

Report

NO₂ Diffusion Tubes for LAQM: Guidance Note for Local Authorities

Prepared for Defra and the Devolved
Administrations

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1 Introduction

This Guidance Note have been produced to assist the many UK Local Authorities who are using diffusive samplers for indicative monitoring of ambient NO₂ concentrations, as part of their Local Air Quality Management (LAQM) activities.

This document has been produced by Netcen on behalf of Defra and the Devolved Administrations, under their contract number RMP 2877, "Support to Local Authorities for Local Air Quality Management".

It is intended as a supplement to the Defra Technical Guidance LAQM.TG(03)¹, bringing together in one convenient source the latest information and guidance on using diffusion tubes and interpreting the results.

Further assistance for Local Authorities in all aspects of LAQM can be obtained from the Local Authority Air Quality Helpdesk, on **0870 190 6050**.

2 Oxides of Nitrogen in the Atmosphere

Oxides of nitrogen, collectively termed NO_x, are air pollutant gases. The most significant of these (in terms of anthropogenic ground level air pollution) are nitric oxide (NO) and nitrogen dioxide (NO₂). Nitrous oxide (N₂O) is the most prevalent oxide of nitrogen in the atmosphere, and although an important "greenhouse gas", it has no known detrimental effect on human health at ambient concentrations. However, nitrogen dioxide (NO₂) is an irritant to the respiratory system, and so can affect human health.

Both NO and NO₂ are formed in high temperature combustion processes, though NO predominates. (The term NO_x, total oxides of nitrogen, is generally used to describe the sum of NO and NO₂ concentrations). According to the National Atmospheric Emissions Inventory (NAEI) at www.naei.co.uk, motor vehicles account for approximately 40% of the UK's total estimated emission of oxides of nitrogen, with power generation also a significant source. However, in urban areas, especially close to major roads, a much higher percentage of the observed oxides of nitrogen will arise from motor vehicles. Almost all oxidised nitrogen pollution is emitted as NO, which at ambient temperatures is oxidised to the more toxic secondary pollutant, NO₂. This process is accelerated in the presence of sunlight, reactive hydrocarbons and ozone.

For the purpose of LAQM, ambient concentrations of nitrogen dioxide are to be reported in units of microgrammes (i.e. 10⁻⁶ grammes) per cubic metre (µg m⁻³). In other contexts, units of parts per billion (ppb) are sometimes also used. To convert to parts per billion (ppb) if necessary, the following relationship should be used:

1 ppb = 1.91 µg m⁻³ for nitrogen dioxide at 293K (20°C) and 1013mb.

NO₂ is one of the key pollutants targeted under the Air Quality Strategy, and is also the subject of EC Limit Values. Table 1 summarises the EC Limit Values and Air Quality Strategy (AQS) Objectives that apply to NO₂.

Table 1: Limit Values and Objectives for Nitrogen Dioxide

Averaging period	EC Limit or AQS Objective	No. of Permitted exceedances	To be achieved by
EC 1st Daughter Directive (1999/30/EC)			
1 hour	200 µg m ⁻³	18 per year	1 st January 2010
Annual Mean	40 µg m ⁻³	-	1 st January 2010
Annual Mean, for protection of vegetation	30 µg m ⁻³ Total NOx	-	19 th July 2001
Air Quality Strategy			
1 hour	200 µg m ⁻³	18 per year	31 st December 2005
Annual Mean	40 µg m ⁻³	-	31 st December 2005
Annual Mean, for protection of vegetation	30 µg m ⁻³ Total NOx	-	31 st December 2000

3 Diffusion Tubes: How They Work

Diffusion tubes are a type of passive sampler; that is, they absorb the pollutant to be monitored directly from the surrounding air and need no power supply. Passive samplers are easy to use and relatively inexpensive, so they can be deployed in large numbers over a wide area, giving good spatial coverage. This has made them a popular choice for Local Authorities, who often use diffusive samplers to complement more expensive automatic monitoring techniques, or at locations where it would not be feasible to install an automatic monitor.

It should be noted that diffusion tubes have two limitations. Firstly, they are an *indicative* monitoring technique. Whilst ideal for screening surveys, or for identifying locations where NO₂ concentrations are highest, they do not provide the same level of accuracy as automatic monitoring techniques. Secondly, as the exposure period is typically several weeks, the results cannot be compared with air quality standards and objectives based on shorter averaging periods such as hourly means.

