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Investigation into Diffusion Tube Bias Adjustment Factors

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Executive Summary

The Scottish Government commissioned this investigation of bias correction factors used by local authorities to correct nitrogen dioxide (NO_2) passive diffusion tubes. This was in recognition of the important role played by diffusion tubes as a source of data to support the National Modelling Framework for Scotland. However, it had been noted that some bias adjustment factors had been falling year on year and the reason for this was unknown. When the correction factors were applied to diffusion tube monitoring data, they reduced the reported concentrations of NO_2 by greater amounts year on year – resulting in a reported improvement in air quality. This contrasted with an examination of uncorrected passive tube data which showed little change over the years, with an apparent fluctuation in automatic monitoring data year on year. The Scottish Government wished to understand more about the role of bias adjustment applied to diffusion tubes and whether current practice might be leading to misleading information on trends in NO_2 concentrations.

Diffusion tube and automatic monitoring data for all co-location sites in Scotland over the period 2008 to 2017 have been examined. Current practice has been determined through questionnaires sent to all 32 local authorities and to the six laboratories being used to supply and analyse the tubes, as well as to the company responsible for quality assurance of the automatic analysers. In addition a detailed update of a previous literature review into factors influencing the performance of diffusion tubes has been prepared. The national co-location site at Marylebone Road in London has allowed a direct comparison to be made between bias adjustment factors for the different laboratories being used.

The main finding is that the apparent evidence for a downward trend in the overall bias adjustment factors for Scottish Laboratories appears to be mainly an artefact of the changes in the sites that have been used to derive the overall factor, together with some chemistry-driven downward trends due to the declining NO_2 and NOx concentrations.

The following are the main observations:

- the literature suggests that key factors affecting bias are a) the chemistry taking place within the tubes during exposure, which will depend on concentrations of NO_2, NOx and O_3 and b) the wind-induced shortening of the diffusion length;
- wind speed has not changed of the period 2008-2017, so is unlikely to be responsible for any change in bias;
- concentrations of NO_2 and NOx have changed over the period 2008-2017, which may well have led to decreasing bias adjustment factors, but this does not necessarily apply to all sites;

- bias adjustment factors can vary significantly from site to site, for example, from 0.60 to 0.94 in one year for tubes exposed at 6 sites in Edinburgh. For a given site there is less variation from year to year;
- site-to-site variations in bias probably relate to microscale exposure effects in terms of wind flow across the sample head that can alter the effective diffusion length. At roadside sites the variations may also be because of small differences in the location of the diffusion tube and the automatic analyser inlet, which may cause one to be closer to the road than the other;
- results for the Queen Street / Wemyss Place co-location site in Edinburgh showed a step change in bias, which was due to a step change in the automatic analyser results. This emphasises that uncertainty in automatic monitors can also affect the bias derived from co-location studies.
- the overall bias adjustment factor from all co-location studies is much more stable when a large number of co-location results is used. For the Scottish laboratories overall factors are based on a limited, and highly varying, number of co-location results (in the range of 1 to 12 sites).

The following observations are made about trends in concentrations in Scotland over the period 2008-2017:

- a significant downward trend of around 2.3%/yr (or 23% over 10 years) is evident for both NO_2 and NOx concentrations, based on results for 43 long-term sites. The downward trend for NO_2 is greater at rural and urban background sites, at around 3.6 to 3.7%/yr.
- The results for the 3 automatic monitors with longer data runs at roadside sites in Edinburgh also show a downward trend over the period 2008-2017 in the range of 3 to 4%/yr. It is therefore to be expected that diffusion tube results, after bias adjustment, would also show a downward trend in concentrations in Edinburgh.

Uncertainty in trends derived from diffusion tubes will be reduced if bias adjustment factors:

- are based on a consistent set of co-locations sites;
- are based on as large a number of co-location sites as possible (especially if sites are changing from year to year);
- are derived from laboratories operating with good precision; and
- are not changed from local to national factors from year to year.

It is recommended that Scottish local authorities should:

- continue to apply laboratory-specific bias adjustment factors to their diffusion tube results, as this will ensure that the overall results for a local authority (but not necessarily those for individual sites) will be closer to the 'true' value as defined by automatic analysers;

- report all their co-location studies to the national database every year;
- take into account laboratory performance when selecting a laboratory for diffusion tube analysis;
- consider whether any changes to their co-location strategies would help reduce the variability of the bias adjustment factors as sites come and go;
- ensure that the diffusion tubes at roadside and kerbside sites are placed at the same distance from the kerb and at the same height as the inlet to the automatic analyser, to the nearest 10 cm if possible;
- avoid different combinations of co-location sites from year to year; and
- use results from as consistent a set of co-location sites as possible, especially if using local co-location sites to derive a local bias adjustment factor.

These recommendations should improve the consistency of diffusion tube results and make evidence of trends more reliable, but there will still be significant differences in diffusion but bias from site-to-site that cannot be overcome by applying bias adjustment factors. Thus absolute values of NO_2 concentrations from diffusion tubes will remain more uncertain than those from automatic monitors.

Finally, it is recommended that the Scottish Government and/or SEPA consider using the findings of this study to prepare guidance for Scottish local authorities on how to generate and apply bias adjustment factors. This should consider, amongst other matters:

- the minimum number of co-location sites to aim for;
- the need to ensure consistency in the co-location sites over time;
- minimum standards for laboratory performance to ensure reliable results;
- whether a long-term site should be established in Scotland, at which all laboratories expose tubes, to accompany the site at Marylebone Road, London;
- the suitability of sites for co-location studies; and
- how best to apply bias adjustment factors.

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1 Introduction

1.1 In the autumn of 2017, the Scottish Government commissioned an investigation of bias correction factors used by local authorities to correct nitrogen dioxide (NO_2) passive diffusion tubes. This was in recognition of the important role played by diffusion tubes as a source of data to support the National Modelling Framework for Scotland. It had been noted that some bias adjustment factors had been falling year on year and the reason for this was unknown. When the correction factors were applied to diffusion tube monitoring data, they reduced the reported concentrations of NO_2 by greater amounts year on year – resulting in a reported improvement in air quality. This contrasted with an examination of uncorrected passive tube data which showed little change over the years, with an apparent fluctuation in automatic monitoring data year on year. The Scottish Government wished to understand more about the role of bias adjustment applied to diffusion tubes and whether current practice might be leading to misleading information on trends in NO_2 concentrations.

1.2 Palmes Diffusion Tubes [1] have been used since the 1980s to measure ambient NO_2 concentrations in the UK (hereinafter Palmes Diffusion Tubes used for the analysis of NO_2 will be referred to as “diffusion tubes”). In the early days of their use, concentrations were derived from the application of the theoretical diffusion coefficient (see details in the Literature Review that is provided separately). It became apparent during their wider use in the 1990s that results could deviate from those of chemiluminescence analysers (which were, and still are, being treated as reference samplers). Some users had started to apply adjustment factors to correct for the bias of the tubes identified from the results of co-location studies. During the 2000s, with the development of Local Air Quality Management, there was a growth in the use of diffusion tubes and of the number of laboratories preparing and analysing the tubes. Reviews of the data in the early 2000s showed that there were systematic differences in the bias, both positive and negative, between laboratories [2]. It was recognised that adjustment factors should be applied to correct for the bias and reduce the uncertainty of published results. In 2003 Defra started publishing the results of co-location studies in the National Diffusion Tube Bias Adjustment Factor Spreadsheet [3], to help users of diffusion tubes allow for the bias before reporting their results. A few years after this, Defra set

1 Palmes diffusion tubes are named after Edward Palmes who developed the concept of using diffusion of gases down a concentration gradient within a tube.

2 For example, in the report prepared for Defra by Laxen, D. and Wilson, P. (2002) Compilation of Diffusion Tube Collocation Studies Carried out by Local Authorities, Air Quality Consultants, available at: http://www.aqconsultants.co.uk/AQC/media/Reports/NO2-Diffusion-Tube-Performance-(Final).pdf

3 Published several times a year and available at: https://laqm.defra.gov.uk/bias-adjustment-factors/national-bias.html . The latest one used for this study was version 09/18, published in September 2018. Local Authorities can choose whether or not to submit results.

up a Working Group on Harmonisation of Diffusion Tubes, which led to the publication of guidance in 2008 [4]. The Working Group identified many differences in the practice of laboratories in preparing and analysing tubes, and the guidance was aimed at harmonising the practice. The principal of the tubes is that a grid coated in tri-ethanol-amine (TEA) at one end of the tube absorbs the NO_2, creating a nitrite compound that is then analysed in the laboratory. The Guidance did not standardise the preparation of the tubes completely and thus there remain two different preparation methods, which, at the basic level, can be categorised into the use of 50% TEA in acetone or 20% TEA in water (previously there had also been tubes prepared with 50% TEA in water or 10% TEA in water). There are also differences allowed for the extraction of the nitrite from the exposed tubes, as well as two approaches to the analysis of the collected nitrite, namely manual colorimetric and automated colorimetric, with the option to use ion chromatography. Despite the attempt to harmonise procedures there are still systematic differences between laboratories and there is a continued need to apply bias adjustment factors.

1.3 This report provides:

- an updated literature review that covers new material published since the detailed literature review published in 2008. The new material has been combined with the findings of the previous review to provide the best possible understanding of the factors affecting the performance of diffusion tubes;
- a summary of the laboratories being used by all Scottish local authorities to supply and analyses diffusion tubes, together with the approach being used to apply a bias adjustment to the published diffusion tube results. Changes that have been made are highlighted;
- an understanding of changes made by laboratories supplying and analysing diffusion tubes and of changes to the automatic monitoring network;
- an analysis of trends in concentrations (NO_2, nitrogen oxides (NOx) and ozone (O_3)) measured using automatic analysers and meteorological parameters (wind speed, temperature and humidity), as these are factors that may influence diffusion tube performance;
- a comparison of the performance of the laboratories used by Scottish Authorities at a fixed site (Marylebone Road in London [5]) in relation to the results of an automatic analyser;
- a detailed analysis of diffusion tube results for the City of Edinburgh using different approaches to bias adjustment;

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4 Report: Diffusion Tubes for Ambient NO_2 Monitoring: Practical Guidance, (AEAT/ENV/R/2504 - Issue 1a), February 2008, Available at: https://laqm.defra.gov.uk/documents/0802141004_NO2_WG_PracticalGuidance_Issue1a.pdf

5 The Marylebone Road site is the only location in the UK where all laboratories expose their tubes. It is a kerbside site alongside a busy main road in central London.

- an analysis of how the selection of co-location sites can affect the overall bias adjustment factors and hence the trend observed; and
- a discussion of the findings and recommendations to improve the quality of the diffusion tube results so as to ensure the best possible indication of trends in concentrations.

1.4 The focus of this study has been on practices since 2008, when the guidance was issued, up until the end of 2017. It is also important to note that, while the focus of the report in on 'bias adjustment factors', there are places where the discussion focusses on diffusion tube 'bias', which is the extent to which the result deviates from the results from an automatic chemiluminescence analyser ("automatic analyser"). A positive bias (i.e. where the tube gives a higher concentration than the automatic analyser) requires application of a bias adjustment factor that is less than 1.

2 Literature Review

2.1 A detailed literature review has been carried out. The Summary from that report is reproduced here, with the full report provided separately.

2.2 The review makes clear that it is well-known that the accuracy (or bias) of a diffusion tube measurement may be influenced by a range of factors in all stages of the diffusion tube method: preparation, exposure conditions, quantification of absorbed nitrite and calculation of the NO_2 concentration. The state of knowledge on these biases was reviewed around 2007-8 when Defra established a Working Group to recommend harmonisation procedures for the diffusion tube methodology in the UK. The following are the key conclusions of the review set out in detail in the full report. It is made clear that the biases act independently; therefore the raw diffusion tube concentration is the net linear summation of all (if any) individual positive and negative biases that influence that diffusion tube deployment. This makes it virtually impossible to disentangle the relative contributions of the different sources of bias from field experiments.

Diffusion Tube Preparation and Analysis

2.3 A dearth of new evidence means it is still unclear whether method of preparation has significant influence on diffusion tube accuracy. The corollary is that no new evidence contradicts the Defra WG recommendation that preparation via dipping grids in 50% TEA in water or pipetting 50 µL of 20% TEA in water have least bias. In principle it should not matter how the TEA is transferred to the grids as long as sufficient TEA is permanently transferred for the TEA to be greatly in excess of the NO_2 to be captured, which should generally be the case.

2.4 The complete absence of published evidence on effect of colour reagent conditions for the colorimetric quantification of absorbed NO_2^- means that no update can be provided. It has to be assumed that where a high standard of laboratory QC/QA procedures is followed, particularly for laboratories subject to regular 'round robin' and other external quality assurance procedures, the extraction and quantification of the absorbed NO_2^- should not contribute a significant source of bias.

Effect of Humidity on Stoichiometric conversion of NO_2 to NO_2^-

2.5 The potential for low ambient humidity during deployment to cause negative bias in TEA-based NO_2 passive samplers is not sufficiently acknowledged by users of diffusion tubes. A recent study has argued that for relative humidity (RH) less than ~75-80% the conversion of NO_2 to NO_2^- is less than unity, and hence concentrations calculated under the assumption that all NO_2 was converted to NO_2^- are biased low. For much of the UK, average RH is around 80%, but there are locations around the UK and/or substantial periods during the year when RH during a diffusion tube exposure is lower than 75% and hence potentially giving rise to negative bias (or 'under-read') from this cause.

Effect of Wind Speed, Humidity and Temperature on Uptake Rate

2.6 Both chamber and field experiments still provide some contradictory results on the significance of wind effects on diffusion tubes. However, it seems clear from consideration of all the literature to date (and from scientific expectation) that positive bias from wind effects exists and can be very large, albeit that the extent of sensitivity of the bias to increasing wind speed is not clear. Under even moderate wind conditions, a number of chamber and field experiments suggest tens of percent positive bias. Close inspection of data across a number of chamber experiments suggests some consistency for an overestimation of the order of 20% compared with the theoretical uptake rate even at the lowest wind speeds that will be routinely encountered in ambient deployments – however, as noted below, this could be due to the assumed value of diffusion coefficient, rather than wind effects (or both).

2.7 Results from chamber experiments also suggest that lower RHs reduce the NO_2 uptake rate of diffusion tubes, consistent with the observation of low RH reducing stoichiometric conversion of NO_2 to NO_2^-.

2.8 Of the three meteorological variables, the evidence suggests that sensitivity of the diffusion tube uptake rate is smallest for temperature, of the order of a few % per 10ºC. Temperature influences the rate of NO_2 diffusion (this is a known, relatively small effect), the relative humidity, and potentially also the physical phase of the TEA, although the latter is not believed to be important for ambient conditions. Due to the link between temperature and relative humidity, it is possible that effects attributed to temperature may be through its effect on relative humidity.

2.9 It is difficult to pinpoint the individual effects of these factors on bias because the bias between a diffusion tube and a reference analyser values may be the net effect of several potential factors acting together, e.g. wind, humidity, within-tube chemistry, and long-term degradation of absorbed NO_2^-. This is particularly the case for field evaluations where diffusion tube exposures can vary between a few days to 5 weeks, and which are subject to varying environmental conditions during exposure that are usually not measured, or measured a long way from the diffusion tube deployments.

2.10 An alternative explanation for chamber exposure data that suggest positive bias compared with the theoretical uptake rate, even at low wind speeds, is that an inappropriate value for the diffusion coefficient of NO_2 in air is being used for the theoretical uptake rate – one that is too low and consequently has the effect of giving rise to a positive bias in derived average NO_2 concentration. This has not been discussed in the literature (but is discussed separately below).

2.11 Considerable accumulated evidence indicates that positive bias from wind effects can be offset either by use of a coarse mesh across the tube and/or with the tubes placed within a shelter. Membranes across the mouth of the tube may overcompensate for wind-induced positive bias by providing resistance to free molecular diffusion and reducing uptake below its theoretical value. At present, local and national network diffusion tubes in the UK are not deployed with either meshes or protective shelters.

Within-Tube Chemical Generation of Additional NO_2

2.12 Model simulations demonstrate potential for intrinsic positive bias from additional NO_2 production from reaction between co-diffusion of NO and O_3. For locations where both NO and O_3 are relatively high compared with NO_2 (e.g. urban background) this positive bias can average as high as ~25%. For roadside locations, where O_3 may be low, and for rural locations where most NOx is already in the form of NO_2, this bias may be only a few %.

2.13 Experimental validation of a chemical bias is again complicated by the presence of other potential biases (wind and humidity effects, long-term absorbent degradation) simultaneously impacting on diffusion tube performance.

Exposure-Duration 'Loss' of absorbed NO_2^-

2.14 Although the evidence is sparse, it is consistent that there may be a small negative bias in diffusion tube-derived NO_2 concentrations associated with a slow chemical degradation of the absorbed NO_2^-, of a few % per week, particularly in sunnier, warmer conditions, which becomes more relevant for exposure durations of several weeks.

Uncertainty in the Value of the NO_2 Diffusion Coefficient

2.15 The original Palmes value for the NO_2 diffusion coefficient (temperature corrected for the UK) has been used in all diffusion tube measurements seemingly without further question. The value was derived from semi-empirical theoretical consideration of gas behaviour because it is very hard to measure experimentally. The one experimental value (from 1937) is a factor 0.89 of the Palmes value. Although semi-empirical methods for estimation of gas diffusion coefficients are well-established, a more recent calculated value is a factor 1.20 of the Palmes value.

2.16 The greater diffusion tube uptake rates measured in some chamber experiments, compared with uptake rates derived using the theoretical equation A.D/L, where A= cross-sectional area of the tube cm^2, D= diffusion coefficient 0.154 cm^2/s at 20ºC, and L = diffusion length down the tube, could be explained if D was in reality greater than the standard Palmes value used. However, it is difficult to control for all variables that may influence uptake experimentally, even in a chamber study. If the true value of D was larger than the Palmes value currently used then NO_2 concentrations currently calculated from diffusion tube measurements are overestimates of the true NO_2 concentrations, i.e. diffusion tube-derived values would be positively biased (and vice versa).

2.17 There should be much greater acknowledgement that the value for D is not known with certainty, and particularly that it is not known to the precision implied by use of a value expressed to 3 significant figures. One evaluation suggests an uncertainty in D of ±35%. This does not mean random uncertainty across individual diffusion tube exposures in the range ±35%, because D has a single true value; instead it means that the true value of D is not known so that all diffusion tube-derived NO_2 values may be an unknown percentage too high or too low. It is important to note, however, that this particular potential source of diffusion tube bias is not an issue for diffusion tubes that are 'bias adjusted' against a chemiluminescence analyser, since if this was the only source of diffusion tube bias at all diffusion tube exposure locations, including the co-location, then it would be accounted for through the bias adjustment factor.

Bias in Comparison Against a Reference Analyser Determination of NO_2

2.18 Diffusion tube bias is assessed by co-location with chemiluminescence analysers. Diffusion tube values calculated using the Defra WG recommended value for D (which assumes an average ambient temperature of 284 K) must be decreased by a factor 284/293 = 0.969 to compare against a chemiluminescence analyser that has been set up to report NO_2 concentrations referenced to the EU reporting temperature of 293 K. Failure to make this adjustment means the diffusion tube-derived value in the comparison is ~3% too high.

2.19 Chemiluminescence analysers using a heated molybdenum NOx-to-NO converter (as is usually the case in the UK) are subject to positive bias in NO_2 measurement from HNO_3, HONO and PAN also present in the air. The bias is much lower (e.g. a few %) for locations close to fresh emissions of NOx, such as roads, compared to locations with more photochemically-aged air. Bias between a 'thermal converter' chemiluminescence analyser and co-located diffusion tube due to this issue would be offset if the other oxidised N-containing gases also gave rise to absorbed NO_2^- in the diffusion tube, but this has not been tested.

2.20 Analyser values may be uncertain by up to ±15%, as set out in the EU Directive for these measurements.

3 Local Authorities Practice

Local Authority Information

3.1 All 32 local authorities in Scotland have been contacted by email with a series of questions (the questions are reproduced in Appendix A1). The aim has been to establish:

- which laboratories are being used to supply and analyse diffusion tubes,
- whether co-location studies are being carried out and, if so, whether the results are being reported to the national database; and
- what bias adjustment factors are being used,

with a particular emphasis placed on changes that have taken place since 2008.

3.2 The response to the questions submitted to the local authorities has been very successful. All local authorities replied, apart from Shetland Council, which is known not to use diffusion tubes. A summary of the responses is provided in Appendix A2.

