WITH DEVELOPMENT (µG/M³)	DIFFERENCE (DCAA) (µG/M³)	IMPACT
R1	19.9	18.0	18.2	0.2	Negligible
R2	20.3	18.0	18.5	0.5	Negligible
R3	15.8	15.3	15.4	0.1	Negligible
R4	18.7	17.0	17.4	0.4	Negligible
R5	19.0	17.2	17.4	0.2	Negligible
R6	16.4	15.5	15.6	0.1	Negligible

RECEPTOR	SCENARIO 1 2018 BASELINE (µG/M³)	PREDICTED CAA NO ₂ (µG/M³)			
		SCENARIO 2 2030 No DEVELOPMENT (µG/M³)	SCENARIO 3 2030 WITH DEVELOPMENT (µG/M³)	DIFFERENCE (DCAA) (µG/M³)	IMPACT
R7	19.4	17.6	17.8	0.2	Negligible
R8	16.5	15.6	15.8	0.2	Negligible
R9	16.1	15.3	15.4	0.1	Negligible
R10	15.6	15.0	15.1	0.1	Negligible
R11	14.3	14.1	14.1	0	Negligible
R12	17.1	15.8	16.1	0.3	Negligible
Jerma MS	20.1	18.0	18.2	0.2	Negligible
Jerma site	16.8	15.7	15.9	0.2	Negligible

TABLE 19: IMPACT ASSESSMENT FOR 2035

RECEPTOR	SCENARIO 1 2018 BASELINE (µG/M³)	PREDICTED CAA PM ₁₀ (µG/M³)				SCENARIO 1 2018 BASELINE (µG/M³)	PREDICTED PCT PM ₁₀ (µG/M³)			
		SCENARIO 4 2035 NO DEVELOPMENT (µG/M³)	SCENARIO 5 2035 WITH DEVELOPMENT (µG/M³)	DIFFERENCE (DCAA) (µG/M³)	IMPACT		SCENARIO 4 2035 NO DEVELOPMENT (µG/M³)	SCENARIO 5 2035 WITH DEVELOPMENT (µG/M³)	DIFFERENCE (DPCT) (µG/M³)	IMPACT
R1	32.5	32.5	32.8	0.3	Negligible	22.8	55.8	56.5	0.7	Moderate
R2	33.0	33.0	33.3	0.3	Negligible	22.8	60.4	61.4	1.0	Substantial
R3	27.5	27.5	27.8	0.3	Negligible	23.7	41.8	42.6	0.8	Slight
R4	30.8	30.8	31.3	0.5	Negligible	33.5	48.6	49.9	1.3	Moderate
R5	31.4	31.4	31.6	0.2	Negligible	25.3	54.4	54.8	0.4	Moderate
R6	27.5	27.5	27.6	0.1	Negligible	22.8	41.5	41.7	0.2	Negligible
R7	31.7	31.7	31.9	0.2	Negligible	23.0	51.0	51.4	0.4	Slight
R8	27.6	27.6	27.8	0.2	Negligible	23.7	42.1	42.4	0.3	Negligible
R9	27.5	27.5	27.6	0.1	Negligible	28.2	42.2	42.3	0.1	Negligible
R10	27.0	27.0	27.1	0.1	Negligible	29.4	40.5	40.7	0.2	Negligible
R11	26.5	26.5	26.5	0	Negligible	35.3	39.5	39.5	0	Negligible
R12	29.7	29.7	30.1	0.4	Negligible	29.4	46.1	46.9	0.8	Slight
Jerma MS	33.7	33.7	34.0	0.3	Negligible	30.1	54.6	55.3	0.7	Moderate
Jerma site	27.6	27.6	27.7	0.3	Negligible	31.0	42.0	42.2	0.2	Negligible

RECEPTOR	SCENARIO 1 2018 BASELINE (µG/M³)	PREDICTED CAA NO ₂ (µG/M³)			
		SCENARIO 4 2035 NO DEVELOPMENT (µG/M³)	SCENARIO 5 2035 WITH DEVELOPMENT (µG/M³)	DIFFERENCE (DCAA) (µG/M³)	IMPACT
R1	13.2	17.8	18.0	0.2	Negligible
R2	13.2	18.1	18.3	0.2	Negligible
R3	13.4	15.0	15.3	0.3	Negligible
R4	15.5	16.6	17.1	0.5	Negligible
R5	13.8	17.0	17.2	0.2	Negligible
R6	13.2	15.4	15.5	0.1	Negligible

RECEPTOR	SCENARIO 1 2018 BASELINE (µG/M³)	PREDICTED CAA NO ₂ (µG/M³)			
		SCENARIO 4 2035 No DEVELOPMENT (µG/M³)	SCENARIO 5 2035 WITH DEVELOPMENT (µG/M³)	DIFFERENCE (DCAA) (µG/M³)	IMPACT
R7	13.2	17.4	17.5	0.1	Negligible
R8	13.5	15.4	15.6	0.2	Negligible
R9	14.7	15.2	15.2	0	Negligible
R10	15.1	14.9	15.0	0.1	Negligible
R11	15.9	14.0	14.1	0.1	Negligible
R12	15.5	15.7	15.9	0.2	Negligible
Jerma MS	14.8	17.8	18.0	0.2	Negligible
Jerma site	15.0	15.6	15.8	0.2	Negligible

4.1 SUMMARY OF IMPACTS

TABLE 20: SUMMARY OF AIR QUALITY IMPACTS

IMPACT TYPE AND SOURCE			IMPACT RECEPTOR		EFFECT AND SCALE							PROBABILITY OF IMPACT OCCURRING	OVERALL IMPACT SIGNIFICANCE	PROPOSED MITIGATION MEASURES	RESIDUAL IMPACT SIGNIFICANCE	OTHER REQUIREMENTS
IMPACT TYPE	SPECIFIC INTERVENTION LEADING TO IMPACT	PROJECT PHASE	RECEPTOR TYPE	SENSITIVITY & RESILIENCE TOWARDS IMPACT	DIRECT/INDIRECT/ CUMULATIVE	BENEFICIAL/ ADVERSE	SEVERITY	PHYSICAL/ GEOGRAPHIC EXTENT OF IMPACT	SHORT/ MEDIUM/ LONG TERM	TEMPORARY/ PERMANENT	REVERSIBLE/ IRREVERSIBLE					
Increased NO ₂ levels from trips generated by the Scheme	Traffic caused by operations	Operations in 2030	R1 to R12, Jerma MS and Jerma site	Medium	Direct	Adverse	Minor	Localised	Long term	Permanent	Irreversible	Likely	Negligible	None	Negligible	N/A
		Operations in 2035		Medium	Direct	Adverse	Minor	Localised	Long term	Permanent	Irreversible	Likely	Negligible	None	Negligible	N/A
Increased PM ₁₀ levels from trips generated by the Scheme	Traffic caused by operations	Operations in 2030	R4	Medium	Direct	Adverse	Minor	Localised	Long term	Permanent	Irreversible	Likely	Minor	Green travel plan	Negligible	N/A
		Operations in 2030	R1 to R3, R5 to R12, Jerma MS and Jerma site	Medium	Direct	Adverse	Minor	Localised	Long term	Permanent	Irreversible	Likely	Negligible	None	Negligible	N/A
		Operations in 2035	R1 to R12, Jerma MS and Jerma site	Medium	Direct	Adverse	Minor	Localised	Long term	Permanent	Irreversible	Likely	Negligible	None	Negligible	N/A
Increased PCT level from trips generated by the Scheme	Traffic caused by operations	Operations in 2030	R6, R8 to R12, Jerma site	Medium	Direct	Adverse	Minor	Localised	Long term	Permanent	Irreversible	Likely	Negligible	None	Negligible	N/A
			R3 and R7	Medium	Direct	Adverse	Minor	Localised	Long term	Permanent	Irreversible	Likely	Minor	Green travel plan	Negligible	N/A
			R4, R5 and Jerma MS	Medium	Direct	Adverse	Minor	Localised	Long term	Permanent	Irreversible	Likely	Moderate	Green travel plan	Minor	N/A
			R1 and R2	Medium	Direct	Adverse	Minor	Localised	Long term	Permanent	Irreversible	Likely	Major	Green travel plan	Moderate	N/A
Increased PCT level from trips generated by the Scheme	Traffic caused by operations	Operations in 2035	R6, R8 to R11, Jerma site	Medium	Direct	Adverse	Minor	Localised	Long term	Permanent	Irreversible	Likely	Negligible	None	Negligible	N/A
			R3, R7, R12	Medium	Direct	Adverse	Minor	Localised	Long term	Permanent	Irreversible	Likely	Minor	Green travel plan	Negligible	N/A

Impact Type and Source			Impact Receptor		Effect and Scale							Probability of Impact Occurring	Overall Impact Significance	Proposed Mitigation Measures	Residual Impact Significance	Other Requirements
Impact Type	Specific Intervention Leading to Impact	Project Phase	Receptor Type	Sensitivity & Resilience Towards Impact	Direct/Indirect/Cumulative	Beneficial/Adverse	Severity	Physical/Geographic Extent of Impact	Short/Medium/Long Term	Temporary/Permanent	Reversible/Irreversible					
			R1, R4, R5, Jerma MS	Medium	Direct	Adverse	Minor	Localised	Long term	Permanent	Irreversible	Likely	Moderate	Green travel plan	Minor	N/A
			R2	Medium	Direct	Adverse	Minor	Localised	Long term	Permanent	Irreversible	Likely	Major	Green travel plan	Moderate	N/A

5 MITIGATION MEASURES AND MONITORING

5.1 EXPECTED IMPACT

During the construction phase, the construction of the planned works will determine the need to prepare a construction site, with the presence of excavation and land filling, storage and handling of inert materials, work vehicle activities, circulation of heavy vehicles for transportation of materials, construction activities. These activities will lead to emissions into the atmosphere primarily related to the operation of the means of work and related to the combustion processes of the engines. Furthermore, the need to move inert materials, as well as their deposit, can also determine the diffusion into the atmosphere of dust and particulate matter, particularly on windy days.

At the end of the works, emissions into the atmosphere are also expected, deriving from the variation in traffic induced by the new road system. The impact is classified as negligible however.

5.2 MITIGATION MEASURES ENVISAGED

In order to reduce impacts brought about by the demolition and construction activities, which generate airborne particulate matter, mitigation measures need to be implemented to minimise dispersion of dust. Possible mitigation systems in the construction phase include:

- a) any heaps of inert material present will be protected from the wind with sheets
- b) Fixed and movable water nebulizers - The nebulizer should be installed during major activities such as demolition and construction.
- c) Dust barriers - Such barriers decrease the wind dispersion of dust beyond the perimeter of the construction site. These barriers must be at least 3 meters.
- d) Wetting of the internal roads of construction sites with trucks containing water. This activity is very important because it reduces the lifting of dust deposited on the ground.
- e) Wheel-washing facility - Wheel-washing facilities are placed at the entrance and exit of the construction site. These systems reduce the dispersion of particulates beyond the perimeter of construction sites.
- f) The transport of inert materials along the ordinary roads pertaining to the site will be carried out using closed or sheeted vehicles.

5.3 PROMOTING SUSTAINABLE TRANSPORT

Transport issues should be considered from the earliest stages of plan-making and development proposals, so that:

- a) the potential impacts of development on transport networks can be addressed;
- b) opportunities from existing or proposed transport infrastructure, and changing transport technology and usage, are realised – for example in

relation to the scale, location or density of development that can be accommodated;

- c) opportunities to promote walking, cycling and public transport use are identified and pursued

At the end of the works, with regard to emissions induced by vehicular traffic, the project may consider:

- a) Creation of a cycle-pedestrian path within the area connected to the urban network, in order to limit travel by car, at least for short distances
- b) Avoid the formation of vehicle traffic queues for access into the complex
- c) Improvement of nearby junctions, to increase the vehicular flow of transit and avoid congestion of vehicular traffic as recommended in the TIA report.



FIGURE 22: A NEBULIZER IN ACTION



FIGURE 23: WETTING OF INTERNAL ROADS



FIGURE 24: EXAMPLES OF WHEEL WASHING FACILITIES



FIGURE 25: A DUST BARRIER INSTALLATION

5.4 GREEN TRAVEL PLAN

A Green Travel Plan is a strategic framework designed to encourage a shift away from single-occupancy private vehicle use towards more sustainable modes of transport, including public transport, walking, cycling, shared mobility solutions, and carpooling. Such plans aim to influence travel behaviour by promoting environmentally responsible transport choices for journeys to and from work, business-related travel, and personal trips undertaken outside working hours.

Green Travel Plans provide an effective mechanism for reducing traffic congestion, particularly during peak travel periods, while simultaneously contributing to improved air quality, reduced greenhouse gas emissions, and enhanced accessibility. By encouraging sustainable travel patterns, these plans support broader environmental objectives and help create healthier and more liveable communities.

The primary objective of adopting a Green Travel Plan for the proposed development is to minimise the environmental impacts associated with vehicular traffic. This can be achieved through a combination of behavioural measures, awareness initiatives, and physical infrastructure improvements aimed at reducing dependency on private car use and increasing the attractiveness of sustainable transport alternatives.

5.5 CONTROL AND MONITORING OF POLLUTANTS

The phase which contributes most significantly to the impact on air quality is the construction phase. Therefore, it is recommended that an expert monitors the

construction phase (including the demolition and excavation activities) to identify the concentrations of pollutants generated by the works. It is important that the concentrations of pollutants do not exceed the limits stipulated in the local and EU Ambient Air Quality regulations.

Directive 2008/50/EC Annex 1, Table 1 states it is an obligation to cover 14% of the calendar year, which correspond to 8 weeks of measurement during the main phases of construction (such as the demolition) or evenly distributed throughout the year, so as to verify that concentrations remain below established limits.

The parameters to monitor include:

- Concentration of Nitrogen Dioxide on the main transit route;
- Particulate matter PM_{10} (test method EN 12341: 2014);
- Analysis on particulate matter PM_{10} filters for metals (Lead, Cadmium, Arsenic and Nickel - test method EN 14902: 2005) and Benzo[a]pyrene (test method EN 15549: 2008).

APPENDIX I

TERMS OF REFERENCE



TERMS OF REFERENCE¹

FOR THE PREPARATION OF AN

AIR QUALITY STUDY

June 2019 version

Legal background:

Regulation 29 of S.L. 549.59, grants ERA the power to issue guidance notes on the conduction of Air Quality Studies which are required by any Regulations issued under the Environment Protection Act including the EIA Regulations (S.L. 549.46).

Part II of Schedule 7 to S.L. 549.59 sets the following (legally binding limit values): an annual limit value of $40\mu\text{g}/\text{m}^3$ for PM_{10} , a daily limit value for PM_{10} of $50\mu\text{g}/\text{m}^3$ which can not be exceeded on more than 35 calendar days (90.4% of the daily readings in a calendar year should be $< 50\mu\text{g}/\text{m}^3$), an annual limit value $40\mu\text{g}/\text{m}^3$ for NO_2 and an hourly limit value of $200\mu\text{g}/\text{m}^3$, which can not be exceeded more than 18 times per calendar year.

Regulations 19 and 20 of S.L. 549.59 give ERA the responsibility to ensure that the above mentioned limits are complied with across Malta and Gozo.

0. Applicability

These terms of reference are applicable to all development applications irrespective of whether or not it qualifies for an Environmental Impact Assessment, as long as the expected increase in traffic flows due to the operation of the project is ≥ 1000 passenger cars AADT or ≥ 200 HDV AADT.

The Air Quality study shall be conducted as follows:

- a) *The relevant details of the proposed development:* This should include an overview of the expected traffic changes when the project is FULLY operational. The report should also include a brief introduction to the sensitivity of the area to increases in traffic flows and changes in air pollution levels keeping in mind the NO_2 levels registered by the passive diffusion tubes (include in ERA's network) sited closest to the site.
- b) *Description of the relevant immission standards with reference to S.L. 549.59.*
- c) *The assessment methods:* This section shall include any relevant details on the methods used in order to monitor the base line levels of NO_2 and PM_{10} , including any proof of equivalence to the reference method(s) as applicable (see 2.i and 2.n below). The section

shall also include a part outlining the core details of the model (including version number) being used in order to predict the impact of the development. The consultants shall also include details on all the input data used and its source, including features of the traffic flows used, speeds, apportionment by vehicle type etc.

- d) *Site selection*: This section shall include the considerations made by the consultants in the selection of the monitoring site. The consultants shall also show how the selected site matches the site selection criteria in Annex I and the additional criteria Section 2 paragraph k). Prior to the commencement of the monitoring campaign the consultants shall together with the method statement include a map with the GIS location of the sampling point. The map shall include any measurements showing that the selected site complies with points v), vi), vii) and ix) of Annex I; the identification of any sensitive receptor in an area determined according to the guidelines in point f), below, as well as any available traffic counts for any thoroughfare within this area. The monitoring campaign cannot start unless the site has been approved by ERA. The rationale behind the selection of the sampling site shall be clearly outlined explaining how the site meets all the site selection criteria especially the criterion in Section 2, paragraph k).
- e) *Model verification*: Model verification involves a comparison between the predicted and the measured values for both PM₁₀ and NO₂. Any errors between modeled and measured values should be adequately corrected. In addition consultants are expected to include estimates of the uncertainties in the traffic flows, vehicle emission factors and background concentrations. Any modeled concentrations should include a cumulative sensitivity analysis for these uncertainties (the effect of each uncertainty should be clearly outlined). The limitations of the model should be clearly stated e.g. the software's inability to model dispersion of air pollutants if the air flow is affected by trees or the inability to model pollutant concentrations in street canyons.
- f) *Identification of sensitive receptors*. For the projects in Annex II to this document and within the scope of S.L. 549.46, the consultants will be required through the use of software modeling traffic flows, to delineate the extent of the area affected by increased traffic flows due to the project. Baseline studies may be required for more than one location. Any sensitive receptor within this area shall be clearly identified through the use of a GIS package. For any other project the consultants may do away with the delineation and identify the sensitive receptors within a 3km radius around the site. Sensitive receptors include schools, retirement homes, residential units, hospitals, etc.

- g) *Description of the baseline conditions.* This section should include details on location of the points at which the air quality monitoring was carried out, the reason for which this particular site was used, the sampling period, data capture, the scale up factors provided by ERA and if possible a break-up of the base line levels of the pollutant by the source.
- h) *Assessment of impact.* Results of the modeling for the “with development” scenario should be clearly set out in tables and also through the use of contour maps (which shall include the sensitive receptors identified in e) above), this should be compared to the “without development” scenario with respect to both the table and the contour map. The comparison between both scenarios shall also be applied to each of the sensitive receptors identified in e) above.
- i) *Determination of the significance of the impact.* The table in section 4 (and the tool made available through the ERA website) shall be used for each of the sensitive receptors identified in e) as well as for the modeled concentrations at the site where the monitoring was carried out.
- j) *Cumulative impacts.* If in the area there are other planned developments, which have already been granted development consent then the contribution of these developments should also be considered at a point in the future when these are fully operational.
- k) *Mitigation measures.* If the effect of the project is substantially adverse or worse, then the report shall include any mitigation measures, which have been identified and, which will reduce the impact of the project to at least slightly adverse. Non-quantifiable measures will not be expected.
- l) *Summary of the report.* The report should be written in clear, concise, grammatically correct English. If the English of the report is unacceptable, the report shall be sent to the consultants for correction and ERA will not take any responsibility for any delays in the process.

2. Base Line Studies

- a) The baseline levels of PM₁₀ and NO₂ shall be established through *in-situ* monitoring;
- b) Baseline levels of PM₁₀ shall be determined using the reference method (EN 12341:2014) for the determination of PM₁₀;

- c) The consultants should use the reference method for the sampling and measurement of PM₁₀;
- d) The design criteria for the samplers shall be as per Annex B to the said standard and shall be as per Section IV of Annex IX: EN 12341: 2014;

Inlet Design	Flow rate		Filters
See Section 5.1.2 and Annex A of EN 12341:2014	To a nominal value of 2.3 m ³ .hr ⁻¹ see Section 5.1.5 of EN 12341:2014	The instantaneous value of the flow rate shall be kept within 5% of the nominal value. The volumetric flow rate averaged over the sampling period shall be within 2% of the nominal value, see Section 5.1.5	Circular: such that the diameter of the exposed area through which the sampled air passes is between 34mm and 44mm.

Table 1 design criteria for the samplers.

- e) The resolution of the balance used for the weighing of filters sampled using an LVS shall be at least 10 µg, Section 5.2.2 of EN 12341:2014;
- f) The filters should be conditioned for at least 48 hours (Section 6.2 of EN12341:2014) at 50% relative humidity (+ or - 5%) with an uncertainty of ≤ 2% RH and at 20 °C (+ or - 1 °C) with an uncertainty of ≤ 0.2 °C, according Table 2, Section 5.2 of EN12341:2014.
- g) The filters should be weighed at least twice for concordance (the difference between successive readings shall ≤ 40µg, Section 6.2 of EN12341:2014) with a time lag of at least 12 hours between the two weightings;
- h) Flow rates are at ambient volumes not at normalised volumes. The weighing shall take place in the same climate controlled room at the same environmental conditions as in f);
- i) Consultants can use alternative sampling and measurement methods if they demonstrate to ERA's satisfaction, equivalence to the above mentioned method under the Maltese air pollution climate. Equivalence shall be determined using the [European Commission's method for the determination of equivalence](#); any other method shall be deemed unacceptable. ERA will accept certificates of equivalence issued by third parties, which have been based on the method herein;

- j) Compliance with non-European standards does not satisfy the requirements above;
- k) Regarding the siting of the sampler/diffusion tube, the consultant shall submit a method statement indicating the location of the sampler/diffusion tube. The sampling point(s) should not be within the site to be developed or exactly adjacent to it, but should be sited at a location representative of the thoroughfare on which the highest traffic impacts (due to the project) are expected. In addition the consultant is obliged to use all the criteria in Annex I to determine the sampling location. In addition the ERA may at its discretion ask the consultant to change the location of the sampler;
- l) The sampling time shall be no less than 6 weeks and extendible by a further 3 weeks depending on the considerations made by the consultants and using the respective penalties in s), below;
- m) The consultants shall discard readings influenced by Saharan dust intrusions. These episodes are characterized by a marked spatial consistency, demonstrated by concomitant peaks in the levels of PM₁₀ (and PM_{2,5}) across the Maltese Islands (see Figure 1 below). The consultants shall use this in conjunction with following two tools to confirm the occurrence of these episodes a) [MACC ensemble](#) and b) [HYSPLIT back trajectory model](#).

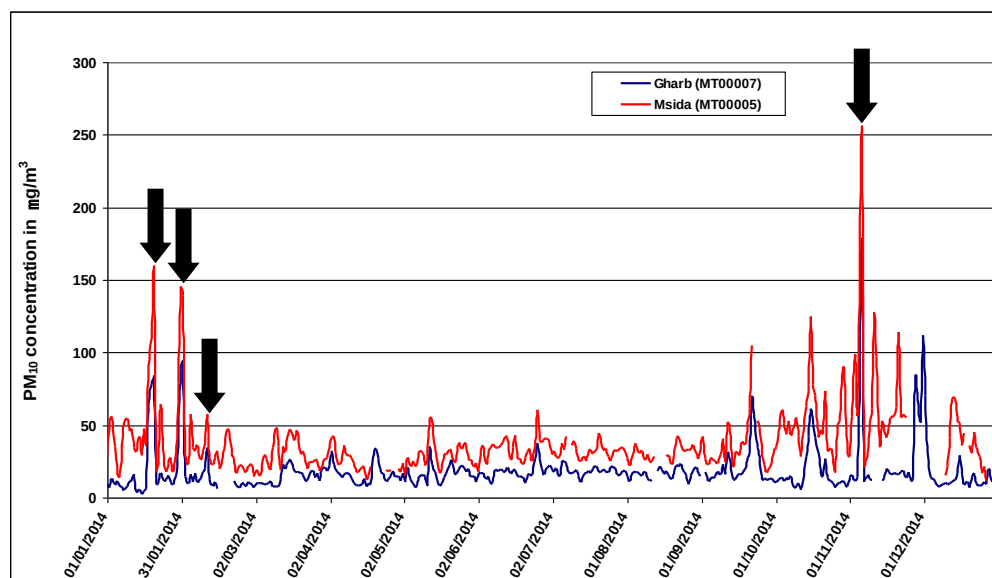


Figure 1: Comparison of the PM₁₀ levels in Għarb (blue) to the PM₁₀ levels in Msida (red) measured in 2014. The black arrows show some of the Saharan events throughout 2014.

- n) The PM₁₀ dataset shall in no case consist of <42 or <63 (depending on whether the baseline monitoring period has been set for 6 or 9 weeks) daily readings, excluding any discarded readings.

Baseline levels of NO₂.

- o) Baseline levels of NO₂ shall be determined using EN 14211:2005. The consultant may use passive diffusive tubes if it is shown that the latter are equivalent to the reference method.
- p) If the consultant opts for passive diffusion tubes, he shall forward at least 1 article in a peer reviewed journal e.g. Pfeffer *et al.* (2010) – *Gefahrstoffe-Reinhalt der Luft*. 11-12, 500-506, which shows that the equivalence of these tubes has been demonstrated for field trials (not exposure chambers) in at least 1 EU Member State. Equivalence should preferably, also have been demonstrated in Malta. The field trial shall include the comparison of at least 40 individual measurements taken throughout a whole calendar year. Equivalence shall be determined using a modification of European Commission's method for the determination of equivalence for PM₁₀; any other method shall be deemed unacceptable
- q) The sampling point for NO₂ shall be the same as for PM₁₀.

Annualisation of the 6 (or 9) week averaged values for PM₁₀ and NO₂.

- r) The factor in l) and p) above shall be based on the use of the following equation (adapted from LAQM TG(16), April 2016 version:

$$CAA = \frac{p_{y+1}^{x \text{ weeks}}}{p_y^{x \text{ weeks}}} \times p_y^{52 \text{ weeks}}$$

Where:

CAA is the corrected annual average;

p_{y+1}^{x weeks} is the concentration of NO₂ or PM₁₀ measured by the consultants throughout the 6 (9) week (baseline) monitoring period;

p_y^{x weeks} is the concentration of NO₂ or PM₁₀ measured throughout the same 6 (9) week monitoring period of the preceding year at a comparable ERA fixed station; and

p_y^{52 weeks} is the annual average of NO₂ or PM₁₀ measured at the comparable ERA fixed station.

Traffic Counts.

- a) The consultant shall also take traffic counts at the main junctions near the monitoring site.
The number and location of the counters are to be approved by ERA, (unless longer term traffic counts are already available).
- b) The traffic count shall take into consideration the vehicle type and the legislation class.
- c) The consultant shall use an appropriate model in order to scale the traffic counts obtained during the 6 (or 9) week period to AADT.

3. Modeling

- a) Once the baseline levels have been obtained the consultant shall determine the impact of the project on air quality through dispersion modeling.
- b) The following models are deemed acceptable by ERA:
IMMIS^{em}
BREEZE Roads.
ADMS-Urban
- c) The model used should use the logic outlined by e) below,
- d) The consultant shall use exclusively the emission factors in the latest version of the Handbook of emission factors for road transport emissions ([HBEFA v 3.3](#)). The average age of the Maltese vehicle fleet shall be taken as 13 years.
- e) The use of other emission factors is not acceptable.
- f) The consultant shall estimate the ambient background levels for both NO₂ and PM₁₀. The approach in Figure 2 below shall be deemed acceptable for both pollutants.

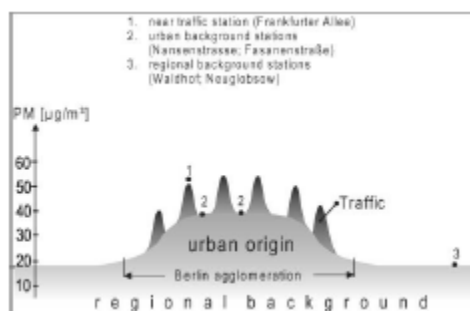


Figure 2: Horizontal profile for PM₁₀ concentration, Lenschow *et al.* (2001) – *Atmospheric Environment* 35, 29-33.

- g) The rural background can be captured through the use of the [EMEP](#) or [LOTOS-EUROS](#) model at a resolution of 50km × 50km (The [GAINS](#) model might have to be used for emissions data for the EU), the urban background can be captured through the use of a model such as [CHIMERE](#) at a resolution of 7km × 7km.
- h) The predictions of the model shall be assessed by comparing the modeled data to the monitoring data provided by the baseline studies. The modeled data must not deviate by more than $\pm 20\%$.
- i) Other methods can be used in order to determine the background levels of NO₂ and PM₁₀, including statistical methods aimed at deriving "horizontal profiles" similar to the ones in Figure 1 (see e.g. Gómez-Losada et al., 2016 – *Atmospheric Environment* 127, 255-261) and based on a full year's dataset, interpolation of data from the nearest ERA diffusion tubes, etc.
- j) The consultant should clearly explain the rationale behind the determination of the background levels.
- k) The consultant shall use the model to project the annual PM₁₀ and NO₂ levels into the future, when the project is fully operational taking into account the cumulative impact of projects in the area, which have been granted development consent.
- l) The consultant shall model two distinct scenarios: A) without the project and B) with the project.
- m) Results shall be displayed as a colour-coded contour map with the modelled annual concentrations of NO₂ and PM₁₀ as well as the calculated 90.4th percentiles for the daily PM₁₀ levels (calculated using the equation in q) within a 3km radius and especially at the sensitive receptors in point 1e. The position of the sensitive receptors shall be clearly labeled.
- n) For the annual averages of NO₂ and PM₁₀ as well as for the 90.4th percentile of the PM₁₀ levels, the contour maps shall show the situation with the scheme and without the scheme.
- o) Contour plots for the 90.4th percentile of the PM₁₀ levels shall include the error in the prediction of this value, which shall be calculated using the equation in q).