The development and use of passive samplers originated in the field of occupational exposure monitoring. However, diffusion sampling techniques have been further developed and tested, and now are widely used for ambient air quality monitoring, where concentrations are generally much lower. NO₂ diffusion samplers are designed either as a badge, or tube configuration. In the UK, most Local Authorities use Palmes-type diffusion tubes. These consist of a small plastic tube, approximately 7cm long, as shown in Figure 1. During sampling, one end is open and the other closed. The closed end contains an absorbent for the gaseous species to be monitored, in this case NO₂.

Diffusion tube samplers operate on the principle of molecular diffusion, with molecules of a gas diffusing from a region of high concentration (open end of the sampler) to a region of low concentration (absorbent end of the sampler).

The movement of molecules of gas (1) through gas (2) is described by Fick's law, which states that the flux is proportional to the concentration gradient:

$$J = -D_{12} \frac{dC}{dz}$$

where:

- J = the flux of gas (1) through gas (2) across unit area in the z direction;
 C = the concentration of gas (1) in gas (2);
 z = the length of the diffusion path; and
 D₁₂ = the constant of proportionality - the molecular diffusion constant of gas (1) in gas (2), with dimensions of length² time⁻¹.

For a tube of area a (m²) and length l (m) then Q (moles), the quantity of gas transferred along the tube in t seconds, is given by:

$$Q = \frac{D_{12} (C_1 - C_0) a t}{l}$$

where: C₀ and C₁ are the gas concentrations at either end of the tube.

In a diffusion tube, the concentration of gas (1) is maintained at zero (by an efficient absorbent) at one end of the tube (i.e. C₀ = zero) and the concentration C₁ is the average concentration of the gas (1) at the open end of the tube over the period of exposure. Hence:

$$C = \frac{Q l}{D_{12} a t}$$

where:

- Q = the quantity of the gas absorbed over the period of exposure;
 a = the cross sectional area of the tube;
 t = the time of exposure; and
 l = the length of the tube.

For the gas monitored, the diffusion coefficient must be determined, or obtained from the literature. The area and length of the tube are determined by measurement.

Triethanolamine (TEA) is the absorbent used for NO₂ in diffusion tubes. The closed end of the tube holds stainless steel mesh discs, coated with a solution of this absorbent. Tubes must be prepared in a clean atmosphere to minimise contamination by atmospheric NO₂. The open end of the tube is then sealed and the tube stored in a sealed container prior to exposure.

For monitoring, the end cap *not* containing the mesh discs is removed and the tube mounted vertically with the open end at the bottom. NO₂ is absorbed as nitrite and after exposure, the lower end cap is replaced and the tubes sent to an analytical laboratory for chemical analysis. Step-by-step instructions for exposing the tubes are given in Section 6.

The tubes must be analysed using a colorimetric or spectrophotometric technique. This generally involves the addition of a solution of sulphanilamide in orthophosphoric acid and naphthyl ethylene diamine dihydrochloride (NEDA) solution, to form an azo dye, the intensity of which is determined on a spectrophotometer at 540nm. The spectrophotometer is calibrated against standard nitrite solutions, to allow the total NO₂ as nitrite, collected by the tube, to be determined. If required, the method can be automated for a large throughput of samples.

4 Factors Affecting Diffusion Tube Performance

NO₂ diffusion tubes are an *indicative* monitoring technique: although ideal for screening studies and for identifying areas of high concentration, they do not offer the same precision and accuracy as the automatic chemiluminescent analyser (which is defined by the European Union as the reference method of measurement for this pollutant). In particular, NO₂ diffusion tubes are affected by several mechanisms, which may cause them to exhibit positive bias (over-read), or negative bias (under-read) relative to the reference technique.

Over-read may be attributed to the individual and combined effect of three interfering factors:

- the shortening of the diffusive path length, by turbulence at the open end of the tube caused by wind^{2,3};
- blocking of UV light by the tube material, resulting in reduced NO₂ photolysis in the tube⁴; or
- the interfering effects of peroxyacetyl nitrate (PAN)³, a pollutant associated with vehicle emissions.

Some factors known to cause under-read are as follows:

- Increasing exposure period. It has been reported that the average of four consecutive one-week, or two consecutive two-week exposures is systematically greater than one four-week exposure^{5,6}. This is considered to be due to the degradation of the absorbed nitrite over time⁵.
- Insufficient extraction of nitrite from the grids.
- The photochemical degradation of the triethanolamine-nitrite complex by light. This has been largely minimised, by the widespread use of opaque diffusive end caps.
- In the specific case of tubes prepared using a 50% v/v solution of TEA in water, it has been reported that there may be a mechanism reducing NO₂ uptake, resulting in negative bias⁷. Such tubes are no longer widely used in the Network. Tubes prepared using other methods (10% or 20% v/v solution of TEA in water, 50% solution of TEA in acetone) appear not to be affected.