3.3 The laboratories being used in Scotland are summarised in Table 1. Most local authorities had used the same laboratory over the period, but 4 had changed laboratory: Falkirk (changed from Socotec to Gradko 50% TEA in acetone in 2015), North Ayrshire (changed from Gradko 20% TEA in water to Glasgow Scientific Services in 2014), Scottish Borders (changed from South Yorkshire Laboratory to Edinburgh Scientific Services (date unknown)), and South Lanarkshire (changed from Glasgow Scientific Services to Edinburgh Scientific Services in 2007), with one, Fife, changing from Tayside to Socotec in 2018 [6]. Changes in laboratory will clearly have an impact on the bias adjustment factor being applied, and may affect information on trends. Tubes prepared using both 20% TEA in water and 50% TEA in acetone have been employed depending on the laboratory used, and for Gradko and Socotec, depending on client choice [7].

[6] If national factors are applied, then additional uncertainty is introduced when changing laboratory mid-way through a calendar year, as there may be seasonal variations in bias adjustment factors that are not allowed for in the use of annual factors. The use of local factors for the two periods should overcome this issue.

[7] Even for these two tube types there are different ways of coating the grids with TEA.

Table 1: Laboratories Used by Scottish Local Authorities in 2017

Laboratory	Tube Type	Number of Local Authorities using the Lab in 2017
Glasgow Scientific Services	20% TEA in Water	13
Edinburgh Scientific Services	50% TEA in Acetone	8
Tayside Scientific Services [a]	20% TEA in Water	4 (reduced by one in 2018)
Aberdeen Scientific Services [a]	20% TEA in Water	3
Gradko	50% TEA in Acetone	1
Gradko	20% TEA in Water	1
Socotec [b]	50% TEA in Acetone [c]	1 (increased by one in 2018)
Diffusion Tubes Not Used	-	1
Total	-	32

[a] The lab analyses the tubes, but the tubes are provided by Gradko.

[b] Formerly ESG Didcot and before that Harwell Scientific Services.

[c] 20% TEA in Water for 2009 and 2010.

3.4 The local authorities have used a range of approaches to applying bias adjustment factors, as is evident in Table 2. Current guidance allows local authorities to choose whether to apply national factors or local factors when adjusting for bias [8]. This will clearly have an effect on bias adjustment factors, which, in turn, is likely to affect the trends in diffusion tube data. There are also some authorities that are developing their own factors by combining local factors with some non-local factors. For instance, Edinburgh Council (using Edinburgh Scientific Services tubes) reports that it combines its local co-location studies with those for the Marylebone Road site and sites in West Lothian to produce an overall factor, while Dundee Council (using Tayside Scientific Services tubes) reports that it derives an overall local factor for its roadside sites and also an overall factor with these same sites, with the Marylebone Road result incorporated. It then uses the highest of the two. There is further discussion of the choice of bias adjustment factors in later sections of this report.

Laboratory Information

3.5 Each of the laboratories set out in Table 1 has been sent a questionnaire (see Appendix A3). The focus has been on changes that have taken place since publication of the diffusion tube harmonisation guidance in 2008. Replies have been received from all but Gradko. In general, the laboratories report that only minor changes have been made since 2008 (see Appendix A4).

[8] Advice on using local or national bias adjustment factors is available at: https://laqm.defra.gov.uk/bias-adjustment-factors/bias-adjustment.html and in Box 7.11 in Technical Guidance, LAQM.TG16 (Defra, 2018b)

Table 2: Approach to Applying Bias Adjustment Factors

Local Authority [a]	Approach
Aberdeenshire Angus Argyll & Bute Clackmannanshire East Ayrshire East Renfrewshire Eilean Siar Glasgow Inverclyde Morary North Lanarkshire Orkney Scottish Borders South Ayrshire South Lanarkshire West Dunbartonshire	Use overall national factors only
Aberdeen Dumfries & Galloway East Lothian North Ayrshire Perth & Kinross West Lothian	Use local factors only
East Dunbartonshire Falkirk Highland Renfrewshire	Use either national or local factors in different years
Dundee Edinburgh Fife Midlothian Stirling	Use combination of local and non-local factors [b]

[a] Shetland does not deploy diffusion tubes.

[b] This is discussed in the text.

Co-Location Studies

Precision

3.6 The bias adjustment factors, whether local or national, are derived from co-location studies, which are mostly based on exposure of triplicate diffusion tubes alongside an automatic monitor. The results from the co-location studies can be used to indicate the precision of the diffusion tube results.

3.7 Defra makes available information on the precision of the co-location studies being carried out (and reported to Defra [9]), according to the laboratory supplying and analysing the tubes. The results for the laboratories used by Scottish local authorities over the full 10 year period 2008-2017 are summarised in Table 3 [10]. Precision (or more importantly, imprecision) will be based on a combination of laboratory factors (in relation to tube preparation and analysis) and the operation of the co-location sites (the handling of the tubes and the precision of the automatic monitors). There is clearly variation between laboratories, with most co-location studies providing results with good precision for most of the time (87-97% and 100% in the case of co-location studies using Tayside tubes). However, in the case of Glasgow Scientific Services, the precision is not very good (only 37% of the precision results are good). It is likely that this is due principally to laboratory imprecision rather than operational imprecision.

Table 3: Precision for Laboratories Used by Scottish Local Authorities 2008-2017

Laboratory	Results with Good Precision
Tayside Scientific Services	100% (n=62)
Edinburgh Scientific Services	97% (n=63)
Gradko 20% TEA in Water	94% (n=318)
Aberdeen Scientific Services	93% (n=46)
Gradko 50% TEA in Acetone	92% (n=180)
Socotec (ESG) 50% TEA in Acetone	87% (n=312)
Glasgow Scientific Services	37% (n=70)

Exposure

3.8 The local authorities reporting their co-location results to the national database are asked to give the distance of the tubes from the inlet to the automatic analyser (in metres). In most cases they report 0 m as the distance, although in one case, Falkirk Council reported a distance of 1.8 m, while in other cases Scottish authorities reported distances for some sites as ~0.15, 0.2 and 1 m for the early years in the dataset, then resorted to reporting the distances as 0 m for the same sites. It is uncertain how accurate the information on distance between tubes and analyser inlet is, and it may well be that 0 m means <0.5 m. There seems to be no recognition that concentrations alongside roads can change rapidly over short distances (both horizontal and vertical). For instance, using the Defra Fall-off with distance calculator [11], a measured

[9] Not all co-location studies are reported to Defra

[10] Precision data issued Sept 2017, available at: https://laqm.defra.gov.uk/assets/tubeprecision2018version0918finalfull.pdf

[11] The calculator is available at: https://laqm.defra.gov.uk/documents/NO2-Fall-Off-With-Distance-from-Roads-Calculator-v4.2.xls

concentration of 45 µg/m^3 at a distance of 0.5 m from the kerb would be 48.2 µg/m^3 at a distance of 0.2 m from the kerb (with a background concentration of 25 µg/m^3). In other words, if the tubes were located 20 cm from the kerb and the analyser inlet at 50 cm then the outcome would be an 'artificial' bias of 1.07, as the diffusion tube would be sampling air with a different concentration of NO_2. This would be before any consideration of bias due to exposure factors or laboratory factors.

Laboratory QA/QC

3.9 Defra and the Devolved Administrations provide quality control standard solutions to laboratories every three months that allow performance to be assessed (of one aspect of the procedure – the analysis). This was formerly called the WASP scheme, which, since April 2014, has been incorporated in the AIR-PT scheme operated by LGC Standards and supported by the Health and Safety Laboratory [12]. Up until March 2009, the scheme was such that the performance reported was based on the results for the best four of each set of five rounds (i.e. if the performance was not good during one of the five rounds, this result was ignored). From April 2008, the performance has been reported in terms of the percentage of the results determined to be satisfactory for each round.

Table 4: Performance of Laboratories Used by Scottish Local Authorities in the AIR-PT Scheme, 2009-2017. Each Entry Shows the % of Results Determined to be Satisfactory in each Round[a]

Round	Aberdeen Scientific Services	Edinburgh Scientific Services	Socotec (ESG)	Glasgow Scientific Services	Gradko	Tayside Scientific Services
R105	100	75	100	75	100	100
R106	75	100	50	100	100	100
R107	100	100	100	100	100	100
R108	100	100	100	50	100	100
R109	100	100	100	100	87.5	100
R110	100	75	100	100	100	100
R111	100	100	100	100	100	100
R112	100	100	100	100	100	100
R113	100	100	100	100	100	100
R114	100	100	100	100	100	100
R115	100	0	100	100	37.5	100
R116	100	100	100	100	100	100
R117	100	100	100	50	100	100
R118	100	100	100	100	100	100
R119	100	100	100	100	100	100
R120	100	100	100	50	100	75

12 Further details available at: https://laqm.defra.gov.uk/diffusion-tubes/qa-qc-framework.html

Round	Aberdeen Scientific Services	Edinburgh Scientific Services	Socotec (ESG)	Glasgow Scientific Services	Gradko	Tayside Scientific Services
R121	100	100	100	25	100	100
R122	100	75	100	100	100	100
R123		100	100	100	100	100
R124	75	100	100	100	100	100
AR1	100	100	100	100	100	
AR3	100	100	100	100	100	100
AR4	100	100	100	100	100	100
AR6	100	75	87.5	100	100	100
AR7	100	100	100	100	100	
AR9	75	100	100	100	100	
AR10	100	100	100	100	100	
AR12	100	100	100	75	100	100
AR13	100	100	75	100	100	
AR15	100	100	75	0	100	100
AR16	100	100	100	100	100	
AR18	100	100	100	100	100	100
AR19	100	100	100	50	100	
AR21	100	100	100	0	100	100
AR22	100	100	100	100	100	

[a] Blank cells had no data submitted

3.10 The results are presented in Table 4 for all of the rounds since April 2009, from the AIR-PT scheme. All the laboratories shows less than 100% performance in at least one or the rounds, however, Tayside Scientific Services shows the best performance, while it is evident that Glasgow Scientific Services has the poorest overall performance. Indeed, the pattern for the laboratories is broadly similar to the precision results presented in Table 3, adding weight to the conclusion that the poor precision for Glasgow Scientific Services is likely to be due principally to laboratory imprecision rather than operational imprecision.

Automatic Monitoring Procedures

3.11 Ricardo Energy and Environment has confirmed that there have been no variations in equipment and procedures for the operation of the AURN monitoring sites; however, information on changes that may have been made by local authorities to their own sites is not available. The same audit and data ratification procedures are applied to all sites. It has, however, been reported that a change took place in 2013 to the handling of zero baseline calibration data that may have a small effect on results from Marylebone Road. This change was not applied to sites in Scotland until the 2017 dataset [13].

Results from National Bias Adjustment Spreadsheet

3.12 The full dataset behind the national bias adjustment spreadsheet published by Defra has been made available to the project team by NPL, who are responsible for collating and publishing the results. While the published spreadsheet contains only a summary of the local authority responses, the full dataset contains all of the raw data submitted by local authorities, including monthly values. This raw data is used by NPL to derive the overall bias adjustment factors using orthogonal regression applied to the raw annual mean diffusion tube and automatic monitor concentrations.

3.13 Clarification has also been sought on the operation of the national co-location study carried out at the Marylebone Road site in London. Tubes are exposed at the same height and distance from the kerb (around 1m) along the length of the housing, which runs for around 10m along the road. It has been clarified [14] that the placement of tubes is completely random from month to month, which should minimise any bias between laboratories brought about by variations in exposure and concentrations along the road.

13 David Hector, Riccardo Energy and Environment, personal communication, July 2018.

14 Nick Martin, NPL, personal communication, July 2018

4 Analysis of Trends

Trend Analysis – Automatic Monitors in Scotland

4.1 The trends in automatic monitoring have been determined for the period 2008 to 2017. Results have been collected from all available Scottish sites during this period [15]. Sites for use in the trend analysis have been filtered, such that only sites with 75% data capture over the full period have been included, and only when at least a year's worth of data are available in both the first two years and last two years. Valid data sets are available for 43 sites, broken down into 31 roadside, 6 rural, and 6 urban background (the sites are listed in Appendix A5). The analyses have been carried out using *openair* software (Carslaw and Ropkins, 2012). Two particular components of *openair* have been used, a smoothTrend fit to the data and a statistical TheilSen linear fit. In each case, monthly mean data have been used in the analysis, with data only included when the 1-hour mean data capture for the month exceeds 75%.

4.2 The **smoothTrend** function in *openair* helps check the linearity of a trend. Monthly averages are calculated from the hourly concentrations and the Generalized Additive Model finds the most appropriate level of smoothing. The plots present the smoothed trend line fitted to the monthly data, along with the 95% confidence interval, which is shown by the shading around the trend line.

4.3 The **TheilSen** function in *openair* provides an analysis of the statistical significance of trends and yields accurate confidence intervals, that are resistant to outliers. The plots show the best fit linear trend line, together with the lines representing the 90% confidence interval (p=0.1). The numerical value of the trend is also output, together with the significance of the trend, which ranges from highly significant to not significant, that is shown as follows: *** for $p<0.001$, ** for $p<0.01$, * for $p<0.05$, + for $p<0.1$ and n/s for not significant (where p stands for probability). All TheilSen trends are presented as values in percent per year (%/yr) rather than microgrammes per cubic metre per year ($\mu g/m^3/yr$), to make comparisons between sites with different concentrations more meaningful. The trend is essentially the change over the full period divided by the number of years, so a 20% reduction over 10 years becomes a 2%/yr reduction.

4.4 In addition to the formal trend analysis using open air and TheilSen linear fits, some analyses in this report are carried out using MS Excel, with linear regression fits.

NO_2 and NOx

4.5 The trends across all sites for NO_2 and NOx are provided in Figure 1. There are clear downward trends for both NO_2 and NOx, with some evidence from the smoothTrend analyses that most of the

15 Data obtained from the Air Quality in Scotland website: http://www.scottishairquality.co.uk/data/

reduction took place in the middle years, being less at the beginning, and towards the end, of the 10 year period. The trends are broadly similar when categorised into roadside [16], rural and urban background sites, as shown in Appendix A6, although the smoothTrend for rural sites shows a steady reduction rather than the pattern of most of the reduction being in the middle years, as is seen for roadside and urban background sites. The trends are summarised in Table 5, together with the significance of the trend. The average rate of reduction for NO_2 is least at roadside sites (-2.3%yr), with higher, but similar, rates at rural (-3.8 %/yr) and urban background (-3.6 %/yr) sites. The average rates of reduction for NOx are also least at roadside sites (-2.4 %/yr) but greatest at urban background sites (-3.8 %/yr). The NOx rate of reduction at rural sites is much smaller than that for NO_2, which reflects the significant change in the NO_2:NOx ratio at rural sites (see below in paragraph 4.7).

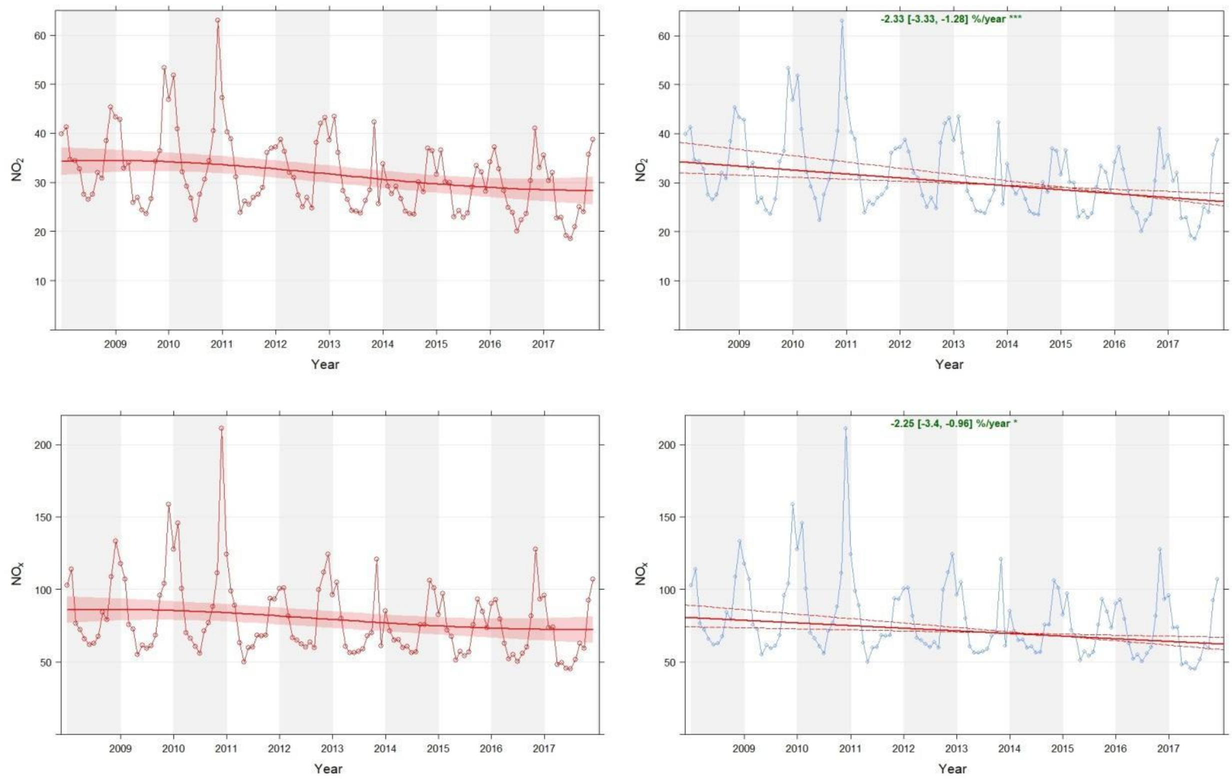

Figure 1: SmoothTrend (left) and TheilSen Trend (right) for NO_2 (top) and NOx (bottom) Concentrations at 43 Automatic Sites in Scotland, 2008-2017

[16] In this report, the term roadside is taken to include kerbside sites.

Table 5: Summary of TheilSen Trends (%/yr) in at Scottish Automatic Monitoring Sites, 2008-2017

Pollutant	Trend (%/yr) and Significance			
	All sites (n=43)	Road (n=31)	Rural (n=6)	Urban Background (n=6)
NO_2 Concentration	-2.33 ***	-2.30 ***	-3.76 ***	-3.59 ***
NOx Concentration	-2.25 *	-2.35 **	-2.64 *	-3.75 ***
NO_2:NOx Ratio	-0.35 *	-0.19 (n/s)	-1.98 ***	+0.09 (n/s)
Ozone Concentration	+0.17 (n/s)	-	+0.02 (n/s)	+0.36 (n/s)

O_3

4.6 For O_3 concentrations there is no significant trend over the 10 year period (Figure 2) and (Table 5), although the smoothTrend plot suggests some variation over this period. This variation is entirely due to the results for the three urban background sites (Aberdeen Errol Place, Edinburgh St Leonards and Fort William), with no pattern seen in the overall result for the six rural sites (Figure 3).