- p) For the three criteria above the consultants shall also draw colour-coded contour maps expressing the difference in the annual levels/90.4th percentile, between the two scenarios (with and without the scheme) in terms of the significance criteria in 4 b) and 4 c).
- q) The minimum acceptable resolution for the model is 50m × 50m and the consultants shall model concentrations at all 50m × 50m grid cells within the area of influence.

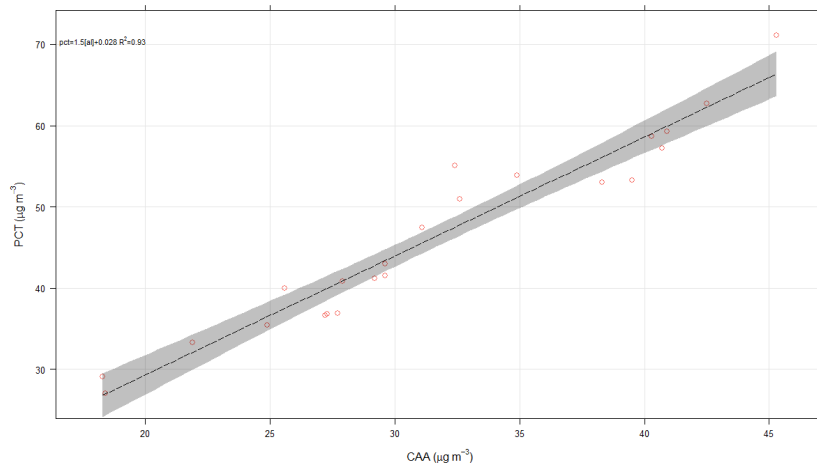


Figure 3: Plot of CAA vs PCT

see e.g. Querol *et al.* (2004) – *Journal of Aerosol Science* 35:9, 1151 – 1172

- r) The consultant shall calculate the baseline of the 90.4th percentile of the daily PM₁₀ using the following equation:

$$PCT = (1.46 \times CAA) + 0.03$$

Error in PCT or ΔPCT should be calculated using the following equation:

$$\Delta PCT = 3.09 \times \left[1.04 + \frac{(CAA - 31.57)^2}{1278.17} \right]^{0.5}$$

The equation for both PCT and ΔPCT shall be updated on a yearly basis by ERA.

The final value of the PCT shall be quoted as PCT ($\pm \Delta PCT$) $\mu\text{g}/\text{m}^3$.

Where CAA (in $\mu\text{g}/\text{m}^3$) is the average of the 6 (or 9) week monitoring period and corrected to an annual average using a factor, which shall be determined by ERA, PCT is the 90.4th percentile of the daily PM₁₀ averages in $\mu\text{g}/\text{m}^3$. The equation above will be modified on a yearly basis by ERA.

- s) If $PCT > 50 \mu\text{g}/\text{m}^3$ (error included) then it is likely that the site is not in compliance with the 90.4th percentile criterion.
- t) The consultant shall also use the modeled annual levels for PM_{10} (AA) to calculate the PCT due to the project (and the error in the PCT) using the same equation as in n) but substituting AA for CAA.
- u) For scaled up annual averages (CAA) $< 30 \mu\text{g}/\text{m}^3$ (errors included) the consultants will not be obliged to analyse for compliance with the 90.4th percentile criterion.
- v) For NO_2 the consultant shall assume that the annual mean is always exceeded before the allowed number of hourly exceedances.
- w) Any assumptions must be clearly stated by the consultant.

4. Significance Criteria

- a) The following criteria of significance (adapted from IAQM's Planning for Air Quality Guidance, January 2017 version) shall be used by the consultant to determine the significance of the impact at all sensitive receptors and at any point within the 3km radius at which the impact of the project on traffic increases is the highest.
- b) A significance criteria tool shall be made available on the ERA website, for guidance and interpretative purposes.
- c) For annual levels of $\text{NO}_2/\text{PM}_{10}$ in $\mu\text{g}/\text{m}^3$.

		Change in the annual $\text{NO}_2/\text{PM}_{10}$ (dAA) levels due to scheme ($\mu\text{g}/\text{m}^3$).			
		$\text{dAA} \leq 0.4 \mu\text{g}/\text{m}^3$	$0.8 \mu\text{g}/\text{m}^3 \leq \text{dAA} \leq 2.0 \mu\text{g}/\text{m}^3$	$2.4 \mu\text{g}/\text{m}^3 \leq \text{dAA} \leq 4.0 \mu\text{g}/\text{m}^3$	$\text{dAA} > 4.0 \mu\text{g}/\text{m}^3$
$\text{CAA for NO}_2/\text{PM}_{10} (\mu\text{g}/\text{m}^3)$	$\text{CAA} \geq 44 \mu\text{g}/\text{m}^3$	MODERATE	SUBSTANTIAL	SUBSTANTIAL	SUBSTANTIAL
	$43.6 \mu\text{g}/\text{m}^3 \leq \text{CAA} \leq 41.2 \mu\text{g}/\text{m}^3$	MODERATE	MODERATE	SUBSTANTIAL	SUBSTANTIAL
	$40.8 \mu\text{g}/\text{m}^3 \leq \text{CAA} \leq 38.0 \mu\text{g}/\text{m}^3$	SLIGHT	MODERATE	MODERATE	SUBSTANTIAL
	$37.6 \mu\text{g}/\text{m}^3 \leq \text{CAA} \leq 30.4 \mu\text{g}/\text{m}^3$	NEGLIGIBLE	SLIGHT	MODERATE	MODERATE
	$\text{CAA} \leq 30 \mu\text{g}/\text{m}^3$	NEGLIGIBLE	NEGLIGIBLE	SLIGHT	MODERATE

- d) For compliance with the 90.4th percentile criterion for PM_{10} .

		Change in the PCT (dPCT) due to scheme ($\mu\text{g}/\text{m}^3$).			
		$\text{dPCT} \leq 0.5 \mu\text{g}/\text{m}^3$	$1.0 \mu\text{g}/\text{m}^3 \leq \text{dPCT} \leq 2.5 \mu\text{g}/\text{m}^3$	$3.0 \mu\text{g}/\text{m}^3 \leq \text{dPCT} \leq 5.0 \mu\text{g}/\text{m}^3$	$\text{dPCT} > 5.0 \mu\text{g}/\text{m}^3$
$\text{PCT } (\mu\text{g}/\text{m}^3)$	$\text{PCT} \geq 55 \mu\text{g}/\text{m}^3$	MODERATE	SUBSTANTIAL	SUBSTANTIAL	SUBSTANTIAL
	$54.5 \mu\text{g}/\text{m}^3 \leq \text{PCT} \leq 51.5 \mu\text{g}/\text{m}^3$	MODERATE	MODERATE	SUBSTANTIAL	SUBSTANTIAL
	$51.0 \mu\text{g}/\text{m}^3 \leq \text{PCT} \leq 47.5 \mu\text{g}/\text{m}^3$	SLIGHT	MODERATE	MODERATE	SUBSTANTIAL
	$47.0 \mu\text{g}/\text{m}^3 \leq \text{PCT} \leq 38.0 \mu\text{g}/\text{m}^3$	NEGLIGIBLE	SLIGHT	MODERATE	MODERATE
	$\text{PCT} \leq 37.5 \mu\text{g}/\text{m}^3$	NEGLIGIBLE	NEGLIGIBLE	SLIGHT	MODERATE

- e) Whenever the impact of the project is determined to be "negligible" no further action will be required from the developer.

- f) If the impact of the project is classified as "substantially adverse" then ERA will not recommend approval unless the project is modified in such a way (including scaling down) that the significance of the impact is measurably lessened to at least "slightly adverse". In this case a green travel plan will not be considered as sufficient.
- g) If the impact of the project is "moderate adverse" then the developer will be asked to modify the project. The modifications can include a green travel plan which has to include specific, measurable² and achievable objectives together with their respective implementation time-frames. The developer will be asked to finance at least in part, the implementation of the green travel plan. The implementation of the plan will have to be audited and eventually updated by the developer on a periodic basis. If the green travel plan does not lower the significance of the impact then the developer will be asked to take additional measures, which may include scaling-down the project.
- h) If the impact of the project is slightly adverse then the developer will be asked to consider alternatives, which will lessen the impact of the project.

² The term measurable in this context means that the green travel plan shall quantify the reduction in the pollutant levels (in $\mu\text{g}/\text{m}^3$), over the scenario leading to the classification of the impact as "moderately adverse".

Concluding Remarks

- a) The air quality study shall consider the **CUMULATIVE** impact of all development taking place and/or which is planned for the site in question irrespective of the number of separate Planning Applications involved.
- b) If the applicant-decides to develop a part of the site at some point in the future, then a full air quality study will be requested and this will have to consider the cumulative impact from the whole site, in line with the ERA Guidelines on the issue. This requirement will apply irrespective of the incremental increase in traffic flow as a result of the latter development.

ANNEX I

Site selection Criteria mention in Section 1 d) and in Section k).

- i. PM₁₀ samplers shall sited at least 500m from:
 - a) dust piles;
 - b) construction/demolition/excavation sites & quarries;
 - c) dirt tracks;
 - d) un-asphalted surfaces;
 - e) surfaces which are visibly covered with dust; and
 - f) any other surface or activity likely to lead to the entrainment of dust
- ii. There shall be absolutely no bends in between the PM₁₀ sampling head/sampling inlet for NO₂ and the analyser.
- iii. The height of the PM₁₀ sampling head/sampling inlet for the NO₂ analyser/NO₂ passive diffusive tube shall be $\geq 1.5\text{m}$ and $\leq 4\text{m}$ above the ground.
- iv. For active samplers, the exhaust outlet shall be positioned in such a way that recirculation of the exhaust air to the sampling inlet is avoided.
- v. The samplers shall be placed at a point, which is representative of a street segment $\geq 100\text{ m}$.
- vi. The distance of the PM₁₀ sampling head/sampling inlet for the NO₂ analyser/NO₂ passive diffusive tubes from the edge of any road junction shall be $\geq 25\text{m}$.
- vii. The PM₁₀ sampling head/sampling inlets for the NO₂ analyser/NO₂ passive diffusive tube shall be placed at $\leq 10\text{m}$ from the kerbside.
- viii. The flow around the PM₁₀ sampling head/sampling inlets for the NO₂ analyser/NO₂ passive diffusive tube shall be unrestricted, without any obstructions in the vicinity of the sampler i.e. free in an arc of at least 270°.
- ix. The PM₁₀ sampling head/sampling inlets for the NO₂ analyser/NO₂ passive diffusive tube shall in no case be at < 0.5 from the nearest building.

Note: The selection of the site is solely the consultants' responsibility. ERA will not waive the requirement for in situ monitoring due to erroneous readings resulting from poorly chosen monitoring sites. The 6 (or 9) week monitoring period will apply regardless of any time constraint the consultants might have. ERA will therefore not assume responsibility for any delays caused by this issue.

ANNEX II

(Projects identified in section 1f).

Projects falling within the scope of the following categories in Schedule I of LN 412 of 2017 are covered by the article above:

All Section 1 (*General land use*) projects depending on the type of project.

The following projects within Section 2 (*Transport Infrastructure Projects*):

Section 2.1 (*Roads*) - Category I

2.1.1.1;

2.1.1.2.

Section 2.1 (*Roads*) - Category II

2.1.2.1.

All projects in Section 2.2 (*Airports*) irrespective of the Category;

The following projects within Section 6 (*Development on the coast or at sea – including ports*):

Section 6.1 (*Ports, Marinas and Waterways*)

6.1.1.1;

6.1.1.2.

All the projects in Section 7 (*Urban Development and Recreational Projects*), with the exclusion of:

Section 7.1 (*Urban Development Projects*)

7.1.2.2;

7.1.2.3 unless it is accompanied by a Section 2, Section 6 or a Section 7 project ,which is not covered by this exclusion.

Section 7.2 (*Recreational or Sporting Establishments*)

7.2.1.1;

7.2.2.3;

7.2.2.4.

The following projects within Section 12 (Industrial Development)

Section 12.7 (*Industrial Estates*)

12.7.2.1.

Section 13.0 (*Changes or Extensions to approved projects, and reactivation of projects*) on a case by case basis.

APPENDIX 2

AADT FOR THE RELEVANT STREETS

TABLE 21: SUMMARY OF AADT TRAFFIC

		2018	2030	2035
Triq Sant Antnin	Network Flows	21,914	24,693	25,953
	Development Flows	0	1,136	1,136
Triq is-Salini	Network Flows	1,417	1,597	1,678
	Development Flows	0	966	966
Triq il-Qaliet (Upper Part)	Network Flows	8,380	9,443	9,924
	Development Flows	0	170	170
Triq il-Qaliet (Lower Part)	Network Flows	8,380	9,443	9,924
	Development Flows	0	951	951
Triq tal-Gardiel	Network Flows	5,448	6,139	6,452
	Development Flows	0	951	951

APPENDIX 3

MONITORING RESULTS

Test Report Air Pollution Measurement

NO2 Nitrogen dioxide measurement by means of passive sampler

customer information

customer: AIS Environment Ltd, Malta
customer ID: MAI
contact person: Sian Pledger
project:
reference:

passive samplers

date received: 15.03.2019
type: tube (Palms)
pollutant: NO2
sampling rate: 0.734 [ml/min]
protective filter: yes

analysis

method: SP01 photometer, Salzmann
analyte: NO2
date: 18.03.2019
place: passam ag

test report

created on: 20.03.2019
created by: I. Anderson
checked on: 27.03.2019
checked by: S. Huber
file name: MAI011901-KF
pages: 1



note: applies to the sample as received; for information on the uncertainty of measurement and detection limit see data sheet: www.passam.ch;
concentration calculated assuming: T = 20°C; p = 1013 hPa; this method is accredited to ISO 17025

measuring site	passive sampler		measuring period					measurement			result		comment
	label	lot no.	start		end		exp. time	blank	dilution	sample value	m analyte/ sampler	C NO2	
			date	time	date	time	[h]	[ABS]		[ABS]	[ug]	[ug/m3]	* remark by customer
1A	3	180919	24/01/2019	13:40	14/02/2019	14:00	504.3	0.006	1	0.190	0.41	18.5	
1B	5	180919	24/01/2019	13:40	14/02/2019	14:00	504.3	0.006	1	0.199	0.43	19.4	
1C	10	180919	24/01/2019	13:40	14/02/2019	14:00	504.3	0.006	1	0.184	0.4	18.0	
2A	4	180919	14/02/2019	14:00	07/03/2019	14:30	504.5	0.006	1	0.248	0.54	24.3	
2B	6	180919	14/02/2019	14:00	07/03/2019	14:30	504.5	0.006	1	0.230	0.5	22.5	
2C	8	180919	14/02/2019	14:00	07/03/2019	14:30	504.5	0.006	1	0.242	0.52	23.4	

ACCREDITATION CERTIFICATE

— National Accreditation Board – Malta —



Sunlab Group Ltd.

Life Sciences Park, San Gwann Industrial Estate,
San Gwann

is accredited by the National Accreditation Board – Malta to undertake testing as detailed in
the Scope of Accreditation bearing the above accreditation registration number,
in compliance with the International Standard

EN ISO/IEC 17025:2005

“General Requirements for the Competence of Testing and Calibration Laboratories”

**This Certificate Must Only Be Read in Conjunction with the Annexed Scope of Accreditation which
defines the tests for which the laboratory has been accredited.**

This Accreditation shall remain in force subject to continuing compliance with NAB-MALTA accreditation
criteria, EN ISO/IEC17025 and any further requirements specified by the National Accreditation Board.

Certificate Number **018/1**

Certificate issue date **21/07/2016**

Accredited Scope **Testing (as described in Scope of Accreditation dated 21/07/2016)**

Chairman – National Accreditation Board

Director - National Accreditation Board

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accrediting the competence of conformity assessment bodies in the field of calibration, testing, inspection,
certification of management systems, products and personnel, and EMAS verifiers in line with EU Reg.
765(2008) Art. 4(1). NAB-MALTA is an EA-MLA signatory for testing, calibration and inspection.

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Tel No. (+356) 23952510
Web: www.nabmalta.org.mt - Email: info@nabmalta.org.mt



Sunlab Group Ltd.

Scope of Accreditation

Contact person	Fillippo Giglio
Address	Life Sciences Park, San Gwann Industrial Estate, San Gwann
Telephone	+35621381391
Company Reg. No.	C44052
Email	info@sunlabgroup.com
Website	N/A

ACCREDITATION INFORMATION - TESTING LABORATORY

Accreditation No.	018
Accreditation Certificate No.	018/1
Accredited according to	EN ISO/IEC 17025:2005
Accreditation Scope No.	S018/1
Date of issue of this Scope	Thursday, 21 July 2016

SCOPE OF ACCREDITATION

Issue No: S018/1

Page 1 of 8

TESTING LABORATORY

Laboratory Locations

Location Details	Activity	Location Code
Address Life Sciences Park, San Gwann Industrial Estate, San Gwann	Head Office	N/A

Site activities performed away from the locations listed above

Location Details	Activity	Location Code
Clients	Environmental Testing	B

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Sunlab Group Ltd.

Scope of Accreditation

SCOPE OF ACCREDITATION

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Material/ Product/ Matrix Tested/ Calibrated	Type of test/ calibration and/or property measured, range of measurment	Standard Specifications/ In- House Methods/ Equipment/ Techniques	Loc. code
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Environmental Monitoring - Ambient Air Quality

Ambient Air Quality	Sampling for the determination of airborne asbestos fibres	DM 06/09/1994 SO n° 129 GU n° 220 20/09/1994 All.2	B
Ambient Air Quality	Sampling for the determination of particulate matter - PM10	DM n° 60 02/04/2002 SO GU n° 87 13/04/2002 + UNI EN 12341:2014	B
Ambient Air Quality	Sampling for the determination of benzo[a]pyrene	EN 15549:2008	B
Ambient Air Quality (PM10 fraction of suspended particulate matter)	Sampling for the determination of Pb, Cd, As and Ni	EN 14902:2005 + EC 1- 2008 (sampling)	B
Ambient Air Quality (Filters)	Sampling for the determination of total particulate matter, total dusts	Internal Method (Sun Lab Group Ltd) IM-01-2015 Rev. 1 del 20/11/2015 (sampling)	B
Ambient Air Quality	Determination of benzene (C6H6)	EN 14662-3:2015	B
Ambient Air Quality	Determination of nitrogen dioxide (NO2), nitrogen monoxide (NO), nitrogen oxides (Nox)	UNI EN 14211:2012	B
Ambient Air Quality	Determination of sulphur dioxide (SO2)	EN 14212:2012	B
Ambient Air Quality	Determination of carbon oxide (CO)	EN 14626:2012	B

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Material/ Product/ Matrix Tested/ Calibrated	Type of test/ calibration and/or property measured, range of measurment	Standard Specifications/ In-House Methods/ Equipment/ Techniques	Loc. code
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Ambient Air Quality	Determination of ozone (O3)	EN 14625:2012	B
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Ambient Air Quality	Sampling for the determination of PM 2,5 mass fraction of suspended particulate matter	EN 12341:2014 (sampling)	B
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Ambient Air Quality	Determination of temperature	EN ISO 7726:2002	B
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Environmental Monitoring - Other

Liquid, granular, paste, coarse, monolithic and Waste	Sampling	UNI 10802:2013	B
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Residential environment and outdoor	Equivalent continuous A-weighted sound pressure level (LAeq,T)	DM 16/03/1998 GU n° 76 01/04/1998 All b	B
-------------------------------------	--	--	---

Soils, land	Sampling	UNICHIM Manual n°196/2 2004 (only paragraph n°5 and 6)	B
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Marine sediments	Sampling of marine sediments	ISO 5667-19:2004	B
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Environmental Monitoring - Stack emissions

Stack emissions (adsorbent solutions)	Sampling for the determination of ammonia	Unichim Method n°632:1984 (sampling)	B
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Sunlab Group Ltd.

Scope of Accreditation

SCOPE OF ACCREDITATION			Page 4 of 8
Material/ Product/ Matrix Tested/ Calibrated	Type of test/ calibration and/or property measured, range of measurment	Standard Specifications/ In-House Methods/ Equipment/ Techniques	Loc. code
Stack emissions	Sampling for the determination of mass concentration of dusts	EN 13284-1:2003	B
Stack emissions	Sampling for the determination of hydrogen sulphide	Unichim Method n°634:1984	B
Stack emissions (vials)	Sampling for the determination of volatile organic compounds: acetone, toluene, hexane, penthane, o-xylene, m-p-xylene, trichloroethylene, 1,1,1-trichloroethane, 4-metil-2-penthane, tetrachloroethylene, ethylacetate, 1-butanholo, 2-butanone, dichloromethane, styrene, 2-butanholo	CEN / TS 13649:2015 (sampling)	B
Stack emissions	Determination of total organic carbon (TOC)	EN 12619:2013	B
Stack emissions	Determination of carbon oxide (CO), carbon dioxide (CO ₂), nitrogen monoxide (NO), nitrogen oxides (NO _x), nitrogen monoxide (NO), sulphur dioxide (SO ₂)	ISO 11042-1:1996	B
Stack emissions	Determination of oxygen	EN 14789:2006	B
Stack emissions	Determination of water vapour	EN 14790:2006	B



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Scope of Accreditation

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Material/ Product/ Matrix Tested/ Calibrated	Type of test/ calibration and/or property measured, range of measurment	Standard Specifications/ In-House Methods/ Equipment/ Techniques	Loc. code
Stack emissions	Determination of flow, velocity, temperature, pressure, humidity vapour	UNI 10169:2001	B
Stack emissions	Determination of flow and velocity	EN ISO 16911-1:2013	B
Stack emissions (filters and absorbent solutions)	Sampling for the determination of arsenic, cadmium, chromium, cobalt, copper, manganese, nickel, lead, antimonium, thallium and vanadium	EN 14385:2004	B
Stack emissions	Determination of the mass concentration of carbon monoxide (CO). Reference method: non-dispersive infrared spectrometry	EN 15058:2006	B
Stack emissions	Determination of mass concentration of nitrogen oxides (NOx). Reference method: chemiluminescence	EN 14792:2006	B
Stack emissions	Determination of mass concentration of sulphur dioxide (SO2)	EN 14791:2006	B
Stack emissions	Sampling for the determination of dioxins and furans	EN 1948-1:2006	B
Stack emissions	Sampling for the determination of polycyclic aromatic hydrocarbons (PAHs)	ISO 11338-1:2003	B

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Material/ Product/ Matrix Tested/ Calibrated	Type of test/ calibration and/or property measured, range of measurment	Standard Specifications/ In- House Methods/ Equipment/ Techniques	Loc. code
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Stack emissions	Sampling for the determination of hydrochloric acid (HCl)	EN 1911:2010	B
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Stack emissions	Determination of hydrochloric acid (HCl) and hydrofluoric acid (HF)c acid (HCl)(sampling)	DM 25/8/2000 All. 2	B
-----------------	---	---------------------	---

Stack emissions	Sampling for the determination of chromium VI	EPA 306: 2014	B
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Environmental Monitoring - Water

Water Treatment Works, Desalination Plants, Reservoirs, Ground waters, Domestic and Industrial Premises, Runoff water, waste waters and effluents, water intended for human consumption and salted waters	Determination of dissolved oxygen	EN ISO 5814:2013	B
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Water Treatment Works, Desalination Plants, Reservoirs, Ground waters, Domestic and Industrial Premises, Runoff water, waste waters and effluents, and water intended for human consumption and water intended for human consumption	Determination of free active chlorine, total chlorine	APAT CNR IRSA 4080 Man 29 2003	B
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Material/ Product/ Matrix Tested/ Calibrated	Type of test/ calibration and/or property measured, range of measurment	Standard Specifications/ In- House Methods/ Equipment/ Techniques	Loc. code
Water Treatment Works, Desalination Plants, Reservoirs, Ground waters, Domestic and Industrial Premises, Runoff water, waste waters and effluents, and water intended for human consumption	Determination of temperature	APAT CNR IRSA 2100 Man 29 2003	B
Waste water, sea water, Superficial water, leachate, ground water and water intended for human consumption	Determination of conductivity	APAT CNR IRSA 2030 Man 29 2003	B
Water, water intended for human consumption, ground water, superficial water, waste water and liquid waste (landfill leacheate, process water, wash water and drain water)	Sampling	APAT CNR IRSA 1030 Man 29 2003	B
Water, water intended for human consumption, ground water, superficial water, waste water and liquid waste (landfill leacheate, process water, wash water and drain water)	Sampling	APAT CNR IRSA 6010 Man 29 2003	B
Water Treatment Works, Desalination Plants, Reservoirs, Ground waters, Domestic and Industrial Premises, Runoff water, waste waters and effluents, and water intended for human consumption	Determination of pH	APAT CNR IRSA 2060	B



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Scope of Accreditation

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Material/ Product/ Matrix Tested/ Calibrated	Type of test/ calibration and/or property measured, range of measurment	Standard Specifications/ In- House Methods/ Equipment/ Techniques	Loc. code
---	--	--	--------------

Water Treatment Works,
Desalination Plants, Reservoirs,
Ground waters, Domestic and
Industrial Premises, Runoff water,
waste waters and effluents, and
water intended for human
consumption

Determination of redox
potential

APHA Standard Methods
for the Examination of
Water and Wastewater ed
22nd 2012, 2580

B

END OF SCOPE

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Web: www.nabmalta.org.mt - Email: info@nabmalta.org.mt



STS Directory

Accreditation number: STS 0149

International standard: ISO/IEC 17025:2005
Swiss standard: SN EN ISO/IEC 17025:2005

passam ltd.
Schellenstrasse 44
8708 Männedorf

Head: Andrea Hangartner
Responsible for MS: Prof. Dr. Jean Marc Stoll
Telephone: +41 44 920 46 44
E-Mail: <mailto:passam@passam.ch>
Internet: <http://www.passam.ch>
Initial accreditation: 27.03.1996
Current accreditation: 01.04.2014 to 31.03.2019
Scope of accreditation see: www.sas.admin.ch
(Accredited bodies)

Scope of accreditation as of 01.04.2014

Testing laboratory for air analysis by diffusive samplers of ambient, indoor and workplace areas and analysis with help of spectrophotometry, gas- and ion chromatography

Group of products or materials, field of activity	Principle of measurement ³⁾ (characteristics, measuring ranges, type of test)	Test methods, remarks (national, international standards, in-house test methods)
Diffusive sampler for		
Ammonia (NH ₃)	Spectrophotometry	In-house test method VP1105_03
Benzene, Toluene, Xylene (BTX)	Gas Chromatography	In-house test method VP1605_03
Carbon monoxide (CO)	Spectrophotometry	In-house test method VP2313_01
Hydrogen chloride (HCl)	Ion chromatography	In-house test method VP2112_01
Hydrogen fluoride (HF)	Ion chromatography	In-house test method VP2212_01
Hydrogen sulphide (H ₂ S)	Ion chromatography	In-house test method VP1805_01
Nitrogen dioxide (NO ₂)	Spectrophotometry	In-house test method VP0105_03 / VP1505_03
Nitrogen oxides (NO _x)	Spectrophotometry	In-house test method VP1205_01
Ozone (O ₃)	DPE-method / Spectrophotometry	In-house test method VP0305_03



STS Directory

Accreditation number: STS 0149

Group of products or materials, field of activity	Principle of measurement ³⁾ (characteristics, measuring ranges, type of test)	Test methods, remarks (national, international standards, in-house test methods)
Ozone (O ₃)	Nitrite method / Ion chromatography	In-house test method VP2005_01
Sulfur dioxide (SO ₂)	Ion chromatography	In-house test method VP1003_03
Test atmospheres		
Principle of permeation	Gravimetry, Flow measurement	In-house test method according to VDI 3490/9

Abbreviation	Signification
V	Validation report of passive sampler system
P	passive sampling system
01	number of passive sampling system
05	year of validation
03	version
VDI	Association of German Engineers

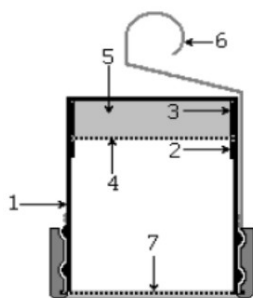
- Validation reports according to Guideline RL 1401 based on the following EN standards:
EN 13528_1 and 13528_2: Ambient air quality - diffusive samplers for the determination of gases or vapours - Requirements and test methods. (September 2002).
- Estimation of uncertainty according to GUM (Guide for the expression of uncertainty, publisher: DIN. Berlin: Beuth 1995)
- specified according ISO/DIS 20988:2004:
Air quality-Guide to estimating measurement uncertainty
Berlin: Beuth 2004

CEN Report: CR14377:2002 E:
Air quality - Approach to Uncertainty for Ambient Air Reference
Measurement Methods

* / * / * / * / *

Review of the application of diffusive samplers in the European Union for the monitoring of nitrogen dioxide in ambient air

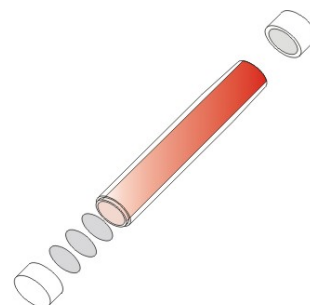
T. Hafkenscheid, A. Fromage-Mariette, E. Goelen, M. Hangartner, U. Pfeffer, H. Plaisance, F. de Santis, K. Saunders, W. Swaans, Y.S. Tang, J. Targa, C. van Hoek and M. Gerboles



Analyst



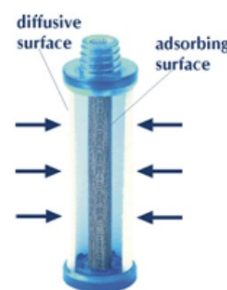
Ogawa



Palmes tube



Passam



Radiello

EUR 23793 EN - 2009

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Contact information

Address: Michel Gerboles.
Joint Research Centre, Via E. Fermi, 2749 - TP 442, I – 21027 Ispra (VA)
E-mail: michel.gerboles@jrc.it
Tel.: +39 0332 785652
Fax: +39 0332 789931

<http://ies.jrc.ec.europa.eu/>
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Executive summary

A number of diffusive samplers that are used for long-term monitoring of nitrogen dioxide in the European Union were subjected to a review of their use and performance characteristics. The information collected was used:

- To draft conclusions about the feasibility of using the samplers for the long-term monitoring of nitrogen dioxide, with the particular aim of checking compliance with the European Union annual limit value of $40 \mu\text{g.m}^{-3}$ (at 20 °C and 101,2 kPa);
- To draft a proposal method for monitoring nitrogen dioxide using diffusive samplers that could be later used by the CEN Technical Committee 264 “Air Quality” Working Group 11 “Diffusive Samplers” to prepare a CEN standard devoted to the measurement of nitrogen dioxide in ambient air.