Of these factors, those causing positive bias are usually the most difficult to eliminate, and positive bias is more common than negative (although the latter is certainly not rare).

5 Guidance on Diffusion Tube Monitoring

General advice on air quality monitoring for the purposes of Air Quality Review and Assessment is provided in Annex 1 of the Technical Guidance (LAQM.TG(03)). This includes general guidance on monitoring strategies, as well as information on how to identify relevant locations for monitoring, and select appropriate monitoring sites.

5.1 WHEN AND WHERE TO USE DIFFUSION TUBES

Diffusion tubes are particularly useful –

- when simple, indicative techniques will suffice;
- to give an indication of longer-term average NO₂ concentrations;
- for indicative comparison with Limit Values and AQS Objectives based on the annual mean;
- for highlighting areas of high NO₂ concentration; and
- where installation of an automatic analyser is not feasible.

They are useful for identifying areas of high NO₂ concentration, particularly when dealing with sources such as traffic emissions, which do not change much from day to day. They are less useful for monitoring ambient concentrations around specific emission sources such as industrial plant, as they cannot identify short-term fluctuations in NO₂ such as may result from fluctuations in wind direction.

5.2 SELECTING DIFFUSION TUBE SITES

For LAQM purposes, sites should be located in areas where people are normally present in daily life, i.e. where there is *relevant public exposure*. The authority should focus on locations where members of the public are likely to be exposed over the averaging period of the objective. Table 2 summarises the locations where the objectives should and should not apply.

Table 2: Typical locations where the objectives should and should not apply

Information from LAQM.TG(03)

Averaging Period	Pollutants	Objectives <i>should</i> apply at ...	Objectives <i>should not</i> generally apply at ...
Annual mean	Nitrogen dioxide	<p>All background locations where members of the public might be regularly exposed.</p> <p>Building facades of residential properties, schools, hospitals, libraries etc.</p>	<p>Building facades of offices or other places of work where members of the public do not have regular access.</p> <p>Gardens of residential properties.</p> <p>Kerbside sites (as opposed to locations at the building facade), or any other location where public exposure is expected to be short term</p>
1 hour mean	Nitrogen dioxide	<p>Kerbside sites (e.g. pavements of busy shopping streets).</p> <p>Those parts of car parks and railway stations etc. which are not fully enclosed.</p> <p>Any outdoor locations to which the public might reasonably expected to have access.</p>	<p>Kerbside sites where the public would not be expected to have regular access.</p>

The immediate area around the sampler location must be open, allowing free circulation of air around the tube. Ideally, samplers would be placed at breathing height, but in order to reduce theft of tubes, it is recommended that tubes are placed at a height of 2-4 m, and in all cases no higher than 5 m.

Section A1.22 and Table A1.4 of the Technical Guidance categorises sites according to the type of environment in which they are located. These categories are reproduced in Table 3 below:

Table 3: Monitoring Site Classifications (from LAQM.TG(03))

Site Type	Description
Urban Centre	An urban location representative of typical population exposure in towns or city centres, e.g. pedestrian precincts and shopping areas.
Urban Background	An urban location distanced from sources and therefore broadly representative of city-wide background conditions, e.g. urban residential areas. (In the NO ₂ Network, this site category was required to be at least 50m from the nearest major or busy road).
Suburban	A location situation in a residential area on the outskirts of a town or city.
Roadside	A site sampling between 1m of the kerb of a busy road and the back of the pavement. Typically this will be within 5m of the kerb, but could be up to 15m.
Kerbside	A site sampling within 1m of the kerb of a busy road.
Industrial	An area where industrial sources make an important contribution to the total pollution burden.
Rural	An open countryside location, in an area of low population density, distanced as far as possible from roads, populated and industrial areas.
Other	Any special source-orientated or location category covering monitoring undertaken in relation to specific emission sources such as power stations, car parks, airports or tunnels.

In the former NO₂ Network, two main site categories were used – roadside and urban background. The majority of NO₂ diffusion tube sites will probably still fall into these categories, and more detailed guidance is given below.