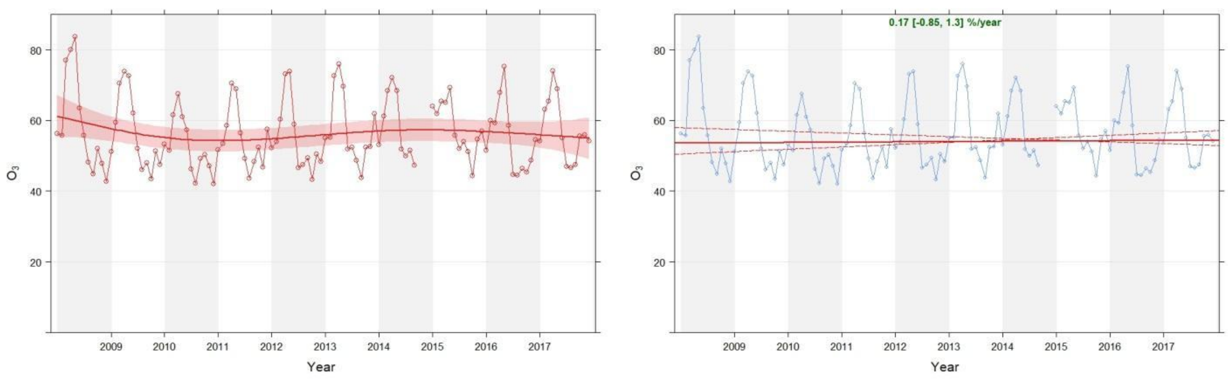

Figure 2: SmoothTrend and TheilSen Trend for O_3 Concentrations at 9 Automatic Sites in Scotland, 2008-2017

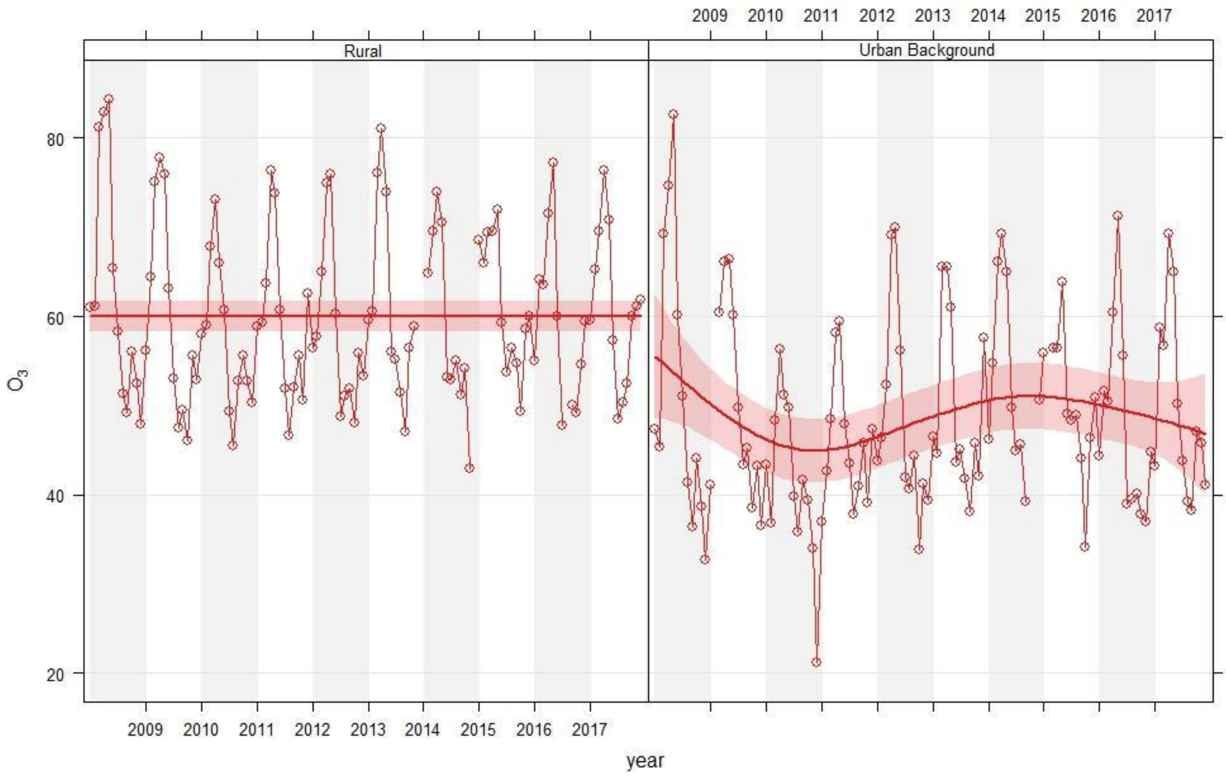

Figure 3: SmoothTrend for O_3 Concentrations at 6 Rural Sites and 3 Urban Background Sites in Scotland, 2008-2017

NO_2:NOx Ratio

4.7 The trends in the ratio of NO_2:NOx (based on the analysis of monthly averages of the hourly NO_2:NOx ratios) for all 43 monitoring sites in Scotland show slight fluctuations over the ten year, with a small downward trend of -0.35 %/yr, which is only significant at the $p<0.5$ level (Figure 4 and Table 5). On the other hand, the fluctuations are greater at the three different site types (Figure 5). It is well known that the ratios will be lower close to roads, where there is a fresh source of NOx emissions, for which the ratio of NO_2:NOx is likely to be of the order of 0.15 (i.e. 15% of the NOx emissions are primary NO_2), whereas in rural locations, the NO_2:NOx ratio will be closer to the conditions driven by photo-chemical equilibrium, which typically gives rise to an annual ratio of around 0.7 (i.e. NO_2 is 70 % of the NOx). The ratios in Figure 5 are, as expected, lower at roadside sites, but surprisingly, at the rural sites they fall from around 0.8 in 2008 to around 0.67 in 2017, at which point they are lower than the values for urban background sites.

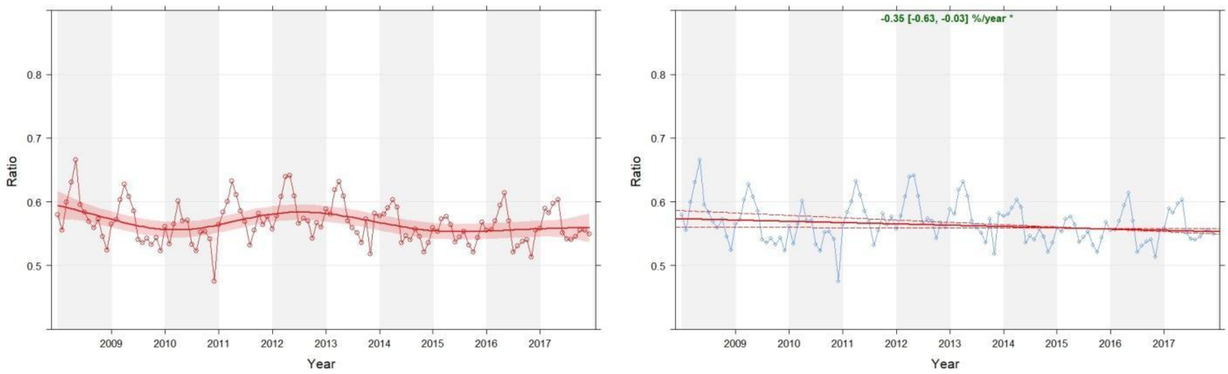

Figure 4: SmoothTrend for NO_2:NOx ratios at 43 Scottish Sites, 2008-2017

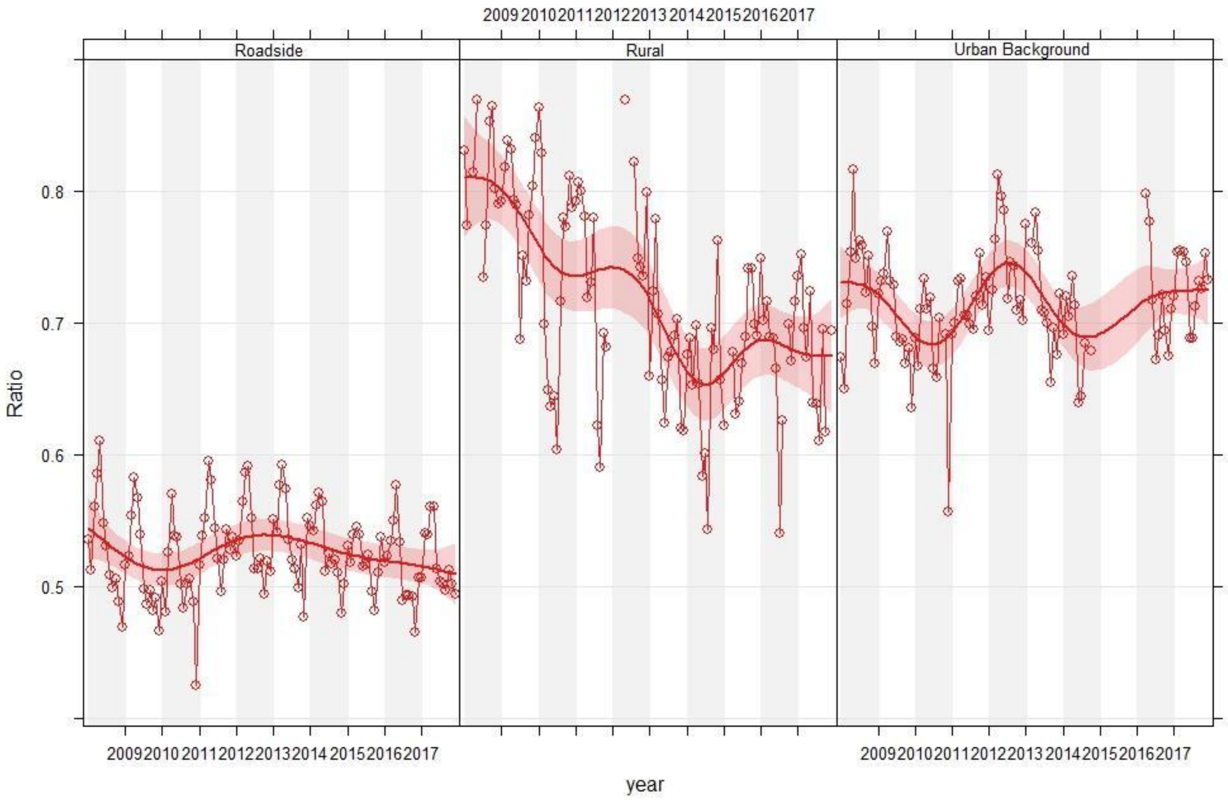

Figure 5: SmoothTrend for NO_2:NOx ratios at 31 Roadside, 6 Rural and 6 Urban Background Sites (bottom), 2008-2017

4.8 Changes in NO_2:NOx ratios at roadside sites will be determined by three factors:

- changes in NOx concentrations (the empirical evidence from other studies is that the NO_2:NOx ratios increase as NOx concentrations decrease (Air Quality Expert Group, 2004), and NOx concentrations at roadside sites in Scotland do decrease over this period (see Table 5 and Appendix A6 for the NOx trend at roadside sites));

- changes in primary NO_2 emissions (ratios will decrease if primary NO_2 decreases); and
- changes in ratios in urban background air being mixed with the roadside emissions (which are neither up or down over this period (see Table 5 and Figure 5)).

The changes in urban background air will, in turn, be related to:

- ratios in fresh urban emissions; and
- ratios in the rural air being mixed in (which have declined significantly over the ten years (see Table 5 and Figure 5)).

There will also be a linkage with urban background O_3 concentrations, which contribute to the conversion of NO to NO_2 (with the NO_2:NOx ratios increasing as O_3 increases), with urban background O_3, in turn, being linked to urban background NOx (O_3 concentrations will increase as NOx concentrations decrease, as is the case for urban background sites over this period (see Table 5 and Appendix A6)), and to any changes in rural O_3 (which shows no significant change).

4.9 The finding set out above suggest that there has been a significant decline in primary NO_2 emissions driving the change in NO_2:NOx ratios seen at roadside sites. The pattern of NO_2:NOx ratios decreasing in rural air is unexpected and currently unexplained, but diffusion tubes are generally not exposed at these locations.

Trend Analysis – Meteorological Parameters

4.10 The trends seen in diffusion tube bias may be driven by meteorological parameters. The literature review (see Chapter 2) identifies a clear influence of wind speed on diffusion tube performance, through the shortening of the diffusion length due to turbulence across the mouth of the tube. As a result, diffusion tube bias will increase as wind speed increases (although perhaps reaching a maximum), which, in turn, leads to a reduction in the bias adjustment factor as wind speed increases. There is also evidence of negative diffusion tube bias at lower relative humidities, namely those below ~78%. Temperature may also have a small positive effect on diffusion tube bias, i.e. a small negative effect on the bias adjustment factor.

4.11 Data from meteorological sites across Scotland have been examined using *openair*. The smoothTrend fits to the monthly-mean data for wind speed for the period 2008 to 2017 are show in Figure 6. The sites are ordered essentially north to south across Scotland (with Carlisle representing southern Scotland). All sites are for measurements made at airports. Average wind speeds lie between 4 and 5 m/s with fluctuations over time at all but one of the sites. There is no consistent pattern to the variations across the sites, but the range in the mean speeds is generally less than 1 m/s. There is considerably more month to month variation but with little apparent consistency, except for a period of higher speeds in the second half of 2011 that is seen at all sites. The TheilSen analysis showed no significant overall trend, apart from at the Inverness site, where a small upward trend is identified of 0.07 m/s per year, which is marginally significant ($p < 0.1$)

4.12 Results for the other parameters, namely temperature and humidity show essentially no trend over time, i.e. the smoothTrend lines are essentially horizontal (see Appendix A7). This includes an analysis of relative humidity below 78% (not shown). The relative humidity results do show a seasonal variation, and monthly mean values below 78% arise at all sites.

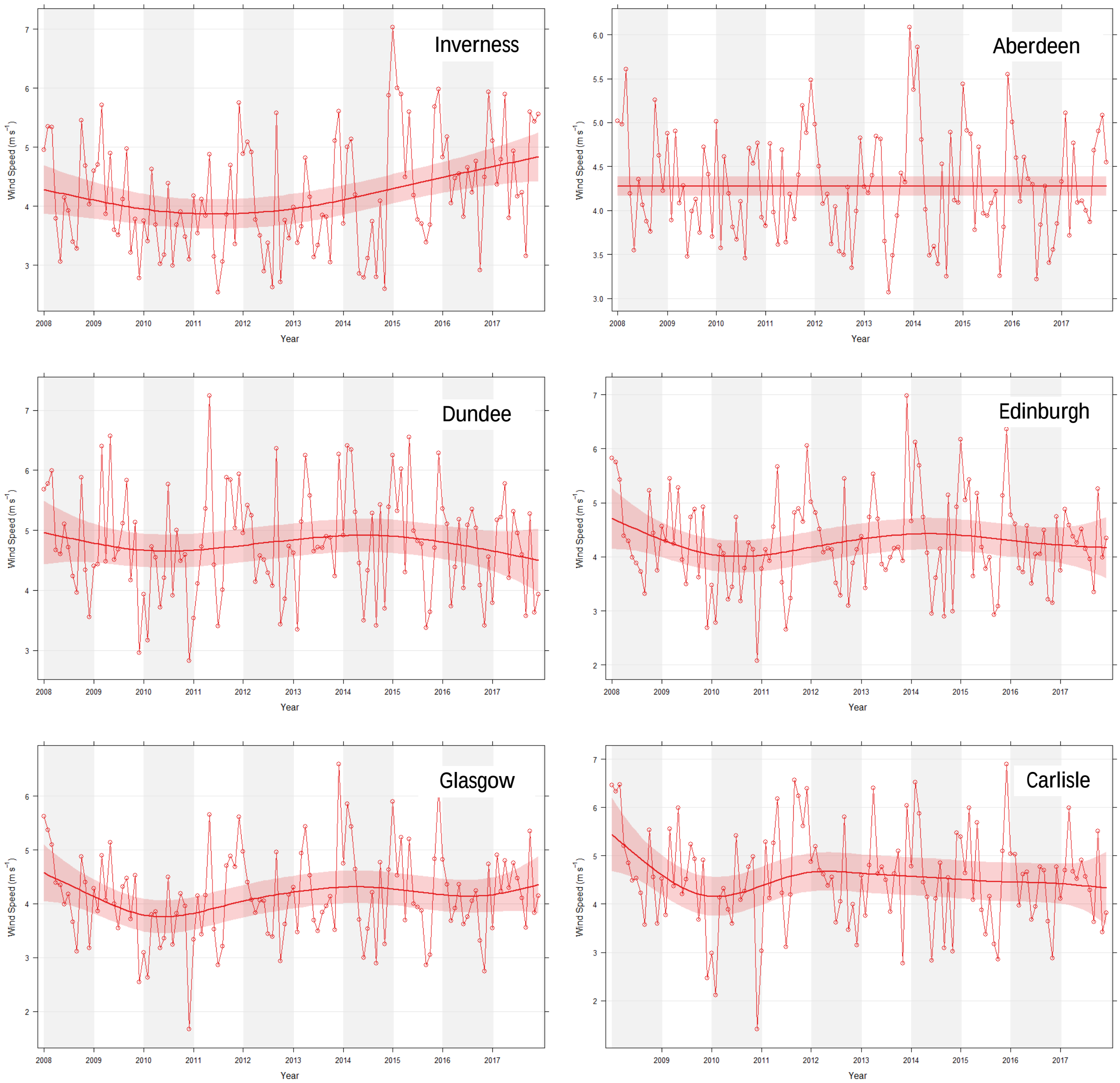

Figure 6: SmoothTrend for Wind Speed, 2008-2017.

Trend Analysis – Diffusion Tube Bias

National Bias Adjustment Factors for Laboratories used by Scottish Authorities

4.13 Changes in national bias adjustment factors for the laboratories used by Scottish local authorities are illustrated in Figure 7. This shows the overall annual factors derived for each laboratory / tube-type used by Scottish local authorities, using published factors from Defra's national database over the period 2008 to 2017 (these will be the factors used by local authorities who rely on national database values). The results for individual laboratories are shown in Figure 8, while the numbers of co-location results making up each of the national factors is set out in Table 6. It should be noted that not only do the number of co-location sites underlying each data point in Figure 7 and Figure 8 vary between years for a given laboratory, so do the proportions of roadside and non-roadside sites (mostly urban background).

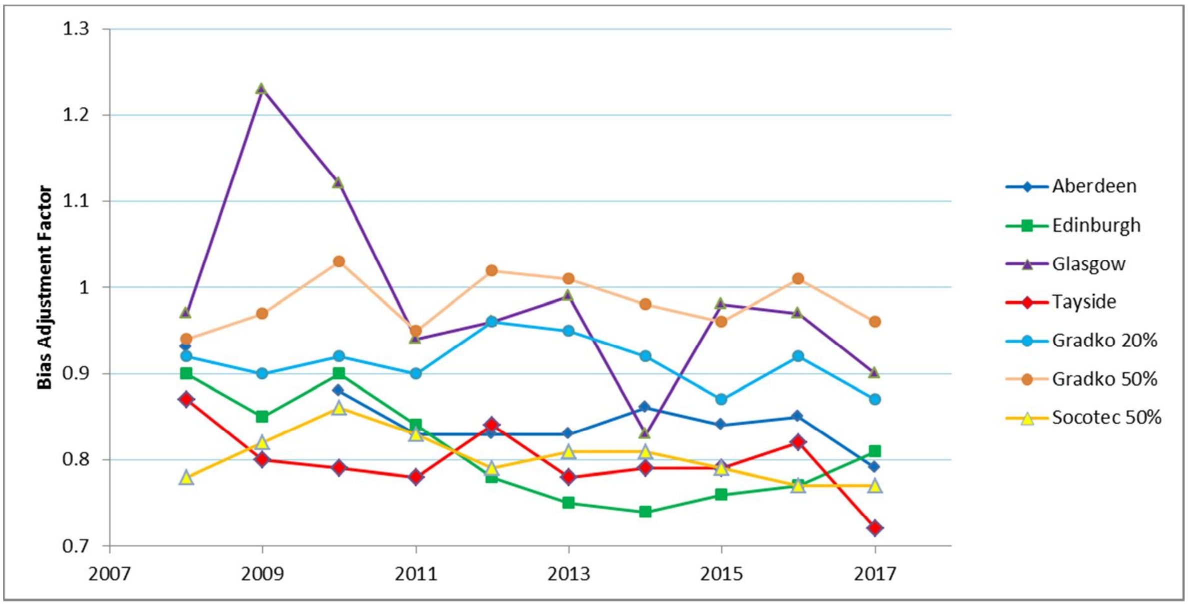

Figure 7: Trend in Published National Bias Adjustment Factors for Laboratories used by Scottish Local Authorities, 2008-2017 (based on v09-18 spreadsheet)

Table 6: Numbers of Co-Location Results for National Bias Adjustment Factors for Laboratories used in Scotland and % Non-Roadside Sites, 2008-2017

Laboratory	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017
Tayside Scientific Services	6 (0%)	6 (0%)	4 (0%)	8	7	1 (0%)	10 (0%)	10 (0%)	5 (0%)	5 (0%)
Edinburgh Scientific Services	2 (0%)	5 (0%)	6 (0%)	8 (0%)	7 (0%)	7 (0%)	7 (0%)	9 (0%)	6 (0%)	6 (0%)
Gradko 20% TEA in Water	21 (14%)	34 (14%)	42 (24%)	41 (20%)	35 (17%)	36 (11%)	22 (18%)	30 (13%)	32 (9%)	39 (18%)
Aberdeen Scientific Services	5 (20%)	-	5 (0%)	6 (17%)	1 (0%)	1 (0%)	7 (14%)	6 (17%)	7 (14%)	7 (14%)
Gradko 50% TEA in Acetone	19 (32%)	16 (31%)	16 (31%)	25 (28%)	21 (24%)	20 (20%)	10 (10%)	15 (20%)	19 (37%)	25 (44%)
Socotec (ESG) 50% TEA in Acetone	14 (36%)	27 (30%)	20 (35%)	45 (22%)	38 (24%)	44 (23%)	31 (32%)	29 (24%)	38 (29%)	30 (27%)
Glasgow Scientific Services	4 (0%)	4 (0%)	6 (33%)	7 (29%)	11 (9%)	5 (0%)	2 (0%)	12 (8%)	9 (11%)	10 (10%)