The main criteria for assessing sampler feasibility for both purposes were:

- Validation level of the samplers based either on application of EN 13528 part 2 or the Guide to the Demonstration of Equivalence of Ambient Air Monitoring Methods, including information about the uncertainty of results obtained using the samplers;
- Potential to meet European Air Quality Directive data quality objectives for indicative and/or fixed measurements;
- Extent or lack of information available to underpin the validity of results obtained using the different samplers;
- Number of different sources providing the above information;
- Differences in performance depending on site type (tube type): traffic, urban, rural;
- Possibility for users to analyse the samplers, e.g., based on procedures specified by manufacturers;
- Their current use throughout the European Union for measuring ambient air quality related to concentrations of nitrogen dioxide.

Of the samplers investigated, two tube-type samplers and a radial sampler were found to be used throughout the European Union for monitoring nitrogen dioxide in ambient air. Other samplers exist that are used mainly for other purposes. In addition, the tube-type samplers are used in monitoring networks for supplementary measurements to the fixed measurements at the level of an indicative method.

Based on the findings of the review, the samplers used in the European Union for ambient air quality monitoring purposes should be of the tube-type design with triethanolamine as sorbent. Sufficient information was available to underpin its potential for meeting European Union data quality objectives, at least for indicative measurements of nitrogen dioxide in ambient air. For other samplers, more supporting information would be needed to draw a similar conclusion.

In conclusion, it is recommended that the proposed method for monitoring nitrogen dioxide using diffusive samplers should be based on the tube-type sampler. If more information becomes available on the performance of the radial sampler, then this sampler could also be included in the standard.

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1 Introduction

Ambient air quality problems associated with levels of nitrogen dioxide (NO₂) are largely due to exceedances of annual limit values. Short-term limit values are only occasionally exceeded in the EU. Diffusive sampling would be an ideal technique for the assessment of compliance with long-term (i.e., annual) limit values for NO₂.

Recent developments indicate that earlier fundamental problems associated with diffusive sampling of NO₂ may have been overcome. Due to modifications in the design of the samplers, potential variations in sampler performance have been eliminated [1,2].

These developments should support the application of diffusive sampling for the assessment of NO₂ in ambient air. Already networks are in operation for routine measurements in many European countries (including Belgium, France, Germany, Switzerland and United Kingdom).

An additional stimulus for applying diffusive sampling is a provision in the ambient air quality directive 2008/50/EC [3] that the number of fixed monitoring sites may be reduced by up to 50 % in zones and agglomerations where supplementary methods for assessment such as modelling and indicative measurements are used. Prerequisites are that:

- The supplementary methods provide sufficient information for air quality assessment;
- The number of sampling points to be installed and the spatial resolution are sufficient to meet the relevant data-quality objectives.

Diffusive sampling methods should be capable of meeting these requirements.

However, the full validation of diffusive sampling methods e.g. according to EN 13528-2, and/or the demonstration of their equivalence with the reference method for NO₂ requires special facilities that are only available to well-equipped institutes/laboratories.

Other smaller institutes and monitoring networks wishing to apply diffusive sampling have to rely on external assistance from commercial/public laboratories. Although small-scale validation experiments and comparisons of diffusive samplers can be performed, it is not clear what the quality and comparability of the results produced by these laboratories could be.

In addition, suppliers of samplers may require that analysis of samplers provided is performed only by themselves. Although perhaps justifiable from a viewpoint of the experience required to correctly perform such analysis, this requirement imposes severe restrictions on the potential application of diffusive sampling.

The availability of a properly validated standard method for the measurement of NO₂ by diffusive sampling would permit the unrestricted use of diffusive samplers by all interested parties.

In August 2006, a New Work Item describing the standardization of a method for the measurement of NO₂ using diffusive sampling methods was submitted to CEN Technical Committee 264 "Air Quality". The proposed New Work Item was accepted.

In order to facilitate the drafting of a future CEN standard, the European Commission made available funding for a group of experts to draft a proposal method for monitoring NO₂ in ambient air with diffusive samplers. The group of experts carried out a literature review of existing information about NO₂ diffusive samplers, to be used as a basis for the subsequent development of the proposal method.

This report summarizes the findings of the literature review. Several different types of diffusive samplers in general use were identified. They may be classified as samplers based on sorption of NO₂ on triethanolamine (TEA), and "other" samplers.

In the chapter devoted to TEA-based samplers, four different samplers are described separately: two tube-type samplers, a badge-type sampler, and a radial-type sampler. In the chapter devoted to other samplers, one badge-type sampler is described.

Other samplers are known to exist, but are not described in this report due to a lack of information. A comprehensive list of samplers may be found in [4].

This report is not intended to specify the various applications of diffusive samplers. Relevant information may be found, e.g., in references [5] and [6].

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2 Samplers based on sorption by triethanolamine

2.1 Introduction

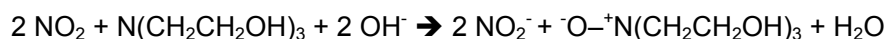
Since their introduction in 1976 for measuring personal exposure to nitrogen dioxide (NO₂) [1], diffusive samplers employing triethanolamine (TEA) as sorbent have been used. Diffusive samplers are an inexpensive method for measuring NO₂ in air over periods from one day to several weeks.

The characteristics of these samplers will be described in separate sections of this report. This section gives an overview of the general properties of TEA-based samplers.

2.2 The sorbent: triethanolamine

Triethanolamine (2,2',2''-nitrilotriethanol (C₂H₄O)₃N, TEA) is a hygroscopic pale yellow liquid with a melting point of 21,6 °C. It has been used as a sorbent for sampling NO₂ since the 1970s, initially in solution in a bubbler or impinger, or in the solid phase on molecular sieve [2]. Its capacity to remove NO₂ from the sampled air is high (90-100 %), as demonstrated using sequential sampling.

The proposed reaction pathway is the following [3].



The collected NO₂ is extracted as nitrite using water. The resulting extract may be analyzed by:

- Colorimetry after derivatization of the nitrite, using the Griess-Saltzman method [4];
- Ion chromatography with conductivity detection [5].

The stoichiometry of the above reaction is dictated to a large extent by the presence of water in the sampled air [3, 6]. The sudden decrease in sampling efficiency below -8 °C [7] suggests that a minimum of around 3 g H₂O m⁻³ is required for TEA to be effective as a sorbent in diffusive samplers.

2.3 Interferences

In addition to its reaction with NO₂, TEA also traps and reacts with other molecules to produce NO₂⁻ ions on extraction into aqueous solution. The two most important potential positive interferences, apart from the reaction of NO with O₃ during sampling, are from peroxyacetyl nitrate (PAN) and nitrous acid (HONO). Dosing of TEA absorbent with NO₃⁻ ions does not produce interference [8]. There is a negligible effect of exposure to O₃ alone in the short term; an atmosphere of 200 ppb of O₃ for 12 h converted less than 10 % of trapped (reacted) NO₂ to NO₃⁻ [9]; active co-sampling of 130 ppb O₃ and 10 ppb NO₂ using TEA on a filter at a relative humidity (RH) of 50 % produced no interference [10].

Interference from PAN is important in that PAN is quantitatively converted to NO₂⁻ on (naturally alkaline) TEA [11]. For tube-type samplers, interference from PAN was lower than 5 % (ppb:ppb) [12]. In practice, interference from PAN is likely to be very small under most exposure conditions, particularly in northern Europe [13]. However, it could be a significant interference in regions with high levels of photochemistry [14].

HONO gives 100 % interference, producing NO₂⁻ on reaction with TEA [10]. However, HONO concentrations in the EU air are likely to be small; even in cities they account for only a few percents of NO₂ concentrations [15].

Not unimportantly, both PAN and HONO would also be measured quantitatively as positive interference by a chemiluminescence NO_x analyzer using thermal conversion of NO₂ (also PAN and HONO) to NO, and would not lead to positive interferences when diffusive samplers are compared with continuous automatic samplers.

Ozone has been reported to interfere through reacting with nitrogen monoxide in the diffusion path of tube-type samplers [16]. However, this finding has not been confirmed by other studies [27].

Sulfur dioxide was found not to interfere with the measurement of NO₂ using tube-type samplers [17].

2.4 Effects of meteorological conditions

2.4.1 Temperature

One of the earliest tests of tube-type samplers showed a 15 % decrease in uptake rate between 27 °C and 15 °C, compared with a theoretical change of less than 2 %. This was attributed to a phase change from solid to liquid of TEA at 21 °C [18]. However, the role of the melting point of TEA was challenged by a later study [19], which showed that TEA solutions did not freeze, but formed a gel even at temperatures as low as -10 °C.

The effectiveness of TEA as a sorbent appears to be dependent on humidity. Some of the reported effects of temperature on uptake rate may be confounded by simultaneous changes in absolute humidity [20], leading to low effective uptake rates at low temperatures that are caused by a lack of water vapour rather than low temperatures *per se* [10, 21, 22]

One laboratory study (designed to evaluate tube-type samplers for use in Greenland) showed almost constant uptake rates from 20 °C down to -8 °C, then a linear decrease to around 30 % of the constant rate, at -28 °C [7]. Another laboratory study found no temperature dependence between 5 and 45 °C [20], while another study found an effect of extremes of temperature and relative humidity on uptake rates, and low uptake rates in the field in winter (by comparison with an automatic monitor) [24].

For short-path 'badge' type samplers the effectiveness of the absorbent may be limited by the rate of diffusion in the liquid phase [25], but this is unlikely to be an issue for the tube type, which has much slower uptake rates. Comparisons of a short path sampler with an active sampler suggest a dependence on temperature of around 1 % per °C [26]. Different designs of sampler have different temperature responses, which must be characterised before they can be used [27].

2.4.2 Relative humidity

The effect of humidity on uptake rate appears to be related to the use of TEA as a sorbent for NO₂, rather than any effect on the diffusion process. Most laboratory studies have used relative humidity (RH) as a measure of water vapour concentration, rather than absolute humidity, which may be more important. Early studies showed no effect of RH between 20 % and 60 % on a short path sampler at room temperature [28]. This was confirmed by subsequent studies with RH higher than 20 % at ambient temperatures [23, 29]. Studies with tube-type samplers between 5 % and 85 % RH at room temperatures (above 22 °C) showed a weak linear dependence of the uptake rate equivalent to an 18 % change in uptake rate between 20 % and 80 % RH [30].

Recent studies demonstrated a dependence on absolute humidity, expressed in terms of the uptake rate for a membrane-capped tube [27], equivalent to a 23 % change in uptake rate between 20 % and 80 % RH at 20 °C.

The effects of variations in absolute humidity on a short path sampler were also reported, with significant reductions in uptake at low RH at low temperature [20, 22].

Effects of humidity on tube-type sampler performance in the field were noted [31], with uptake changing by 17 % between 20 % and 80 % RH at 20 °C with wind velocity of 1 m.s⁻¹. If the uptake rate is dependent on absolute humidity, the above figures may not present a true picture of the dependence on temperature and relative humidity, because RH is a function of water vapour concentration (absolute humidity) and temperature.

However, in comparing results from diffusive samplers with those from automatic analyzers, it is important to note that automatic NO₂ analyzers also have a dependence on humidity, which may not

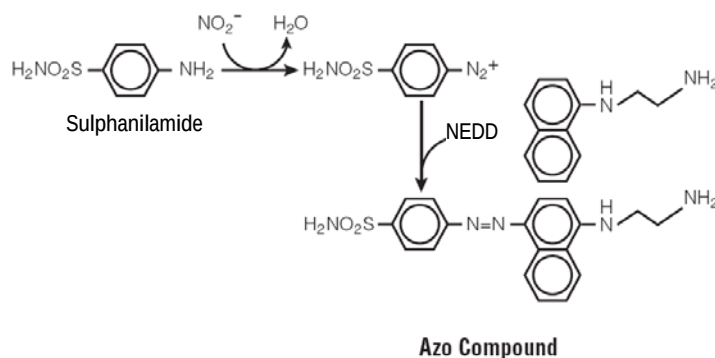
have been allowed for in comparing the response of diffusion tubes relative to automatic methods. The response of a chemiluminescence analyzer typically decreases by 0,5 % per g/m^3 of water vapour [32]. This is equivalent to a change of 5 % between 20 % and 80 % RH at 20 °C.

2.4.3 Air velocity

The effects of air velocity are highly dependent on the sampler design and will be discussed in the sampler-specific sections of the report.

2.5 Analysis of TEA-based samplers

The original method used by Palmes [1] for measurement of the trapped NO_2 relied on the colorimetric determination of NO_2^- using the diazotisation reaction with acidified sulphanilamide and N-(1-naphthyl)-ethylene diamine dihydrochloride (NEDD, sometimes also referred to as NEDA), with detection and quantification of the pink colour produced using photometric absorption spectroscopy at 537 - 542 nm. This colour reagent, or 'Saltzman reagent' has long been used for the quantification of NO_2^- in solution.



However, several authors used ion chromatography (IC) to quantify NO_2 uptake. The benefit of using IC was recognised over 20 years ago, in terms of a greatly improved limit of detection using tube-type samplers, compared with colorimetric analysis [5]. Using gradient elution IC, the limit of detection for tube-type samplers was measured as 4 ppb.hour, compared with 33 ppb.hour for a colorimetric method [12]. Other authors have shown a 14-fold decrease in the limit of detection [33].

2.6 Conclusions

Diffusive sampling of NO_2 using TEA-based samplers dates back 35 years. Meanwhile, a substantial number of studies have been devoted to investigating the behaviour of TEA-based diffusive samplers and their dependence on environmental conditions (presence of interferences, temperature, humidity).

Humidity is probably the most important environmental variable that affects the performance of diffusive samplers using TEA as absorbent. TEA does not perform quantitatively at low humidity. The data of Hansen et al. [7] suggest a loss of efficiency below -8 °C, equivalent to an air concentration of water vapour of about 3 g.m^{-3} , or 35 % RH at 5 °C. At any given temperature, the effect of a change in relative humidity between 20 % and 80 % is to change uptake rates by about ± 15 % relative to the values at 50 % RH. In practice, the dependence on humidity has rarely been tested in the field, and the interaction between humidity and the reaction of TEA with NO_2 has not been investigated systematically.

The dependence of uptake rate on temperature is small and predictable, except in cold dry air. This deviation from theory is related to the use of TEA as the sorbent and appears to be caused by a lack of sufficient water vapour to ensure quantitative conversion of trapped NO_2 to NO_2^- ions. The availability of water is crucial to the way in which TEA reacts with NO_2 . As noted above, the sudden decrease in sampling efficiency below -8 °C suggests that a minimum of around $3 \text{ g H}_2\text{O.m}^{-3}$ is required for TEA to be effective as the sorbent in diffusive samplers. This is unlikely to be a problem under most EU conditions, except for very cold, dry weather.

A number of compounds, particularly PAN and HONO are known to produce positive biases when co-sampled with NO₂. However, under typical EU conditions the biases are expected to be small.

Moreover, the current reference method for the measurement of NO₂ in ambient air which is based on thermal conversion of NO₂ to NO with detection of chemiluminescence, suffers from similar biases. Consequently, when comparing TEA diffusive samplers with this reference method, the effects of the interference cannot be quantified.

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3 The Palmes tube

3.1 Sampler design

The traditional NO_2 Palmes tube consists of an acrylic tube (of 71,16 $\pm$ 0,20 mm long and 10,91 $\pm$ 0,15 mm internal diameter) open at one end and two or three stainless steel mesh discs coated with a solution containing triethanolamine (TEA) at the closed end (see figure 3.1, a). A removable cap is used to close the open end of the tube after exposure. The NO_2 molecules diffuse through the air into the tube, following the concentration gradient and are trapped as nitrite ion on TEA. In a recent study, Gerboles et al. [1] proposed a modification of the traditional Palmes diffusion tube by fitting a Teflon membrane at the open end of the tube (see figure 3.1, b). This membrane was used to obtain a sampler free of wind speed effect. In the United Kingdom, a Teflon mesh is used instead of a membrane [2]. All ready-to-use Palmes tube components are commercially available.

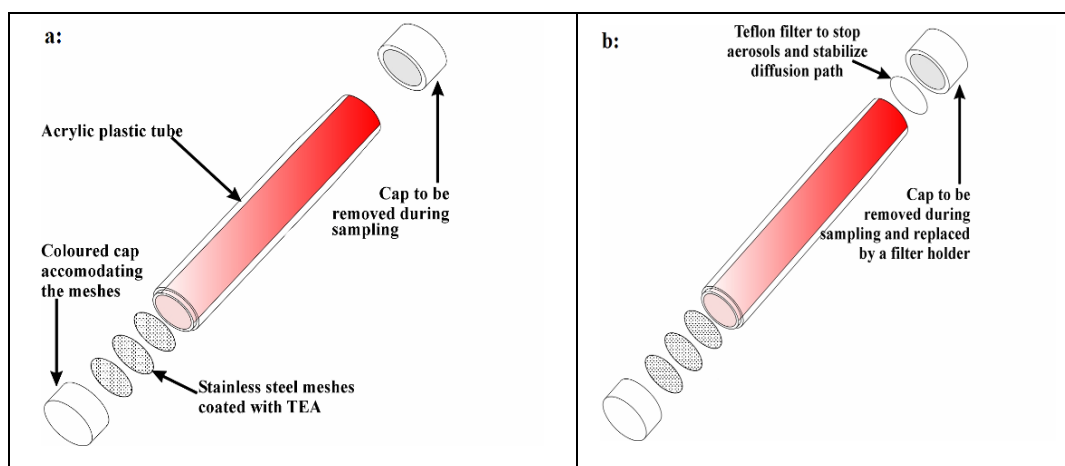


Figure 3.1.a: The traditional Palmes diffusion tube, b: The membrane-closed Palmes tube proposed by Gerboles et al. [1].

The coloured cap needs to be completely opaque and without cracks [2].

Samplers are mounted vertically, with the cap containing the coated discs uppermost. Positions allowing unrestricted movement of air around the sampler are selected. Diffusion tube samplers are fixed by spring clips to the supports (pylons or posts) using supports or spacers of different types. The samplers are, as far as practicable attached at 3-4 meter above the ground in order to avoid vandalism. To attenuate the effect of wind turbulence and improve the precision of measurements by Palmes tubes, it is recommended to use a protective device as for example, shown in Figure 3.2.



Figure 3.2: Cylindrical protective box

The decision to use a protective device should come first (before using a spacer). Criteria to use the protective box may be:

- To prevent exposure to direct sunlight;
- To prevent turbulence in the tube entrance (but at least $0,2 \text{ m.s}^{-1}$ should be ensured);
- To avoid ingress of rain.

In the case of the membrane-closed Palmes tube proposed by Gerboles et al. [1], the protective box is not necessary since the membrane introduced at the open end of tube is intended for isolating the molecular diffusion path from air movements.

3.2 Sampler preparation

The Palmes tube described here needs to be assembled from individual parts. The tube, Teflon membrane and caps are cleaned in a glass container filled with ultra high purity water under magnetic stirring and changing the water every half an hour for 3 h. All components are then placed in an oven at 45°C until they are completely dry. The stainless-steel mesh discs are cleaned in an ultrasonic bath at 60°C for 5 h, with the water changed every half an hour. They are then placed in an oven and flushed with nitrogen at 125°C until they are completely dry. Three clean and dry discs are placed in the coloured cap with tweezers. Then, a tube is placed onto the coloured cap [1].

In practice, this procedure may be quite tedious. Less stringent procedures are described in [3] and [4].

In addition, the coating of the sampling substrate needs to be performed by the user itself. Different procedures for preparation are described [e.g. 5]. Methods of proven validity are:

- 50 % solution of TEA in acetone, grids dipped into solution and dried before assembly;
- 20 % solution of TEA in deionised water, 50 μl of solution pipetted onto grids already placed in end cap;

- 10 % solution of TEA in deionised water with 0,3 % of wetting agent (e.g. Brij-35), 40 µl of solution pipetted onto grids already placed in end cap.

3.3 Extraction and analysis

To determine the quantity of nitrite sampled by the Palmes tube, the Griess-Saltzman method is generally used. The Saltzman reagent consists of a solution of sulphanilamide (2 % w/v) and N-(naphthyl-1) ethylene diamine dihydrochloride (0,007 % w/v) in 5 % v/v ortho-phosphoric acid. A known volume of colorimetric reagent solution is introduced into the tube, and extraction is effected either by:

- Vortex shaking for a minimum of 15 s;
- Vibrating for a minimum of 10 min at 750 rpm.

Nitrite reacts in the phosphoric acid solution with sulphanilamide to give a diazonium salt that couples with naphthalene derivative to form an azo dye. It is recommended to allow the colour to develop at ambient temperature in the dark for a minimum time of 1 h. The absorbance of the azo dye is measured at 542 nm [4].

3.4 Expression of the NO₂ concentration

To calculate the airborne NO₂ concentration, the equation 3.1 is generally applied.

$$C_{NO_2} = \frac{(m_s - m_b)}{v \times t \times 10^{-6}} \quad (\text{eq. 3.1})$$

where

C_{NO_2} = NO₂ concentration in µg.m⁻³ at actual average temperature and pressure during the exposure;

m_s = mass of nitrite measured in the exposed sampler in µg;

m_b = mass of nitrite in the blank in µg;

v = uptake rate in cm³.min⁻¹;

t = sampling time in min.

Several authors also prefer to use equation 3.2 for the calculation of NO₂ concentration, with the uptake rate expressed in ng.ppb⁻¹.min⁻¹.

$$C_{NO_2} = 1,91 \frac{(m_s - m_b)}{u \times t} \quad (\text{eq. 3.2})$$

where

C_{NO_2} = NO₂ concentration in µg.m⁻³ at 20 °C and 101,3 kPa;

m_s = mass of nitrite measured in the exposed sampler in ng;

m_b = mass of nitrite in the blank in ng;

u = uptake rate in ng.ppb⁻¹.min⁻¹;

t = sampling time in min.

The coefficient 1,91 is used to convert ppb to µg.m⁻³ at 20 °C and 101,3 kPa.

3.5 Application range and conditions

The Palmes tube may be exposed for 1 to 5 weeks sampling periods according to results of field validation tests obtained from many sites across Europe [1, 2, 6-9]. Some users have exposed tubes for up to 8 weeks [10].

Results of validation studies described below suggest that the Palmes tube sampler, when properly prepared and exposed with sufficient protection from adverse influences, may be used over a temperature range from -5 °C to 40 °C, and a relative humidity range from 30% to 95%.

Detection limits for a one-week sampling period were found to be 1,4 [1] and 1,9 $\mu\text{g}\cdot\text{m}^{-3}$ [3], depending on the preparation procedure (see section 3.2). In a field experiment, the upper limit for NO_2 that was found in practice to lead to valid results for 5-week sampling was 150 $\mu\text{g}\cdot\text{m}^{-3}$ [2].

When stored in a clean refrigerator at 4°C before exposure, an unexposed tube may be stable for up to 1 year [11].

Stability tests of Palmes tubes after exposure were performed by Gerboles et al. [11] in a feasibility study of the preparation and certification of a reference material for NO_2 in diffusive samplers. The Palmes tubes were stored under two different conditions: at room temperature (22°C) in the dark and at 4°C in a refrigerator. It was demonstrated that the samples may be stable for at least one year under both conditions of storage. The results were in agreement with those obtained previously by Palmes et al. [12], where the samplers were found to be stable for at least 6 months.

3.6 Uptake rate

For the traditional Palmes diffusion tube without membrane, the theoretical uptake rate (72,8 $\text{cm}^3\cdot\text{h}^{-1}$) calculated using the diffusion coefficient of NO_2 in air and the dimensions of the sampler is currently the most common value. It has also been confirmed by test results in exposure chambers under standard conditions ($T=20^\circ\text{C}$, $\text{RH}=50\%$ and wind speeds between 0,1 and 0,3 $\text{m}\cdot\text{s}^{-1}$) [8].

The uptake rate is dependent on the air temperature and pressure during exposure. In appendix 2 of reference [2], a correction for the uptake rate is proposed (equation 3.3). Temperature correction raised to the power 1,5 instead of 1,81 have been proposed by other authors [4]. In most cases, the pressure correction may be neglected.

$$v_{T,P} = v_{\text{ref}} \left(\frac{273,2 + T}{273,2 + T_{\text{ref}}} \right)^{1,81} \frac{P_{\text{ref}}}{P} \quad (\text{eq. 3.3})$$

where

$v_{T,P}$ = uptake rate in $\text{cm}^3\cdot\text{min}^{-1}$ at temperature T and pressure P during sampling;

v_{ref} = uptake rate in $\text{cm}^3\cdot\text{min}^{-1}$ at the reference temperature and pressure;

T = actual temperature during sampling in $^\circ\text{C}$;

T_{ref} = reference temperature in $^\circ\text{C}$ at which v_{ref} rate is given (for example if v_{ref} was calculated using a value of 0,154 $\text{cm}^2\cdot\text{s}^{-1}$ for the diffusion coefficient of NO_2 in air, the reference temperature is 21,1 $^\circ\text{C}$);

P = actual pressure during sampling in kPa;

P_{ref} = reference pressure in kPa at which v_{ref} is given, in general 101,3 kPa.

To improve the accuracy of measurements by Palmes tubes, some authors established empirical equations to estimate the uptake rate as a function of influential environmental parameters. These equations were defined from the results of complete programs of tests in exposure chamber.

Plaisance et al. [8] proposed a first equation which allows the effects of temperature and humidity to be taken into account on the uptake rate of the open Palmes tube exposed in cylindrical box for 2-week sampling:

$$v = 72,8 \times (2,85 \times 10^{-3} \times [T] - 1,62 \times 10^{-4} \times [\text{RH}] + 4,96 \times 10^{-5} \times [T] \times [\text{RH}] + 0,9) \quad (\text{eq. 3.4})$$

where

v = uptake rate in $\text{cm}^3\cdot\text{h}^{-1}$;

T = temperature in $^\circ\text{C}$.

Buzica et al. [9] provided another model-predicted uptake rate. It was deduced from tests in exposure chamber carried out by applying a fractional factorial plan of experiments with 5 factors at two levels

(wind speed, temperature, humidity, NO₂ concentration level and sampling time). The equation predicts the uptake rate of the Palmes tube without membrane exposed from 1 to 2 weeks:

$$v = 7,4 \times 10^{-4} + 2,72 \times 10^{-5} \times T + 1,43 \times 10^{-5} \times RH + 5,81 \times 10^{-4} \times w \quad (\text{eq. 3.5})$$

where

v = uptake rate in ng.ppb⁻¹.min⁻¹;
 T = temperature in °C;
 RH = relative humidity in %;
 w = wind speed in m.s⁻¹.

For the Palmes tube equipped with a Teflon membrane proposed by Gerboles et al. [1], the membrane introduced a resistance to molecular diffusion. Therefore the uptake rate of the sampler could not be determined using the first Fick's law, but was instead estimated by laboratory experiments in exposure chamber. Gerboles et al. carried out the same program of tests as described in [9] and derived a model-predicted uptake rate for the membrane-closed Palmes tube exposed from 3 to 14 days:

$$v = \frac{1}{2} (134 + 0,86RH - 0,00130 t + 1,28T + 3,18w) 10^{-5} \times \left(1 + \sqrt{1 - \frac{0,64 \cdot 10^{-5} m}{t ((134 + 0,86RH - 0,00130 t + 1,28T + 3,18w) 10^{-5})^2}} \right) \quad (\text{eq. 3.6})$$

where

v = uptake rate in ng.ppb⁻¹.min⁻¹;
 T = temperature in °C;
 RH = relative humidity in %;
 w = wind speed in m.s⁻¹;
 m = mass of nitrite in ng;
 t = exposure time in min.

3.7 Environmental effects

3.7.1 Air velocity

Some studies [8, 9, and 13] reported that the greatest effect on the uptake rate of a traditional open Palmes tube may be attributed to wind velocity. An increase in uptake rate was observed with increasing air velocities usually following a logarithmic trend [8, 13]. The effect starts from very low wind velocities (between 0,1 m.s⁻¹ and 0,2 m.s⁻¹).

The magnitude of the uptake increase was found to be about 60 % over the wind velocity range of 0 m.s⁻¹ to 7 m.s⁻¹ [13]. Other authors [8, 9] confirmed that the increase rate was high, about 40 % from 1 m.s⁻¹ to 2.8 m.s⁻¹. An effective and practical way for reducing the effect of air turbulence was demonstrated by the use of a cylindrical protective box (figure 3.2).

Buzica et al. [9] observed that for the open Palmes tube the effect of the wind speed was ±25 % of the average uptake rate, while the effects of the relative humidity and temperature were smaller, at ±10 % and ±7 %, respectively.

Gerboles et al. [1] proposed the addition of a porous membrane at the open end of the Palmes tube. It removes the high influence of wind speed and wind direction on uptake rate. With the addition of the membrane, the wind becomes a minor influencing factor.