5.2.1 Roadside and kerbside sites

These sites often reflect the maximum concentration of NO₂ to which people may be regularly exposed, even if only for short periods, close to a busy main road (A-road). The road with maximum traffic flow within the area may not produce the highest ambient concentrations, if it is situated in an open area, for instance a dual carriageway. Higher concentrations may be observed at a less busy road with tall buildings on either side (the street canyon effect), for instance in a town centre. In general, unless data from other sources exists, local knowledge will be required to select the most appropriate sites.

Roadside diffusion tubes should be sited between **1-5 m from the kerb edge**, and mounted ideally either on a lamp post or road sign on the pavement, or on the face of a building adjoining the pavement. Kerbside sites should be within 1m of the kerb, and are usually fixed to street furniture. Avoid locations where the tubes are likely to be affected by turbulence from passing fast traffic, as this may cause them to over-estimate the NO₂ concentration. Measurements from roadside and kerbside sites will only be representative over a very small area, as NO₂ concentrations close to sources vary considerably, even over short distances.

5.2.2 Urban background, urban centre and suburban (i.e. non-roadside) sites

At distances of more than 50m from a busy road, it is anticipated that NO₂ concentrations will have been diluted to the local urban background concentration. Hence, measurements made in this type of location are likely to be representative of a fairly large area, and can be reliably compared with similar locations in other urban areas.

Urban background sites must be located:

- >50 m from any major source of NO₂, such as multi-storey car parks;
- >30m from any very busy road (> 30,000 vehicles per day). The old NO₂ Network required urban background sites to be at least 50m from any busy road;
- >20m from a busy road (10,000 – 30,000 vehicles per day) or from any medium sized sources, e.g. petrol stations or ventilation outlets from catering establishments;
- >10m from *any* road; and
- >5m from anywhere where vehicles may stop with their engines idling.

Examples of typical urban background sites are on lampposts or street signs in quiet residential areas, schools or other public buildings, either close to the town centre or in suburbs bordered by a busy arterial road. When street furniture is used, even on quiet roads, the sampler must be more than 1 m from the kerb.

It is recommended that Local Authorities include some urban background sites in their diffusion tube monitoring programme, and in particular, continue to operate any urban background sites which were formerly included in the NO₂ Network: as these have been running for several years, they can provide useful information about local trends in background levels of NO₂.

5.3 DETAILED SITING OF THE SAMPLER

Diffusion tubes must be held vertically with the open end downwards during sampling. Generally, a permanent clip (e.g. Terry clip or plastic clip) is mounted so that the tubes can be changed easily (see Figure 2). The clip and spacer (see below) may be simply mounted at the monitoring site with PVC tape, double sided tape, or cable tie as appropriate.

It is important that the open end of the tube is exposed to free circulation of air. Also, certain surfaces may act as absorbers for NO₂ leading to a thin layer of reduced atmospheric concentrations immediately adjacent to the surface. For these reasons tubes must not be fixed directly to walls etc., even when the objective is to monitor at a building façade. A spacer block of at least 5 cm must be used between the surface and the tube, as indicated in Figure 2. A small block of wood or plastic can be used as the spacer. The open end of the tube must be located below the lower surface of the spacer, as shown in Figure 2. Ideally the tube with spacer block should be mounted on some projection 0.5 - 1 m horizontal distance from the face of the building, or on a drainpipe or similar structure. Avoid placing diffusion tubes in any form of recess. Some examples of how diffusion tubes can be fixed in place are shown in Figures 3 and 4.

Although it is important to place diffusion tubes where there is free circulation of air around the tube, the opposite extreme should also be avoided, i.e. areas of higher than usual turbulence. For this reason, the tube should not be located on the corner of a building. Care must be taken to avoid any very localised sources, or sinks of NO₂, or disturbances to the airflow. For example, close proximity (less than 10 m) to the following must be avoided:

- heater flues (particularly low level balanced flues);
- trees and other vegetation;
- air conditioning outlets;

- extractor vents; or
- underground ventilation shafts.

The site should be open to the sky, with no overhanging vegetation or buildings.

5.4 DURATION OF MONITORING PROGRAMME

It is recommended that NO₂ diffusion tube monitoring is carried out for a full year, as the objective is usually assessment against the AQS Objective for the annual mean. In any case, the Technical Guidance specifies that all surveys should be carried out for a minimum of six months. Nitrogen dioxide concentrations often show seasonal variation, so the six months should comprise three summer and three winter months, e.g. January to June inclusive or July to December inclusive. Section A1.39 of the Technical Guidance gives more information on this: six-month mean NO₂ concentrations are likely to be within 15% of the annual mean, while three-month means are likely to be within 20% of the annual mean.