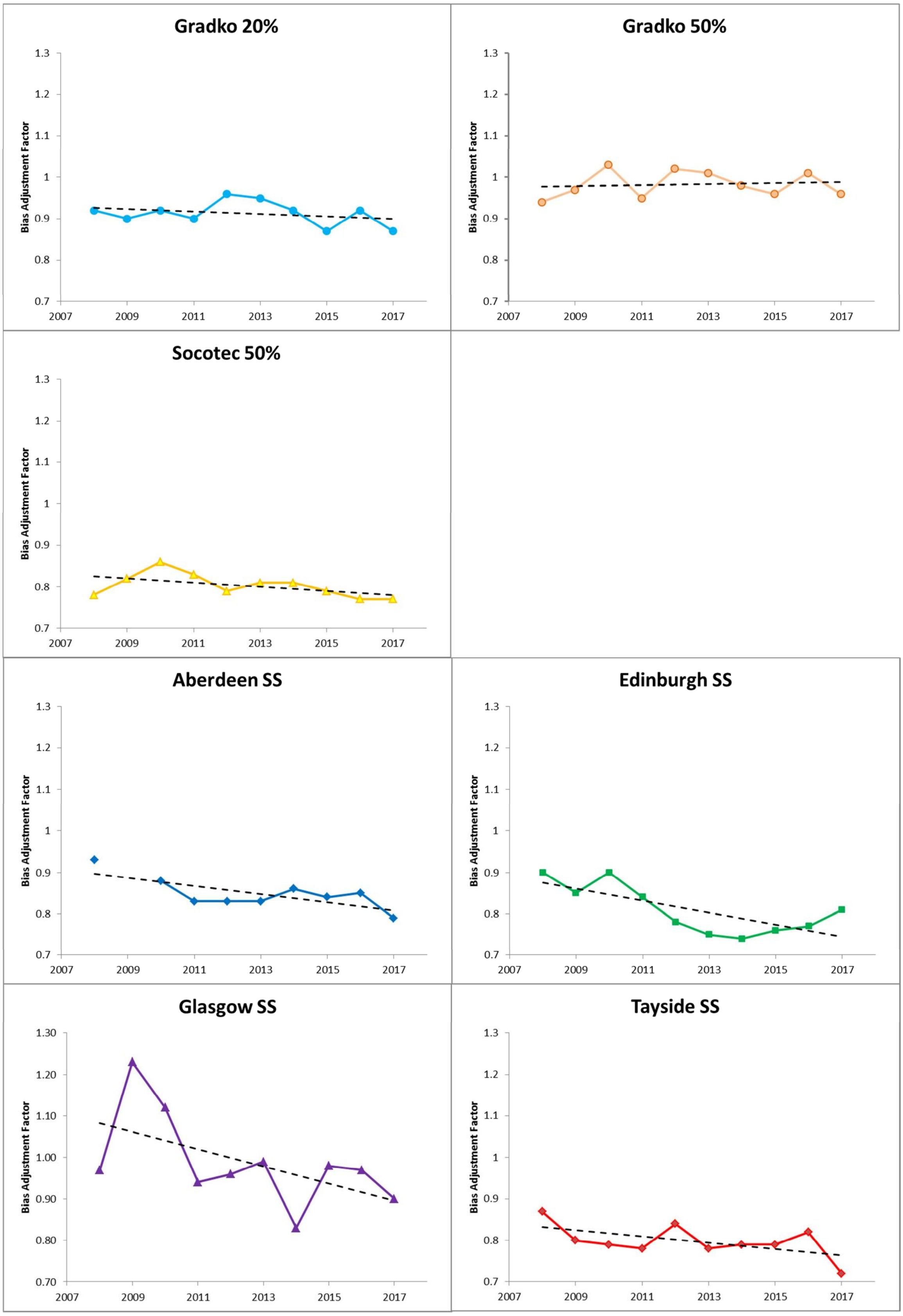

Figure 8: Trend in Published National Bias Adjustment Factors for Laboratories used by Scottish Local Authorities, 2008-2017 (based on v09-18 spreadsheet)

4.14 It is evident from Figure 7 that there are significant differences in the bias adjustment factors for the different laboratories, despite the harmonisation introduced in 2008. There is also some year-to-year variation, although this is less evident in the results for Gradko and Socotec, which are based on a large number of co-location results. The greatest year-to-year variation in bias adjustment factors is seen for Glasgow Scientific Services, which is a likely consequence of the generally poor precision achieved by this laboratory, as evidence by the co-location results and the results for the quality control solutions (see paragraphs 0 to 3.10). While the year-to-year changes could be due to factors such as wind speed or humidity, this is unlikely, as any changes would be likely to be in unison across the laboratories, which is clearly not the case (Figure 7 and Figure 8). There is also an apparent tendency for the overall bias adjustment factors to reduce over time for the Scottish laboratories, i.e. for bias to increase over time, however, only the results for Edinburgh Scientific Services tubes reach statistical significance at the $p<0.05$ level. On the other hand, the Gradko and Socotec tubes, based on a much larger number of sites, show no significant trend over the 10-year period (nor an apparent trend). The apparent downward trends in bias adjustment factors for the Scottish laboratories may reflect an element of a real increase in bias over this period, but as the trend is only significant for one laboratory it is likely to be largely an artefact of the changing mix of co-location results used to generate the national bias adjustment factors, as discussed in subsequent sections. It is also noted that while the trend in the overall bias adjustment factors for Edinburgh Scientific Services reaches statistical significance ($p=0.015$) the initial downward trend between 2010 and 2014 seems to have been replaced by an upward trend since 2014.

4.15 An analysis of the results for co-location sites in Edinburgh is presented in section 5. It is therefore appropriate to present the individual co-location results for the bias adjustment factors for Edinburgh Scientific Services tubes. These are shown in Figure 9, together with the national factor derived from these individual results, and in Figure 10 with the co-location sites visually linked to show trends at individual sites.

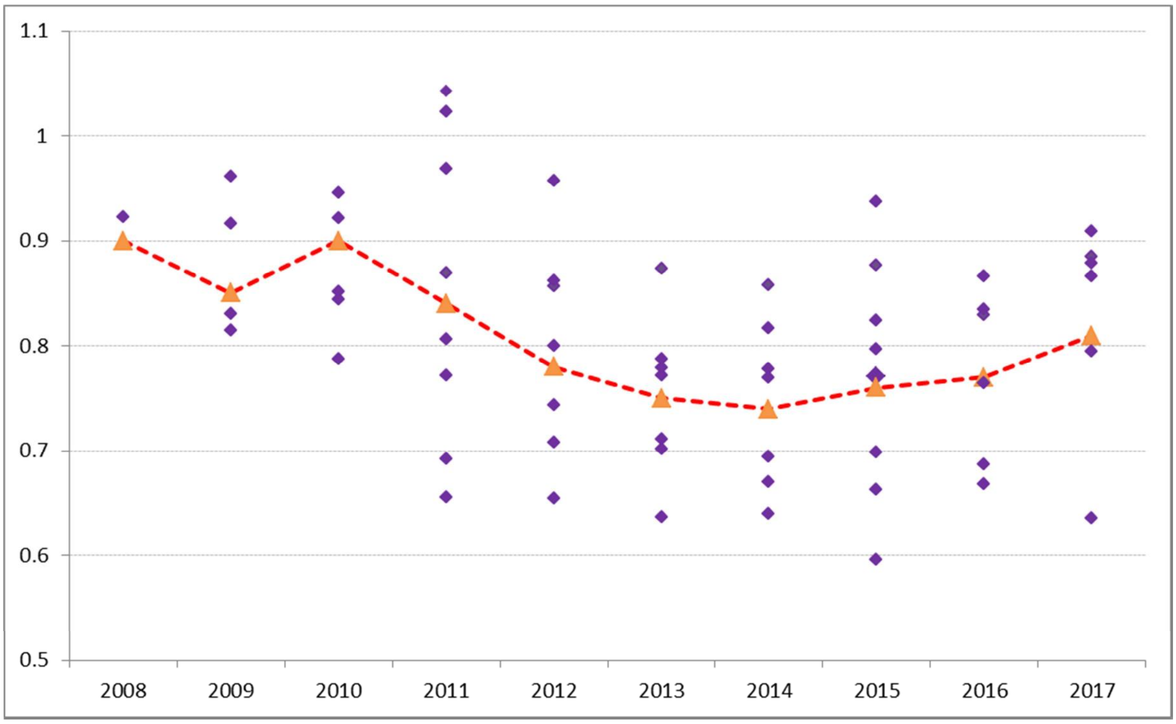

Figure 9: Individual Co-Location Bias Adjustment Factors for Edinburgh Scientific Services and the Overall National Factor (dashed line)

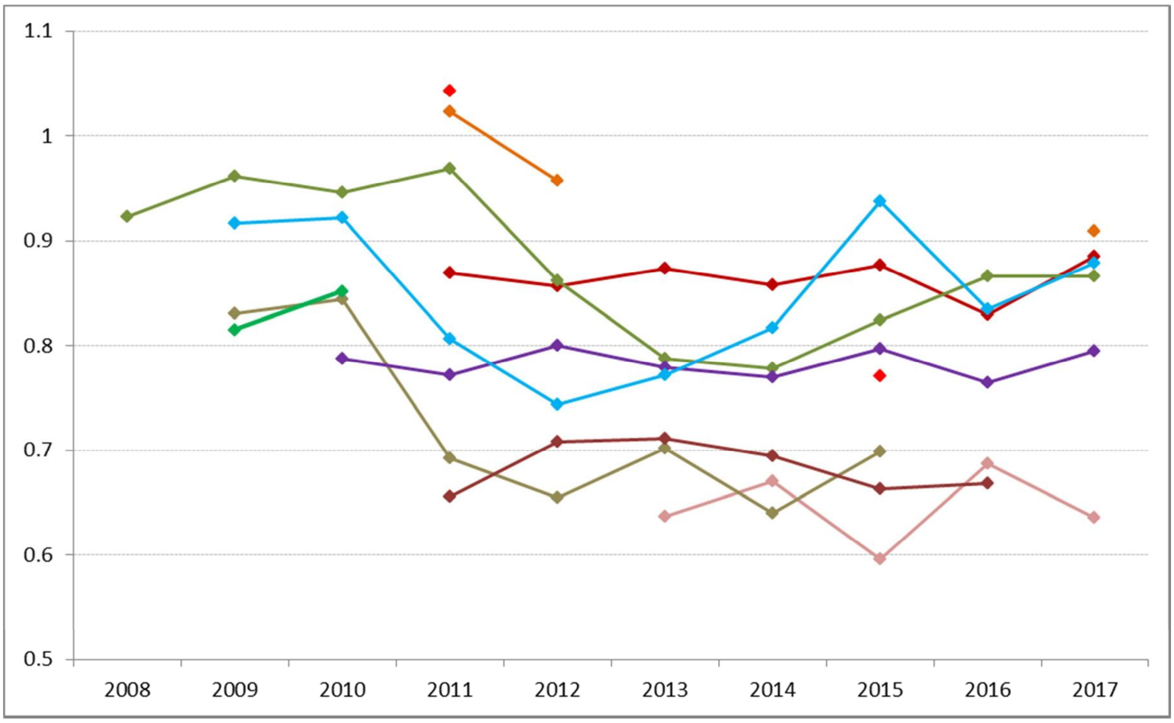

Figure 10: Individual Co-Location Bias Adjustment Factors for Edinburgh Scientific Services Linked by Co-Location Site

4.16 The results for individual co-location sites for Edinburgh Scientific Services tubes show evidence of substantial differences in the bias adjustment factors that are largely site dependent (the range is from 0.60 to 0.94 in 2015). There is also evidence of the bias adjustment factor declining at some sites between around 2010 and 2013, but this is not clear cut at other sites where trends have been more stable. This is discussed further in later sections of the report.

Bias Adjustment Factors for Laboratories used by Scottish Authorities at the Marylebone Road Site in London

4.17 To help understand the effect of laboratory on the bias (and hence bias adjustment factor) an analysis has been carried out of the intercomparison study that laboratories take part in with their tubes exposed at Marylebone Road. This reduces the number of factors that might influence bias.

Trends in NO_2 concentrations and Diffusion Tube Bias

4.18 The trend in NO_2 concentrations at Marylebone Road, measured by the automatic monitor, and those for the unadjusted diffusion tubes, are shown in Figure 11. There is a clear downward trend in the concentrations over the 10 year period at this site (further discussion of trends in concentrations at the Marylebone Road site is provided in 4.22). This is also evident in the TheilSen trend results presented in Table 7.

4.19 It is notable, however, that the patterns for the raw diffusion tube results are different for all laboratories, both in relation to each other and to the automatic monitor. This is evidence that the tube behaviour is laboratory dependent rather than site dependent, and furthermore, within a laboratory the behaviour is also dependent on the tube preparation method (Gradko results).

Table 7: Summary of TheilSen NO_2 Trends (%/yr) at Marylebone Road for the Automatic Monitor and the Raw (Unadjusted) Diffusion Tubes for Different Suppliers, 2008-2017

Source	Trend (%/yr) and Significance
Automatic Monitor	-2.52 ***
Aberdeen Scientific Services	-2.28 ***
Edinburgh Scientific Services	-2.98 ***
Glasgow Scientific Services	-2.52 ***
Tayside Scientific Services	-2.94 ***
Socotec (ESG) 50% TEA in Acetone	-2.58 ***
Gradko 20% TEA in Water	-1.43 ***
Gradko 50% TEA in Acetone	-2.54 ***

4.20 The results are also shown as change in bias over the 10 years in Figure 12. Again, there is considerable variation from laboratory to laboratory, but there is evidence of significant increases in bias at this site for tubes from all laboratories, although the magnitude of the change is very different across the laboratories (Table 8). This means that the bias adjustment factors would decrease over this period, which is not entirely consistent with the findings in the analysis of all co-location studies discussed in paragraphs 4.13 and 4.14. This suggests that there may be a factor(s) at Marylebone Road that is giving rise to a real change in bias at this site, which is not present more generally. Further discussion is provided in paragraphs 4.23 to 4.24.

Table 8: Summary of TheilSen Trends in Bias (%/yr) at Marylebone Road for Different Suppliers, 2008-2017

Source	Trend (%/yr) and Significance
Aberdeen Scientific Services	+0.49 $^{+}$
Edinburgh Scientific Services	+1.86 ***
Glasgow Scientific Services	+1.23 $^{+}$
Tayside Scientific Services	+0.86 ***
Socotec (ESG) 50% TEA in Acetone	+1.21 ***
Gradko 20% TEA in Water	+2.98 ***
Gradko 50% TEA in Acetone	+1.71 ***

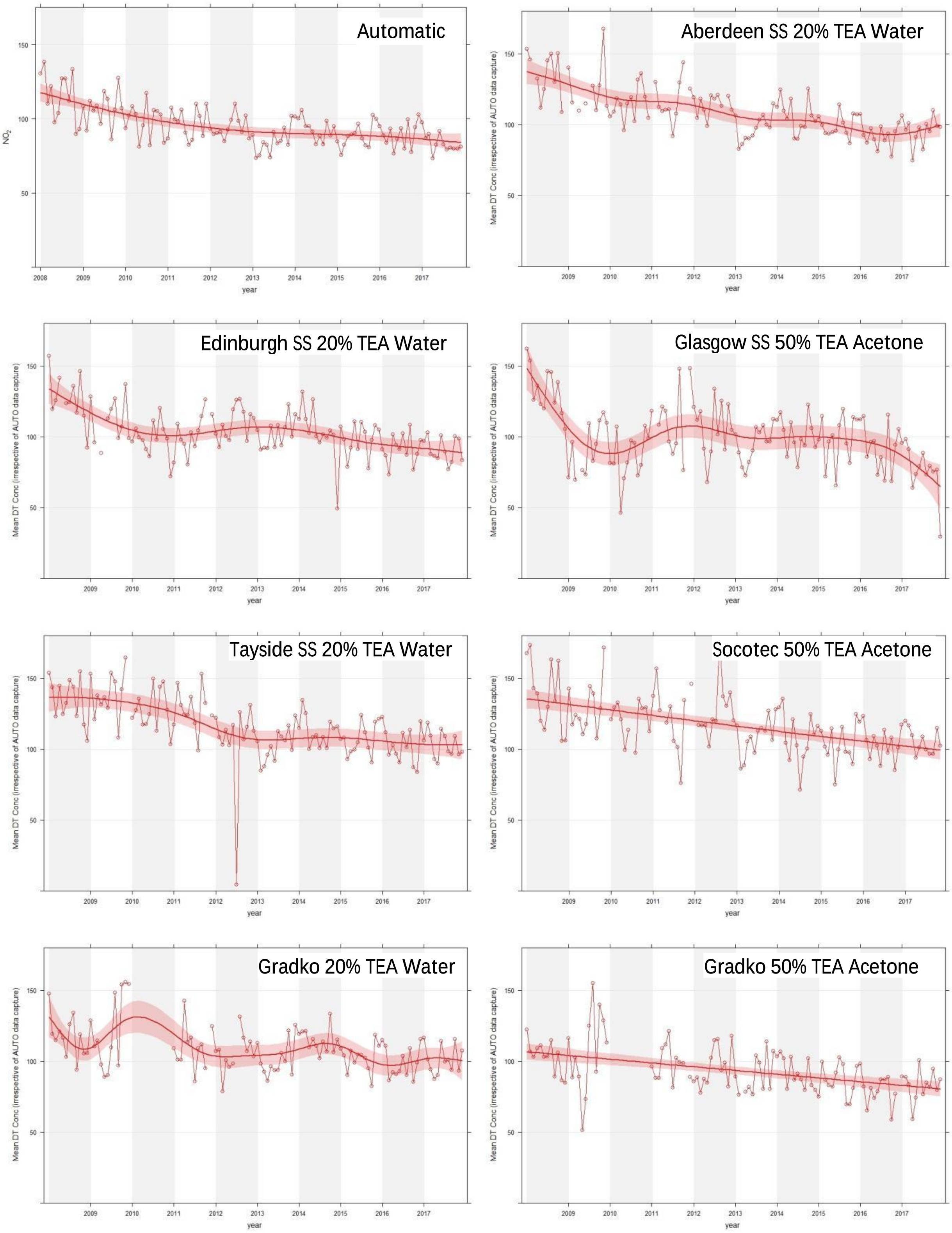

Figure 11: SmoothTrend in NO_2 Concentrations at Marylebone Road ($\mu g/m^3$). Automatic Monitor and Unadjusted Diffusion Tube Results, 2008-2017

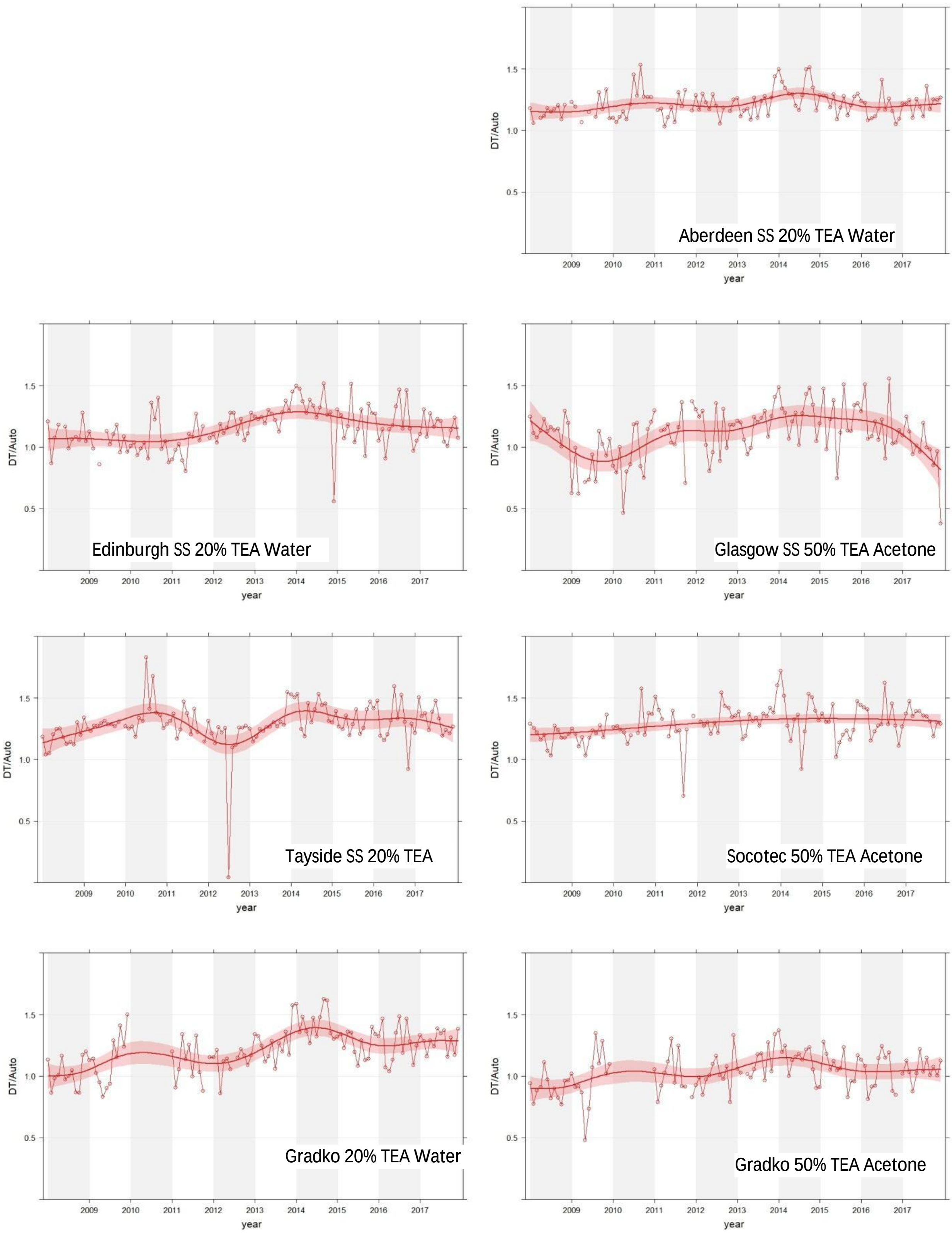

Figure 12: SmoothTrend in Bias at Marylebone Road, 2008-2017

4.21 It is known that a step change in data handling for the automatic monitor at Marylebone Road took place in 2013 to be in line with EU eReporting requirements. This involved zero baseline processing using calibration data down to one decimal place (previously it had been an integer)[17]. There is no clear step change in the NO_2 or NOx data from the automatic monitor that coincides with this change (Figure 13), nor in the bias adjustment factors (Figure 12), so it is unlikely that the change has had a material effect on the concentrations reported by the automatic monitor.