3.7.2 Temperature and relative humidity

Temperature and humidity were found to have a smaller influence on the response of the sampler (see above) with the uptake rate increasing linearly by 0,3 %.°C⁻¹, in agreement with the theoretical dependence of the diffusion coefficient of NO₂ on temperature.

A maximum bias in the uptake rate of nearly +10 % was observed under particularly extreme conditions (temperature higher than 30 °C and relative humidity higher than 80 %) [8].

3.7.3 Interferences

Potential interferences from nitrous acid (HONO) and peroxyacetyl nitrate (PAN) which give rise to nitrite ion must be recognised. However, neither compound is likely to be present at sufficient concentrations or over sufficiently long periods to cause serious interferences in most situations. Gair et al. [14] found only a positive interference lower than 6 % which they considered non-significant.

Heal et al. [15] and Jenkins [16] showed that the chemical reaction between O₃ and NO within diffusion tubes may lead to an overestimation of the measured NO₂ concentration. The light transmission characteristics of the acrylic tube used for sampling showed some attenuation in the photochemically important region, possibly leading to changes in the photochemical equilibrium in the air actually inside the sampler.

This information, together with ozone data, was used to model the system for typical conditions of exposure of urban and rural areas. The model showed an increase in NO₂ of about 11 % in rural and 6 % in urban areas. The photochemical reaction is only of importance during daylight and even in the more sensitive rural areas the effect would be difficult to detect.

In field tests carried out by Atkins et al. [17] and Bush et al. [18], no differences were found in the performance of the diffusion tube at rural and urban locations. Likewise, the laboratory experiments in an exposure chamber [1] revealed no bias of O₃ on the NO₂ measurements by Palmes tubes.

3.8 Validation of sampler performance

3.8.1 Comparisons with reference methods

Palmes tubes were validated for outdoor use in several studies. The first extended outdoor evaluation was carried out by Atkins et al. [17] at two sites (rural and urban locations) using the Palmes tubes (10 % TEA/water solution with 0,3 % of the wetting agent Brij-35) and the theoretical uptake rate.

Precision was found to be satisfactory with coefficients of variation for batches of 10 Palmes tubes between 5 % and 8 % for NO₂ concentrations above 5 ppb, which appeared to be independent of NO₂ level and sampling duration (1 week or 4 weeks). Parallel measurements using chemiluminescence analysers and diffusion tubes revealed a good agreement between the two methods. Regression analysis on 42 paired measurements produced a line with a slope not significantly different to 1 and a correlation coefficient above 0,98, over a range of concentrations of 3 ppb to 60 ppb. There was no difference in the performance of the Palmes tube at the rural (NO₂ lower than 30 ppb) and urban (NO₂ higher than 30 ppb) locations.

Glasius et al. [6] confirmed the good agreement between NO₂ measurements carried out with Palmes tube and co-located chemiluminescence analysers at three sites in Denmark and Italy. However, samplers (33 % TEA/acetone solution) at sheltered locations slightly overestimated NO₂ (less than 10 % of overestimation) at concentration levels above 15 ppb. An opposite trend was found at concentrations lower than 15 ppb.

Heal et al. [15] observed overestimations of NO₂ measured by Palmes tubes (50 % TEA/acetone solution) against co-located chemiluminescence analyser at an urban site in Edinburgh (UK). The average ratios of Palmes tube to analyser NO₂ were 1,27 (n=22), 1,16 (n=34) and 1,11 (n=7) for exposures of 1, 2 and 4-weeks, respectively. Based on further modelling of the diffusion, the authors concluded that the overestimation of NO₂ by Palmes tubes could be explained by the generation of excess NO₂ due to the reaction of NO with O₃ inside the tube.

Bush et al. [18] co-located Palmes tubes (50 % TEA/acetone solution) with chemiluminescence analysers at 17 urban monitoring stations in the UK for a one year period. Highly significant correlations (above 0,95) were found between all Palmes tube exposure types (sampling time of 2

and 4 weeks with sheltered and unsheltered samplers) and co-located chemiluminescence analysers. The uncertainty calculated from the overall differences between Palmes tube measurements and the chemiluminescence measurements of NO₂ was estimated to be between ±24 % and 38 % for individual Palmes tube measurements, but reduced between ±10 % and 18 % for annual averages. Differences due to the exposure period and exposure procedure were found, but these were not large.

Tang et al. [10] compared measurement results obtained with Palmes tubes (both open and equipped with a membrane, using protective shelters consisting of a sheet of curved stainless steel painted black, open to the air on 3 sides) with those from chemiluminescence reference analyzers. Comparative measurements were performed at 5 sites: 3 urban sites and 2 rural sites.

Exposure periods were 1, 2, 4 and 8 weeks. In general, it was found that open tubes overestimated NO₂ concentrations at urban sites (average levels around 20 ppb) by almost 30 % to 35 % on average. At the rural site (average levels around 4 ppb) the results agreed much better (ratios between 0,98 and 1,03).

Results obtained with membrane tubes were 10 % lower on average than the reference values for the 4-week sampling period, but were in excellent agreement with those obtained over an 8-week exposure period. At the rural site, the membrane tubes yielded levels that were about 75 % of those of the reference analyzers.

During 2001-2002, CEN/TC264 WG11 (Diffusive sampling) performed a small-scale pilot study at two locations in which 6 replicate samplers of different types of diffusion samplers were exposed for two weeks, in parallel with measurements from a chemiluminescence analyser. These results have not been published and were provided by CEN for the purpose of the present report. Samplers were analysed by the suppliers. The results for two Palmes tube samplers are reported in table 3.1.

Table 3.1: Results of CEN pilot study for Palmes tube samplers

Willebroek	NO ₂ (µg.m ⁻³)	Ratio Palmes/reference
<i>Reference</i>	40,8	
Palmes 1	52,8	1,30
Palmes 2	57,1	1,40
Teddington	NO ₂ (µg.m ⁻³)	Ratio Palmes/reference
<i>Reference</i>	13,8	
Palmes 1	17,6	1,28
Palmes 2	18,7	1,36

Both Palmes tubes were found to overestimate NO₂ concentrations.

Buzica et al. [19] organized a series of 4 comparisons in which different samplers operated by different laboratories were exposed both under laboratory and field conditions. Each sampler was exposed in replicate (6) for a period of 14 days, except in the laboratory trial “high” (see table 3.2).

Table 3.2: Laboratory conditions (intercomparison of Buzica et al.)

Parameter	High	Low
Exposure time (d)	7	14
Concentration (µg.m ⁻³)	80	40
Air velocity (m.s ⁻¹)	2,5	1,0
Temperature (°C)	25	5
Relative humidity (%)	75	30

Five laboratories participated with different implementations of the Palmes tube (with and without shelter; with membrane). The results obtained for the samplers are presented in table 3.3.

Table 3.3: Results field tests, (intercomparison of Buzica et al.)

Lab high	NO₂ (µg.m⁻³)	Ratio Palmes/reference
<i>Chemiluminescence</i>	76,8	
Palmes open 1	125,8	1,64
Palmes open 2	138,5	1,80
Palmes sheltered 1	96,5	1,26
Palmes sheltered 2	97,0	1,26
Palmes membrane	71,5	0,93
Lab low	NO₂ (µg.m⁻³)	Ratio Palmes/reference
<i>Chemiluminescence</i>	43,5	
Palmes open 1	46,0	1,06
Palmes open 2	37,2	0,86
Palmes sheltered 1	32,6	0,75
Palmes sheltered 2	35,8	0,82
Palmes membrane	40,4	0,93
Genevilliers	NO₂ (µg.m⁻³)	Ratio Palmes/reference
<i>Chemiluminescence</i>	41,6	
Palmes open 1	45,2	1,09
Palmes open 2	42,5	1,02
Palmes sheltered 1	47,2	1,14
Palmes sheltered 2	40,5	0,97
Palmes membrane	40,5	0,97
Fontainebleau	NO₂ (µg.m⁻³)	Ratio Palmes/reference
<i>Chemiluminescence</i>	14,1	
Palmes open 1	13,1	0,93
Palmes open 2	12,4	0,88
Palmes sheltered 1	11,6	0,82
Palmes sheltered 2	11,8	0,83
Palmes membrane	12,4	0,88

Apart from the results of the laboratory trial “high”, the results are comparable with those of the reference method (chemiluminescence, CLS).

The precision of the replicate measurements ranged from 3 % to 9 %, except for the laboratory trial “high”, where some values exceeded 10 %.

Plaisance et al. [8] produced a large series of comparison data (n = 52) between diffusion tubes (10 % TEA/water solution with 0,3 % of the wetting agent Brij-35) with and without protection device (cylindrical box) and the chemiluminescence analyser carried out at four French urban monitoring stations for ten months. No systematic differences in measurements were observed between the two techniques, using both the theoretical uptake rate and model-predicted uptake rate (see section 3.6).

A lower scattering of points around the regression line (the slope was not significantly different from 1) was found for Palmes tubes set in the protective device and with the model-predicted uptake rate, revealing a significant improvement in the precision of measurements.

The ISO 13752 standard (1998) was used to evaluate the expanded uncertainty of the Palmes tubes under field conditions. Using the model-predicted uptake rate and the protective device, the expanded uncertainty is reduced to < 25%, implying that this diffusion sampler fulfils the uncertainty requirement for indicative measurements of EU Directive 2008/50/EC.

Buzica et al. [9] investigated the performance of Palmes tube (10 % TEA/water solution with 0,3 % of the wetting agent Brij-35) at one background location in comparison with the chemiluminescence analyser. The use of the theoretical uptake rate gave a high coefficient of correlation ($r^2 = 0,97$) between the measurements of two methods, but resulted in a substantial underestimation (slope 0,75) of the NO₂ concentration measured by the Palmes tube. By applying the model-predicted uptake rate established in this study (see section 3.6), this bias was corrected. For individual measurements, the Palmes tube was shown to comply with the 25% uncertainty requirement.

Gerboles et al. [1] carried out the field tests of the membrane-closed Palmes tube (10 % TEA/water solution with 0,3 % of the wetting agent Brij-35) at the EMEP station in Ispra (I). Forty pairs of data (passive samplers vs chemiluminescence) were collected over a range of concentrations from 8 to 45 µg.m⁻³. Data were analysed to evaluate the equivalence of this sampler to the reference method for NO₂ (chemiluminescence method) in accordance to the Guide to the Demonstration of Equivalence of ambient air monitoring methods [20]. The relative between sampler uncertainty was found to be 3,7%, a value that satisfies the requirement for NO₂ (≤5%) defined in the Guide.

The regression line obtained by applying the method of ISO 6143 (2001) for the reference results of the chemiluminescence analyzer versus those of the membrane-closed Palmes tube revealed no systematic bias in measurements (a slope of $1,05 \pm 0,045$ and an intercept of $-0,24 \pm 0,93$).

To determine the NO₂ concentrations measured by the membrane-closed Palmes tube, the model-predicted uptake rate was used (see section 3.6). From the results of these field tests and in accordance with the Guide of Demonstration of Equivalence, the expanded uncertainty was calculated to be 17% for an individual sampler measurement when the NO₂ concentrations were higher than 20 µg m⁻³. For the estimation of annual average concentrations, the relative expanded uncertainty was found to be 12% at the limit value of 40 µg.m⁻³, satisfying the data quality objective for indicative measurements (25%). According to these experiments, the membrane-closed Palmes tube for NO₂ could become equivalent to the reference method even for fixed measurements [21].

Through AEA Technology (United Kingdom), annual average data for a large number of monitoring sites for both Palmes tube samplers and reference monitors [22] were provided. In summary, two methods were used for the preparation of the sampler substrates:

- 50 % solution of TEA in acetone, grids dipped into solution and dried before assembly;
- 20 % solution of TEA in deionised water, 50 µl of solution pipetted onto grids already placed in end cap.

The two datasets derived from different preparation methods were evaluated according to the methodology of the Guide for the Demonstration of Equivalence [20]. By applying an orthogonal regression forced through the origin (0,0), the results given in the figures 3 and 4 were obtained. One may notice that using an orthogonal regression forced through the origin, the intercept is still be slightly different from (0,0).

<i>REGRESSION OUTPUT</i>		
slope, b	1,023	
uncertainty of b	0,014	
intercept, a	0,6	
uncertainty of a	0,59	
number of data pairs	83	
<i>EQUIVALENCE TEST RESULTS</i>		
random term	5,2	$\mu\text{g.m}^{-3}$
bias at LV	1,5	$\mu\text{g.m}^{-3}$
combined uncertainty	5,4	$\mu\text{g.m}^{-3}$
relative uncertainty	13,6%	
reference uncertainty	1,0	$\mu\text{g.m}^{-3}$
limit value	40	$\mu\text{g.m}^{-3}$

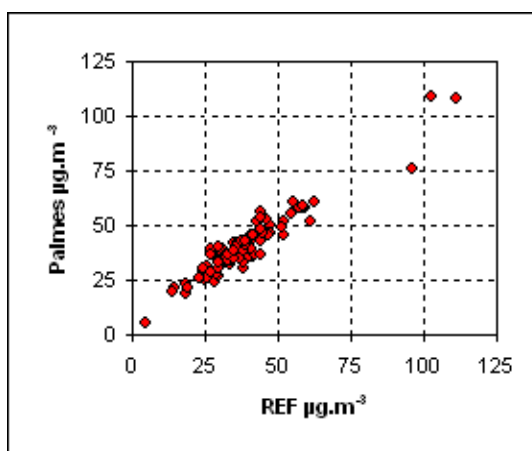


Figure 3.3: Uncertainty for annual averages according to the Guide to the Demonstration of Equivalence, Palmes substrate 20 % TEA in water vs chemiluminescence analyser

<i>REGRESSION OUTPUT</i>		
slope, b	0,906	
uncertainty of b	0,014	
intercept, a	-0,3	
uncertainty of a	0,71	
number of data pairs	116	
<i>EQUIVALENCE TEST RESULTS</i>		
random term	7,6	$\mu\text{g.m}^{-3}$
bias at LV	-4,1	$\mu\text{g.m}^{-3}$
combined uncertainty	8,6	$\mu\text{g.m}^{-3}$
relative uncertainty	21,6%	
reference uncertainty	1,0	$\mu\text{g.m}^{-3}$
limit value	40	$\mu\text{g.m}^{-3}$

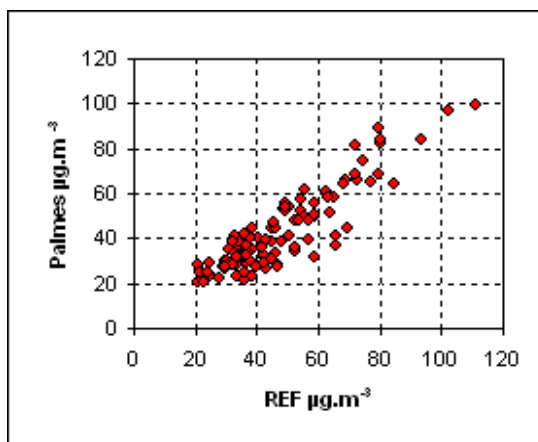


Figure 3.4: Uncertainty for annual averages according to the Guide to the Demonstration of Equivalence, Palmes substrate 50 % TEA in acetone vs chemiluminescence analyser

The results suggest that preparation of the sampling substrate using 20 % TEA in water leads to a better comparability with reference data.

Currently, a comparison is ongoing in the United Kingdom in which Palmes tube samplers and Radiello samplers are exposed at a traffic site in London. Results of this comparison were not available at the time of the drafting of this report.

3.9 Measurement uncertainty

3.9.1 GUM approach

A French Guide [24] is fully devoted to the assessment of measurement uncertainty from the application of the Palmes tube for measurement of NO_2 . In a fully worked example based on practical data, the relative expanded uncertainty at NO_2 concentration of $37 \mu\text{g.m}^{-3}$ was calculated to be 32 % for a single measurement of 2 weeks duration.

The main contribution to this uncertainty (around two thirds of total uncertainty) was from the uptake rate. The uncertainty of the uptake rate was assessed from tests performed by JRC using Palmes

tubes with a cylindrical protective box in an exposure chamber, under two extreme environmental conditions, yielding low and high values of uptake rate [19] which represented worst case scenarios. Hence, the 32 % represents a worst-case estimate. Practical values are expected to be lower.

3.9.2 Direct approach

From the comparisons described above, estimates of the uncertainty associated with NO₂ measurements performed with Palmes tubes were made.

Based on a series of 52 comparison data using an ISO 13752 approach, Plaisance et al. [8] estimated the expanded uncertainty to be < 25 % for a sampler in protective box, using a model-predicted uptake rate.

This finding was confirmed by Gerboles et al. [1], and by Buzica et al. [21], again when using a modelled uptake rate. For the membrane tube, the relative expanded uncertainty of individual measurement results at the level of the annual limit value (40 µg.m⁻³) was estimated to be 17 %.

When aggregating individual results to form an annual average, the relative expanded uncertainty reduced to 12 %. To reach this level of uncertainty, knowledge of average temperature, pressure and relative humidity and wind speed during exposure is a prerequisite.

3.10 Application in EU monitoring networks

Palmes tube samplers are extensively used e.g. in Denmark, France, the Netherlands, Spain and the United Kingdom for supplementary measurements to fixed measurements at the level of an indicative method. Other applications include identification of hot spots, mapping, zoning, trend analysis, source apportionment, impact on vegetation, assessment of exposure of population, verification of dispersion models etc.

3.11 Conclusions

The Palmes tube-type diffusive sampler is suitable for long-term monitoring of NO₂ in ambient air. Exposure periods of 1 to 8 weeks are feasible. The lower detection limit for a 1-week sampling period varied with the meticulousness of the sampler preparation procedure, and generally was between 1,4 µg.m⁻³ and 2 µg.m⁻³. The upper limit for a 5-week exposure period was at least 150 µg.m⁻³.

Information about the precision of the sampler showed that it is usually better than 5 % when using a barrier or shelter to reduce effects of wind-induced turbulence. Without these, the precision was generally higher.

Comparisons of sampler results with those obtained from reference monitors (chemiluminescence) gave varying results; however, the results are generally consistent within the uncertainties of the methods. At urban sites, where unprotected open tubes were used, a tendency was observed towards overestimation of NO₂ concentrations.

When using membrane-capped tubes in combination with model equations describing the uptake rate as a function of temperature, humidity, wind speed etc. the comparability improved.

When the uncertainty associated with the measurement results was evaluated according to the Guide to the Expression of Uncertainty in Measurement, the relative expanded uncertainty of individual results was estimated to be 32 % for worst-case conditions (when using a single value for the uptake rate independent of environmental conditions). When assessing measurement uncertainty by direct approaches, e.g., from parallel measurements with the reference method for measurement of NO₂, better results were obtained (generally < 25 %).

These findings suggest that the Palmes tube is at least suitable for performing long-term measurements of NO₂ for indicative purposes, and possibly even for fixed measurements.

When aggregating results to form annual average values, the relative expanded uncertainty may be further reduced to levels below 15 % due to the reduction of random effects on uncertainty.

3.12 References

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4 The Passam sampler

4.1 Sampler design

The Passam sampler, which is based on the Palmes tube design, is shown in figure 4.1 and consists of an opaque polypropylene tube. The tube is slightly conical. The dimensions of the tube have been measured by Ecole de Mines de Douai [1, p. 46] (see figure 4.1).

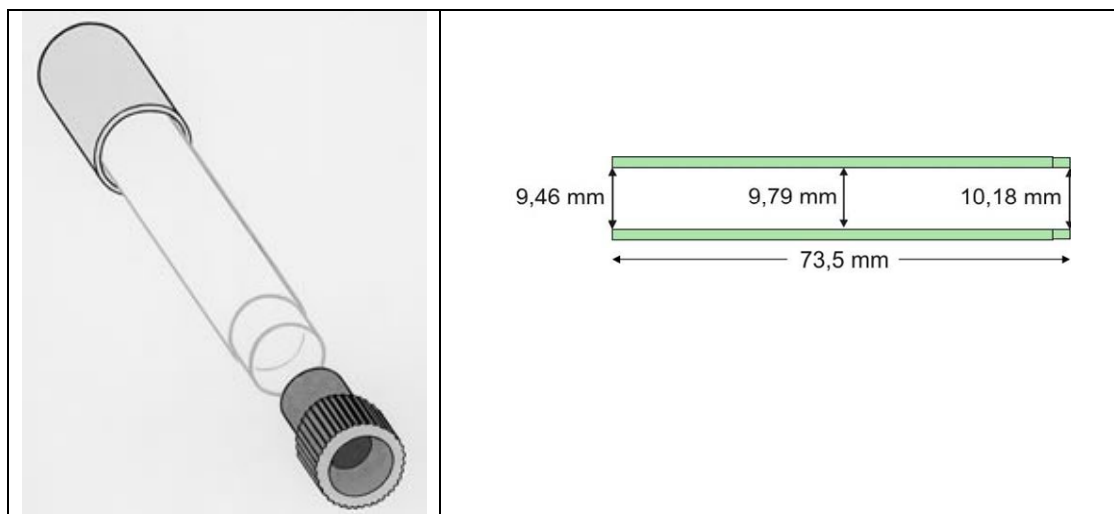


Figure 4.1: Passam tube design

At the narrow end, 3 stainless steel screens are mounted, which are coated by dipping into a solution of TEA - acetone 1:7. Shelf life of the sampling substrate of up to 2 years has been found [2]. Passam tubes are exposed in specific shelters [3]. These shelters are designed to protect the samplers from environmental factors such as rain, excessive radiation and wind. The shelters are an integral component of the measurement method (see figure 4.2).



Figure 4.2: Passam protective shelter

In order to reduce the effect of wind-induced turbulence the sampler may be equipped with a membrane or a glass frit [4].

4.2 Extraction and analysis

The manufacturer describes the determination of the collected NO₂ by colorimetry, after reaction with sulphanilic acid and N-1-naphthylethylenediamine [3].

4.3 Application range and conditions

Information on application ranges and conditions given in table 4.1 was provided by the manufacturer [3].

Table 4.1: Application ranges and conditions

Parameter		Application ranges/Conditions
Sampling time		1 – 4 weeks
Working range		1 – 200 µg.m ⁻³
Detection limit		0,8 µg.m ⁻³ for 1-week exposure 0,4 µg.m ⁻³ for 2-week exposure
External influences	Wind speed	Influence of wind speed < 10 % up to 4,5 m.s ⁻¹ when using protective shelter
	Turbulence at kerb sites	Use of membrane recommended because of potential increase of uptake rate
	Temperature	No effect between 5 and 40 °C
	Humidity	No effect between 20 and 80 % RH
Storage	Before use	12 months
	After exposure	4 months
Cross sensitivity		Nitric oxide and sulfur dioxide do not interfere
		Presence of PAN will lead to high results

Field studies showed that exposure periods of up to 6 weeks are feasible without introducing differences [4].

4.4 Uptake rate

The uptake rate of the Passam tube was determined in a series of laboratory experiments [5] designed as prescribed in EN 13528 part 2. In addition, the results of a series of comparisons performed by Buzica *et al.* [6] were used to validate these earlier results.

The manufacturer reported a nominal uptake rate of 0,85 cm³.min⁻¹ ± 11 % for a reference temperature of 9 °C and a reference pressure of 950 mbar.

When applying Fick's first law of diffusion, an uptake rate of 0,947 cm³.min⁻¹ was calculated at a temperature of 21 °C and pressure of 101,3 kPa [1, p. 47].

For practical purposes, users may correct the uptake rate to actual conditions of temperature and pressure by applying equation 3.3. In most cases, the pressure correction may be neglected. Other authors proposed e.q. 4.1 with a temperature correction raised to the power of 1.5 instead of 1.81 ([1], page 74):

$$v_{T,P} = v_{ref} \left(\frac{273,2 + T}{273,2 + T_{ref}} \right)^{1,5} \frac{P_{ref}}{P} \quad (\text{eq. 4.1})$$

where

- $v_{T,P}$ = uptake rate in cm³.min⁻¹ with temperature T and Pressure P during sampling;
- v_{ref} = uptake rate in cm³.min⁻¹ at reference temperature and pressure;
- T = actual temperature during sampling in °C;
- T_{ref} = reference temperature in °C at which v_{ref} rate is given;
- P = actual pressure during sampling in kPa

P_{ref} = reference pressure in kPa at which v_{ref} is given.

When applying a glass frit [4] to reduce effects of wind-induced turbulence, the uptake rate reduces to $0,827 \text{ cm}^3 \cdot \text{min}^{-1}$.

4.5 Environmental effects

4.5.1 Air velocity

The migration of NO_2 molecules to the absorption layer at the lower end of the diffusive sampler is determined by the length of the diffusion path. Eddies created by wind turbulence can shorten the diffusion path, thereby increasing the uptake rate and producing higher results. This phenomenon can be eliminated in one of two ways:

- by using protective shelters;
- by equipping the sampler inlet with a membrane.

Protective shelters

Protective shelters reduce the wind velocity at the sampler openings (the sampler and the shelter are an integral system): $0,5 \text{ m} \cdot \text{s}^{-1}$ outside corresponds to about $0,1 \text{ m} \cdot \text{s}^{-1}$ inside the shelter [3, 6] (see figure 4.3).

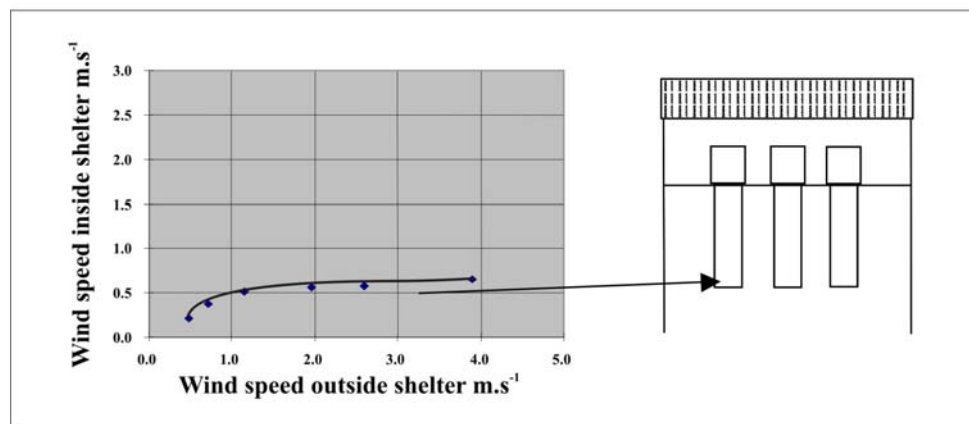


Figure 4.3: Effect of protective shelter on wind velocity inside the shelter

Effect of diffusion barrier like membranes or glass frit

The effect of using a polyethylene membrane on the relative uptake rate is illustrated in the figure 4.4.

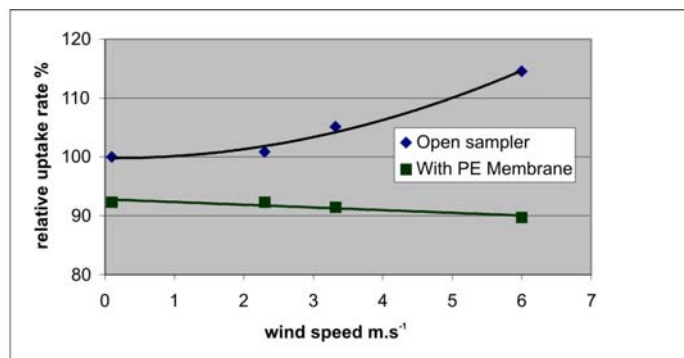


Figure 4.4: Relative uptake rate with and without membrane.

However, membranes affect the uptake rate of a diffusive sampler. The tested membranes (Fluoropore $1 \mu\text{m}$, Glass fibre EPM 2000 and Polyethylene $15\text{--}45 \mu\text{m}$) produced a decrease around

10% $\pm$ 4%. The results of the tests with different membranes are reported in table 4.2. The tests were conducted in a glass chamber with concentrations of 50 and 100 $\mu\text{g.m}^{-3}$ and wind speeds of 0,01 and 0,5 m.s^{-1} . By using membranes, an additional resistance to the diffusion of NO_2 towards the absorbent is introduced (see section 3.7.1). This resistance tends to change with sampling conditions and creates another source of uncertainty. However, this uncertainty was found to be lower than the effect of wind velocities above 2 – 3 m.s^{-1} for open tubes without protective shelters.

Table 4.2: Uptake rate for membrane closed Passam samplers relative to open tube

Membrane type	50 $\mu\text{g.m}^{-3}$ 0,5 m.s^{-1}	100 $\mu\text{g.m}^{-3}$ 0,01 m.s^{-1}	100 $\mu\text{g.m}^{-3}$ 0,5 m.s^{-1}
Fluoropore 1 μm	90 %	95 %	94 %
Glass fibre EPM 2000	91 %	93 %	94 %
Polyethylene 14-45 μm	87 %	90 %	89 %

4.5.2 Relative humidity

No influence of relative humidity between 20 and 80% was observed [8]. No data are available for extreme conditions such as dry desert areas and wet tropic areas.

Under European climatic conditions, no humidity effects were reported [9].

4.5.3 Temperature

To investigate the influence of temperature, two glass chambers were set up in series. Six laboratory tests were performed. One chamber was always set at a controlled temperature of 20°C, while the second one was set at different temperatures between -15 and 50 °C (see figure 4.5). For each test, paired uptake rates (one at 20 °C and one at the temperature under test) were determined by exposure and analysis of several samplers in the chambers. For each paired uptake rate, a relative difference with reference to the uptake rate at 20 °C was calculated. Figure 4.5 shows that in the range of 5 to 40 °C, the uptake remained nearly constant and that it does not need any correction [8] according to temperature during exposure.