Box A1.3 of the Technical Guidance advises on how the annual mean can be estimated from the results of a survey based on a shorter period. However, given the relatively low cost of diffusion tubes, it is recommended that a full year's monitoring is carried out where possible.

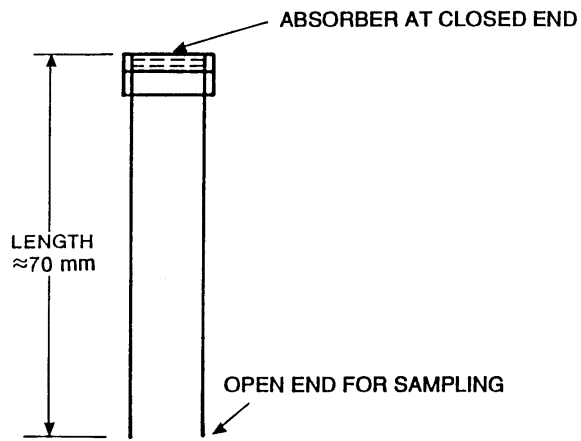


Figure 1 Diffusion Tube Sampler

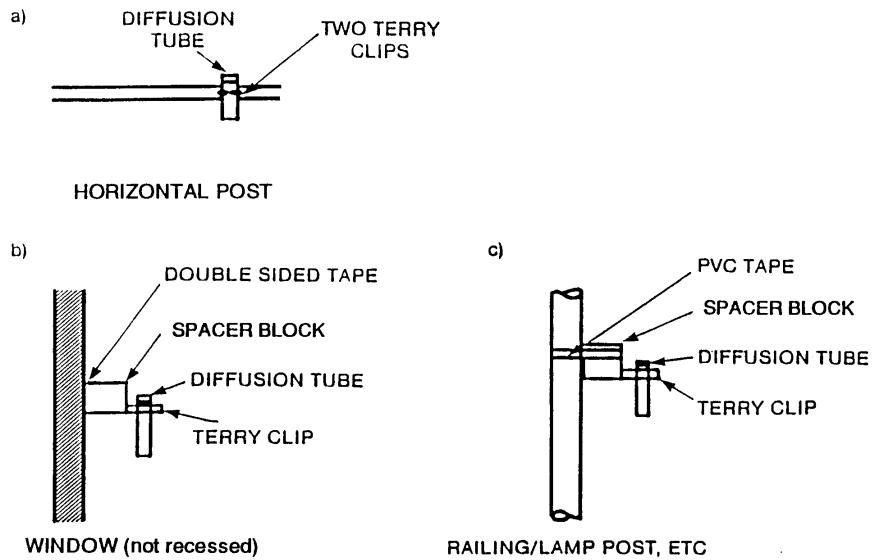


Figure 2 Suggested Mounting Methods for Diffusion Samplers



Figure 3: Example of how diffusion tubes can be fixed to a lamppost or similar.

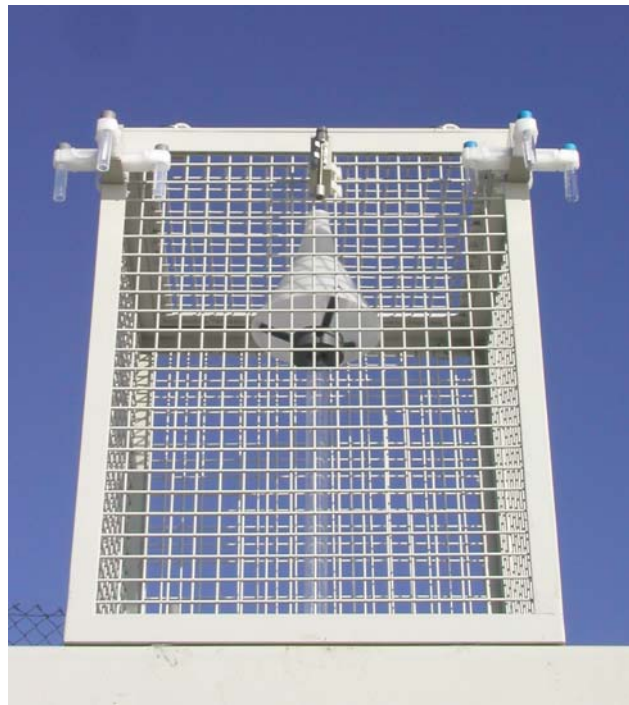


Figure 4: Example of how diffusion tubes can be fixed at an automatic monitoring site (for co-location study).