Trends in Factors that might Influence Diffusion Tube Bias

4.22 To understand better those factors that might give rise to the changes in bias seen at Marylebone Road (Figure 12), further information is provided on a) NO_2, NOx and O_3 concentrations and the NO_2:NOx ratio at Marylebone Road, b) NO_2, NOx and O_3 concentrations and the NO_2:NOx ratio at the London Bloomsbury site, which is representative of background concentrations at Marylebone Road, and c) meteorological parameters taken from the meteorological station at London City Airport.

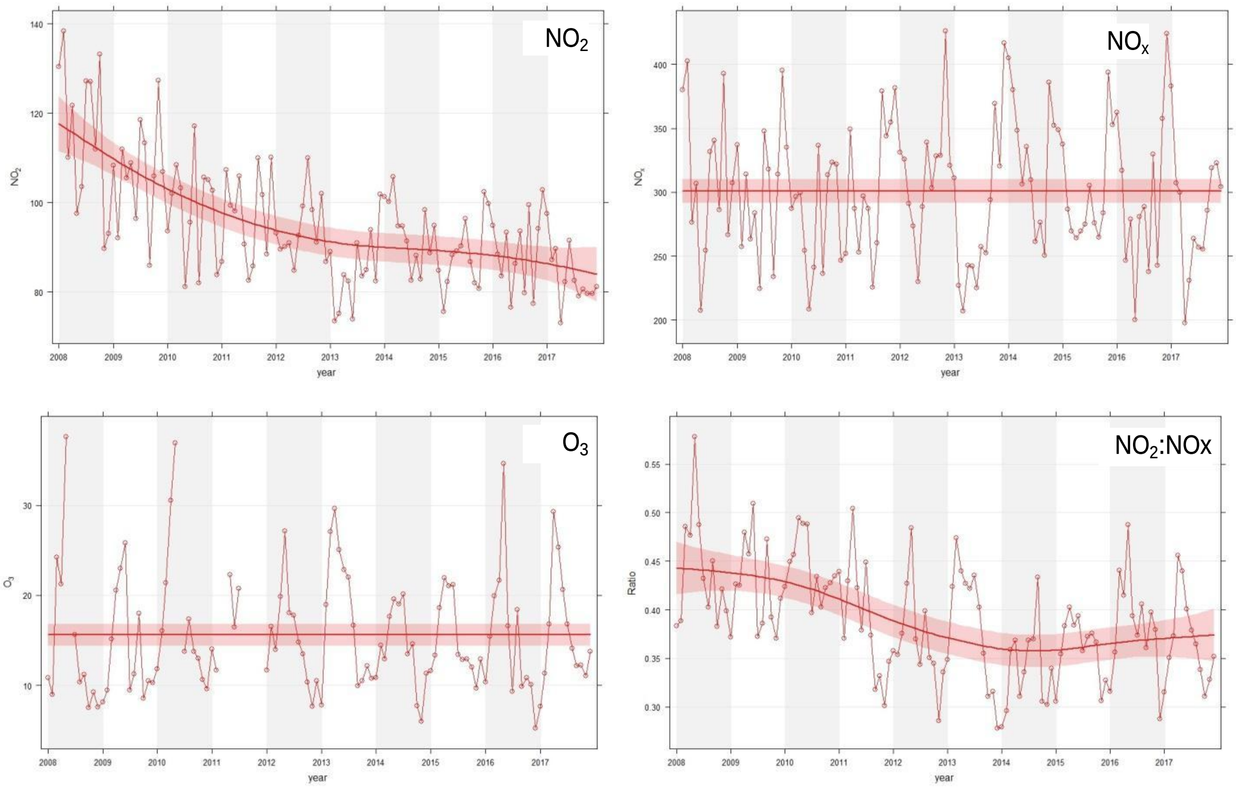

Figure 13: SmoothTrend in NO_2, NOx and O_3 Concentrations (mg/m^3) and NO_2:NOx Ratio at Marylebone Road, 2008-2017

17 David Hector, Riccardo, personal communication July 2018.

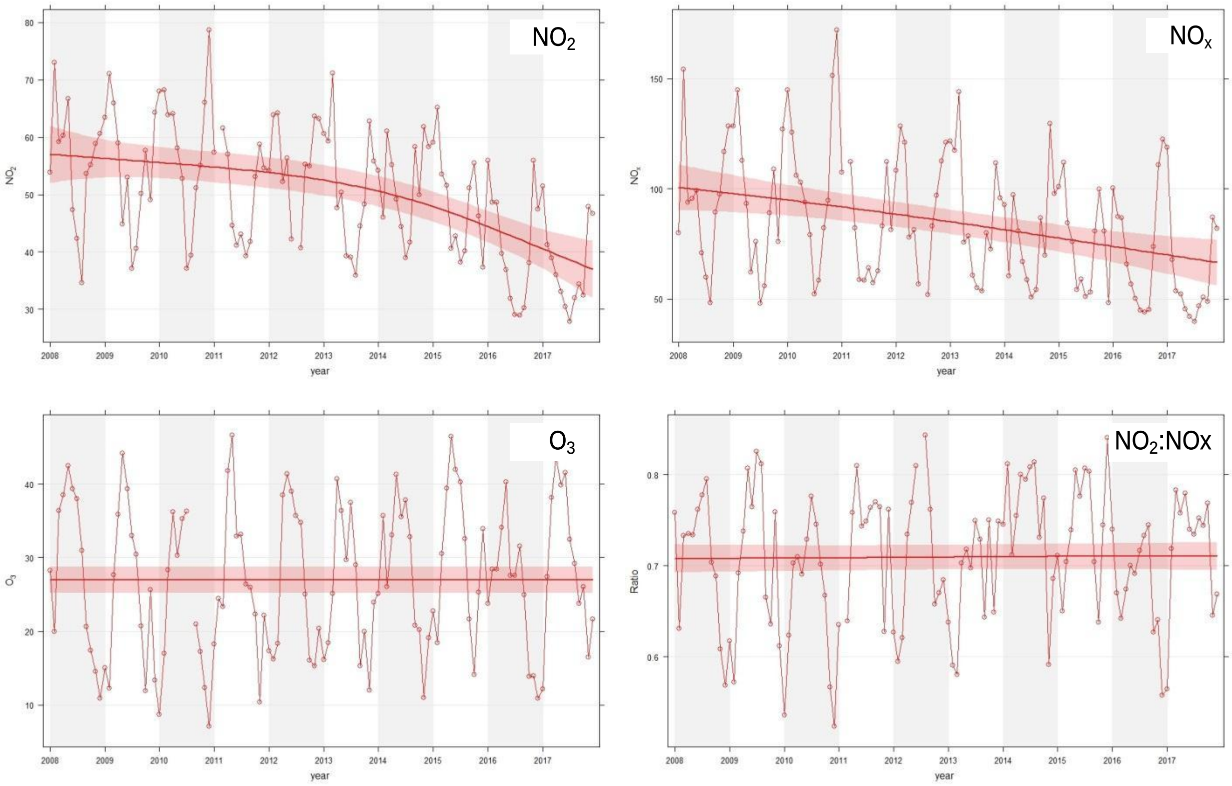

Figure 14: SmoothTrend in NO_2, NOx and O_3 Concentrations ($\mu g/m^3$) and NO_2:NOx Ratio at London Bloomsbury Urban Background Site, 2008-2017

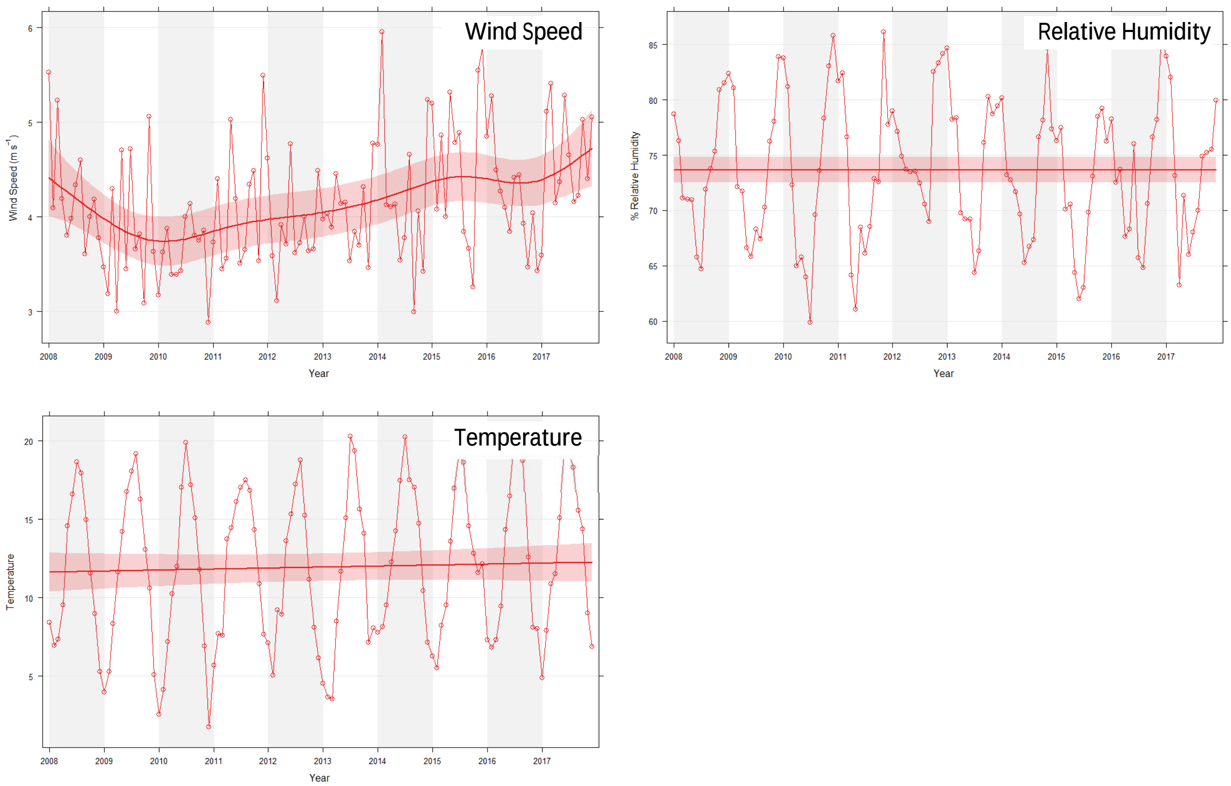

Figure 15: SmoothTrend in Wind Speed, Relative Humidity and Temperature at London City Airport, 2008-2017

Table 9: Summary of TheilSen Trends (%/yr) at Marylebone Road, 2008-2017

Pollutant	Trend (%/yr) and Significance			
	NO_2	NOx	O_3	NO_2:NOx
Marylebone Road	-2.52 ***	-0.19 (n/s)	+0.38 (n/s)	-2.13 ***
London Bloomsbury	-3.25 ***	-3.63 ***	+0.79 (n/s)	+0.25 (n/s)

4.23 The results for Marylebone Road show a significant reduction in NO_2 concentrations over the last 10 years, but no commensurate reduction in NOx and no change in O_3 (Figure 13). The NO_2 reduction is steep at the beginning, 2008-2013, but then levels out somewhat from 2014-2017. The resultant NO_2:NOx ratio (based on the monthly averages derived from the hourly mean ratios) decreases over this time. The nearby background site, London Bloomsbury, also shows reductions in NO_2, although the pattern for NO_2 is opposite to that seen at Marylebone Road, with little reduction in the earlier years 2008-2013 and a steeper reduction in recent years, 2014-2017. However, in contrast to Marylebone Road, NOx concentrations at London Bloomsbury decline over this period. For O_3, there is no significant change in concentration over the whole period at London Bloomsbury, as is the case for Marylebone Road. There is also no change in the NO_2:NOx ratio derived from the hourly data at London Bloomsbury.

4.24 Assuming that London Bloomsbury, in Russell Square, is a good indicator of background air at the Marylebone Road site, which is only 2 km away, implies that NOx emissions from road traffic have increased at Marylebone Road (to compensate for the reduction in background NOx in the air being mixed with the fresh emissions). Furthermore, the additional road traffic emissions must have considerably less primary NO_2 to drive the commensurate reduction in NO_2 concentrations (although part of this reduction will be due to the reduction in background NO_2). These changes imply that there is more NO within the increased NOx emissions, giving rise to higher total NO concentrations at Marylebone Road. An increase in NO concentrations would imply a reduction in the O_3 concentrations, due to the reaction of NO and O_3 to form NO_2, however, O_3 concentrations have remained constant over the period. This in turn would suggest that O_3 concentrations in the background air have been increasing, to compensate for the expected reduction in O_3 as a result of the additional fresh NO. The results for London Bloomsbury do not really support this; there is a non-significant increase in O_3 of <1% per year (Table 9).

4.25 It is recognised that the chemistry taking place within the diffusion tubes can affect the bias. In particular, the reaction of NO with O_3 leads to overestimation of NO_2 (positive bias). Heal and Cape (1997) showed that the extent of the overestimation depends on the instantaneous NO:NO_2 ratio and on the relative concentrations of NO and O_3. There is no simple method to calculate the bias as it is not simply related to average NO:NO_2 or NO:O_3 ratios, but to the dynamic behaviour throughout the sampling period. However, the model simulations indicate a general trend for bias to increase with decreasing NO_2 concentration, for a given NO_2:NOx ratio and given O_3 concentration. This role of the chemistry was supported by a study of 252 separate long-term co-location studies (Laxen and Marner, 2006), which demonstrated that there was a linkage between bias and the NOx or NO_2 concentration, with bias being increased as concentrations are reduced, this being clearest at higher concentrations; above ~80 µg/m^3 NOx. The fits to the data imply that a reduction in concentration from 200 µg/m^3 to 100 µg/m^3 NOx would increase bias by around 9%, while a reduction from 80 µg/m^3 to 40 µg/m^3 NO_2 would increase bias by around 13%. The effect would be to reduce the bias adjustment factors, such that a factor of 0.9 at the higher concentration would become 0.83 or 0.80 at the lower NOx and NO_2 concentrations respectively.

4.26 What remains unclear from the chemistry model is exactly how changing primary NO_2 emissions at Marylebone Road may have affected the in-tube chemistry. Nevertheless, the pattern of increasing bias at Marylebone Road, where NO_2 and NOx concentrations are high, is consistent with this change being driven by chemistry within the tube. Indeed, the drop in the NO_2 concentration over the 10 years of around 30 µg/m^3, would increase bias by around 10%, on the basis of the empirical relationship derived by Laxen and Marner (2006). The increases observed at Marylebone Road range from around 5% to 30% for the different laboratories, with an average of 10%.

5 Examination of Data for Sites in Edinburgh

Trends at NO_2 and NOx at Automatic Sites

5.1 The automatic monitors at three sites in Edinburgh with long-term data (meeting the criteria described in paragraph 4.1), and at one site just outside (to provide a local rural background), all show a significant downward trend in both NO_2 (Figure 16) and NOx (Figure 17) concentrations. The reductions are broadly similar for NO_2 and NOx, at around 3-4 %/yr (Table 10). These are all sites with valid data sets for trend analysis (see paragraph 4.1). Two of these sites, Georgie Road and St John's Road, are also co-location sites. The NO_2 and NOx trend patterns for the St Leonards site are more variable than the other sites.

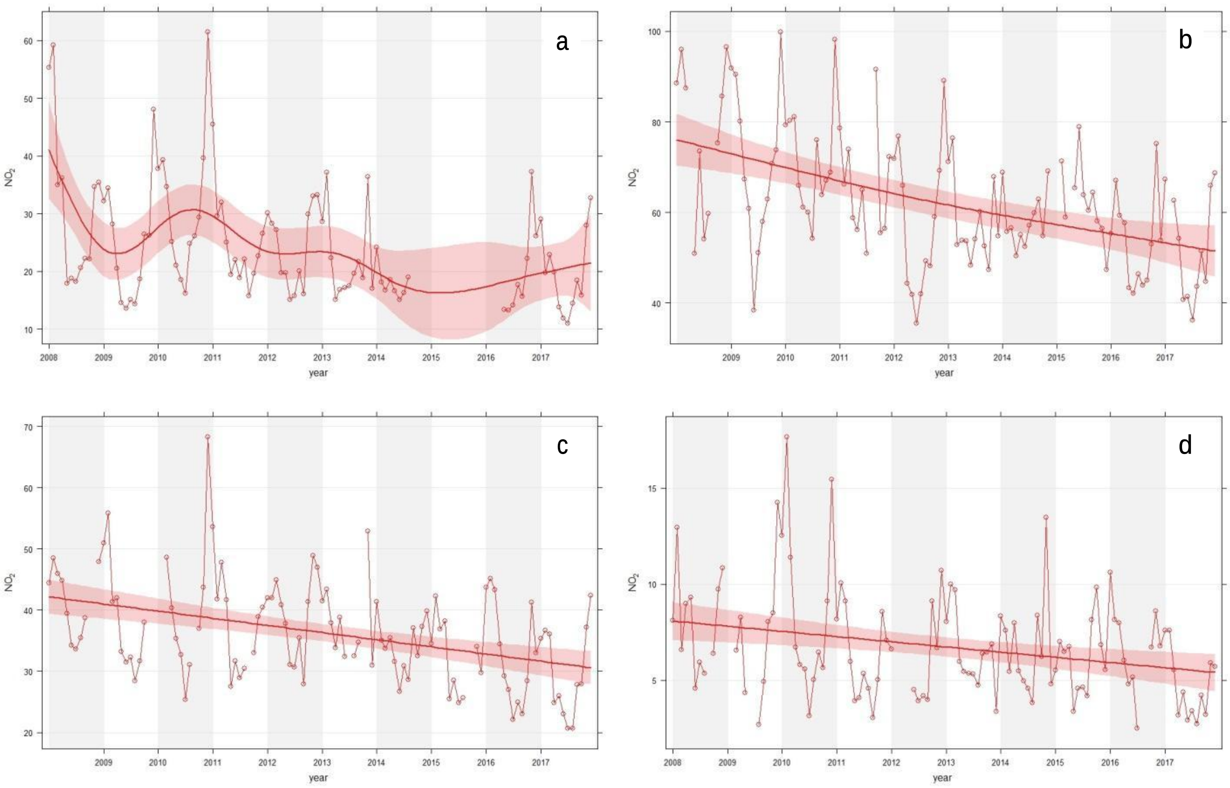

Figure 16: SmoothTrend for NO_2 Concentrations (µg/m^3) at Four Automatic Sites in or near Edinburgh with Long-Term Data, 2008-2017

(a) St Leonards (urban background), (b) St John's Road (kerbside), (c) Gorgie Road (roadside), and (d) Bush Estate (rural)