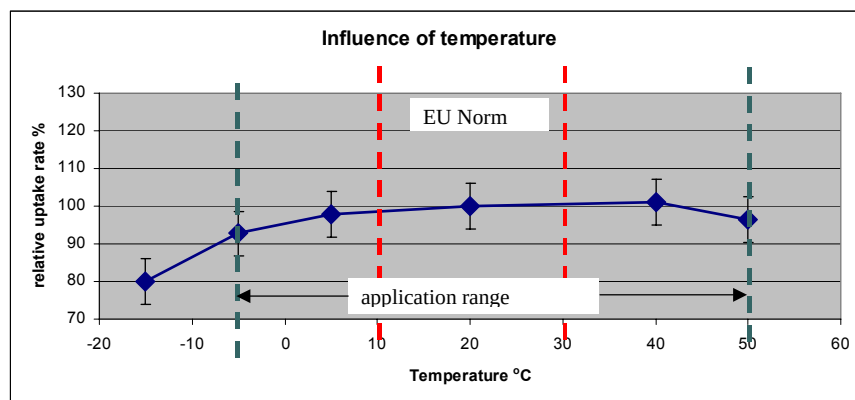


Figure 4.5: Effect of temperature on uptake rate, error bars represent the standard deviation of the relative uptake rates

In a year-long study conducted in Switzerland at 3 monitoring sites, where meteorological data were collected, comparisons between measurements by Passam samplers and chemiluminescence analysers were carried out [8]. A correlation analysis was performed between the meteorological factors and the ratios of NO₂ concentrations measured by the analysers to the diffusive sampler values. In total, 78 2-week pairs of measurements were available. All samplers were equipped with protective shelters. No influence of wind velocity and radiation was observed (see table 4.3). There was a slight correlation with temperature and humidity, although the median test was negative in all cases.

Table 4.3: Correlation coefficients of meteorological parameters with the ratios of NO₂ measurements carried out with chemiluminescence analyses out of diffusive samplers

	Temperature	Humidity	Wind speed	Radiation
Unit	°C	% rel.	m/sec	Watt/m ³
Correlation r	0.136**	0.113**	0.021	-0.019
Range _{min}	-0.7	42	0.7	15
Range _{max}	23	85	2.6	273
Median	11.2	67	1.4	112
Median test	n.s.	n.s.	n.s.	n.s.

** = 99% significance level.

In a Swiss alpine Valley 1800 m above sea level, a measurement comparison between a chemiluminescence monitor and the Passam samplers was performed. The mean temperature in the coldest season was -4,1 °C. No differences in results of the two methods were observed for temperatures above - 5 °C [3].

4.5.4 Pressure

A pressure effect of 0,5 % decrease in uptake rate with an increase in ambient air pressure of 10 mbars has been observed [8].

4.5.5 Interferences

Burri has studied the interferences of NO, SO₂ and ozone. No effects could be shown when single substances were applied [10].

4.6 Validation of sampler performance

4.6.1 Comparisons with reference methods

Basic validation studies 1986 – 1988

To validate the diffusive sampling system, comparisons with continuous monitors were performed [10]. The comparisons were made at 5 different monitoring sites over one year. 184 weekly monitoring pairs were collected. The concentration values of the monitors were standardized to 9 °C and 950 mbar. The results are compiled in figure 4.6.

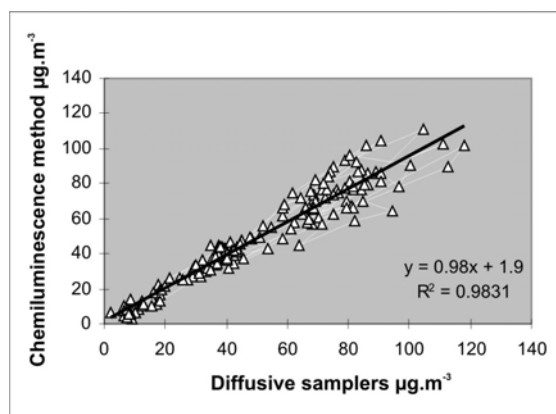


Figure 4.6. Relationship between results of Passam and chemiluminescence monitors

Reports from cantons of Switzerland

Comparisons of yearly means

In figure 4.7, the results of comparisons of annual NO_2 averages are shown. Each point is characterized by 50 to 70 diffusive sampler measurements over one year and a complete data set of chemiluminescence analyser results. The exposure period was two weeks. Under these conditions, varying meteorological factors such as humidity, wind, temperature etc. were automatically considered.

The 95 % confidence interval was calculated to be $\pm 4 \mu\text{g.m}^{-3}$ at the level of the Swiss long-term limit value of $30 \mu\text{g.m}^{-3}$. This figure is valid for the investigations conducted from 1987 to 1994. Figure 4.7 shows that the uptake rate of the sampler remained constant from 1987 to 1994 and from 1995 to 2000. The ratio of NO_2 measured by samplers vs monitors was 0,98 from 1987 to 1994. The same ratio (1,01), was not significantly different from 1995 to 2000. The difference in R^2 values may be explained by the larger range of NO_2 concentrations measured between 1987 and 1994.

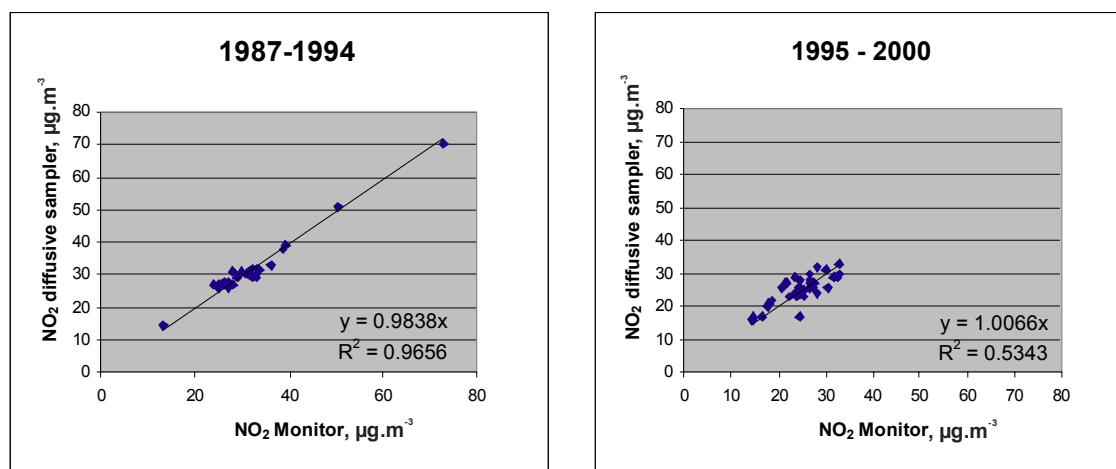


Figure 4.7. Relationship between results of Passam and chemiluminescence monitors

Comparisons of single pairs

Table 4 gives a regression analysis for individual NO_2 concentrations measured using Passam samplers and chemiluminescence analysers. The data were communicated by the Environmental Agencies of the cantons of Grison, Basel and Bern (CH). For each sampling site, the slope/intercept of the regression line, the percentage of variation expressed by the regression line (R^2) and the number of samples are given. Samplers were exposed for 2 weeks.

Table 4.4: Comparisons of individual NO₂ measurements by Passam samplers and chemiluminescence analyser at field sites. Results of environmental agencies in Grison, Basel and Bern (CH)

Canton	Type of site	Year	Slope	Intercept	R ²	n
Bern	city background	2005	1,15	-3,4	0,939	26
		2006	0,96	-0,91	0,975	26
		2007	0,94	-0,03	0,928	26
	agglomeration, highway	2005	1,49	-25	0,780	26
		2006	1,12	-9,1	0,889	26
		2007	1,22	-12,7	0,889	26
Basel	city	2001/02	1,15		0,954	124
Grison	industrial	2001-2003	0,94	-6,8	0,700	166
	traffic		0,94	-3,1	0,840	54
	rural		0,9	-1,1	0,890	113
	mountain city, suburb		1,09	-0,9	0,850	128
	mountain city, traffic		1,08	-7,3	0,860	41
	traffic		1,12	-11,4	0,570	25
	mountain		1,16	-11,1	0,750	24
	highway		0,97	-1,2	0,740	231
	mountain village		1,26	-5,8	0,930	15
	highway		0,26	16,4	0,130	58
Neuchatel	city	2005	1,13	0	0,927	27

Near highways and in cities, site-specific discrepancies were sometimes observed (see figure 4.8). In general, an overestimation of the concentration of NO₂ in the vicinity of highly trafficked streets was observed [11]. The deviations are most likely due to traffic-induced vertical air turbulence.

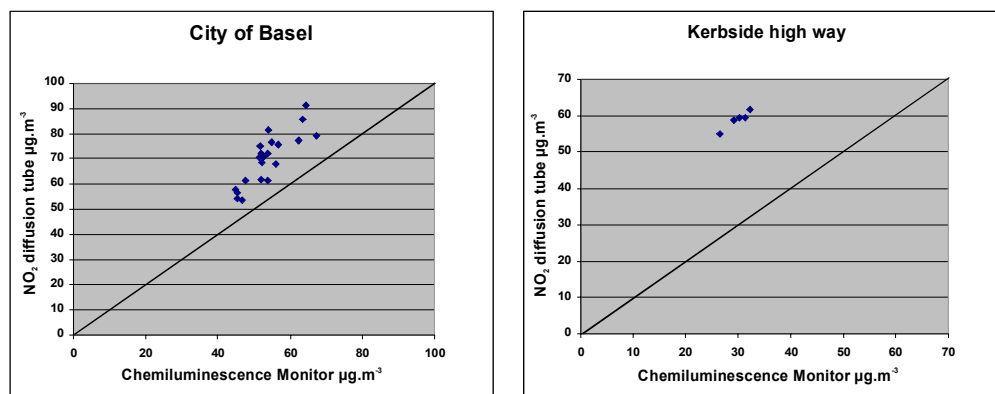


Figure 4.8. Examples of relationships between results of Passam and chemiluminescence monitors for specific city and highway conditions

Reports from outside Switzerland

In 2001-2002, CEN/TC264 WG11 performed a small-scale pilot study at two locations in the UK. At each location, 6 replicate samplers of different NO₂ passive samplers were exposed for two weeks, in parallel with measurements from a reference chemiluminescence analyser. Samplers were provided and analysed by the suppliers. The unpublished results for the exposed Passam samplers are reported in table 4.5.

Table 4.5: Results of CEN pilot study for Passam samplers

Willebroek	NO ₂ (µg.m ⁻³)	Ratio Passam/reference
Reference	40,8	
Passam	55,0	1,35
Teddington	NO ₂ (µg.m ⁻³)	Ratio Passam/reference
Reference	13,8	
Passam	20,2	1,46

Passam samplers were found to overestimate NO₂ concentrations.

Experiments in France at various sites also concluded that the Passam tubes overestimated NO₂ concentrations, when using the uptake rate of 0,85 cm³.min⁻¹ (see figure 4.9). In order to obtain correct values, a uptake rate of 0,947 (21 °C, 101,3 kPa) should be used, reducing the results of the Passam tubes by about 11 %. [1, p. 47].

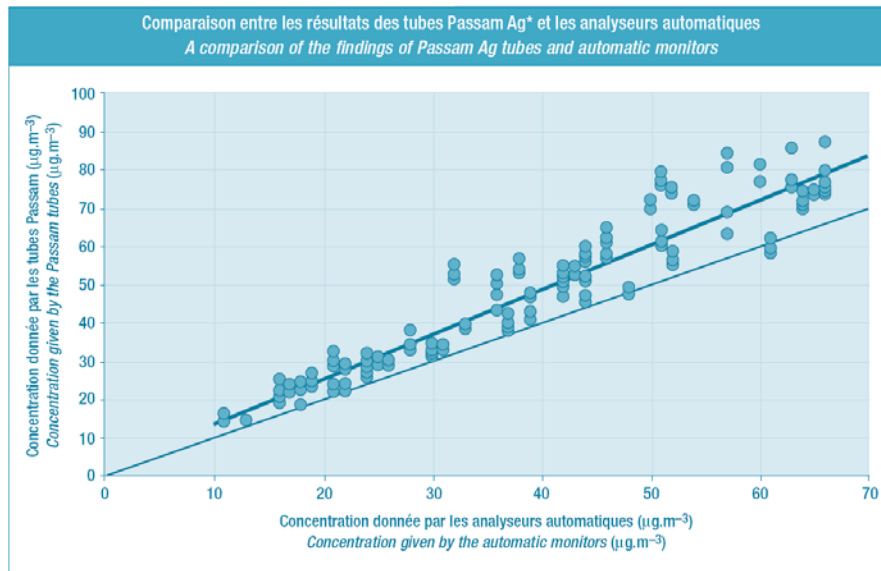


Figure 4.9: Relationship between results of Passam and chemiluminescence monitors

ASPA (the French air quality Alsace network) reported slopes of linear regressions between results of chemiluminescence monitors and Passam tubes from 0,95 to 1,15 (see table 4.6). The NO₂ concentrations were corrected to 20 °C and 1013 mbar according to equation 4.1. The slope/intercept of the regression line, the percentage of variation expressed by the regression line (R²) and the number of samples are given. Samplers were exposed for 2 weeks.

Table 4.6: Comparisons of individual NO₂ measurements by Passam samplers and chemiluminescence analyser at field site. Results of ASPA in France

ASPA	Type of site	Year	Slope	Intercept	R ²	n
1	agglomeration	2005	1,15	-3,42	0,939	25
2	rural	2005	0,964	-0,91	0,975	25
3	agglomeration	2005	0,953	-0,03	0,928	25
4	city centre	2005	1,006	1,29	0,963	25
5	city centre	2005	1,023	2,36	0,989	25

Buzica et al. [6] organized a series of 4 comparisons in which different samplers operated by different laboratories were exposed both under laboratory and field conditions. Each sampler type was exposed in batches of 6 samplers for a period of 14 days, except in the laboratory trial “high” (see table 4.7).

Table 4.7: Laboratory conditions (intercomparison of Buzica et al.)

Parameter	High	Low
Exposure time (d)	7	14
Concentration ($\mu\text{g.m}^{-3}$)	80	40
Air velocity (m.s^{-1})	2,5	1,0
Temperature ($^{\circ}\text{C}$)	25	5
Relative humidity (%)	75	30

The results obtained for the Passam sampler (implemented by an external laboratory following the Passam protocol), are presented in table 4.8.

Table 4.8: Results of Passam sampler analysed by an external laboratory (intercomparison of Buzica et al.)

Location	CLS ($\mu\text{g.m}^{-3}$)	Passam ($\mu\text{g.m}^{-3}$)	Ratio
Laboratory, high	76,8	97 ± 5	1,27
Laboratory, low	43,5	$39,5 \pm 0,7$	0,91
Genevilliers	41,6	$53,1 \pm 0,3$	1,28
Fontainebleau	14,1	$15,7 \pm 0,4$	1,11

CLS: chemiluminescence method

The Passam tubes were found to overestimate NO_2 concentrations, confirming the findings reported in [1] (see table 4.8). This was attributed to the use of an uptake rate for reference conditions differing considerably from the exposure conditions.

In 2004-2005, Pfeffer et al. [4] performed an extensive study into the use of Passam tubes. Tubes were exposed for periods from 2 to 6 weeks at 10 different sites in North-Rhine Westphalia in Germany (LANUV network)). In this investigation, a diffusion barrier consisting of a porous glass membrane was fitted at the open end of all samplers. The uptake rate of the tubes, derived from the comparison with reference method according to EN 14211 was $0,8270 \pm 0,0085 \text{ cm}^3.\text{min}^{-1}$. When comparing concentrations measured with the reference method and the modified Passam sampler by linear regression, the site-specific slope derived for each monitoring site generally did not differ significantly from the slope calculated from the complete data set at the 95% confidence level. The site-specific slopes varied between 0,93 and 1,11. The between-sampler uncertainty obtained from replicate sampling was $1,2 \mu\text{g.m}^{-3}$. The tubes were subsequently used in the LANUV monitoring network. They were further investigated for consistency with the reference method. No deviations were observed when comparing 789 data pairs of results [12].

In France, Passam samplers were extensively compared to the chemiluminescence reference method [13]. During the years 2005, 2007 and 2008 samplers were exposed side-by-side with the reference method at 6 locations (5 in 2005) with exposure periods of 4 weeks, resulting in a total of 181 valid data pairs. From the results reported, it was observed that the data capture of the Passam samplers (100%) was higher than that of the reference method (95,5%). Further, when subjecting the data to the evaluation of equivalence [14], the results presented in figure 4.10 were found. The evaluation revealed excellent agreement between the results of both methods. The resulting uncertainty, 13 % for a 95 % confidence level, fulfils the 15 % uncertainty requirement for fixed measurements of NO_2 . The ratio of the overall means of diffusive sampling results and reference results was 0,98.

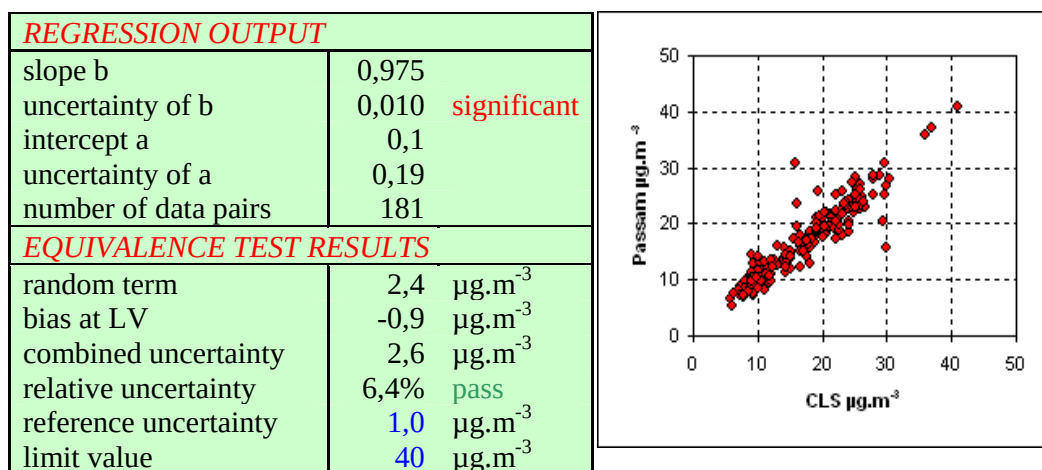


Figure 4.10: Uncertainty for annual averages according to the Guide to the Demonstration of Equivalence, Passam sampler vs chemiluminescence analyser

4.7 Measurement uncertainty

4.7.1 GUM approach

Passam applied the (indirect) GUM approach for the evaluation of the uncertainty associated with the measurement of NO_2 using the Passam tube [15]. The uncertainty assessment was based on the following measurement equation:

$$C_{\text{NO}_2} = \frac{(m_d - m_b) \cdot 10^6}{v \cdot t} \quad (\text{eq 4.2})$$

where

C_{NO_2} = ambient concentration in $\mu\text{g.m}^{-3}$;
 m_d = mass of desorbed analyte in μg ;
 m_b = blank of analyte in μg ;
 v = diffusive uptake rate in $\text{cm}^3.\text{min}^{-1}$;
 t = exposure time in min.

The input quantities and their uncertainties are defined as follows:

u_{md} : Uncertainty of the mass of measured nitrite. The standard uncertainty is characterised by the standard deviation of the calibration function;
 u_{mb} : Blank values: the variation of blank value has to be added to u_{md} in absolute terms;
 u_v : Uncertainty of uptake rate. The variation of this term is given by the standard deviation of repeated verification experiments in standard atmospheres;
 u_t : Exposure time. This term is in general negligible at exposure times of more than one week.

An additional term is introduced, which covers the uncertainties associated with between-sampler precision, micro-environmental factors, variations in the geometry of samplers etc.

u_P : Variation of multiple samples at the same site. The size of this term is estimated by the median of triplicate samplers in the field.
 u_{ext} : External influences such as temperature, wind speed, humidity. This term has to be taken into account, if the samplers are used in extreme conditions. This term has to be estimated.

The combined uncertainty u_c is calculated using equation 4.3.

$$u_c^2 = u_v^2 + u_{md}^2 + u_{mb}^2 + u_p^2 + u_t^2 + u_{ext}^2 \quad (\text{eq. 4.3})$$

The expanded uncertainty is calculated by using a coverage factor of 2. Detailed figures for u_v , u_p and u_{mb} are given in [16]. The coefficient of variation of replicates is reported in [17] to be 1,7 %. The uncertainty figures are re-evaluated every year [16].

The expanded uncertainty calculated in the above manner varies between 20 % and 25 % (see figure 4.11). The data quality objective of EU Directive 2008/50/EC for indicative measurements is generally fulfilled.

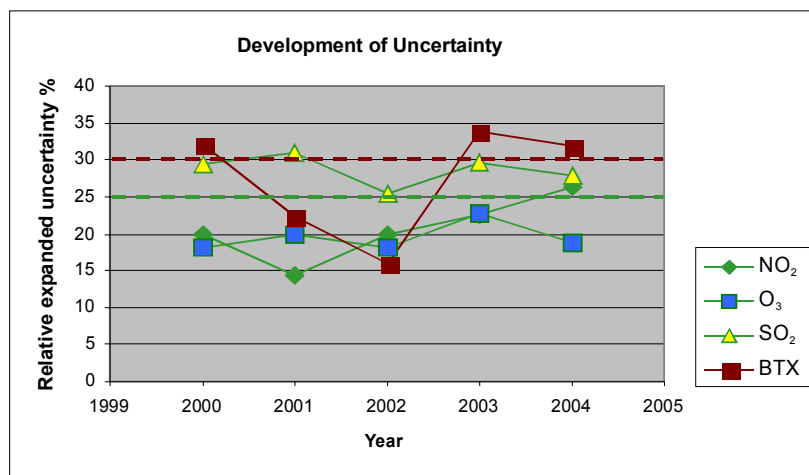


Figure 4.11: Relative expanded uncertainty of Passam results from 2000 to 2004 as monitored by the manufacturer

4.7.2 Direct approach

A comprehensive uncertainty evaluation using a direct approach was performed by Pfeffer et al. [4]. At 10 monitoring sites, parallel measurements were performed with Passam samplers and the EU reference method (EN 14211) for more than one year. A modified Passam tube equipped with a porous glass membrane was used.

From the comparisons with reference values obtained from the chemiluminescence monitors, a relative expanded uncertainty for single results between 21 % and 25 % at $40 \mu\text{g.m}^{-3}$ was calculated for exposure periods of 2 to 6 weeks. Calculation according to the guide to demonstration of equivalence for 4-weeks exposure resulted in an expanded uncertainty of 22 %. In this calculation, the uncertainty of the reference method results was set to zero. Consequently, the uncertainty represents the worst case [18].

It is unlikely that these results were biased, since the estimation of the uptake rate was based on NO₂ values measured using the reference method (EN 14211). The estimation of the uptake rate was performed using measurements at 10 different monitoring sites and over 14 months (as the slope of the mass uptake versus sampled dose, see figure 4.12). With all these different sampling conditions, the influencing parameters (either chemical or meteorological) encompassed a large range of possible values. It is therefore likely that most of the sources contributing to the uncertainty of the reference method and of the diffusive sampling method were randomised. For this reason, it seemed to be justified to divide the uncertainty of single values by the square root of 12 when calculating annual averages from 12 monthly values. Consequently, the uncertainty of annual averages based on monthly measurements should be less than 10 %. This means that the EU data quality objective of 15 % is safely met for annual means.

In 2004/2005, the uptake rate was evaluated by parallel measurements with chemiluminescence analysers. It was found to be $0.827 \text{ cm}^3.\text{min}^{-1}$ (see figure 4.12). At this time, the monitors in the

monitoring network were logically not type approved according to the new CEN standard EN 14211 published in 2005.

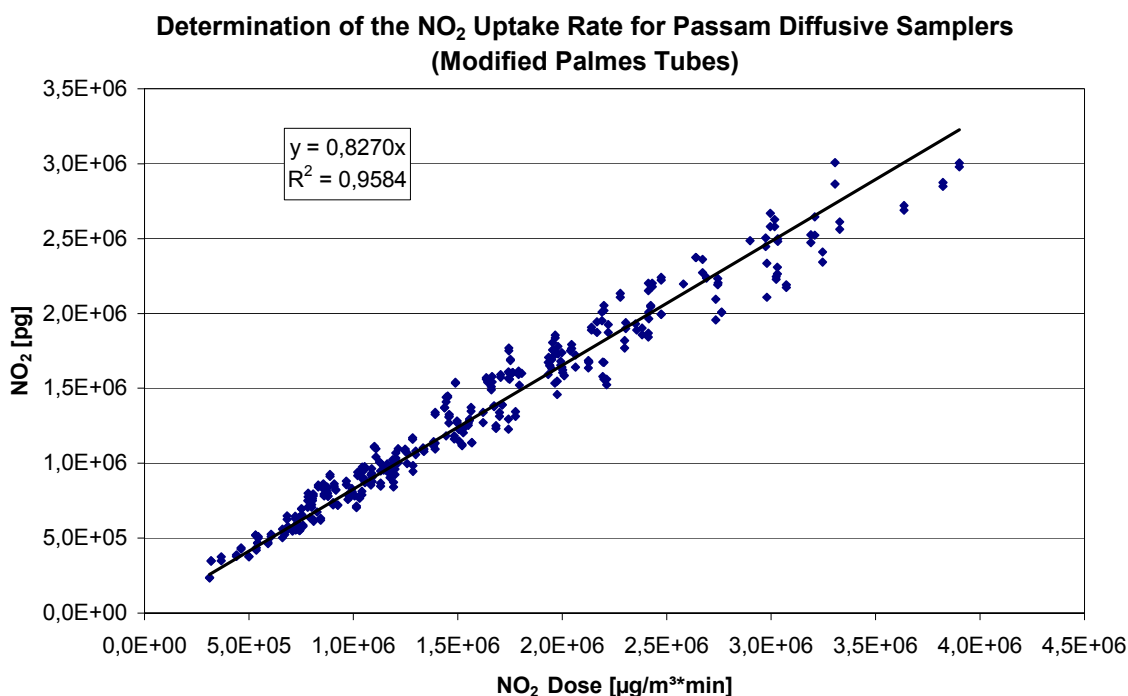


Figure 4.12: Relationship between mass of NO₂ obtained by analysis and NO₂ dose sampled

The uptake rate found in the validation experiments was continuously checked by ongoing parallel measurements with the chemiluminescence method from 2006 to 2008 at six to eight stations. Results for 2006 showed an excellent congruence of the annual averages measured by the chemiluminescence method and with the diffusive samplers [12, 18].

In 2007 and 2008, slight and increasing differences were found at various stations showing higher values of the continuous measurements compared with the diffusive samplers [12].

Comprehensive investigations were performed to find technical reasons for this phenomenon. It was shown that all handling details of the diffusive sampler technique remained unchanged over the years. But in the network of continuous analysers, old instruments were replaced stepwise by new monitors that were type approved according to EN 14211 in order to meet the requirements of Annex VI D of the new European directive 2008/50/EC. The new generation of instruments therefore appears to give higher results for NO₂ in some situations, especially in high ambient humidity conditions. Similar effects were found during inter-laboratory comparisons in the German networks [19].

When sufficient data of parallel measurements are available, it may be necessary to adjust the uptake rate of the diffusive samplers accordingly.

ASPA performed parallel measurements with Passam samplers and the EU reference method (EN 14211) at 5 monitoring sites (rural to city sites) for 1 year using two-week exposure periods [1] (see figure 4.13). The raw data of diffusive samplers, delivered by Passam, were corrected for temperature and pressure according to equation 4.1. Applying the direct approach described in EN-ISO 20988, an expanded uncertainty of 14,4 % at 40 µg.m⁻³ was obtained. This figure is similar to the results obtained when evaluating uncertainty for the 3-year data set of monthly measurement results provided by Lig'air [13].

This shows that the uncertainty tends to meet the data quality objective of EU Directive 2008/50/EC for fixed measurements.

NO₂: Comparison with reference method: France

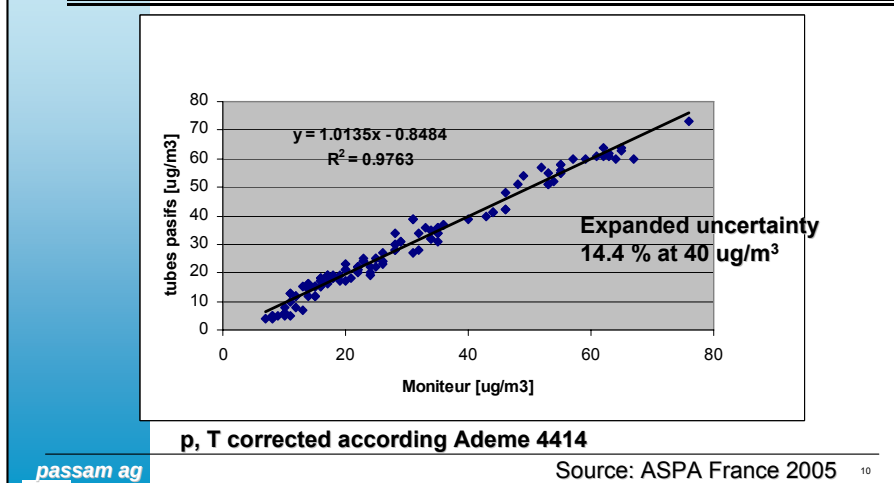


Figure 4.13: Relationship between results of Passam tubes and chemiluminescence monitors, Field site in France (ASPA)

4.8 Application in EU monitoring networks

Passam tube samplers are used e.g. in Cyprus, France, Germany, Italy, Lithuania and Romania for supplementary measurements to the fixed measurements at the level of an indicative method. Other applications include identification of hot spots, mapping, zoning, trend analysis, source apportionment, impact on vegetation, assessment of exposure of population, verification of dispersion models etc.