6 Instructions for Exposing Diffusion Tubes

The following procedures should be followed:-

- Remove tubes from the refrigerator on the day that they are to be put out, and ensure each one is clearly labelled with an identification number (if this hasn't already been done by the supplying laboratory). The labelling must be weatherproof!
- Take tubes to the site in a snap-seal bag. Travel blanks, where applicable, should be identified and their code numbers noted on the exposure details form provided by your analytical laboratory.
- At each site, select a tube. Record its ID number, and the site at which it is to be exposed on the exposure details form.
- With the absorbent (coloured) end cap uppermost, remove the bottom (white or clear) end cap and clip the tube into the holder. Ensure the tube is positioned vertically with its open end downwards
- Record the date and time of the start of the exposure period on the exposure details form, and make a note of any site irregularities (for example building/road works, traffic diversions).
- Keep the end caps in the bag, for use when the exposure period is completed.

On the appropriate date, the samplers will need to be changed and a new batch of tubes identified for exposure. The following procedures should be followed:-

- Transport the new batch of unexposed tubes to site, together with the end caps from the last batch, any travel blanks as appropriate, and exposure details forms for both batches.
- At each site, remove the exposed tube from the sample holder and replace the end cap tightly.
- Record the time and date of the end of the exposure period on the exposure details form, against the appropriate tube number.
- Make a note of any site irregularities (building/road works, traffic diversions), also anything which might affect, or even invalidate, the tube's results (for example tube found on the ground, insects, dirt, or liquid inside the tube) on the form.
- Select a new tube for exposure. Remove its end cap and place it open end down in the holder, as above. Record tube ID details, date and time. Tubes that are damaged or have splits in the end-caps should not be used.
- Keep the tubes in a sealed container, in a cool place (a fridge is best) until they can be returned to the laboratory for analysis, which should happen as soon as possible.

- Ensure that the tubes are used and analysed within the specified "use by" date – usually this is within 3 months of preparation.

Tubes should always be capped securely after exposure; any tubes returned uncapped to the laboratory will be rejected. When visiting sites, it is recommended that the operator takes some spare tube end caps, also some spare mounting clips and spacer blocks to replace any missing or damaged.

More precise results will be obtained by using groups of three or more tubes together, rather than single tubes alone. However, this has to be balanced against the additional cost, and multiple tube exposure is not essential, except in the case of co-location studies (see below) when it is advisable to expose tubes in triplicate.

6.1 BIAS ADJUSTMENT FACTORS

Diffusion tubes have become widely used by Local Authorities for air quality monitoring as part of the ongoing Review and Assessment process. However, as explained in section 4, diffusion tube measurements may exhibit substantial bias compared to the reference method. Clearly, this is a problem in any situation where diffusion tube results are to be compared with air quality standards or objectives. Furthermore, diffusion tubes analysed by different laboratories may exhibit very different bias, even when the tube preparation technique, tube materials, and analytical techniques are broadly the same. The reasons for this are still not fully understood.

As a result, Defra's Technical Guidance LAQM.TG(03) recommends that Local Authorities making use of nitrogen dioxide diffusion tubes in their Review and Assessment should carry out their own investigation of diffusion tube bias, then apply an adjustment factor to the annual mean if required. This investigation should be based on a co-location study of at least nine months' duration, with diffusion tubes exposed in triplicate at a suitable automatic monitoring site (their own, or alternatively a suitable AURN site).

6.2 CO-LOCATION WITH AUTOMATIC ANALYSERS

As explained above, if an annual mean based upon diffusion tube results is to be used for comparison with AQS objectives, it is important that any over- or under-estimation by the tubes (often referred to as "bias") should be quantified, and (where necessary) corrected for. This should be done by means of a co-location study: that is, by exposing diffusion tubes alongside an automatic chemiluminescent analyser, and comparing the results of the two techniques. When carrying out a co-location study:-

- Diffusion tubes should be placed within 3m of the automatic analyser inlet (1m if possible), but care should be taken that they do not block the inlet in any way.
- If the co-location study is being carried out at a roadside monitoring station, ensure that the tubes are the same distance from the road as the analyser inlet.
- The co-located diffusion tubes should be exposed in triplicate (i.e. groups of three) if possible. Ideally they should be spaced at least 10cm apart.
- The duration of the study should be at least 9 months.
- Exclude data from any months when the automatic analyser does not achieve at least 90% data capture.