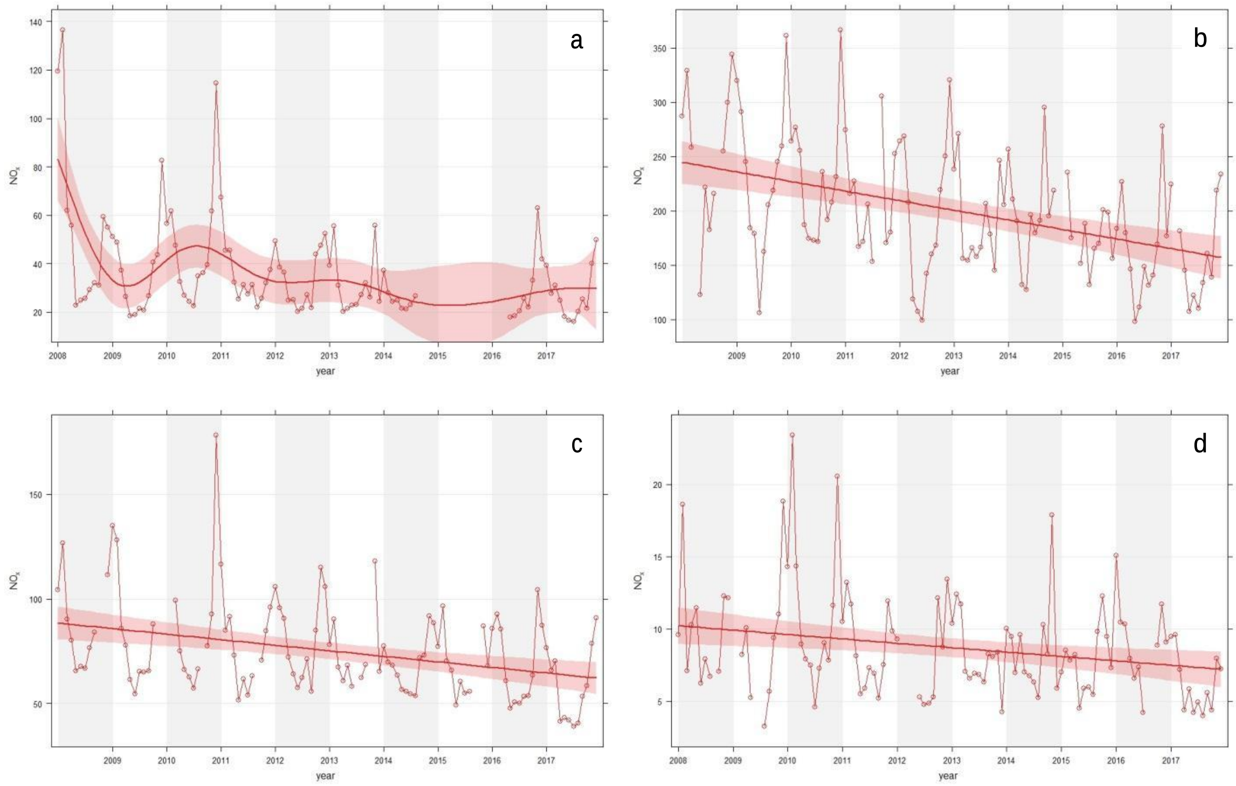

Figure 17: SmoothTrend for NOx Concentrations (µg/m^3) at Four Automatic Sites in or near Edinburgh with Long-Term Data at Automatic Sites, 2008-2017

(a) St Leonards (urban background), (b) St John's Road (kerbside), (c) Gorgie Road (roadside), and (d) Bush Estate (rural)

Table 10: Summary of Trends (%/yr) in Scotland 2008-2017

Pollutant	Trend (%/yr) and Significance			
	St Leonards	St John's Road	Gorgie Road	Bush Estate
NO_2 Concentration	-3.97 ***	-3.33 ***	-2.90 ***	-3.24 *
NOx Concentration	-3.98 ***	-3.88 ***	-2.98 ***	-2.85 **

Trends in NO_2 at Co-Location Sites in Edinburgh

5.2 Results for monthly mean concentrations of NO_2 from both automatic monitors and unadjusted diffusion tubes at 6 co-location sites in Edinburgh with several years of data, are shown in Figure 18. The automatic monitors show downward trends at six of the eight sites. The trends for raw diffusion tube data are also downward at all six sites. Indeed, the trends for both the automatic and diffusion tube monitors are essentially the same at each site (i.e. the regression lines are essentially parallel), with the exception of the Queen Street / Wemyss Place monitor, for which the raw diffusion tube data do not decline as fast as the automatic data. The results for Queen Street / Wemyss Place imply that the diffusion tube bias is increasing at this site, resulting in a decreasing bias adjustment factor to correct the results to match the NO_2 concentrations from the automatic monitor. Figure 19 illustrates the trends in bias for the six Edinburgh sitesThe results for Queen Street / Wemyss Place are discussed further in paragraph 5.5.

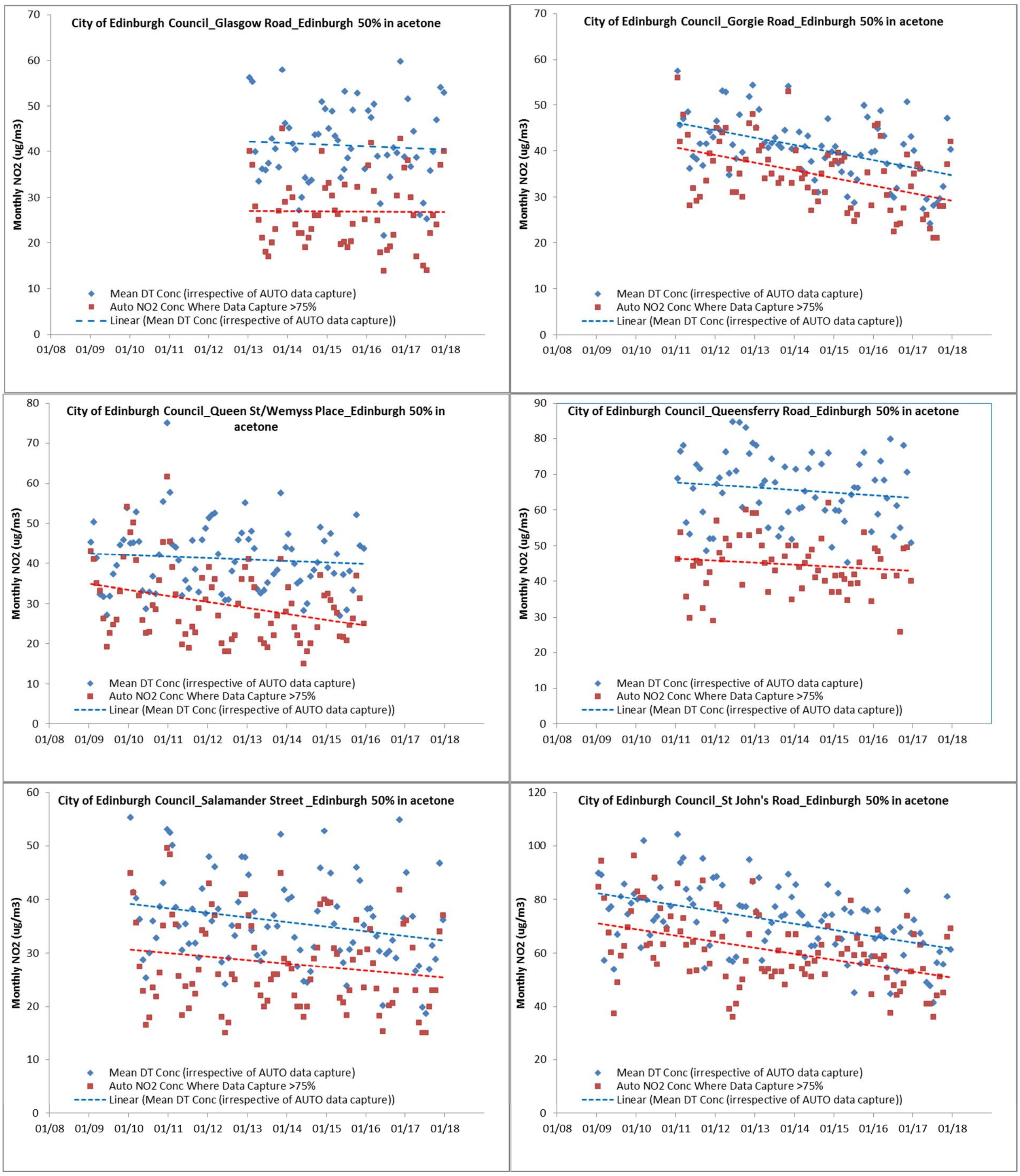

Figure 18: Trends in Raw Diffusion Tube and Automatic NO_2 Concentrations (µg/m^3) at Co-Location Sites in Edinburgh, 2008-2017

The automatic data are only shown if there are diffusion tube results for the same month

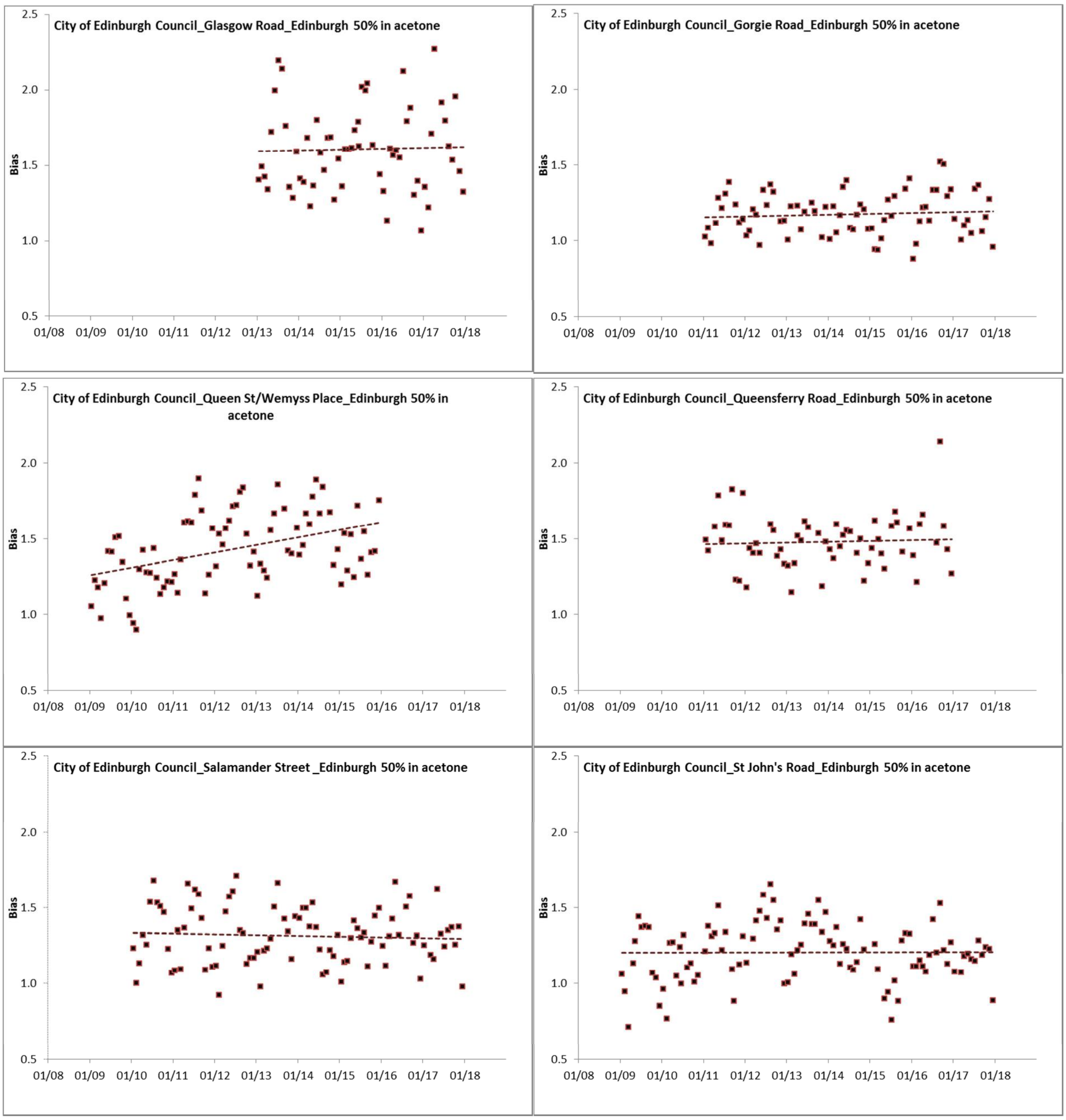

Figure 19: Trends in Diffusion Tube Bias at Co-Location Sites in Edinburgh, based on Monthly Results, 2008-2017

Trends in Bias Adjustment Factors

5.3 Edinburgh City Council has submitted the results of the co-location studies for its sites in Edinburgh to the national database throughout the 10 year period, 2008-2017. These are combined with the results for other local authorities using tubes supplied and analysed by Edinburgh Scientific Services, including those for the national co-location study being carried out at Marylebone Road, to provide an overall bias adjustment factor for Edinburgh Scientific Services that is published on the national spreadsheet (the full data are presented Figure 9 in and Figure 10 in Section 4). The bias adjustment factors for co-location studies in Edinburgh are shown in Figure 20. It is clear that the number of sites varies from year to year and while in some years the national factor for Edinburgh Scientific Services' tubes lies in the middle of the range, in other years the national factor is different, for example in 2010 and 2011 the national factor is well above the mid-point of the Edinburgh factors. The national factors are derived from these Edinburgh sites together with four sites in other locations (one in Stirling, two in West Lothian and Marylebone Road in London). One reason for the departure between bias adjustment factors for Edinburgh tubes and the national factors is that sites change over the years (see Figure 21). For instance, the Queensferry Road and Glasgow Road sites cover only part of the period, 2011 to 2016 and 2013 to 2017 respectively. They have much lower bias adjustment factors (the tubes have higher bias) and this will have contributed to bringing the national factor down during this period.

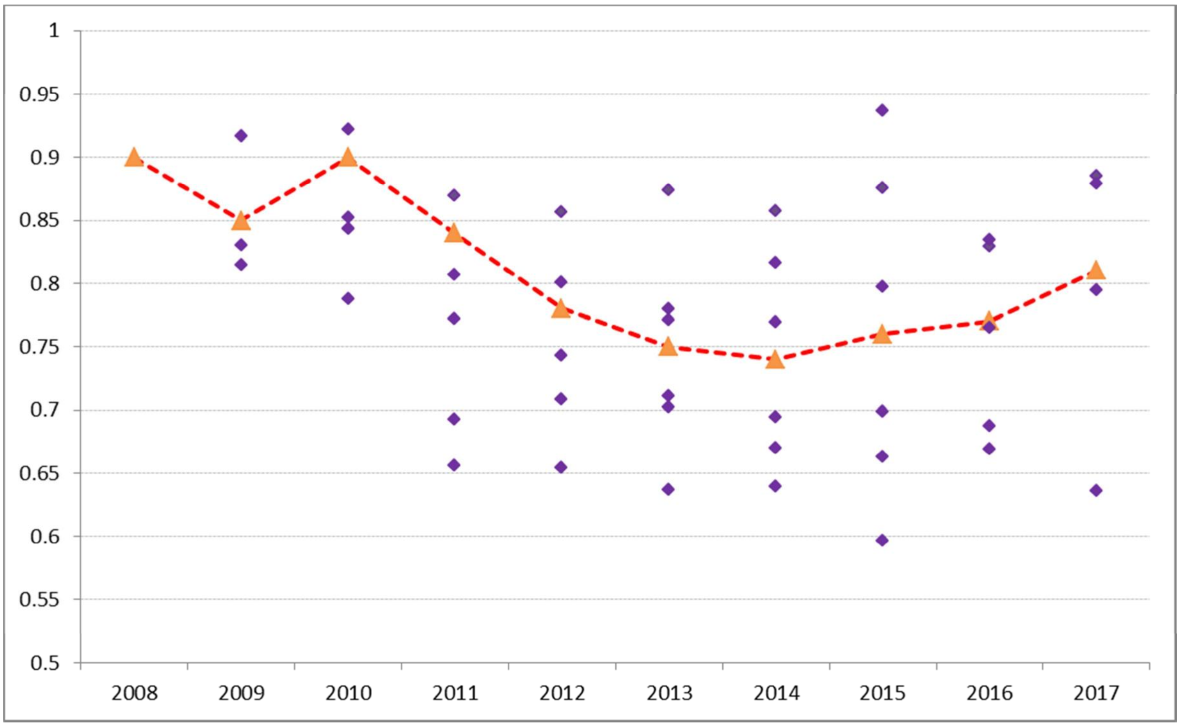

Figure 20: Bias Adjustment Factors for Co-Location Studies in Edinburgh and the National Bias Adjustment Factors for Edinburgh Scientific Services Tubes (dashed line), 2008-2017

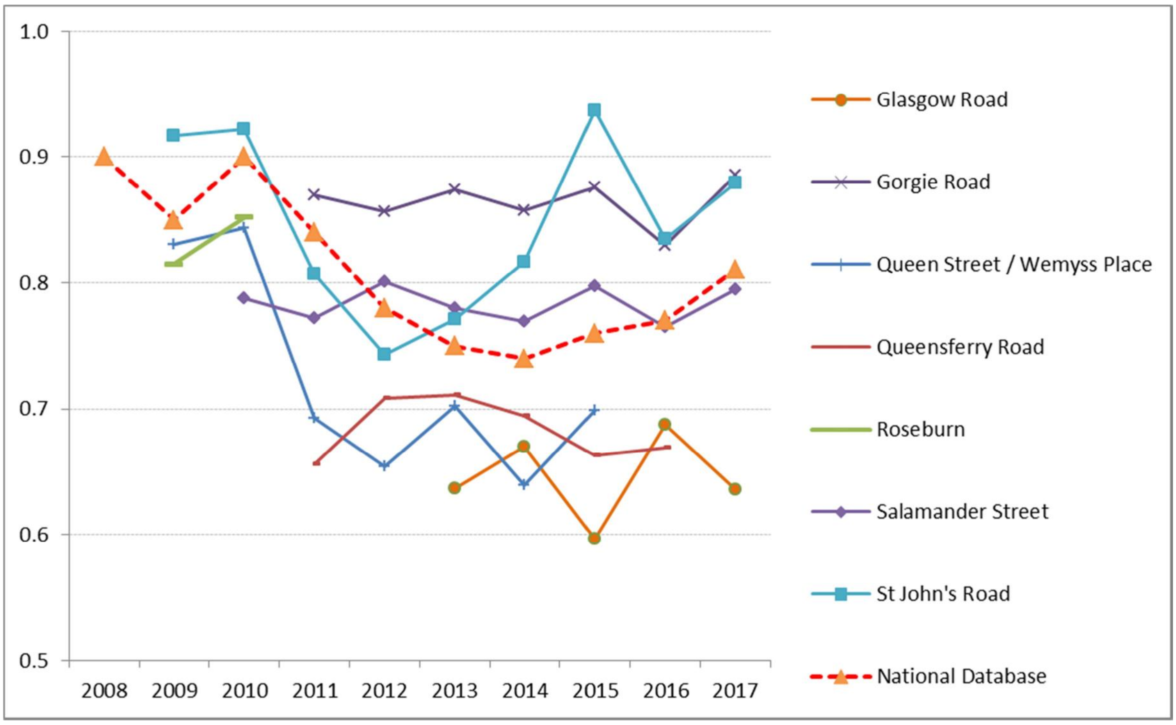

Figure 21: Bias Adjustment Factors for All Co-Location Studies in Edinburgh and the National Bias Adjustment Factors for Edinburgh Scientific Services (dashed line), 2008-2017

5.4 There is some evidence in Figure 21 that bias adjustment factors decreased between 2010 and 2013 (as is also noted in paragraph 4.16), in particular for the Queen Street / Wemyss Place site, and to some extent for St John's Road, although the latter decline was temporary. The other site contributing to the national factors that showed a decline was Marylebone Road. However, not all sites showed a decline during this period, e.g. Salamander Street. Indeed, the evidence from Figure 19 is that, of the Edinburgh co-locations sites, only the Queen Street / Wemyss Place site showed a reduction in the bias adjustment factor (as the bias increased over the 10 years), the other sites being essentially constant over this period.