4.9 Conclusions

The Passam tube-type diffusive sampler is suitable for long-term monitoring of NO₂ in ambient air. Exposure periods of 1 to 6 weeks are feasible. The lower detection limit for a 2-week sampling period is reported to be 0,4 µg.m⁻³.

Information about the precision of the sampler indicates that this is usually better than 5 %.

The comparability of sampler results with those obtained from continuous reference monitors (chemiluminescence) vary somewhat, with ratios of average results generally ranging from 0,9 to 1,3. This variability may be reduced, when :

- Uptake rates are converted to actual conditions of temperature and pressure;
- Membranes are introduced into the sampler inlet, particularly for traffic-related sites.

When the uncertainty associated with the measurement results is evaluated according to the Guide to the Expression of Uncertainty in Measurement, relative expanded uncertainties of individual results were between 20 and 25 %. When assessing measurement uncertainty by direct approaches, e.g., from parallel measurements with the reference method for measurement of NO₂, similar and even better results were obtained.

These findings suggest that the Passam tube is at least suitable for performing long-term measurements of NO₂ for indicative purposes and possibly even for fixed measurements.

When aggregating results to form annual average values, the relative expanded uncertainty may be further reduced to levels below 15 % due to the reduction of random effects on uncertainty.

4.10 References

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5 The Ogawa badge

5.1 Sampler design

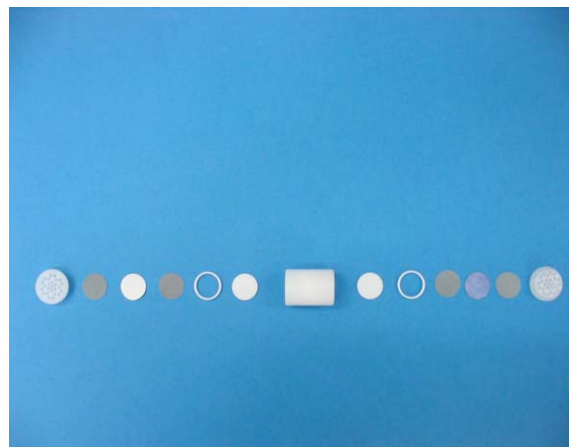
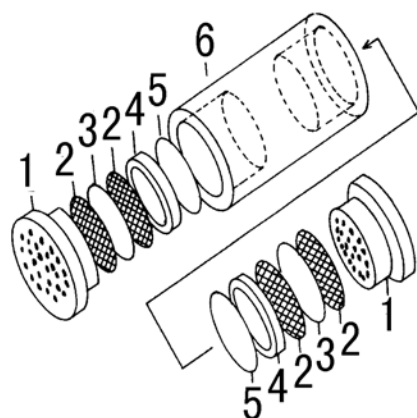


Figure 5.1: Ogawa sampler design

1. Diffuser end cap
2. Stainless steel mesh
3. Sampling filter (14,5 mm ϕ)
4. Teflon ring
5. Teflon disk
6. Body (15 mm ID; 19 mm OD; 6 mm length)

The Ogawa sampler [1] (see figure 5.1) is a badge-type sampler that can be equipped with a sampling filter on either side of the sampler body. Sampling filters consist of cellulose fibre. Both filters can be coated with triethanolamine (TEA) for the sampling of NO_2 in ambient air. Coated filters may be supplied by the manufacturer. However, literature reveals that filters may also be coated by users themselves [2].

The presence of a second filter permits the simultaneous collection of NO_2 and nitrogen oxides equal to the concentration of nitrogen monoxide (NO) plus NO_2 . In this case, the second filter is coated with TEA and 2-phenyl-4,4,5,5-tetramethyl imidazoline-3-oxide-1-oxyl (PTIO), which is a specially prepared reagent for oxidising NO to NO_2 . This filter then collects both species as NO_2 . The concentration of NO can be obtained as a difference in NO_2 concentrations found on the two differently coated filters.

5.2 Extraction and analysis

The manufacturer recommends the determination of the collected NO_2 by colorimetry after reaction with sulphanilamide and N-1-naphthylethylenediamine. However, literature reveals the use of ion chromatography for the measurement of nitrite on the filter [3,4]. In that case, co-sampled sulfur dioxide can also be simultaneously measured.

5.3 Application range and conditions

The manufacturer recommends exposure periods from 24 to 168 hours, but indicates that for low concentrations it is possible to sample for up to 30 days. In practice, samplers have been exposed for up to 4 weeks [4].

Although not explicitly stated in [1], the information provided suggests that the samplers may be used over a temperature range from -10°C to 40°C , and a relative humidity range from 50 % to 80 %.

The sampler should always be exposed with a shelter as provided by the manufacturer.

Detection limits given by the manufacturer are 2,3 ppb for 24-hour sampling, and 0,32 ppb for 1-week sampling. The upper limit for 1-week sampling is reported to be 3600 ppb.

The manufacturer specifies the following conditions for storage of coated filters, samplers and sampled filters upon refrigeration:

- Coated filters sealed in original glass vial with aluminium pouch : 90 days
- Sampler loaded with coated filter(s) placed in bag in sealed brown vial : 60 days
- Exposed sampler placed in bag in sealed brown vial : 14 days*
- Filter extract in sealed amber glass vial : 90 days.

* Filters should be analyzed as soon as possible after exposure.

5.4 Uptake rate and environmental effects

The Ogawa Protocol [1] provides information about the uptake rate of the sampler in the form of a coefficient α , which is a function of temperature and relative humidity. After analysis of an Ogawa sampler, NO_2 is calculated using equation 5.1

$$C_{\text{NO}_2} = \alpha \cdot \frac{m}{t} \quad (\text{eq. 5.1})$$

where

C_{NO_2} = concentration of NO_2 in ppb;

α = dose according to the uptake mass in $\text{ppb} \cdot \text{min} \cdot \text{ng}^{-1}$, (converse of an uptake rate);

m = mass of nitrite determined by analysis on a single filter in ng;

t = exposure time in min.

α may be calculated for a given temperature and relative humidity using the semi-empirical equation 5.2.

$$\alpha = \frac{10^4}{0,677 \cdot P \cdot RH + 2,009 \cdot T + 89,8} \quad (\text{eq 5.2})$$

where

RH = ambient air relative humidity in %;

T = ambient temperature in °C.

P is calculated using equation 5.3.

$$P = \left[\frac{2P_n}{P_T + P_n} \right]^{\frac{2}{3}} \quad (\text{eq. 5.3})$$

where

P_n = saturated water vapour pressure at 20 °C in mm of Mercury (Hg) = 17,53

P_T = saturated water vapour pressure at temperature T in mmHg.

The variation of α as a function of temperature and relative humidity is presented in table 5.1 and figure 5.2.

Table 5.1: Variation of α in ppb.min.ng-1 as a function of temperature and relative humidity

RH (%) / T (°C)	0	5	10	15	20	25	30	35	40
20	92,4	85,3	79,3	74,2	69,7	65,7	62,2	59,0	56,0
30	85,2	79,4	74,5	70,3	66,5	63,2	60,2	57,4	54,8
40	79,0	74,3	70,3	66,8	63,7	60,9	58,3	55,8	53,5
50	73,6	69,8	66,5	63,6	61,0	58,7	56,5	54,4	52,4
60	68,9	65,8	63,1	60,7	58,6	56,7	54,8	53,0	51,3
70	64,8	62,2	60,0	58,1	56,4	54,8	53,2	51,7	50,2
80	61,2	59,0	57,2	55,7	54,3	53,0	51,8	50,5	49,2
90	57,9	56,1	54,7	53,5	52,4	51,4	50,4	49,3	48,2

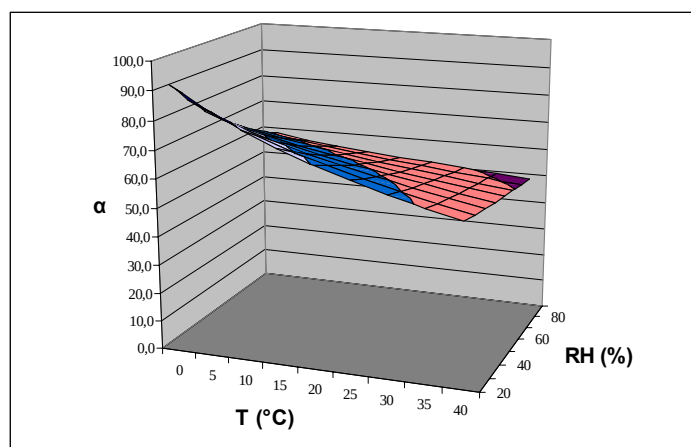


Figure 5.2: Variation of α in ppb.min.ng-1 according to Temperature (T) and relative humidity (RH)

In order to calculate a uptake rate in more common units of $\text{cm}^3 \cdot \text{min}^{-1}$, equation 5.4 can be used for the conversion.

$$V = \frac{10^3}{\alpha} \cdot \frac{V_{m,air}}{46,0055} \quad (\text{eq. 5.4})$$

where

$V_{m,air}$ = molar volume of the sampled air.

5.5 Validation of sampler performance

5.5.1 Comparisons with reference methods

The Ogawa protocol describes a comparison between the results of the sampler and a reference method performed within the frame of the original validation of the sampler (Yokohama City Research Institute of Environmental Science, Yokohama, Japan, Report No. 128, March 1997; see [1]). The results are presented in figure 5.3. The y-axis represents results obtained with the sampler, the x-axis results of the reference method. Unfortunately, the sampling period is unknown.

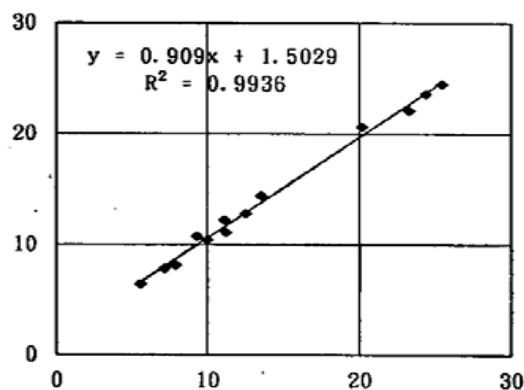


Figure 5.3: Comparison between results of the Ogawa sampler with the chemiluminescence method. X and y axis represent the results of the diffusive sampling method and reference method, respectively

In a further Japanese report supplied by Ogawa USA (no reference available), a comparison was reported between the Ogawa sampler and chemiluminescence monitoring at Funakoshi environmental station. Samplers were exposed during two 5-week periods in July/August 1999 and January/February 2000. Sampling periods of 1, 2, 3, 4 and 5 weeks were used, samplers being exposed in triplicate. The sampler results obtained were internally consistent over the 5-week period. Ratios of results of samplers and chemiluminescence monitors ranged between 0,95 and 1,16, with better comparability observed in the winter period. No information was provided of sampler precision.

Bytnerowicz et al. [5], in a study devoted to the measurement of several air pollutants in Sequoia National Park, measured NO₂ over the period of May to October 1999 both by the chemiluminescence method and by using the Ogawa sampler. The samplers were exposed in duplicate for consecutive two-week periods. The mean values found by the Ogawa sampler and the chemiluminescence method were 2,6 and 2,0 ppb, respectively. The precision of mean value determined by the Ogawa sampler was 5,6 %.

Buzica et al. [6] organized a series of 4 comparisons in which different samplers operated by different laboratories were exposed both under laboratory and field conditions. Each sampler type was exposed in batches of 6 samplers for a period of 14 days, except in the laboratory trial “high” (see table 5.2).

Table 5.2: Laboratory conditions (intercomparison of Buzica et al.)

Parameter	High	Low
Exposure time (d)	7	14
Concentration ($\mu\text{g.m}^{-3}$)	80	40
Air velocity (m.s^{-1})	2,5	1,0
Temperature ($^{\circ}\text{C}$)	25	5
Relative humidity (%)	75	30

The results obtained for the Ogawa sampler operated by Lab L – following the Ogawa protocol – are presented in table 5.3.

Table 5.3: Results of Ogawa sampler operated by Lab L (intercomparison of Buzica et al.)

Location	CLS ($\mu\text{g.m}^{-3}$)	Ogawa ($\mu\text{g.m}^{-3}$)	Ratio
Laboratory, high	76,8	132 $\pm$ 19	1,72
Laboratory, low	43,5	46,4 $\pm$ 2,6	1,07
Genevilliers	41,6	41,4 $\pm$ 0,9	1,00
Fontainebleau	14,1	14,8 $\pm$ 3,1	1,05

CLS: chemiluminesce method

Apart from the results of the laboratory trial “high”, the results were comparable with those of the reference method (chemiluminescence, CLS). An explanation for the aberrant results at high air velocity may be that Lab L did not use a protective cover in the laboratory trials. The laboratory “high” trial yielded large variations in results for all participants, with mean results ranging from 54 to 188 $\mu\text{g.m}^{-3}$. The precision of the results was also variable, ranging from 2 % to 20 %.

Singer et al. [7] validated the samplers e.g. by parallel measurements with a chemiluminescence analyser. Samplers were exposed for 1 week. They reported a good correlation, with samplers producing slightly lower results (8 % on average). They reported the precision for the sampler to be better than 5 %. The detection limit for a 1-week sampling period was reported to be 0,2 ppb (analysis performed by colorimetry).

Swaans and Goelen [8] reported the results of field tests in Belgium in which a number of diffusive samplers were compared by parallel measurements with a reference monitor. The exposure period was 14 days; each sampler was exposed in triplicate. The results are presented in table 5.4.

Table 5.4: Results field tests in Belgium

Location	CLS ($\mu\text{g.m}^{-3}$)	Ogawa ($\mu\text{g.m}^{-3}$)	Ratio
Borgerhout	44,7	47,3 $\pm$ 5,2	1,06
Gent	21,0	22,4 $\pm$ 2,1	1,07
Borgerhout	51,4	50,6 $\pm$ 0,2	0,98
Gent	27,3	25,6 $\pm$ 2,7	0,94

Again, results obtained with the Ogawa sampler were comparable to those obtained with the chemiluminescence method. However, the precision of the triplicate results was rather high for 3 trials (≈ 10 %).

Additional work performed by these authors involved a comparison of analyses by ion chromatography and colorimetry. The colorimetric method was found to give a lower detection limit (factor 3). Otherwise, the results obtained were similar.

Sather et al. [9] compared results of 24- and 96-hour diffusive samplers with those from a chemiluminescence analyser. Correlations were good, improving with prolonged sampling duration. Duplicate samplers yielded mean absolute differences of 1,6 to 1,9 ppb for average levels of 22 ppb to 23 ppb.

Sather et al. [4] performed parallel measurements of Ogawa samplers with the US-EPA Federal Reference Method (FRM: the chemiluminescence method) for one year at 6 locations in El Paso, Texas. The extensive dataset resulting from these comparisons was kindly made available by Dr. Sather of US-EPA. Unfortunately, the results received were rounded which may affect comparability at low levels.

The samplers were exposed for different periods: 2, 3 and 4 weeks. All samplers were exposed in duplicate. The mean average difference found between sampler pairs is 0,3 ppb. All results of the trials are presented in tables 5.5 to 5.7.

Table 5.5: Measurement by the US Federal Reference Method (FRM) and Ogawa sampler at two monitoring sites. Exposure period: 2 weeks; results in ppb. Bold figures represent averages.

UTEP			Skyline		
<i>FRM</i>	<i>Ogawa</i>	<i>Ratio</i>	<i>FRM</i>	<i>Ogawa</i>	<i>Ratio</i>
25	29	1,16	17	17	1,00
22	23	1,05	12	13	1,08
23	25	1,09	13	12	0,92
23	25	1,09	15	13	0,87
18	19	1,06	9	10	1,11
19	19	1,00	11	11	1,00
14	16	1,14	7	7	1,00
17	18	1,06	8	8	1,00
16	16	1,00	8	7	0,88
15	14	0,93	7	7	1,00
14	14	1,00	6	5	0,83
14	12	0,86	6	6	1,00
12	12	1,00	6	6	1,00
14	13	0,93	7	6	0,86
12	12	1,00	6	5	0,83
15	14	0,93	7	6	0,86
14	14	1,00	8	6	0,75
13	14	1,08	7	6	0,86
20	21	1,05	10	9	0,90
13	15	1,15	7	6	0,86
16	17	1,06	8	9	1,13
17	20	1,18	8	12	1,50
18	20	1,11	8	11	1,38
19	21	1,11	10	12	1,20
23	26	1,13	13	16	1,23
23	25	1,09	14	17	1,21
17,3	18,2	1,06	9,2	9,3	1,02

Table 5.6: Measurement by the US Federal Reference Method (FRM) and Ogawa sampler at two monitoring sites. Exposure period: 3 weeks; results in ppb. Bold figures represent averages.

Ascarate			Santa Teresa		
<i>FRM</i>	<i>Ogawa</i>	<i>Ratio</i>	<i>FRM</i>	<i>Ogawa</i>	<i>Ratio</i>
21	26	1,24		7	
22	23	1,05	6	6	1,00
22	22	1,00	5	4	0,80
18	19	1,06	5	4	0,80
16	18	1,13	3	3	1,00
19	16	0,84	2	1	0,50
16	13	0,81	1	0	
18	13	0,72	1	0	
13	12	0,92	3	2	0,67
10	9	0,90	3	2	0,67
13	12	0,92	4	3	0,75
15	14	0,93	3	3	1,00
18	17	0,94	5	5	1,00
18	17	0,94	4	3	0,75
19	20	1,05	6	6	1,00
20	20	1,00	6	6	1,00
26	26	1,00	7	7	1,00
17,9	17,5	0,98	4,0	3,6	0,91

Table 5.7: Measurement by the US Federal Reference Method (FRM) and Ogawa sampler at two monitoring sites. Exposure period: 4 weeks; results in ppb. Bold figures represent averages.

Socorro			Desert View		
FRM	Ogawa	Ratio	FRM	Ogawa	Ratio
17	20	1,18	14	14	1,00
17	18	1,06	12	11	0,92
14	14	1,00	11	10	0,91
13	12	0,92	7	5	0,71
12	9	0,75	8	6	0,75
12	8	0,67		3	
7	7	1,00		4	
9	8	0,89		6	
10	9	0,90		6	
12	11	0,92	11	9	0,82
14	14	1,00	9	8	0,89
15	15	1,00	12	13	1,08
19	19	1,00	15	15	1,00
13,2	12,6	0,94	11,0	8,5	0,90

By studying the ratios of the mean results obtained by the FRM and the Ogawa sampler, their comparability was evaluated. It was observed that results were comparable for a 2-week exposure period, with the samplers slightly overestimating the reference concentrations. Sampler results for 3- and 4-week periods were generally lower than those of the FRM.

Using this extensive dataset, an attempt to evaluate the equivalence of the sampler with the reference method according to the Guide to the Demonstration of Equivalence [10] was made. The results are presented in figure 5.4.

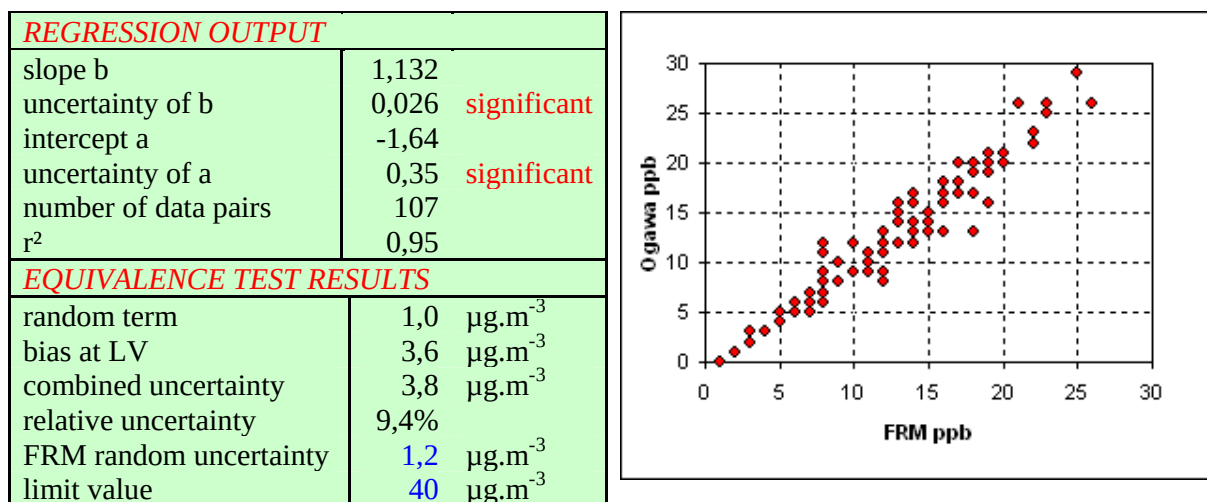


Figure 5.4: Uncertainty for annual averages according to the Guide to the Demonstration of Equivalence, Ogawa sampler vs chemiluminescence analyser (FRM)

The evaluation indicated that, without a recalibration of the uptake rate, keeping the slope and intercept results obtained, this sampler did not meet the data quality objective (DQO) of the EU directive for fixed measurements, as its expanded uncertainty exceeds 15 %, but satisfied the DQO for indicative measurements.

Mosqueron et al. [11] performed a comparison between the sampler and reference method within the frame of quality assurance of an indoor and ambient air exposure study.

The ratio between the means of 49 paired results was 0,97 for an exposure period of 48 hours. When exposing the sampler at both ends, a good correlation was observed between the two results.

Sarnat et al. [12] determined a series of performance characteristics for the sampler when sampling for a period of 24 hours. They found detection limits of 6,4 and 10,8 ppb depending on the sampling season. By measuring with a collocated reference method they determined the precision and accuracy of the sampler to be 17 % and 106 %, respectively.

Van Roosbroeck et al. [13] performed a comparison between the sampler and reference method within the frame of quality assurance of the application of the sampler.

They reported a mean relative difference of 3 %, and a correlation coefficient of 0,96 for an exposure period of 48 hours. The precision of duplicate sampler measurements was reported to be < 5 %.

5.5.2 Miscellaneous information about performance characteristics

A number of publications reported additional information about practical detection limits and precision of the sampler.

Gilbert et al. [3] used samplers to study levels of NO₂ near highways. Employing ion chromatography for analysis, they reported a detection limit for 1-week sampling of 0,7 ppb. The precision of results for duplicate samplers ranged from 6 to 20 %.

Yang et al. [14] used samplers to measure concentrations of NO₂ in indoor air and the penetration of NO₂ from outside to indoor air. Samples were taken over 24-hour periods. Each week duplicate measurements were performed, resulting in an average precision of 8,3 %.

Mukerjee et al. [15] performed a field comparison between samplers and reference monitors. The samplers were exposed for 3, 4 and 7 days for 3 consecutive weeks, with 7-day sampling paralleling 3+4-day sampling. Due to monitor malfunctioning, no definitive conclusions about correlations between results were presented. The study provided information about repeatability and detection limits. Unfortunately, the authors did not report the internal consistency of the 3+4- and 7-day results. The sampler precision was found to be better than 5 %. The detection limit found was lower than 1,3 ppb.

5.6 Measurement uncertainty

No information was found in the literature of (systematic) assessments of measurement uncertainties associated with the use of the Ogawa sampler, e.g., performed according to the Guide to the Expression of Uncertainty in Measurement. When using results from [4] and [6] to make a direct estimation of uncertainties, results found are between 3 % and 23 % expanded relative uncertainty indicating the suitability of the sampler for indicative long-term monitoring of NO₂. However, further systematically obtained information is needed to substantiate such a claim.

5.7 Application in EU monitoring networks

The Ogawa sampler has been used in Spain. To date, there is no reference found of the sampler being used for ambient air monitoring purposes in the EU. Applications are in the field of indoor air monitoring.

5.8 Conclusions

The Ogawa badge-type diffusive sampler is suitable for long-term monitoring of NO₂ in ambient air. Exposure periods of 2 to 4 weeks are feasible. Lower detection limits reported vary somewhat, but are certainly below 1 µg.m⁻³ for a 2-week exposure period.

Information provided about the precision of replicate samples again is variable. Results range from 2 to 20 %. However, frequently precisions better than 5 % are reported.

It is not always clear, though, whether the results of duplicated measurements are based on application of two separate samplers or on analysis of the two filters on either side of the sampler.

When exposed for 14 days or more in the field, the comparability of sampler results to those obtained with continuous reference monitors (chemiluminescence) were good, with ratios of average results ranging from 0,90 to 1,07. The availability of sampler results upon long-term exposure is better than 90 %. Absence of data in comparisons is due to malfunctioning of reference monitors rather than malfunctioning of the sampler.

When using the methodology of the EU Guide to the Demonstration of Equivalence to the results of the US-EPA El Paso study, the sampler is found to pass the uncertainty requirement for indicative measurements. The random uncertainty found for the relation between sampler results and reference method indicate that by correcting the uptake rate the sampler may pass the criterion for fixed measurements. However, the study has been performed in conditions that are atypical of the EU.

No information has been found about any uncertainty assessment of the results obtained with the sampler, e.g., according to the Guide to the Expression of Uncertainty in Measurement.

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6 The Radiello radial sampler

6.1 Sampler design

The Radiello sampler is a radial-type diffusive sampler that was developed by Fondazione Salvatore Maugeri in Italy [1]. Its cylindrical outer surface acts as diffusive membrane: the gaseous molecules move axially parallel towards an adsorbent bed which is cylindrical too and coaxial to the diffusive surface [2] (see figure 6.1).

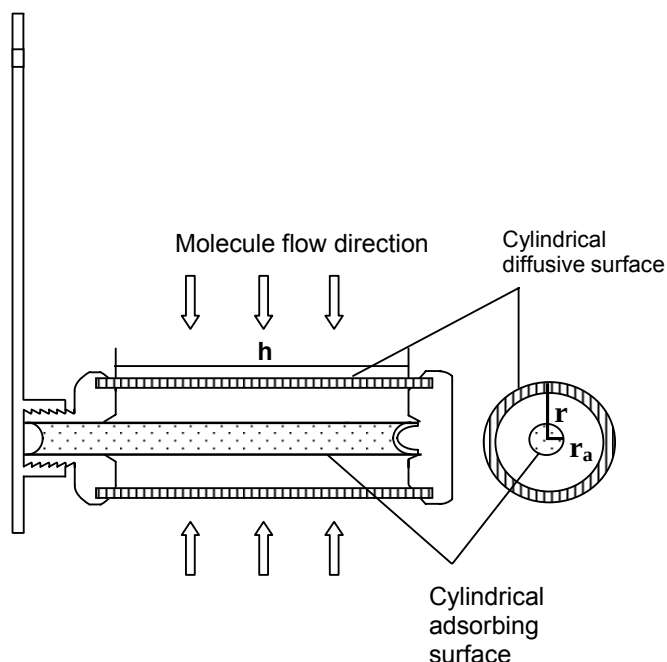


Figure 6.1: Radiello sampler design

According to manufacturer's general instructions, exposure for a long time in a wet atmosphere generally does not affect the sampling performances of the Radiello sampler. Nevertheless the sorption of large quantities of water by the cartridges can sometimes affect the sampler performance. Therefore a shelter is important to protect Radiello samplers from rain.

For outdoor exposures, a mountable polypropylene shelter is available (see figure 6.2). It was designed to be mounted easily and without any tool in the field. The shelters are open on three sides. Pylons and posts are recommended as carriers [3]. Once assembled, it ensures the best compromise between protection against rain and wind. It can house up to four samplers and is able to fit a wide range of pole diameters.



Figure 6.2: Radiello shelter

The diffusive body can be fitted on a supporting plate either in a vertical or horizontal position as shown in figure 6.3.



Figure 6.3: Supporting plate for the Radiello sampler

The adsorbing cartridges are impregnated with a mixture of TEA/water, which also contains traces of ethanol. Further details on the coating and preparation protocol were requested from the manufacturer, but were not provided due to reasons of confidentiality.

The manufacturer recommends and describes the determination of the collected NO_2 by colorimetry after reaction with sulphanilamide and N-1-naphthylethylenediamine [4].

6.2 Application range and conditions

According to the manufacturer [4], the uptake rate of NO_2 is constant in the range from $2000 \mu\text{g}\cdot\text{m}^{-3}\cdot\text{min}$ to $10^7 \mu\text{g}\cdot\text{m}^{-3}\cdot\text{min}$ (1 ppb to 500 ppb NO_2 for 7-day exposure or 0,5 ppb to 250 ppb for 14-day exposure). The limit of quantification after 7 days exposure is 1 ppb.

The range of meteorological conditions where the use of the Radiello sampler is applicable is given in table 6.1. Exposures up to 15 days are feasible for NO_2 , but if relative humidity is higher than 70 % for the entire sampling duration, the manufacturer recommends a sampling time shorter than or equal to 7 days. Due to the fact that TEA is very hygroscopic, even if water does not actually interfere with sampling or analysis, the excess water adsorbed by the cartridge could cause some loss of adsorbing medium by percolation.

Table 6.1: Application range of NO_2 Radiello sampler [4]

Parameter	Range where no effect on uptake rate is observed
Temperature	-10 °C to 40 °C
Relative humidity	15 % to 90 % (maximum RH value 70 % for 14-day exposure); avoid moisture condensation upon the membrane
Wind speed	$0,1 \text{ m}\cdot\text{s}^{-1}$ to $10 \text{ m}\cdot\text{s}^{-1}$ The outdoor shelter is required for ambient air measurements
Sampling duration	Up to 15 days If $\text{RH} > 70 \%$: preferably not longer than 7 days

According to the manufacturer [4], the cartridges are stable for at least 12 months before and 4 months after exposure, if stored in the dark at 4 °C. Expiry date is printed on the plastic bag. At least two cartridges belonging to the same lot should be kept as blanks.