- It is of paramount importance to ensure that the data from the analyser are of good quality, so good QA/QC procedures (see LAQM.TG(03)) must be applied to the automatic monitoring.
- The co-located diffusion tubes should be prepared, handled and analysed in exactly the same way as those from the other (non co-located) monitoring sites in the survey. Exposure periods should be the same, to within +/- 2 days.

Details of how to calculate a bias adjustment factor are given in Box 6.4 of the Technical Guidance, on page 6-7, so have not been reproduced here.

At the time of writing, it has not been established whether diffusion tube performance varies between roadside and urban background locations. However, there are theoretical reasons why this might be the case, so if the majority of the other sites in your survey are (for example) roadside, it makes sense to use a roadside site for the co-location study, if you have the choice.

It is not necessary for every Local Authority to do its own co-location study, and it is recognised that it would not be feasible for every LA to do this. Instead, results from studies carried out by other Local Authorities, or Netcen, or the tube supplier/analyst can be used to generate a suitable bias adjustment factor. However, it is important to ensure that:-

- the tubes are identical, being prepared and analysed by the same laboratory, using the same materials and techniques;
- the exposure period is the same as in your own survey; and
- the duration of the co-location study is at least 9 months.

A spreadsheet has been developed for Local Authorities who use NO₂ diffusion tubes as part of their air quality monitoring. It is designed to assist diffusion tube users in calculating the precision and accuracy of their results, in co-location studies where diffusion tubes are compared with automatic analysers. It can be used to calculate a bias adjustment factor (with a 95% confidence interval as an estimate of the uncertainty on the bias adjustment factor), and then to apply the bias adjustment factor to annual mean results from other NO₂ diffusion tube sites.

You can find it on the "LAQM tools" section of the Air Quality Archive at <http://www.airquality.co.uk/archive/laqm/tools.php> .

One frequently asked question is whether it is better to use a locally-derived bias adjustment factor, or one based on results from several studies at different sites. The answer to this question depends on several factors, and this issue is dealt with as an FAQ on the Review and Assessment Helpdesk site, at <http://www.uwe.ac.uk/aqm/review/> . The following text is taken directly from the FAQ on this web site, with the permission of Defra:

"The most important factors to be considered when deciding which bias adjustment factor to use are the following:

- - *Tube exposure time (1 week, 2 weeks, 1 month)*
- - *Length of the monitoring study*
- - *QA/QC of the chemiluminescence analyser*
- - *QA/QC of diffusion tubes*
- - *Siting of the co-location study*
- - *Siting of other tubes in the survey*

Local Authorities using diffusion tubes as part of their Review and Assessment are advised to report both the adjustment factor from their local study, and the "national" bias adjustment factor. However, the decision of which to use will depend upon a number of factors that will need to be considered. At the end of the day it will be up to each Local Authority to take account of these factors and set out the reasons for the choice made. Specific factors that should be addressed are:

Cases Where the Locally Obtained Bias Adjustment Factor May be More Representative:

- *Where the diffusion tube exposure periods are weekly or fortnightly (or anything other than monthly – the national database of co-location results only covers monthly exposure.)*
- *If the co-location site is unusual in some way: for example, affected by specific large NO_x sources other than road traffic, such as local industrial processes. (This is a strong indication in favour of using a locally-derived factor).*
- *For tubes exposed in a similar setting to the co-location site (open/shelter, height...)*
- *Where the duration of the whole diffusion tube study is less than one year, especially if it is less than 9 months (when adjustment is best made for a matched time period, rather than using an annual factor).*
- *Where the Review and Assessment Helpdesk spreadsheet contains data from few (i.e. less than five) other studies using the same laboratory and preparation technique – although the local result can be added to the national values to derive a new national value (see below).*
- *Where the co-location study is spread across more than one calendar year, e.g. October 2003 to September 2004 – especially where there is evidence of different national adjustment factors for different calendar years.*
- *For co-location sites with good precision for the diffusion tubes and with high quality chemiluminescence results, i.e. to national AURN standards.*

Cases Where the Combined Bias Adjustment Factor May be More Representative:

- *Where the survey consists of tubes exposed over a range of settings, which differ from the co-location site, e.g. the co-location site is in a very exposed setting and the tubes being assessed are on a building façade in a canyon-like street.*
- *Where the co-location study is for less than 9 months, although the diffusion tube monitoring is for a longer period.*
- *Where the automatic analyser has been operated using local, rather than national, QA/QC procedures.*
- *Where data capture from the automatic analyser is less than 90%, or there have been problems with data quality*
- *For co-location sites with poor precision. "*

Finally, although the chemiluminescent analyser is defined as the reference technique for NO₂, it should be remembered that it, too, has a certain amount of uncertainty associated with the results: typically around 10-15% for the annual mean (although at present, Local Authorities are not required to take this into account in Review and Assessment).