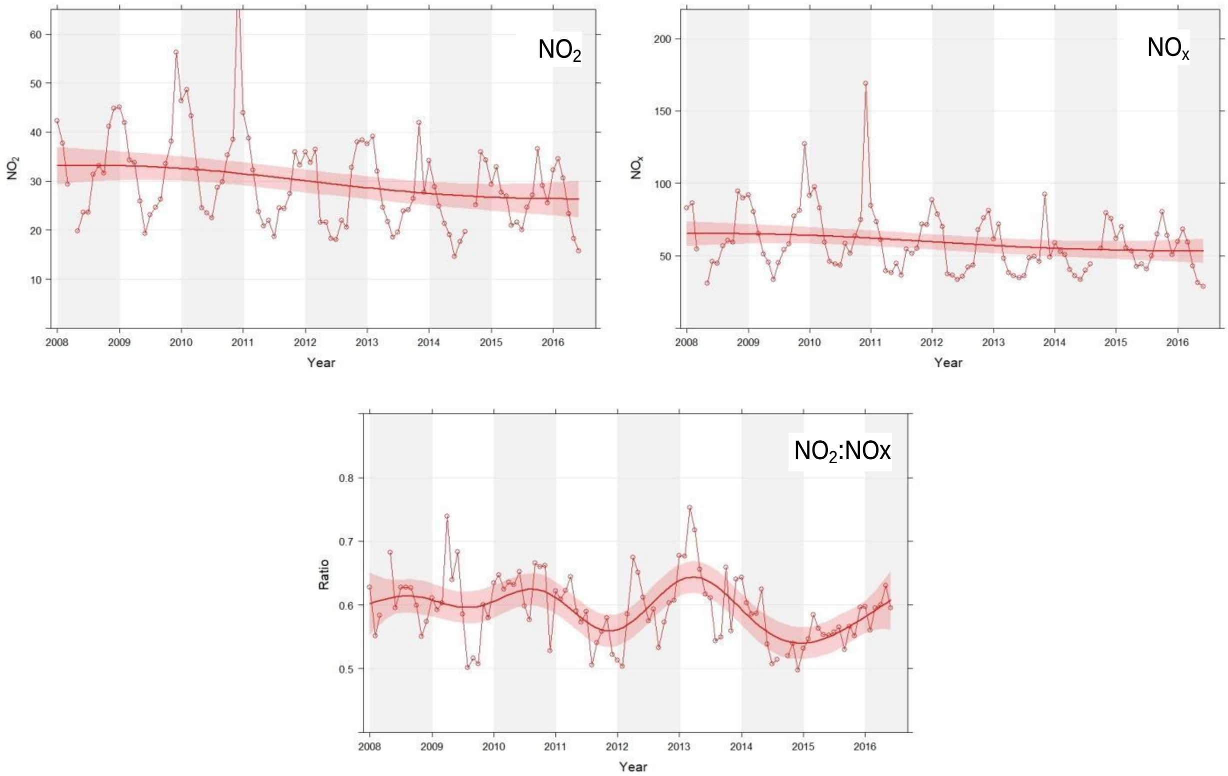

Figure 22: SmoothTrend in NO_2 and NOx concentrations (µg/m^3) and NO_2:NOx ratios at the Queen Street / Wemyss Place Co-Location Site in Edinburgh, 2008-2017

5.5 This raises the question as to why the bias increased at the Queen Street / Wemyss Place site, but not the other sites in Edinburgh. A similar effect was seen in the results for Marylebone Road in London which was shown to be consistent with chemistry taking place within the tubes (see paragraphs 4.17 to 4.26). The NO_2 and NOx concentrations and the ratio NO_2:NOx at the Queen Street / Wemyss Place site are shown in Figure 22. There are significant (TheilSen) reductions in concentrations; -3.26%/yr for NO_2 and 3.07%/yr for NOx, as well as a small but significant (TheilSen) reduction in the NO_2:NOx ratio of 0.86%/yr (indicating an decrease in primary NO_2, as at Marylebone Road). The absolute reduction in NO_2 is around 10 µg/m^3 and for NOx around 20 µg/m^3. Using the relationships identified by Laxen and Marner (2006), the increase in bias due to these reductions would be around 3% (from the NO_2) or 2% (from the NOx relationship) over the 7 years (see also paragraphs 4.25 and 4.26). The actual increase in the bias over the 7 years was around 28% (Figure 19). The change observed is thus unlikely to be related to chemistry within the tube. The data for the Queen Street / Wemyss Place site have been examined further and show two distinct periods with different bias values, one up to March 2011 at around 1.2 and one from this date at around 1.5 (Figure 24). These results would suggest that something changed at this site, but not at the other sites in Edinburgh. The results for the raw (unadjusted) diffusion tube concentrations and the automatic analyser concentrations are also shown in Figure 24. It is apparent that the change in concentrations responsible for the change in bias was in the automatic analyser results, which showed a step drop at this time. The local authority had noted this step change in 2011 and discussed it in its annual Updating and Screening Assessment (City of Edinburgh Council, 2012). No changes were identified in laboratory procedures or those for the automatic analyser. Indeed it was reported that the examination *"included a review of calibration data, site service reports, site audit and data scaling, by AEA Technology. Checks for discrepancies with raw data bases were also investigated. AEA confirmed that there were no issues with the real time data".* However, change in the bias at the Queen Street / Wemyss site can be put down to a step change in the results from the automatic analyser, although the reason for this is unclear. The large reduction in the bias adjustment factor for this site is therefore an anomaly that does not apply to other sites in Edinburgh, and does not represent a change in laboratory procedures by Edinburgh Scientific Services.

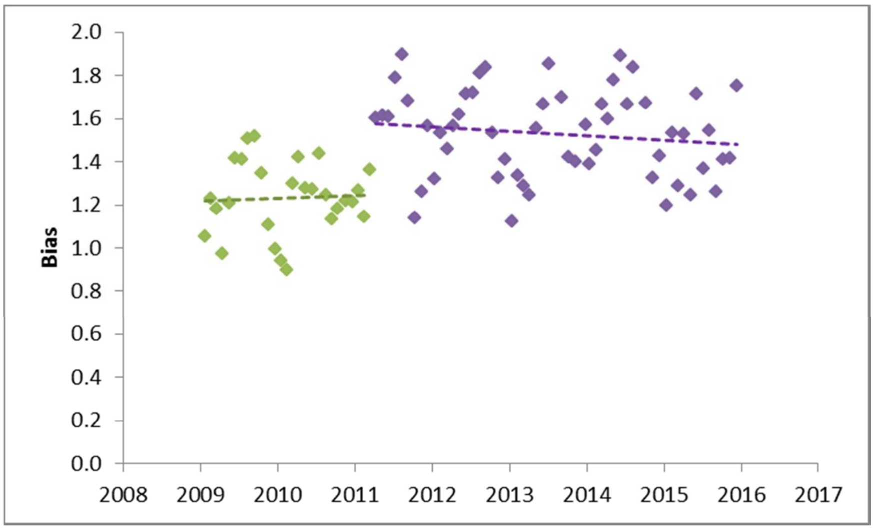

Figure 23: Trends in Monthly Bias at the Queen Street / Wemyss Place Co-Location Site in Edinburgh for Two Periods between 2009-2015

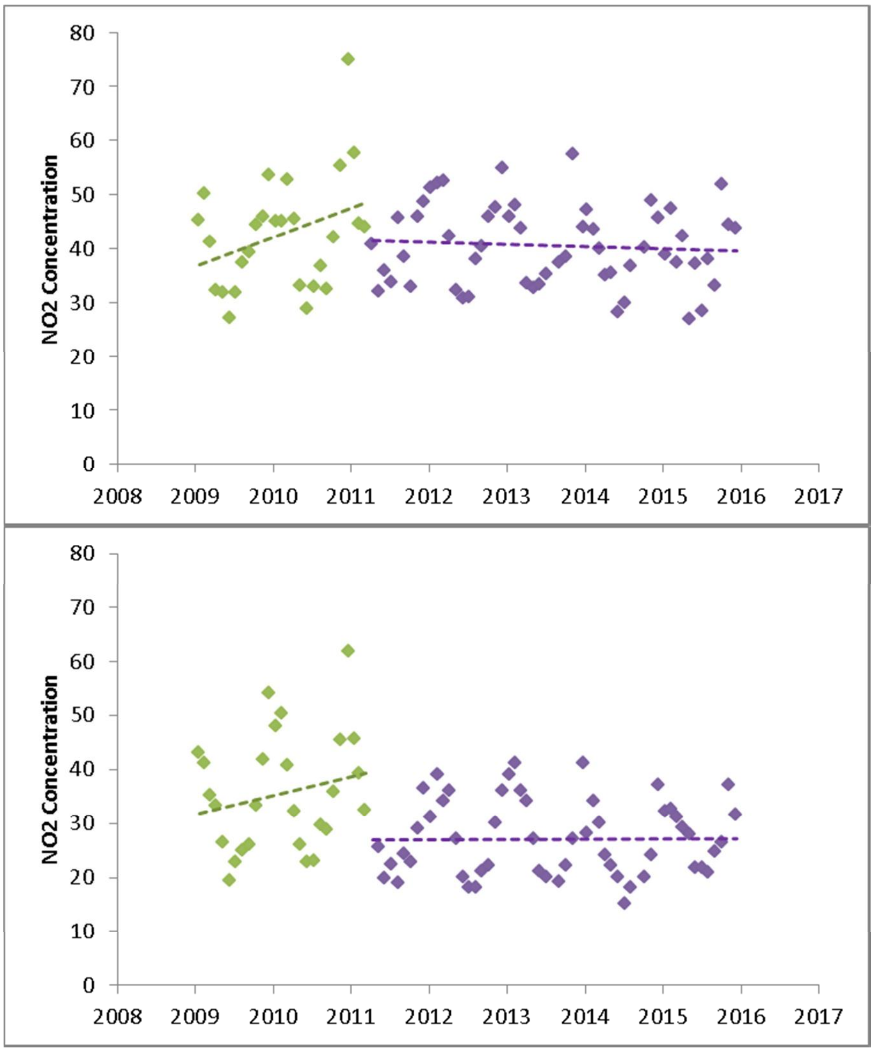

Figure 24: Trends in Monthly Raw Diffusion Tube Data (Top) and Monthly Automatic Analyser Data (Bottom) (Concentrations in μg/m^3) at the Queen Street / Wemyss Place Co-Location Site in Edinburgh for Two Periods between 2009-2015

5.6 Greater credence should be given to co-location studies that cover the full or a large part of the period. There are 2 sites in Edinburgh with long-term data for Edinburgh Scientific Services tubes: Salamander Street and St John's Street, with 8 and 9 co-location results respectively. The bias adjustment factors for these sites are shown in Figure 25.

5.7 The data presented in Figure 25 can be looked at in a different way, to demonstrate how the choice of bias adjustment factor might affect trends in reported concentrations. To do this, a scenario has been created in which the raw (unadjusted) diffusion tube NO_2 concentrations are the same every year at 40 μg/m^3, with the bias adjustment factors applied to show the nominal 'true' concentration, i.e. the concentration that would be reported. The outcome is a broadly similar pattern of concentrations derived from these two sources of adjustment factors in Edinburgh

(Figure 26). The concentrations have also been derived using the national bias adjustment factors and provide a not dissimilar set of results.

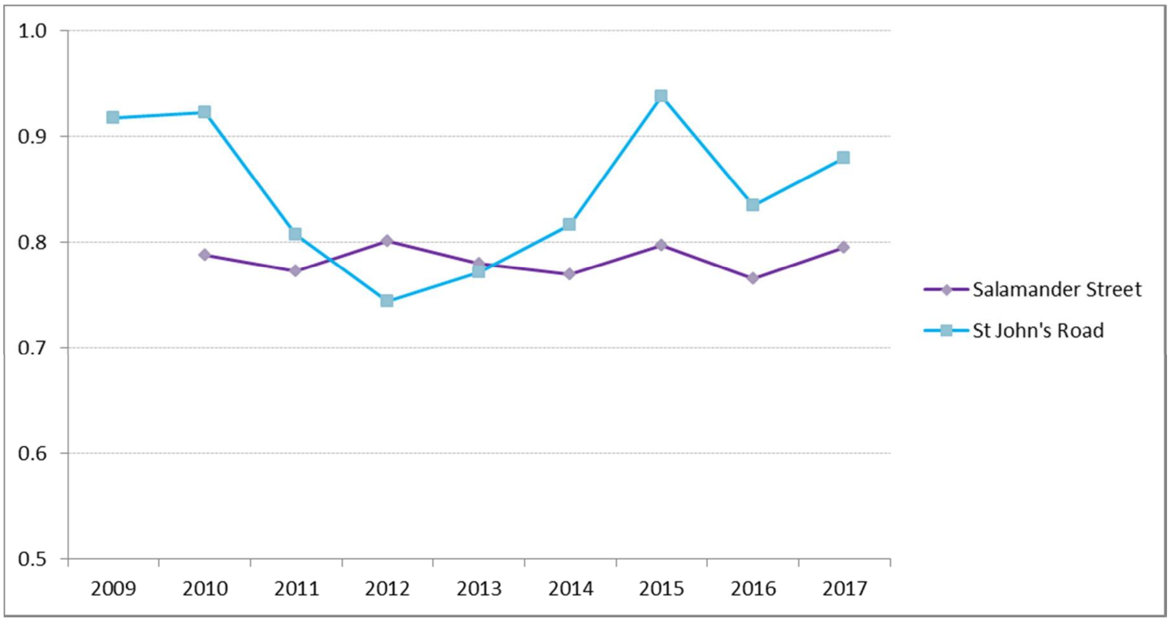

Figure 25: Bias Adjustment Factors for Edinburgh Scientific Services Tubes for Longer Term Co-Location sites in Edinburgh, as well as National Bias Adjustment Factors (dashed line), 2010-2017

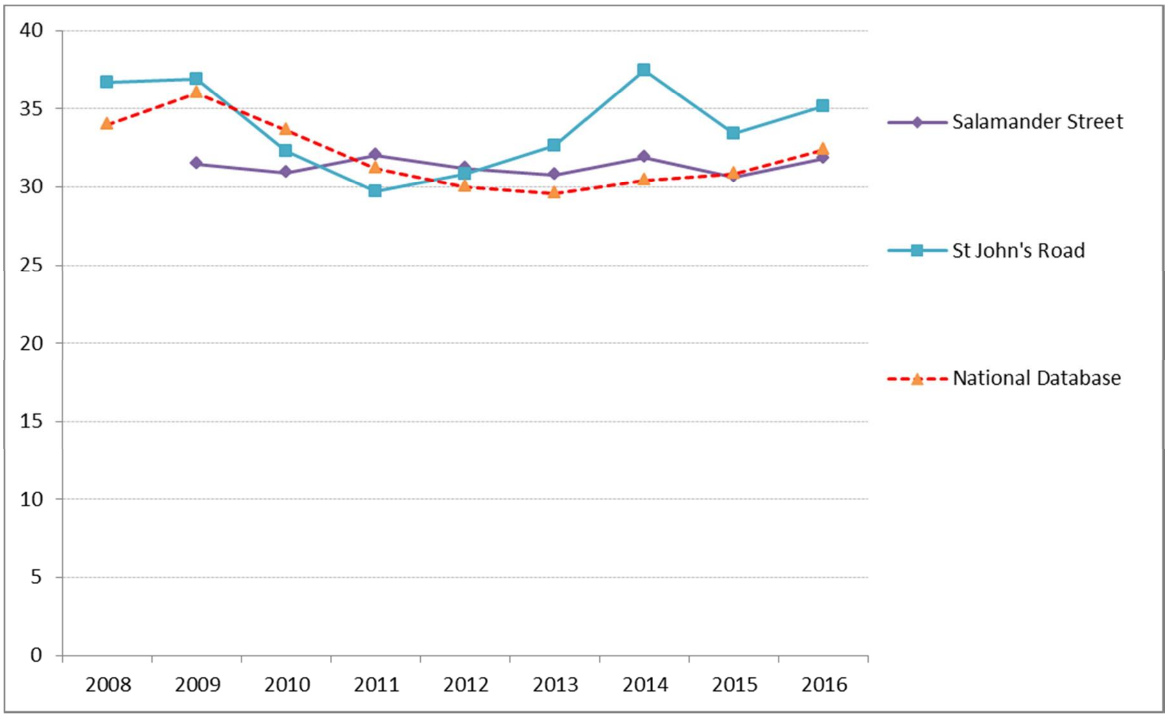

Figure 26: Nominal NO_2 Concentrations for a Constant Raw Diffusion Tube Concentration of 40 $\mu g/m^3$, using Site Specific Bias Adjustment Factors and Factors from the National Database (dashed line), 2008-2017

5.8 In conclusion, the downward trend in bias observed in Edinburgh during the early years of the 2010s, that helped identify the need for this study (see paragraph 1.1) seems to be a feature of the large differences between bias adjustment factors at different sites, and the chance effect of the year-on-year changes in both which sites and how many sites were feeding into the derivation of the overall national factors for Edinburgh Scientific Services tubes, coupled with evidence of real changes in bias at the co-location site at Marylebone Road in London, and a step change at the Queen Street / Wemyss Place site in Edinburgh, which seems to be the result of a step change in concentrations from the automatic monitor.. This would suggest that the changes in bias adjustment factors for Edinburgh Scientific Services are not related to changes in laboratory performance.

6 Uncertainty in Overall Bias Adjustment Factors

Influence of a Single Co-Location Site on the Overall Bias Adjustment Factor

6.1 The results discussed in section 5 for the Edinburgh co-location sites makes clear that the number of sites, and their continuity, will affect the calculation of the overall bias adjustment factors. To provide further understanding of the variability in the calculated overall bias adjustment factor, an analysis has been carried out for each laboratory used in Scotland, involving the stepwise removal of one of the results and re-calculation of the overall bias adjustment factor using orthogonal regression (the method used to combine results for the national database). The results are shown in Figure 27 for the four Scottish laboratories, all of which have a relatively limited number of co-location studies, and in Figure 28 for the two other laboratories used by local authorities in Scotland, both of which have a large number of co-location studies (Gradko shown separately for the two tube preparations, 20% TEA in water and 50% TEA in acetone).

6.2 The results of this analysis show that the overall bias adjustment factor for a given year could vary considerably if just one site is removed, especially in the case of the four Scottish laboratories. This is much less so for the Socotec and Gradko results. This reflects the greater number of co-location studies forming the Socotec and Gradko results. Clearly, the greater number of co-location results, the less the sensitivity of the overall bias adjustment factor to sites coming and going from year to year. There are, nevertheless, still variations from year to year, which are largely due to the substantial variations in bias adjustment factors from one co-location site to another and the year-to-year variations in which and how many sites are included in the overall factor (as discussed in sections 4 and 5 and further in this section)

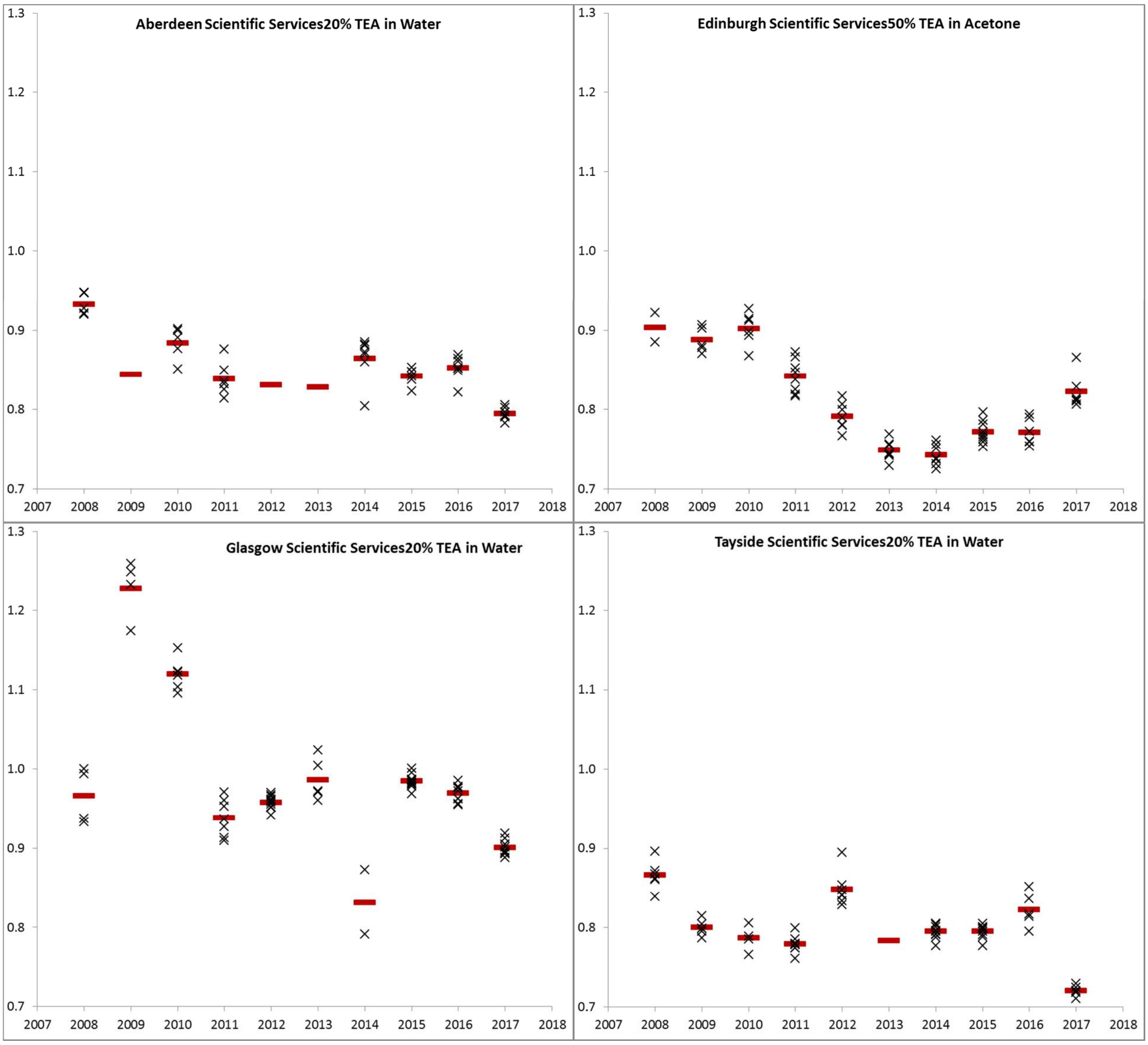

Figure 27: Effect of Removing One Site at a time from the Calculated Overall Bias Adjustment Factor (marked with an X), as well as the Value with No Sites Removed (red bar), for the Four Scottish Laboratories, 2008-2017