6.3 Extraction and analysis

Information on procedures for extraction of sampler cartridges and analysis of sample extracts are available from the manufacturer [4]. The analytical procedures comprise both colorimetry using the Griess-Saltzman method for NO₂ and ion chromatography for SO₂. An alternative ion chromatographic procedure is available from Swaans et al. [5]. The extraction procedure appears to be a critical factor. During a laboratory and field comparison of NO₂ diffusive samplers by the Joint Research Centre [6], extraction of nitrite from the Radiello cartridge using a vortex shaker for 1 minute at 2500 rpm was found not to be sufficient and needed 1 or 2 repetitions before complete extraction. Another method based on ultrasonic extraction for 25 minutes of the cartridge placed in a glass container with 10 ml of Millipore water gave complete recovery of nitrite.

After tubes were vigorously shaken for two minutes, the contact period between absorption liquid and cartridge was also extended to 1,5 hours by Swaans et al. [5] to ensure complete extraction of nitrite.

6.4 Expression of the NO₂ concentration

To calculate the airborne NO₂ concentration, equation 6.1 is generally applied:

$$C_{\text{NO}_2} = 1,91 \frac{(m_s - m_b)}{u \times t} \quad (\text{eq 6.1})$$

where

- C_{NO_2} = NO₂ concentration in µg m⁻³ at 20 °C and 101,3 kPa;
- m_s = mass of nitrite measured in the exposed sampler in ng;
- m_b = mass of nitrite measured in a blank sampler in ng;
- u = uptake rate in ng.ppb⁻¹.min⁻¹;
- t = sampling time in min.

The coefficient 1,91 is used to convert the NO₂ concentration from ppb in µg m⁻³ at 20 °C and 101,3 kPa.

6.5 Uptake rate

The uptake rate was determined by the manufacturer as 31,5 cm³.min⁻¹ at 25 °C (corresponding to 0,141 ng.ppb⁻¹.min⁻¹). The laboratory validation data used for the current model of Radiello NO₂ sampler were supplied by the manufacturer. They are presented in table 6.2. They included the results of two sets of exposure tests at two temperature levels (25 °C and 2 °C) each including three sets of six samples exposed for variable sampling time (approx. 3, 5, 7 days). For one temperature level (9,5 °C), an average value was given while for the other two levels all the individual values were reported.

Table 6.2: Validation data of the Radiello sampler supplied by the manufacturer

First test: temperature 25 °C									
Exposure 1									
<i>Camp</i>	<i>μg</i>	<i>T</i> (°C)	<i>NO₂</i> (ppb)	<i>Exposure time</i> (min)	<i>NO₂</i> (ppb*min)	<i>ν</i> (ng/ppb*min)	<i>ν</i> mean	<i>St.</i> <i>dev.</i>	<i>% rsd</i>
1°-1	12,90	25,1	22,5	3684	82852	0,156			
1°-2	9,67	25,1	22,5	3684	82852	0,117			
1°-3	11,76	25,1	22,5	3684	82852	0,142			
1°-4	10,24	25,1	22,5	3684	82852	0,124			
1°-5	11,38	25,1	22,5	3684	82852	0,137			
1°-6	7,84	25,1	22,5	3684	82852		0,135	0,015	11,4
Exposure 2									
<i>camp</i>	<i>μg</i>	<i>T</i> (°C)	<i>NO₂</i> (ppb)	<i>Exposure time</i> (min)	<i>NO₂</i> (ppb*min)	<i>ν</i> (ng/ppb*min)	<i>ν</i> mean	<i>St.</i> <i>dev.</i>	<i>% rsd</i>
2°-1	20,54	25,1	23,2	6777	157125	0,131			
2°-2	23,89	25,1	23,2	6777	157125	0,152			
2°-3	22,50	25,1	23,2	6777	157125	0,143			
2°-4	18,52	25,1	23,2	6777	157125	0,118			
2°-5	22,69	25,1	23,2	6777	157125	0,144			
2°-6	21,62	25,1	23,2	6777	157125	0,138	0,138	0,012	8,7
Exposure 3									
3°-1	30,21	25,0	22,9	9650	220877	0,137			
3°-2	35,78	25,0	22,9	9650	220877	0,162			
3°-3	30,53	25,0	22,9	9650	220877	0,138			
3°-4	32,11	25,0	22,9	9650	220877	0,145			
3°-5	37,48	25,0	22,9	9650	220877	0,170			
3°-6	33,50	25,0	22,9	9650	220877	0,152	0,151	0,013	8,7
						<i>ν overall</i> <i>mean</i>	0,141		
Second test: temperature 2 °C									
Exposure 1									
<i>camp</i>	<i>μg</i>	<i>T</i> (°C)	<i>NO₂</i> (ppb)	<i>Exposure time</i> (min)	<i>NO₂</i> (ppb*min)	<i>ν</i> (ng/ppb*min)	<i>ν</i> mean	<i>St.</i> <i>dev.</i>	<i>% rsd</i>
1°-1	8,91	2,2	27,0	3962	107008	0,083			
1°-2	7,21	2,2	27,0	3962	107008	0,067			
1°-3	6,83	2,2	27,0	3962	107008	0,064			
1°-4	7,52	2,2	27,0	3962	107008	0,070			
1°-5	9,04	2,2	27,0	3962	107008	0,084			
1°-6	4,99	2,2	27,0	3962	107008		0,074	0,009	12,8
Exposure 2									
2°-1	12,77	2,1	27,0	6900	186166	0,069			
2°-2	15,99	2,1	27,0	6900	186166	0,086			
2°-3	14,41	2,1	27,0	6900	186166	0,077			
2°-4	17,00	2,1	27,0	6900	186166	0,091			
2°-5	14,54	2,1	27,0	6900	186166	0,078			
2°-6	17,19	2,1	27,0	6900	186166	0,092	0,082	0,009	11,2

Table 6.2: Validation data of the Radiello sampler supplied by the manufacturer (continued)

Exposure 3									
<i>camp</i>	μg	<i>T</i> (°C)	<i>NO</i> ₂ (ppb)	<i>Exposure time</i> (min)	<i>NO</i> ₂ (ppb*min)	ν (ng/ppb*min)	ν <i>mean</i>	<i>St. dev.</i>	<i>% rsd</i>
3°-1	17,95	2,1	26,9	9688	260828	0,069			
3°-2	21,93	2,1	26,9	9688	260828	0,084			
3°-3	20,29	2,1	26,9	9688	260828	0,078			
3°-4	24,08	2,1	26,9	9688	260828	0,092			
3°-5	23,20	2,1	26,9	9688	260828	0,089			
3°-6	26,80	2,1	26,9	9688	260828		0,082	0,009	11,3
						ν <i>overall mean</i>	0,080		
Third test: temperature 9,5 °C									
<i>T</i> (°C)	<i>NO</i> ₂ (ppb)	<i>Exposure time</i> (min)		<i>NO</i> ₂ (ppb*min)	ν (ng/ppb*min)		ν <i>mean</i>		
9,5	22	10080		221760			0,100		

6.6 Environmental effects

6.6.1 Air velocity

The uptake rate was reported to be invariant with wind speed between 0,1 m.s⁻¹ and 10 m.s⁻¹ [4].

6.6.2 Relative humidity and temperature

The uptake rate was reported to be invariant with humidity in the range 15 % to 90 % [4].

However, a significant effect of temperature and relative humidity on uptake rate was observed by Swaans et al. [5]. The temperature effect from 10 °C to 30 °C corresponds to the temperature effect given by the supplier of the samplers (see section 6.7.1). High relative humidity (70 % to 80 %) caused a strong non-reproducible decrease of uptake rate for NO₂ at 24 hour experiments, but this effect was not observed at longer exposures except for the tests at -5 °C. At temperature below zero, in combination with high relative humidity, the sampler showed anomalous behaviour for NO₂. The possible effect of concentration level and exposure time for NO₂ needs further research.

The NO₂ uptake rate at 25 °C and 101,3 kPa should be corrected so as to reflect the actual sampling conditions. According to the manufacturer's instruction manual [4], the temperature effect for NO₂ on the uptake rate is taken into account using equation 6.2.

$$\nu_T = \nu_{25} \left(\frac{273+T}{273+T_{ref}} \right)^{7,0} \quad (\text{eq. 6.2})$$

where

ν_T = uptake rate at the temperature T ranging from -10 to 40 °C in ng.pp⁻¹.min⁻¹;

ν_{25} = reference uptake rate at 25 °C; 0.141 ng.pp⁻¹.min⁻¹;

T = temperature ranging from -10 to 40°C;

T_{ref} = reference temperature of 25 °C.

The exponential coefficient of 7,0 is derived from the results of the laboratory validation study performed by the manufacturer (see section 6.5).

6.6.3 Pressure

The effect of atmospheric pressure (P) on the uptake rate of the Radiello sampler (ν) is usually insignificant. Even though ν linearly depends on P, the extent of variation of atmospheric pressure

rarely exceeds 3 kPa about the average value of 101,3 kPa at sea level. An error of $\pm 3 \%$ on uptake rate and usually within $\pm 1,5 \%$ results if no correction for pressure is applied.

6.7 Validation of sampler performance

6.7.1 Laboratory tests

During the course of year 2002, the NO₂ Radiello sampler was changed by the manufacturer. Since then the cartridges have been made from microporous polyethylene instead of polyester fibre. Afterwards the sampler's manual was also modified a number of times.

Consequently, the results from studies performed using the old type of Radiello cannot be considered in this review. This concerns e.g. results from validation studies performed by the Joint Research Centre Institute for Environment and Sustainability [11], and results from the Resolution project¹. The validation data presented here relate to the latest version of the Radiello NO₂ diffusive sampler.

In 2005, a validation study of Radiello combined NO₂-SO₂ diffusive sampler [5] was performed by the Flemish Institute for Technological Research (VITO, Belgium). This was the result of lack of agreement between NO₂ samplers and chemiluminescence analyzers from the VMM automatic network, particularly in case of frost, after changes to the sampler by the supplier. The sampler was first validated under controlled laboratory conditions and subsequently compared with NO₂-(SO₂) results of 3 other type of samplers in a field comparison at two locations: Ghent-Mariakerke and Borgerhout in Flanders.

Laboratory exposures at different temperatures (-5, 10 and 30 °C) and relative humidities (0, 50 and 80 % RH) in combination with varying concentration levels and exposure times were carried out, with a focus on extreme conditions (see table 6.4). Typical environmental levels at the monitoring locations of the VMM network for acidic deposition during former campaigns were 10, 20 and 40 µg.m⁻³ NO₂. Under laboratory conditions, exposures were carried out at higher concentrations levels during shorter times within the linear range of 3000–5.10⁶ ppb.min according to manufacturer's instructions [4]. By choosing this approach, a better accuracy of the generated higher gas concentrations was achieved. This made it possible to draw better conclusions about the effects on the uptake rate.

Table 6.4: Laboratory validation set up

NO ₂ (ppb)	Temperature (°C)	Relative humidity (%)	Exposure time
73	-5	80	24 h
18	-5	80	4 days
73	10	0	24 h
73	10	50	24 h
146	10	50	24 h
293	10	50	24 h
73	10	80	24 h
146	10	80	24 h
293	10	80	24 h
11	10	80	14 days (336 h)
73	30	0	24 h
73	30	50	24 h
73	30	80	24 h
18	30	0	4 days
18	30	80	4 days

¹ RESOLUTION Development of a high spatial resolution atmospheric monitoring model to verify the actual emissions reduction of ozone precursors foreseen by Auto-Oil program), LIFE99ENV/IT/081, http://ec.europa.eu/environment/life/project/Projects/index.cfm?fuseaction=home.createPage&s_ref=LIFE96%2520ENV%252FIT%252F000070&area=2&yr=1996&n_proj_id=1114

The average uptake rate for NO₂ for 24 hour exposures at 10 °C and 50 % RH and tested concentration levels (73, 146 and 293 ppb NO₂) was $0,076 \pm 0,011$ ng ppb⁻¹ min⁻¹. Uptake rates during all experiments were lower than the uptake rate given in the instruction manual of the sampler. As already mentioned in section 6.6.2, a significant effect of temperature and relative humidity on the sampler uptake rate was observed. The temperature effect from 10 to 30 °C corresponds to the temperature effect given by the supplier of the samplers. Exposures to high relative humidity (70 to 80 %) for 24 hours caused a strong non-reproducible decrease of uptake rate for NO₂ (see figure 6.3). However, this effect was not observed for longer exposures, except for the tests at -5 °C. At temperatures below zero in combination with high relative humidity, the sampler showed anomalous behaviour for NO₂.

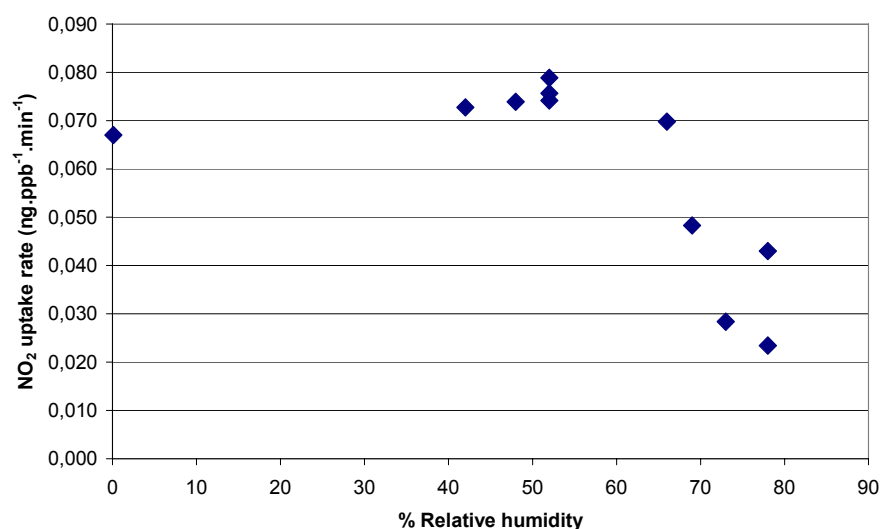


Figure 6.3: NO₂ uptake rate of Radiello sampler at 10 °C versus % relative humidity (24 h exposure)

6.7.2 Comparisons with reference methods

Buzica et al. [6] organized a series of 4 comparisons in which different samplers operated by different laboratories were exposed both under laboratory and field conditions. Each sampler type was exposed in batches of 6 samplers for a period of 14 days, except in the laboratory trial “high” (see table 6.5).

Table 6.5: Laboratory conditions (intercomparison of Buzica et al.)

Parameters	High	High
Exposure time (d)	7	14
Concentration (µg.m ⁻³)	80	40
Air velocity (m.s ⁻¹)	2,5	1,0
Temperature (°C)	25	5
Relative humidity (%)	75	30

The results obtained for the Radiello sampler operated by Lab H, following the manufacturer protocol, are presented in table 6.6.

Table 6.6: Results of Radiello sampler operated by Lab H (intercomparison of Buzica et al.)

Location	CLS (µg.m ⁻³)	Radiello (µg.m ⁻³)	Ratio
Laboratory, high	76,8	54,1 ± 1,5	0,70
Laboratory, low	43,5	30,0 ± 1,0	0,69
Genevilliers	41,6	44,7 ± 1,3	1,075
Fontainebleau	14,1	12,0 ± 0,9	0,85

During the laboratory tests, the samplers were not protected by a shelter, but a holder was used. For the NO₂ laboratory exposures, the uptake rate was calculated using the model equation given in the previous operating manual (2002). By applying the equation of the operational manual version 01/2003 to the laboratory tests (the one given in equation 6.2), the corrected concentrations were in closer agreement with the reference values than with those calculated with the previous model of the uptake rate.

Swaans and Goelen [5] reported the results of field tests in Belgium in which a number of diffusive samplers have been compared by parallel measurements with a reference monitor. The exposure period was 14 days; each sampler was exposed in triplicate. The results are presented in table 6.7. The Radiello samplers were desorbed using a vortex shaking method (a method based on ultrasonic desorption has also been used).

Table 6.7: Results of field tests in Belgium

Location	CLS ($\mu\text{g.m}^{-3}$)	Radiello ($\mu\text{g.m}^{-3}$)	Ratio
Borgerhout	55	52,8 ± 8,8	0,96
Gent	37	33,2 ± 7,3	0,92
Borgerhout	44,7	47,4 ± 5,1	1,06
Gent	21,0	16,0 ± 2,1	0,76
Borgerhout	51,4	35,1 ± 3,0	0,68
Gent	27,3	18,2 ± 3,5	0,67

The agreement between measurements performed with Radiello samplers and chemiluminescence analyzer was acceptable, but in some cases the relative standard deviation of the replicates exceeded 30 %. The ratios Radiello samplers/NO₂ analyzer for the different site campaigns ranged from 0,67 to 1,06. In general, the performance of the Radiello sampler was better in the field than during laboratory validation (see table 6.6), although for certain periods samplers gave lower NO₂ concentrations than the continuous analyzer. Conditions were more extreme during the laboratory validation than during the field tests.

Results of comparative measurements between NO₂ Radiello diffusive samplers and chemiluminescence analyzers from 3 French air quality monitoring networks are given in table 6.8.

The results from French studies (personal communication to the authors) confirmed that the Radiello sampler tends to underestimate the concentrations of NO₂ measured by the chemiluminescence analyzers.

Ratios found ranged from 0,57 to 0,99 with one exception (1,42) for concentrations ranging from 22 to 49 $\mu\text{g.m}^{-3}$. For a 7-day exposure period the effect appears to be larger than for 14-day exposure.

Other available validation data regarding the NO₂ Radiello sampler exist, but do not apply to the current sampler [7 - 9]. Also the data from the CEN/TC 264 WG11 pilot study date from 2000-2001 and do not apply to the current sampler since the sampler was changed in 2002.

Currently, a comparison is ongoing in the United Kingdom in which Palmes tube samplers and Radiello samplers are exposed at a traffic site in London. Results of this comparison were not available at the time of the drafting of the report.

Table 6.8: Results of French studies

Laboratory	Sampling site	Nb of samplers	Sampling time (days)	Start	End	NO2 tube (ppb)	NO2 tube ($\mu\text{g.m}^{-3}$)	NO2 chemiluminescence ($\mu\text{g.m}^{-3}$)	Ratio Tube / Chemiluminescence	Température	Mass of nitrite (μg)
ATMOSF/AIR Bourgogne		1	7	23/10/07	30/10/07	12,8	20,9	36,9	0,57	8,4	0,171
ATMOSF/AIR Bourgogne		1	7	30/10/07	6/11/07	13,5	21,7	36,6	0,59	6,6	0,168
ATMOSF/AIR Bourgogne		1	7	13/11/07	20/11/07	16,8	25,5	41,2	0,62	1,3	0,158
ATMOSF/AIR Bourgogne		1	7	20/11/07	27/11/07	19,8	31,7	49,0	0,65	6,5	0,168
ATMOSF/AIR Bourgogne		1	7	27/11/07	4/12/07	15,6	24,6	38,1	0,64	4,6	0,164

Laboratory	Site	Nb of samplers	Exposure	Start	End	NO2 $\mu\text{g}/\text{m}^3$ - tube 1	NO2 $\mu\text{g}/\text{m}^3$ - tube 2	NO2 chemiluminescence ($\mu\text{g.m}^{-3}$)	Ratio Tube / Chemiluminescence
LIM/AIR	Urban	2	14	10/10/06	24/10/06	37,4	26,1	22,4	1,42

	Site	Nb of samplers	Exposure	Start	End	NO2 $\mu\text{g}/\text{m}^3$ tube 1	NO2 $\mu\text{g}/\text{m}^3$ tube 2	NO2 $\mu\text{g}/\text{m}^3$ - tube 3	NO2 chemiluminescence in $\mu\text{g}/\text{m}^3$	Ratio Tubes mean / Chemiluminescence	Ratio Tube 1 / Chemiluminescence	Ratio Tube 2 / Chemiluminescence	Ratio Tube 3 / Chemiluminescence
	ARLES												
AIRFOBEP	Urban	2	14	2/23/2007	3/9/2007	20,3	25,4		27,4	0,84	0,74	0,93	
AIRFOBEP	Urban	1	14	3/9/2007	3/26/2007	21,3			27,8	0,77	0,77		
AIRFOBEP	Urban	2	14	3/26/2007	4/11/2007	25,9	26,3		31	0,84	0,84	0,85	
AIRFOBEP	Urban	1	14	10/24/2007	11/7/2007		28,3		33	0,86		0,86	
	SALON												
AIRFOBEP	Urban	2	14	2/23/2007	3/9/2007	21,5	18,2		21,7	0,91	0,99	0,84	
AIRFOBEP	Urban	2	14	3/9/2007	3/26/2007	26,4	25,2		28,8	0,9	0,92	0,88	
AIRFOBEP	Urban	2	14	3/26/2007	4/11/2007	31,8	30,4		31,4	0,99	1,01	0,97	
AIRFOBEP	Urban	2	14	10/24/2007	11/7/2007	17,7	15,5		26,4	0,63	0,67	0,59	
	MARIGNANE												
AIRFOBEP	Urban	3	14	2/23/2007	3/9/2007	38	43,4	37,9	42,3	0,94	0,9	1,03	0,9
AIRFOBEP	Urban	3	14	3/9/2007	3/26/2007	27,2	25,7	26,7	32,9	0,81	0,83	0,78	0,81
AIRFOBEP	Urban	2	14	3/26/2007	4/11/2007	38,6	38,4		44,3	0,87	0,87	0,87	
AIRFOBEP	Urban	2	14	10/24/2007	11/7/2007	38,3		39	46,9	0,82	0,82		0,83

6.8 Measurement uncertainty

6.8.1 GUM approach

The manufacturer in its instruction manual reports an uncertainty of 11,9 % for NO₂ measurements for a probability of 95 % that the true value is within the resulting interval. The method of calculation was requested from the manufacture but was not available.

VITO estimated the NO₂ expanded uncertainty as being 30 % at a 95 % confidence level for the Radiello sampler used to simultaneously determine NO₂ and SO₂ [5]. This uncertainty was estimated using the results of 24-hours laboratory experiments performed in an exposure chamber at 10 °C and 50 % of relative humidity. The estimation was carried out according to the GUM method based on equation 6.3. The contributions of all parameters affecting the uncertainty of measurements are given in table 6.9.

$$C = 1,91 \frac{(m_d - m_b) \cdot 10^6}{v \cdot t} \quad (\text{eq. 6.3})$$

where

- C = ambient concentration in $\mu\text{g} \cdot \text{m}^{-3}$;
- m_d = mass of desorbed analyte in μg ;
- m_b = blank of analyte in μg ;
- v = diffusive uptake rate in $\text{ng ppb}^{-1} \cdot \text{min}^{-1}$;
- t = exposure time in min.

Table 6.9: Uncertainty of NO₂ measurements by Radiello calculated using VITO laboratory experiments

Uncertainty source	x	u(x)	u(x)/x
nitrite in desorption liquid mg/l	1,3	0,02	0,02
volume of desorption liquid (ml)	6,00	0,08	0,01
absolute amount of nitrite on sampler (μg)	7,62	0,2	0,02
nitrite in desorption liquid from blank sampler (mg/l)	0,09	0,009	0,1
volume of desorption liquid (ml)	6,00	0,08	0,01
absolute amount of nitrite on blank sampler (μg)	0,54	0,05	0,1
nitrite mass after blank-correction (μg)	7,08	0,2	0,03
temperature (T) during measuring period (K)	277,2	1	0.0036
uptake rate ($\text{ng ppb}^{-1} \cdot \text{min}^{-1}$) at T	0,064	0,010	0,151
sampling duration (min)	20108	10	0,0005
NO₂ Concentration in ambient air (ppb)	5,46	0,8	0,15

The relative standard uncertainty of the measured NO₂ concentration is 15 %, the expanded uncertainty at a 95 % confidence level ($k=2$) is then 30 %. This measurement uncertainty is not valid in case of sampling time of 24 hours combined with high relative humidity since a strong decrease of uptake rate may occur under these exposure conditions.

The major source of uncertainty is found to be the uptake rate.

6.8.2 Direct approach

When combining data reported in tables 6.6, 6.7 and 6.8 for all field comparisons of Radiello samplers exposed for 14 days with the chemiluminescence reference method, a total of 26 sets of comparison data were available. These were used to make an estimate of the uncertainty of NO₂ concentrations

measured with the Radiello sampler by applying the approach described in the Guide to the Demonstration of Equivalence [10]. The result of this estimation is given in figure 6.4.

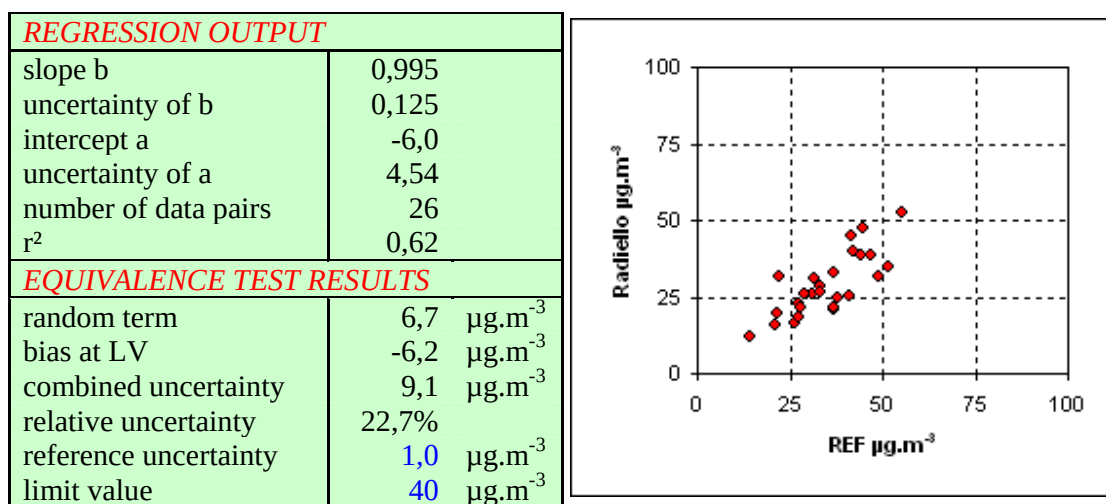


Figure 6.4: Uncertainty for annual averages according to the Guide to the Demonstration of Equivalence, Radiello sampler vs chemiluminescence analyser (REF)

The relative standard uncertainty calculated in this way was 22,7 %, leading to an expanded uncertainty (95 % confidence) of 45 %. The uncertainty is affected significantly by a systematic underestimation of concentrations by about 6 $\mu\text{g.m}^{-3}$.

6.9 Application in EU monitoring networks

Radiello samplers are used e.g. in Belgium, France, Italy, Slovakia and Spain for surveys aimed at, e.g. identification of hot spots, mapping, zoning, trend analysis, source apportionment, impact on vegetation, assessment of exposure of population, verification of dispersion models etc.

6.10 Conclusions

The Radiello radial-type diffusive sampler may be used for long-term monitoring of NO_2 in ambient air. Exposure periods of 1 day to 2 weeks are feasible. The lower detection limit for a 2-week sampling period was reported to be 0,9 $\mu\text{g.m}^{-3}$. Results of a laboratory study in which the sampling period was restricted to one day showed an underestimation of NO_2 concentrations by a factor of 2 when applying the uptake rate specified by the manufacturer. The reason for this may be a transient period of sorption at the beginning of the sampling period.

Information about the precision of the sampler from field campaigns revealed that the precision relative standard deviation varied around 10 %.

The comparability of sampler results with those obtained with continuous reference monitors (chemiluminescence) varied, with ratios of average results ranging from 0,6 to 1,4. In general, Radiello showed a trend to underestimate concentrations measured by reference monitors. However, the number of field data available was too limited to be conclusive.

When the uncertainty associated with the measurement results for a one-day exposure was evaluated according to the Guide to the Expression of Uncertainty in Measurement, a relative expanded uncertainty of individual results of 31 % was found. When assessing measurement uncertainty by direct approaches, e.g., from parallel measurements with the reference method for measurement of NO_2 , similar results were obtained.

These findings suggest that the Radiello sampler did not satisfy the uncertainty data quality objective for indicative measurements of NO_2 , for which an uncertainty ≤ 25 % is required.

When aggregating results to form annual average values, the relative expanded uncertainty was further reduced to levels below 25 % due to the reduction of random effects on uncertainty.

The information collected about the uncertainty of individual measurement results did not correspond with information supplied by the manufacturer stating an expanded measurement uncertainty of 12 %. However, information about the assessment approach used by the manufacturer was (currently) unavailable.

The possible effect of concentration level, high humidity and exposure time for NO₂ needs further research.

6.11 References

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7 Other samplers : the Analyst

7.1 Sampler design

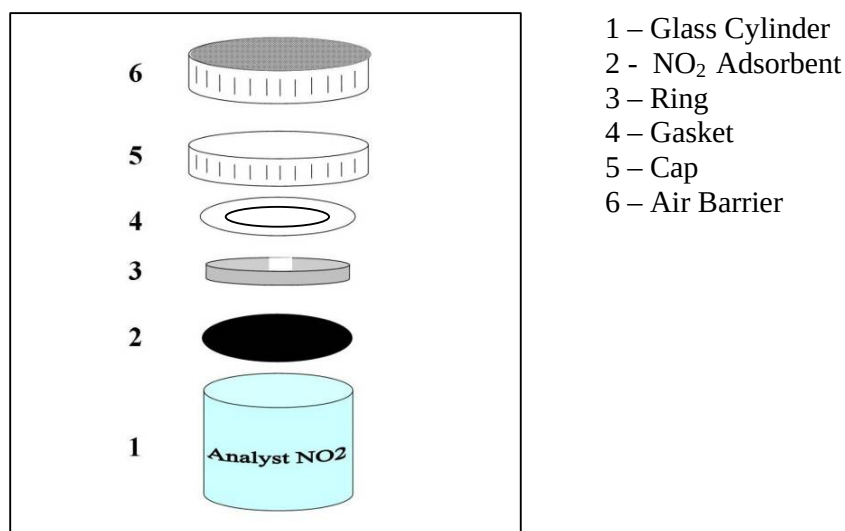


Figure 7.1: Analyst sampler design

The body of the sampler (see figure 7.1, part 1) is a cylindrical glass vial (inner =2,04 cm, length=2,54 cm) with a threaded cap at one end (parts 4 and 5). NO₂ is collected on a disc of impregnated carbon paper filter (part 2) placed at the bottom of the vial and held in position by a stainless steel ring (part 3). To avoid turbulent diffusion inside the vessel, the open end is protected during sampling using a fine stainless steel and plastic screen (part 6). Before and after sampling, the screen is replaced with a polyethylene cap (part 5), which houses a silicone gasket (part 4).