6.3 INTERPRETATION OF RESULTS

As explained in section 6.2 above, Netcen have developed a spreadsheet for Local Authorities who use NO₂ diffusion tubes as part of their air quality monitoring. It is designed to assist diffusion tube users in calculating the precision and accuracy of their results, in co-location studies where diffusion tubes are compared with automatic analysers. It can be used to calculate a bias adjustment factor (with a 95% confidence interval as an estimate of the uncertainty on the bias adjustment factor), and then to apply the bias adjustment factor to annual mean results from other NO₂ diffusion tube sites.

You can find it on the "LAQM tools" section of the Air Quality Archive at <http://www.airquality.co.uk/archive/laqm/tools.php>.

6.3.1 Application of Bias Adjustment Factors

Having calculated the bias adjustment factor from your co-location study (or obtained a bias adjustment factor from another source, e.g. the Review and Assessment website <http://www.uwe.ac.uk/aqm/review/diffusiontube270206.xls>), this should be applied to the annual mean when comparing this parameter with the AQS objective of 40 ug m⁻³ for the annual mean NO₂ concentration.

Some points to remember when using bias adjustment factors are as follows: -

- Apply a bias adjustment factor to the *annual mean* NO₂ concentration only, not to individual monthly results. Performance of diffusion tubes can vary from month to month depending on meteorological and other factors, so it is not valid to adjust monthly values in this way.
- The performance of diffusion tubes can vary over time, so is not valid to apply a bias adjustment factor obtained from a recent study to previous years' data.
- When using a bias adjustment factor in Review and Assessment reports, always report the unadjusted annual means as well. Give full details of how the bias adjustment factor was obtained.

6.3.2 When to Reject Diffusion Tube Results

Any tubes arriving from the supplier with split end caps, cracks, or other damage should not be exposed, but should be returned to the supplier. The same applies to any tubes containing large drops of liquid (fine condensation is OK).

After exposure, the following factors may cause a diffusion tube result to be unreliable, and should be recorded on the exposure sheet:

- Tube found on the ground at the end of the exposure period (reject, as it's not possible to know when it fell from its fixing);
- Insects or spiders inside the tube;

- Dirt in the tube; or
- Bonfires etc. near the site, or unusual traffic activity.

Sometimes, a diffusion tube result may be much higher or lower than usual results from the site. The first step should be to check with the analyst, to ensure that the result has been correctly calculated and reported. Have details such as the exposure period been correctly reported?

Having ruled out calculation or reporting errors, it will be necessary to decide whether the value should be rejected. Some general guidelines are as follows:

- Low concentrations (3 $\mu\text{g m}^{-3}$ or less) are rare at urban background or roadside sites in built up areas. If such a low concentration is measured at an urban site, where measured NO₂ concentrations are usually much higher, it is unlikely to be genuine, and more likely due to a faulty diffusion tube. (Of course, this does not apply at rural sites, where such low concentrations may well be typical).
- High concentrations, unless there is a reason why the result is likely to be spurious, it is best to err on the side of including high values rather than rejecting them.

6.3.3 Identifying Outlying Values from Triplets

Where groups of three or more diffusion tubes are exposed together, occasions may arise where one or more of the results differs substantially from the others, and may be considered suspect.

If four or more diffusion tubes are exposed together, it is possible to use a statistical test (such as Grubb's test or Dixon's test) to identify an outlying value. However, in the more usual case of triplicate exposures, these tests are not valid.

Instead, it is possible to use the following "common sense" approach to help identify and exclude an outlying value:

1. Calculate the coefficient of variation (CoV, sometimes also called the relative standard deviation) of all the triplets in your survey. This is the ratio of the standard deviation to the arithmetic mean, expressed as a percentage.
2. The CoV of the "suspect" triplet should be compared with those of the rest of the survey. If it is substantially higher, this may indicate a problem with one or more of the three results.
3. In some cases, there may be one result that is clearly much higher or lower than the other two, and this can confidently be rejected. However, on other occasions there may be considerable "spread" in the three results, but with no clear outlier.
4. From experience with Palmes type NO₂ diffusion tubes, a CoV of around 10% or less would be expected. A CoV of more than 20% would indicate that the precision of the triplet of results is relatively poor.

7 References

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