Application range and conditions

The following information was compiled for the application range and conditions of the sampler [1].

Detection limit: 1 ppb (corresponding to 3 standard deviations of 12 blanks for a one-week exposure).

Exposure time: From 1 week to 2 months. Shorter exposure times for high concentrations

Shelter: The experience gained in many monitoring study showed that a rain and wind shield (see figure 7.2 a) was sufficient for an effective protection of the Analyst sampler. When a strong influence of wind is expected it is recommended to use the shelter shown in figure b.

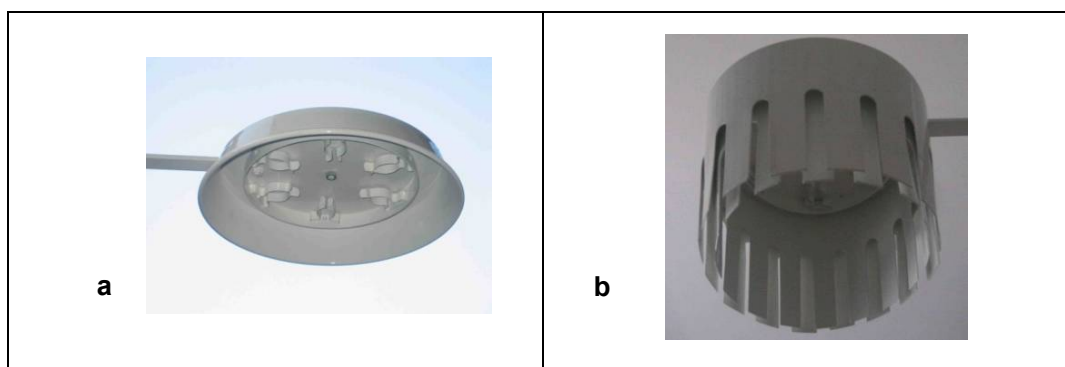


Figure 7.2: Shelters for the Analyst sampler

7.2 Sampler storage

Before use: 6 months.

After exposure: 2 months in a cold and dry place.

The stability of the nitrite collected decreases if the samplers are withdrawn from the field, when they have been recently exposed to very high relative humidity (e.g. rain). If the samplers cannot be analysed immediately (within two or three days after exposure), the manufacturer advises to collect the samplers when the weather is fine and stable for one or two days before ending the sampling. If this is not possible, the samplers must be dried over silica gel or allowed to equilibrate indoors before closing them and storing them in a fresh and dry place.

7.3 Extraction and analysis

Nitrogen dioxide, adsorbed as nitrite, can be determined by ion chromatography. A method using the standard Griess-Saltzman reaction for nitrite followed by colorimetric analysis can also be used.

After exposure, the filters are extracted with eluent (2,7 mM Na₂CO₃ and 0,3 mM NaHCO₃). The extraction of nitrite is carried out in the same sampler by adding 5 ml of the extraction solution (eluent). The nitrite ion concentration is determined using ion chromatography (Dionex equipped with a column IONPAC AS12A). The concentration of nitrite is calculated from calibration graphs with sodium nitrite standards.

Stock standard solutions of 1000 µg.ml⁻¹ may be purchased as certified solutions from different manufacturers, or can be prepared by dissolving 0,7499 g of oven-dried sodium nitrite in 0,5 l of de-ionised water. The working standard solutions for the preparation of the calibration curve are made as follows:

- 10 ml of the stock solution are added to a 200 ml flask that is filled to the mark with the Dionex eluent;
- Subsequent dilutions are carried out using a 10 ml pipette and the appropriate volumetric flasks;
- A set of standards in the range 0 to 3,0 of µg.ml⁻¹ nitrite anion are prepared to calibrate the ion chromatograph.

For low-level applications, more diluted standards may be necessary.

7.4 Calculation of ambient air concentration

Equation 7.1 is used to calculate the NO₂ concentration in air (expressed in µg.m⁻³) in which ν is 11.7 cm³.min⁻¹ at 20 °C (see 7.5).

$$C_{\text{NO}_2} = \frac{(m_s - m_b)}{\nu \times t \times 10^{-6}} \quad (\text{eq 7.1})$$

where

C_{NO_2} = NO₂ concentration in µg m⁻³ at 20 °C;

m_s = mass of nitrite measured in the exposed sampler in µg;

m_b = mass of nitrite measured in a blank sampler in µg;

ν = uptake rate in cm³.min⁻¹ at 20 °C;

t = sampling time in min.

This formula assumes that the average temperature during sampling is 20 °C. If the temperature T is significantly different, a correction to C_{NO_2} can be applied multiplying by coefficient calculated using equation 7.2.

$$\nu_{T,p} = \nu_{\text{ref}} \left(\frac{273,2 + T}{273,2 + T_{\text{ref}}} \right)^{1,8} \quad (\text{eq. 7.2})$$

where

- v_T = uptake rate in $\text{cm}^3 \cdot \text{min}^{-1}$ at temperature T during sampling;
 v_{ref} = uptake rate in $\text{cm}^3 \cdot \text{min}^{-1}$ at the reference temperature of 20 °C, 11.7 $\text{cm}^3 \cdot \text{min}^{-1}$;
 T = actual temperature during sampling in °C;
 T_{ref} = reference temperature in °C at which v_{ref} rate is given (20 °C).

7.5 Uptake rate and environmental effects

The NO_2 uptake rate may be calculated directly from the theoretical diffusion coefficient of NO_2 and the geometry of the sampler. The rate at which NO_2 is transferred through the vial depends on the average concentration in the ambient air according to Fick's law which is integrated along the diffusion path length to give equation 7.3.

$$m = \frac{(C - C_0)DA t}{L} \quad (\text{eq. 7.3})$$

where

- m = mass uptake in μg ;
 C = concentration of NO_2 in $\mu\text{g} \cdot \text{m}^{-3}$;
 C_0 = concentration of NO_2 at the surface of the sorbent in $\mu\text{g} \cdot \text{m}^{-3}$ (close to zero);
 D = diffusion coefficient of NO_2 in air in $\text{m}^2 \cdot \text{min}^{-1}$;
 A = cross-sectional area of the diffusion path in m^2 ($3,27 \cdot 10^{-4} \text{ m}^2$);
 t = exposure time in min;
 L = length of the diffusion path in cm (0,0254 cm).

By substitution and using the diffusion coefficient at 25 °C, the NO_2 uptake rate was calculated using equation 7.3 and found to be $12,3 \pm 0,5 \text{ cm}^3 \cdot \text{min}^{-1}$.

The uptake rate was also determined by comparing measurements of the chemiluminescence reference method and of the Analyst samplers for concentrations between 100 and 1300 $\mu\text{g} \cdot \text{m}^{-3}$ at 20 °C and 50 % of relative humidity. When calculating the slope of the regression line of the two methods of measurements, the uptake rate of the Analyst sampler was $11,7 \pm 0,6 \text{ cm}^3 \cdot \text{min}^{-1}$ [1].

The fairly good agreement between the estimation of the uptake rate using the theory of diffusion and by indirect measurements demonstrates both that NO_2 absorption on the carbon coated surface is very rapid and that the C_0 term in equation 7.3 must be close to zero.

A series of laboratory tests were undertaken to demonstrate the effect of fluctuating concentrations of NO_2 on the sampler response. In these experiments, dilution of NO_2 from a permeation tube was varied over the exposure time by using a pump. NO_2 changed between 50 (i.e. when the pump was on) and 500 $\mu\text{g} \cdot \text{m}^{-3}$ (i.e. when the pump was off) every hour. This concentration change was repeated overnight. The results of these experiments showed that the uptake rate of variable NO_2 concentrations was within 5 % of those obtained at constant concentration [1].

To study the influence of relative humidity on the collection efficiency of the sampler, the amount of nitrite collected per unit time and concentration was determined over a range of 20 % to 80 % relative humidity at 500 $\mu\text{g} \cdot \text{m}^{-3}$ of NO_2 for 10 h at 25 °C. The uptake rates were unaffected by relative humidity and averaged around $11,9 \pm 0,8 \text{ cm}^3 \cdot \text{min}^{-1}$.

The interference of ozone was studied by exposing samplers previously loaded with NO_2 to an ozone mixture in an exposure chamber (3 samplers were exposed to 400 $\mu\text{g} \cdot \text{m}^{-3}$ O_3 for 5 h). Ozone was measured using UV absorption analyzer. Ozone had no measurable interference effect.

7.6 Validation of sampler performance

In 2001-2002 CEN/TC264 WG11 “Diffusive samplers” performed a small-scale pilot study at two locations in which 6 samplers were exposed for two weeks, accompanied by parallel measurements with a reference monitor. The results for the exposed Analyst samplers are reported in table 7.1.

Table 7.1: Results of CEN pilot study for the Analyst sampler

Willebroek	NO ₂ (µg.m ⁻³)	Ratio Analyst/reference
Reference	40,8	
Analyst	112	2,74
Teddington	NO ₂ (µg.m ⁻³)	Ratio Analyst/reference
Reference	13,8	
Analyst	18,0	1,30

Analyst samplers were found to overestimate NO₂ concentrations. The overestimation for the experiment at Willebroek could be explained by the fact that the sampler was exposed without a shelter in very windy conditions in an open field, contrary to manufacturer recommendations.

A validation study carried out at an urban background site (Villa Ada, Rome, Italy), side-by-side with a chemiluminescence analyser, showed that the Analyst sampler for NO₂ is characterised by an expanded uncertainty lower than 21 %, well within the limit required by EU Directive 2008/50/EC for indicative measurements [1].

This field validation consisted of two elements:

- A study into the integrated response of samplers over different sampling periods;
- A comparison with a reference analyzer according to ISO 13752.

The study entailed the comparison of 35 pairs of results from the chemiluminescence analyser and the Analyst sampler over a full range of average wind-speed conditions ranging from 1,4 m.s⁻¹ to 2,0 m.s⁻¹ over fortnight sampling periods. Average daily wind velocity values ranged from 0,7 m.s⁻¹ to 4,2 m.s⁻¹.

Buzica et al. [2] organized a series of 4 comparisons in which different samplers operated by different laboratories were exposed both under laboratory and field conditions. Each sampler type was exposed in batches of 6 samplers for a period of 14 days except in the laboratory trial “high” (see table 7.2).

Table 7.2: Laboratory conditions (intercomparison of Buzica et al.)

Parameter	High	Low
Exposure time (d)	7	14
Concentration (µg.m ⁻³)	80	40
Air velocity (m.s ⁻¹)	2,5	1,0
Temperature (°C)	25	5
Relative humidity (%)	75	30

The results obtained for the Analyst sampler operated by Lab B are presented in table 7.3.

Table 7.3: Results of the Analyst sampler operated by Lab B (intercomparison of Buzica et al.)

Location	CLS (µg.m ⁻³)	Analyst (µg.m ⁻³)	Ratio
Laboratory, high	76,8	111 ± 5	1,44
Laboratory, low	43,5	43,3 ± 1,0	1,00
Genevilliers	41,6	55,9 ± 1,4	1,34
Fontainebleau	14,1	15,0 ± 0,5	1,06

These results show a somewhat “mixed” performance, although the laboratory “high” trial yielded large variations in results for all participants, with mean results ranging from 54 to 188 $\mu\text{g}\cdot\text{m}^{-3}$. The precision of the results was good, usually within 10 %.

7.7 Measurement uncertainty

The accuracy of the samplers in comparison to the chemiluminescence technique, expressed as percent relative error was found to be better than ± 20 % at 20 ppb of NO_2 . The relative standard deviation on 12 samplers is 7 % [1].

No further information is available, e.g. assessments based on application of the Guide to the Expression of Uncertainty in Measurement.

7.8 Application in EU monitoring networks

Applications appear to be mostly in indoor air monitoring, e.g., for studies into protection of cultural heritage. No references to applications in ambient air monitoring have been found.

7.9 Conclusions

The Analyst badge-type diffusive sampler may be used for long-term monitoring of NO_2 in ambient air. Exposure periods of 1 to 2 weeks are feasible. The lower detection limit for a one-week exposure period was reported to be 1,9 $\mu\text{g}\cdot\text{m}^{-3}$.

The precision of replicate samples was generally within 10 %. However, the number of studies reported is limited.

The comparability of sampler results with those obtained with continuous reference monitors (chemiluminescence) was acceptable, with ratios ranging from 1,0 to 1,4. However, it must be emphasized that the number of studies on which this conclusion was based is limited.

No information was available on the availability of sampler results upon long-term exposure. However, from the laboratory experiments it could be concluded that an exposure period of at least 4 months is feasible for sites characterized by concentrations up to 200 $\mu\text{g}\cdot\text{m}^{-3}$.

When assessing measurement uncertainty by direct approaches, e.g., from parallel measurements with the reference method for measurement of NO_2 , the accuracy was reported to be ± 20 %.

No information was found about any uncertainty assessment of the results obtained with the sampler, e.g., according to the Guide to the Expression of Uncertainty in Measurement.

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8 Summary of findings, conclusions and recommendations

8.1 Summary of findings

A number of diffusive samplers that are used for long-term monitoring of nitrogen dioxide (NO₂) were subjected to a review of their use and performance characteristics. The samplers were selected on the basis of their general availability in the European Union:

- The Palmes tube sampler;
- The Passam tube sampler;
- The Ogawa badge sampler;
- The Radiello radial sampler;
- The Analyst badge sampler.

The IVL sampler, although a sampler in frequent use throughout the European Union, was not included in the review, since most information about this sampler is considered a proprietary secret by the manufacturer.

The information collected was used to:

- Draft conclusions about the feasibility of using the samplers for the long-term monitoring of NO₂, with the particular aim of assessing compliance with the European Union annual limit value of 40 µg.m⁻³ (at 20 °C and 101,2 kPa);
- Draft a proposal method for monitoring NO₂ using diffusive samplers, for future use by CEN Technical Committee 264 “Air Quality” Working Group 11 “Diffusive Samplers” as a CEN standard devoted to the measurement of NO₂ in ambient air.

Main criteria for the assessment of sampler feasibility for both purposes were:

- The validation level of the samplers, based either on application of EN 13528 part 2 or the Guide to the Demonstration of Equivalence of Ambient Air Monitoring Methods, including information about the uncertainty of results obtained using the samplers;
- From this: the potential to meet European Air Quality Directive data quality objectives for indicative and/or fixed measurements;
- The extent or lack of information available to underpin the validity of results obtained using the different samplers;
- The number of different sources providing the above information;
- Differences in performance depending on site type (tube type): traffic, urban, rural;
- The possibility for users to analyse the samplers, e.g., based on procedures specified by manufacturers;
- Their current use throughout the European Union for measuring ambient air quality related to concentrations of NO₂.

The conclusions for each individual sampler are reported below.

8.1.1 The Palmes tube sampler

Palmes tube samplers are extensively used e.g. in Denmark, France, the Netherlands, Spain and the United Kingdom for supplementary measurements to the fixed measurements at the level of an indicative method. Other applications include identification of hot spots, mapping, zoning, trend analysis, source apportionment, impact on vegetation, assessment of exposure of population, verification of dispersion models etc.

A number of methods exist for the preparation of the TEA-based sampling substrate. Only 3 of these have been proven to give reliable results in practice.

Palmer tube samplers are generally analysed by colorimetry applying the Griess-Saltzman methodology.

The Palmer tube-type diffusive sampler is suitable for long-term monitoring of NO₂ in ambient air. Exposure periods of 1 to 8 weeks are feasible. The most commonly used exposure period is 2 or 4 weeks. The lower detection limit for a 2-week sampling period will vary with the meticulousness of the sampler preparation procedure, and will generally be between 0,7 and 1 µg.m⁻³. The upper limit for a 2-week exposure period is at least 375 µg.m⁻³.

Unused and exposed samplers may be stored for several months under specific conditions (dark; air tight; reduced temperatures).

A large body of literature evidence from various sources was available about the application of Palmer tube samplers for the monitoring of NO₂ in ambient air. A considerable number of studies reported the performance in side-by-side comparisons with reference monitors (chemiluminescence).

Generally, these comparisons gave varying results; however, the results are generally consistent within the uncertainties of the methods. At urban sites, where unprotected open tubes were used, a tendency was observed towards overestimation of NO₂ concentrations.

When using membrane-capped tubes in combination with model equations describing the uptake rate as a function of temperature, humidity, wind speed etc., the comparability improved.

When the uncertainty associated with the measurement results was evaluated according to the Guide to the Expression of Uncertainty in Measurement, the relative expanded uncertainty of individual results was estimated to be 32 % for worst-case conditions (when using a single value for the uptake rate independent of environmental conditions).

Assessments of measurement uncertainty by direct approaches, e.g., from parallel measurements with the reference method for measurement of NO₂, generally gave relative expanded uncertainties below 25 %. These findings suggest that the Palmer tube is at least suitable for performing long-term measurements of NO₂ for indicative purposes, and possibly even for fixed measurements.

When aggregating results to form annual average values, the relative expanded uncertainty may be further reduced to levels below 15 % due to the reduction of random effects on uncertainty.

8.1.2 The Passam tube sampler

Passam tube samplers are used e.g. in Cyprus, France, Germany, Italy, Lithuania and Romania for supplementary measurements to the fixed measurements at the level of an indicative method. Other applications include identification of hot spots, mapping, zoning, trend analysis, source apportionment, impact on vegetation, assessment of exposure of population, verification of dispersion models etc.

The preparation of the TEA-based sampling substrate is performed by the manufacturer.

Passam tube samplers are generally analysed by colorimetry applying the Griess-Saltzman methodology.

The Passam diffusive sampler is suitable for long-term monitoring of NO₂ in ambient air. Exposure periods of 1 to 6 weeks are feasible. The lower detection limit for a 2-week sampling period is reported to be 0,4 µg.m⁻³. The most commonly used exposure period is 2 or 4 weeks.

Unused and exposed samplers may be stored for several months under specific conditions (dark; air tight; reduced temperatures).

A large body of literature evidence from various sources was available about the application of Passam tube samplers for the monitoring of NO₂ in ambient air. A considerable number of studies reported the performance in side-by-side comparisons with reference monitors (chemiluminescence).

The comparability of sampler results with those obtained with reference monitors varied somewhat, with ratios of average results generally ranging from 0,9 to 1,3. This variability may be reduced, when:

- Sampling rates are converted to actual conditions of temperature and pressure;
- Membranes are introduced into the sampler inlet particularly for traffic-related sites.

When the uncertainty associated with the measurement results was evaluated according to the Guide to the Expression of Uncertainty in Measurement, relative expanded uncertainties of individual results from 20 to 25 % resulted. When assessing measurement uncertainty by direct approaches, e.g., from parallel measurements with the reference method for measurement of NO₂, similar and even better results were obtained. When combining results from a number of studies in France, a relative expanded uncertainty of 13 % was calculated, qualifying the sampler for the fixed measurement regime of EU Directive 2008/50/EC.

These findings suggest that the Passam tube is at least suitable for performing long-term measurements of NO₂ for indicative purposes and possibly even for fixed measurements.

When aggregating results to form annual average values, the relative expanded uncertainty may be further reduced to levels below 15 % due to the reduction of random effects on uncertainty.

8.1.3 The Ogawa badge sampler

The Ogawa sampler has been used in Spain. To date, there is no reference found of the sampler being used for ambient air monitoring purposes in the EU. Applications are mainly in the field of indoor air and exposure monitoring. The preparation of the TEA-based sampling substrate is performed by the manufacturer.

Ogawa samplers are generally analysed by colorimetry applying the Griess-Saltzman methodology.

The Ogawa badge-type diffusive sampler is suitable for long-term monitoring of NO₂ in ambient air. Exposure periods of 2 to 4 weeks are feasible. Lower detection limits reported vary somewhat, but are below 1 µg.m⁻³ for a 2-week exposure period.

Unused and exposed samplers may be stored for several months under specific conditions (dark; air tight; reduced temperatures).

A number of studies from various sources were available about the application of Ogawa samplers for the monitoring of NO₂ in ambient air mainly in the United States of America. A limited number of studies reported the performance in side-by-side comparisons with reference monitors (chemiluminescence).

When exposed for 14 days or more in the field, the comparability of sampler results to those obtained with continuous reference monitors (chemiluminescence), was good, with ratios of average results ranging from 0,90 to 1,07. The availability of sampler results upon long-term exposure was better than 90 %. Absence of data in comparisons was due to malfunctioning of reference monitors rather than malfunctioning of the sampler.

No information is available about any uncertainty assessment of the results obtained with the sampler, e.g., according to the Guide to the Expression of Uncertainty in Measurement.

When using the methodology of the EU Guide to the Demonstration of Equivalence to the results of the US-EPA El Paso study, the sampler was found to pass the uncertainty requirement for indicative measurements. The random uncertainty found for the relation between sampler results and reference

method indicated that by correcting the uptake rate the sampler may pass the criterion for fixed measurements. However, the study was performed under conditions that are atypical of the EU.

8.1.4 The Radiello radial sampler

The Radiello sampler is used in the EU e.g. in Belgium, France, Italy, Slovakia and Spain for surveys aimed at, e.g. identification of hot spots, mapping, zoning, trend analysis, source apportionment, impact on vegetation, assessment of exposure of population, verification of dispersion models etc.

The preparation of the TEA-based sampling substrate is performed by the manufacturer.

Radiello radial samplers are generally analysed by colorimetry applying the Griess-Saltzman methodology.

The Radiello radial-type diffusive sampler may be used for long-term monitoring of NO₂ in ambient air. Exposure periods of 1 day to 2 weeks are feasible. The lower detection limit for a 2-week sampling period was reported to be 0,9 µg.m⁻³. Results of a laboratory study in which the sampling period was restricted to one day showed an underestimation of NO₂ concentrations of a factor of 2 when applying the uptake rate specified by the manufacturer. The reason for this may be a transient period of sorption at the beginning of the sampling period.

The comparability of sampler results with those obtained with continuous reference monitors (chemiluminescence) varied, with ratios of average results ranging from 0,6 to 1,4. In general, Radiello showed a trend to underestimate concentrations measured by reference monitors. However, the number of field data available was too limited to be conclusive.

When the uncertainty associated with the measurement results for a one-day exposure was evaluated according to the Guide to the Expression of Uncertainty in Measurement, a relative expanded uncertainty of individual results of 31 % was found. When assessing measurement uncertainty by direct approaches, e.g., from parallel measurements with the reference method for measurement of NO₂, similar results were obtained.

These findings suggest that the Radiello does not satisfy the uncertainty data quality objective for indicative measurements of NO₂, for which the uncertainty shall not exceed 25.

When aggregating results to form annual average values, the relative expanded uncertainty may be further reduced to levels below 25 % due to the reduction of random effects on uncertainty.

The information collected about the uncertainty of individual measurement results does not correspond with information supplied by the manufacturer stating an expanded measurement uncertainty of 12 %. However, information about the assessment approach used by the manufacturer is (currently) unavailable.

The possible effect of concentration level, high humidity and exposure time for NO₂ needs further research.

8.1.5 The Analyst badge sampler

Applications of the Analyst sampler appear to be mostly in indoor air monitoring, e.g., for studies into protection of cultural heritage. No references to applications in ambient air monitoring were found apart from the ones of the manufacturer.

To date, the preparation of the sampling substrate is performed by the manufacturer.

Analyst samplers are generally analysed by ion chromatographic determination of the nitrite formed after sorption on the sampling substrate.

The Analyst diffusive sampler is suitable for long-term monitoring of NO₂ in ambient air. Exposure periods of 1 to 2 weeks are feasible. The lower detection limit for a one-week exposure period is 1,9 µg.m⁻³.

The comparison of sampler results with those obtained with continuous reference monitors (chemiluminescence) showed ratios ranging from 1,0 to 1,4. On one occasion a ratio of 2,7 has been found in an early study. However, the number of studies was very limited.

No information was available on the availability of sampler results upon long-term exposure, e.g. for a period of one year.

When assessing measurement uncertainty by direct approaches, e.g., from parallel measurements with the reference method for measurement of NO₂, a single study reported the accuracy to be ± 20 %.

No further information was found about any uncertainty assessment of the results obtained with the sampler, e.g., according to the Guide to the Expression of Uncertainty in Measurement.

8.2 Conclusions and recommendations

Based on the findings summarised above, the following conclusions were drawn.

- The Palmes tube, Passam tube and Radiello radial sampler are in general use in the European Union for monitoring NO₂ in ambient air. Of these, the two tube-type samplers are used in ongoing air quality monitoring for supplementary measurements to the fixed measurements at the level of an indicative method.
- The Ogawa badge and Analyst badge are not in general use in the European Union for ambient air monitoring of NO₂.
- The extent to which results of validation studies are available differs considerably between samplers. For the tube-type samplers, a substantial number of sources were identified. For the Ogawa badge and Radiello radial sampler information was more restricted. For the Analyst badge information was even scarcer.
- The available information suggests that, in general, the tube-type samplers may at least meet the EU uncertainty data quality objectives for indicative measurements. Application of membranes or shelters generally improves their performance. In some cases uncertainties were found that would qualify the samplers for fixed measurements.
- For the Ogawa badge sampler, the current limited information available suggests a potential to meet the EU uncertainty requirement for indicative measurements. However, the conditions of the study on under which this finding is based were not really representative for average European Union conditions. More information would be needed to draw firmer conclusions about the validity of the results produced by the sampler for monitoring NO₂ in ambient air.
- For the Radiello radial sampler, the current limited information available suggests that the sampler is not able to meet the EU uncertainty requirement for indicative measurements. The sampler generally appears to systematically underestimate NO₂ concentrations. More information would be needed to draw firmer conclusions about the validity of the results produced by the sampler for monitoring NO₂ in ambient air. It is recommended to further investigate the possible effects of concentration level, high humidity and exposure time for NO₂.
- For the Analyst badge insufficient information is currently available to draw a quantitative conclusion about its potential to meet EU data quality objectives for the monitoring of NO₂ in ambient air. The limited information available gives mixed findings. More information would be

needed to draw firmer conclusions about the validity of the results produced by the sampler for monitoring nitrogen dioxide in ambient air.

On the basis of the above conclusions it is recommended that experts draft, a proposal method, based on the tube-type sampler, for monitoring nitrogen dioxide using diffusive samplers to be later used by CEN/TC 264 Working Group 11 "Diffusive Samplers" to prepare a new standard. Should further information become available in time on the performance of the Radiello radial sampler, which provides supporting evidence of its validity and its potential to meet EU data quality objectives, this sampler may still be considered and be included in the standard.

Contributors to the review

The following experts have contributed to this review report.

- *TEA general*
J. Neil Cape – Centre for Ecology and Hydrology, Edinburgh, United Kingdom
- *Palmes tube sampler*
Hervé Plaisance – Ecole de Mines de Douai, Douai, France
Jaume Targa, Alison Loader - AEA Technology, Harwell, United Kingdom
Sim Tang - Centre for Ecology and Hydrology, Edinburgh, United Kingdom
- *Passam sampler*
Markus Hangartner - Passam, Männedorf, Switzerland
Ulrich Pfeffer – Landesamt für Natur, Umwelt und Verbraucherschutz NRW, Recklinghausen, Germany
- *Ogawa sampler*
Theo Hafkenscheid, National Institute for Public Health and Environment, Bilthoven, Netherlands
- *Radiello sampler*
Wendy Swaans and Eddy Goelen, Flemish Institute for Technology and Research, Mol, Belgium
- *Analyst sampler*
Franco de Santis, Central Institute for Research, Rome, Italy
- *Study Group Members*
Anne Fromage-Mariette – Air Languedoc-Roussillon, Montpellier, France
Michel Gerboles – Joint Research Centre Institute for Environment and Sustainability, Ipra
Kevin Saunders – Keris Ltd., Heckfield, United Kingdom
- *Editor*
Theo Hafkenscheid, National Institute for Public Health and Environment, Bilthoven, The Netherlands
- *Language revision*
Sim Tang - Centre for Ecology and Hydrology, Edinburgh, United Kingdom
- *Secretariat*
Caroline van Hoek, NEN, Netherlands Standardization Institute, Delft, The Netherlands

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Author(s): T. Hafkenscheid, A. Fromage-Marriette, E. Goelen, M. Hangartner, H. Plaisance, S. Tang, U. Pfeffer, F. de Santis, , K. Saunders, W. Swaans, C. van Hoek and M. Gerboles

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Abstract

A number of diffusive samplers that are used for longer-term monitoring of nitrogen dioxide in the European Union were subjected to a review of their use and performance characteristics. The information collected was used to evaluate the capacity of diffusive samplers for monitoring the European Union annual limit value of 40 $\mu\text{g.m}^{-3}$.

A bibliographic review was carried out to determine the availability of validation data for these samplers, their capacity to meet the data quality objectives for indicative and/or fixed measurements of the European Directive, the possibility for users to analyse the samplers and their current use throughout the European Union for measuring ambient air quality.

Two tubes-type samplers and a radial sampler were found to be used throughout the European Union. Based on the findings of the review, only for tube-type samplers based on the application of triethanolamine as the sorbent, sufficient information was available to underpin the potential of these samplers for meeting the European Union data quality objectives for nitrogen dioxide monitoring.

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