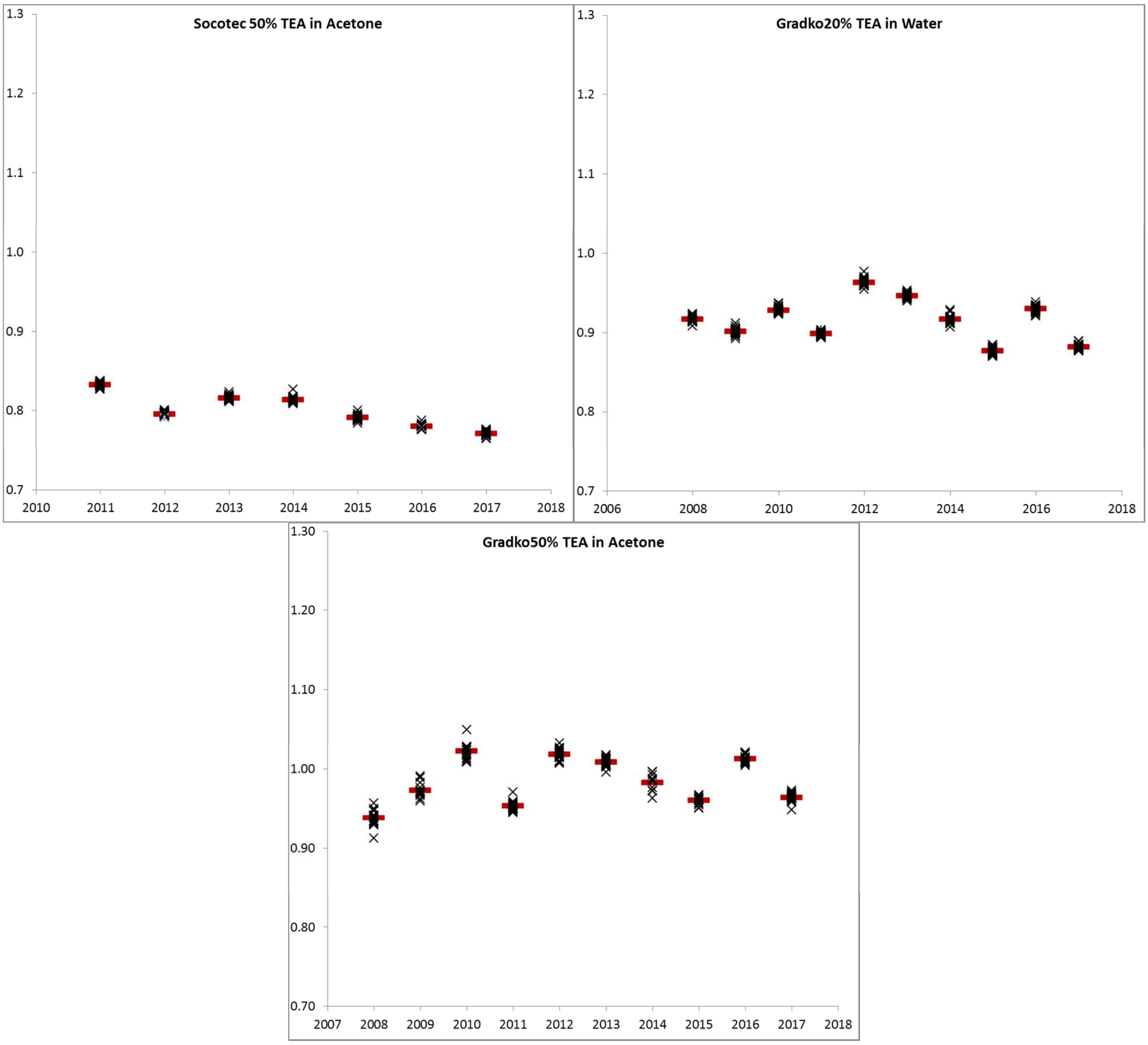

Figure 28: Effect of Removing One Site at a time from the Calculated Overall Bias Adjustment Factor (marked as X), as well as the Value with No Sites Removed (red bar), for the Socotec and Gradko Laboratories also used in Scotland, 2008-2017

6.3 The effect of removing even more sites becomes greater when site numbers are smaller. For example, in the case of Edinburgh Scientific Services tubes there are between 2 and 9 co-location results in any one year. The effect of randomly leaving out three tubes is shown in Figure 29 (cf. leaving out just one site in Figure 27). There is no result for 2008, as there were only two tubes in that year. For other years, the range in the calculated overall bias adjustment factor is from around 0.1-0.2, in other words, the reported overall bias adjustment factor in a particular year could be very different if three sites were randomly excluded. Thus in this scenario, the reported overall bias adjustment factor in 2011 could be anywhere in the range 0.76 to 0.94, depending on which sites are included.

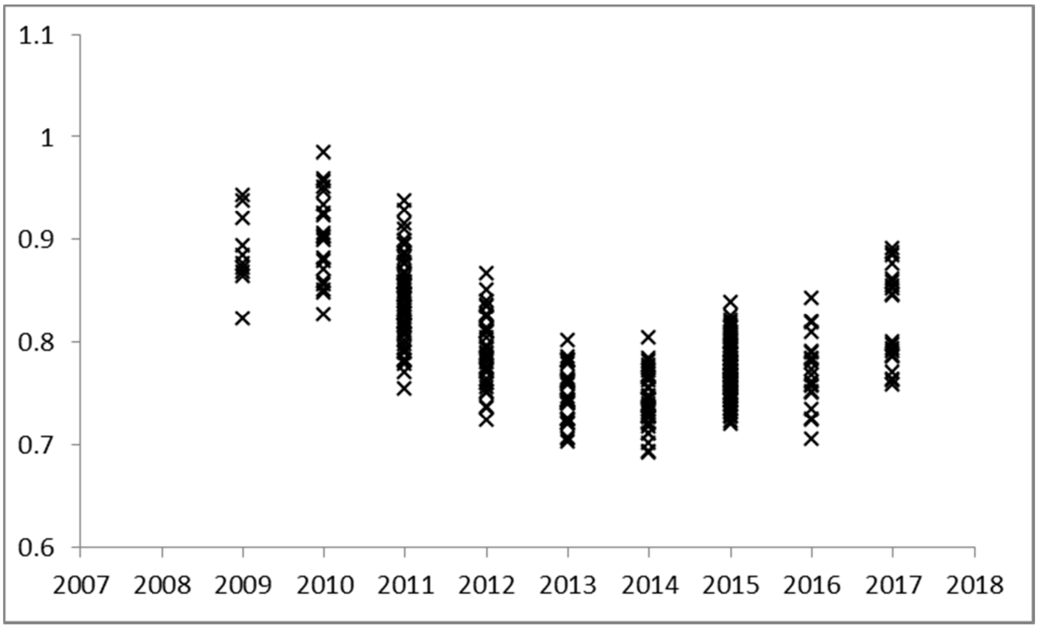

Figure 29: **Effect of Randomly Removing Three Sites at a time from the Calculated Overall Bias Adjustment Factor (marked as X), for Edinburgh Scientific Services Tubes, 2008-2017**

Influence of the Selection of Sites on the Overall Bias Adjustment Factor

6.4 A further analysis has been carried out to demonstrate the influence of site selection on the overall bias adjustment factor. This is based on the results for Gradko 20% TEA in water tubes, where a comparison has been made between the overall factors as published on the national spreadsheet and a calculated subset of the results for sites in England and Scotland that are to the north of, but include, Lancaster and Scarborough. These sites were chosen as being most representative of what might be happening in Scotland, where there was evidence of a downward trend in the bias adjustment factors for the Scottish laboratories (see Figure 7 and Figure 8). The results are shown in Figure 30, together with the number of co-location results available in each year in Table 11. The calculated overall factors for the northern sites have been calculated using orthogonal regression, as is the case for the national factors.

Table 11: **Numbers of Co-Location Results for Northern Sites and National Database for Gradko 20% TEA in Water Tubes, 2008-2017**

Laboratory	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017
Northern Sites	0	3	9	7	7	6	4	4	4	7
National Database	21	34	42	41	35	36	22	30	32	39

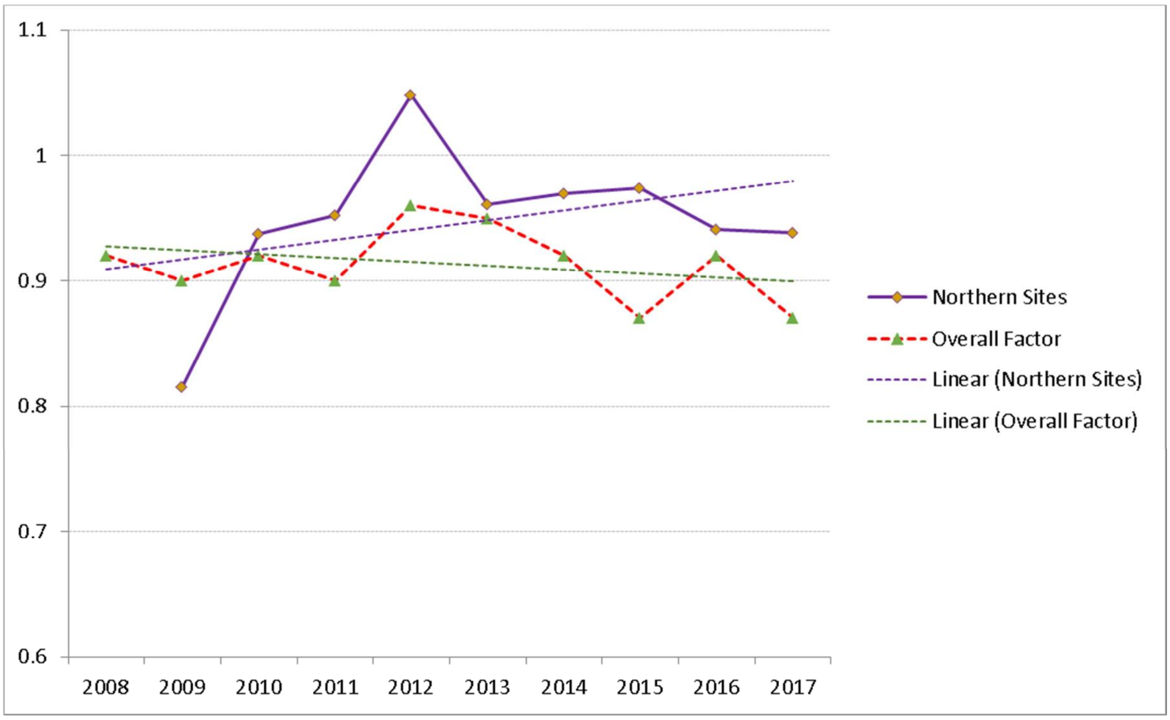

Figure 30: Calculated Overall Bias Adjustment Factor for Northern Co-Location Sites and the Overall National Factors, all for Gradko 20% TEA in Water Tubes, 2008-2017

6.5 It is clear that there is much less variation from year to year in the overall national bias adjustment factors, which are based on between 21 and 42 co-location results in each year, than in the overall bias adjustment factors for the Northern sites, which are based on between 3 and 9 co-location results in each year. The national database factors for Gradko 20% TEA in water tubes show little change over this time (as previously shown in Figure 8), however the northern sites show an apparent increasing trend, although this is entirely dependent on the result for 2009, which is based on only 3 sites.

6.6 This reinforces the view that the overall bias adjustment factors are highly dependent on the sites for which co-location results are available in any one year. The significant differences in the bias adjustment factors from site to site (see paragraph 4.16) mean that there can be a significant impact on the overall factor depending on which sites are included, but this impact will be less if there are a large number of co-location sites.

7 Observations and Recommendations

Observations

7.1 The following observations can be made from the analyses set out above:

Diffusion Tube Bias and Bias Adjustment Factors

- there are many factors that can influence diffusion tube bias, both within the laboratory and during exposure;
- the literature review suggests that key factors affecting bias are a) the chemistry taking place within the tubes during exposure, which will depend on concentrations of NO_2, NOx and O_3 and b) the wind induced shortening of the diffusion length. There may also be a role for relative humidity affecting the collection on the grid, and a small role for temperature;
- the analysis of trends shows that relative humidity and temperature have not changed over the period 2008-2017 and they will therefore not be influencing any changes in bias. Wind speed also shows no overall trend over this period, and while there are some patterns of increasing and decreasing average wind speed, there is no apparent relationship with any change in bias;
- there have been changes in concentrations of NO_2, NOx and the ratio of NO_2:NOx over the period 2008-2017. There is evidence, both in the literature and in the monitoring data, that these changes may well have led to increasing diffusion tube bias and hence decreasing bias adjustment factors, but this does not necessarily apply to all sites;
- the range in the site-dependent bias adjustment factors can be large, for example, from 0.60 to 0.94 in one year for tubes exposed at 6 sites in Edinburgh. Furthermore, for individual sites the bias is generally consistently higher or lower than the overall bias for that laboratory, emphasising that bias is site dependent. For a given site there is less variation in the bias adjustment factors from year to year; sites with a low bias adjustment factor will tend to always have a low factor, and vice versa;
- the site-to-site variations in bias are not fully understood but probably relate to microscale exposure effects in terms of wind flow across the sample head that can alter the effective diffusion length. At roadside sites the variations may also be because of small differences in the location of the diffusion tube and the automatic analyser inlet, which may cause one to be closer to the road than the other; concentrations can vary significantly over a few tens of centimetres, both in horizontal and vertical distance;
- the year-to-year variations in the overall diffusion tube bias are not consistent from one laboratory to another, which suggest that changing exposure factors (e.g. wind speed) are not

driving these changes. It is more likely that these year-to-year variations are related to changes in the mix of co-location results from year-to-year;

- the results for the Marylebone Road site suggest that there is a real increase in the bias over the 10 years. This is different from laboratory to laboratory, but the average increase is around 10%, which is consistent with the scale of change predicted from a previous study that showed increasing bias with decreasing NO_2 concentrations. This is likely to be due to the chemistry within the diffusion tube, in particular the reaction of NO with O_3 to create additional NO_2 whose relative influence on bias changes as the relative concentrations of NO_2, NO and O_3 at the site change;
- the results for the Queen Street / Wemyss Place co-location site in Edinburgh show an apparent increasing trend in bias over the seven years this site was in operation. Detailed examination showed that this was due to a step change in the results from the automatic analyser. This emphasises that uncertainty in automatic monitors can also affect the bias derived from co-location studies.
- the overall bias adjustment factor from all co-location studies is much more stable when a large number of co-location results is used. This is not the case for the Scottish laboratories where the overall factors are based on a limited, and highly varying, number of co-location results (in the range of 1 to 12 sites);
- the evidence for a downward trend in the overall bias adjustment factors for Scottish Laboratories appears to be an artefact of the sites that have been used to derive the overall factor, coupled with some chemistry-driven downward trends due to the declining NO_2 and NOx concentrations.

Trends in Concentrations in Scotland

- An analysis has been carried out of trends in concentrations of NO_2, NOx and O_3 over the period 2008-2017 for 43 long-term sites across Scotland with automatic monitors, of which 31 are at roadside sites. The overall picture is of a significant downward trend for NO_2 and NOx concentrations over the period of around 2.3%/yr (or 23% over 10 years). The overall downward trend at roadside sites is also around 2.3%/yr. At rural and urban background sites, which are fewer in number, the downward trends are greater, at around 3.6 to 3.7%/yr.
- The results for the 3 automatic monitors with longer data runs at roadside sites in Edinburgh also show a downward trend over the period 2008-2017 in the range of 3 to 4%/yr. It is therefore to be expected that diffusion tube results, after bias adjustment, would also show a downward trend in concentrations in Edinburgh.

Recommendations

7.2 Uncertainty in trends derived from diffusion tubes will be reduced if bias adjustment factors are:

- based on a consistent set of co-locations sites, at which the diffusion tubes also remain consistently positioned with respect to the analyser inlet;
- based on as large a number of co-location sites as possible (especially if sites are changing from year to year);
- derived from laboratories operating with good precision; and
- not changed from local to national factors from year to year.

7.3 On this basis Scottish local authorities should:

- continue to apply laboratory-specific bias adjustment factors to their diffusion tube results, as this will ensure that the overall results for a local authority (but not necessarily those for individual sites) will be closer to the 'true' value as defined by automatic analysers;
- be encouraged to report all their co-location studies to the national database every year (there are several dates for reporting during the year);
- take into account laboratory performance when selecting a laboratory for diffusion tube analysis;
- consider whether any changes to their co-location strategies would help reduce the variability of the bias adjustment factors as sites come and go; and
- use results from as consistent a set of co-location sites as possible, especially if using local co-location sites to derive a local bias adjustment factor.

7.4 This study has shown that there are significant variations in diffusion tube bias from site-to-site, which, for roadside sites, may be in part due to the small-scale difference in the placement of the tubes and the inlet to the automatic analyser. This will lead to an 'artificial' bias due to sampling real differences in concentrations, as concentrations alongside roads vary considerably over short distances, both horizontally and vertically. To minimise this effect on the derivation of bias adjustment factors at co-location sites, local authorities should:

- ensure that the diffusion tubes are placed as close as possible (ideally within 10 cm) to the automatic analyser inlet. Where a separation distance is essential, then effort should focus on ensuring that both the tube and the inlet are the same distance from the kerb and the same height.

7.5 These recommendations, if followed through, should improve the consistency of diffusion tube results, and hence make evidence of trends more reliable. It should, nevertheless, be recognised that there can still be significant differences in diffusion tube bias from site-to-site, which cannot be fully overcome by applying bias adjustment factors. As a consequence, the absolute values of NO_2 from diffusion tubes will remain more uncertain than those from automatic monitors.

7.6 Any changes made following these recommendations, either to the laboratory being used to supply and analyse the diffusion tubes or to the placement of the tubes, should be applied from the beginning of a new monitoring year, i.e. as near as practicable to 1 January, to avoid additional uncertainties due to applying bias adjustment factors for different laboratories to separate parts of the year or to the bias at a site changing due to revised tube placement. Any changes made should also be clearly documented.

7.7 Finally, it is recommended that the Scottish Government and/or SEPA consider using the findings of this study to prepare guidance for Scottish local authorities on how to generate and apply bias adjustment factors. Amongst other matters, this should consider:

- the minimum number of co-location sites to aim for;
- the need to ensure consistency in the co-location sites over time;
- whether a long-term site should be established in Scotland, at which all laboratories expose tubes, to accompany the site at Marylebone Road, London;
- minimum standards for laboratory performance to ensure reliable results;
- the suitability of sites for co-location studies; and
- how best to apply bias adjustment factors.

8 References

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9 Glossary

AQC	Air Quality Consultants
AURN	Automatic Urban and Rural Network
Defra	Department for Environment, Food and Rural Affairs
EU	European Union
LAQM	Local Air Quality Management
$\mu g/m^3$	Microgrammes per cubic metre
NO	Nitric oxide
NO_2	Nitrogen dioxide
NOx	Nitrogen oxides (taken to be NO_2 + NO)
O_3	Ozone

10 Appendices

A1 Questionnaire for Local Authorities

A1.1 The following questions were included in an email sent to all Scottish local authorities:

> To help us carry out our investigations we would like to know about your practices within the time frame 2000 to 2017. We would therefore be grateful if you would provide answers to the following questions:
>
> 1. Which laboratory currently provides your tubes and analyses your tubes?
> 2.
>   a. Can you please list any changes to the laboratory used and when they were introduced?
> 3. What bias adjustment factors do you currently use to adjust your diffusion tube results?
> 4.
>   a. Are they from the National database?
>   b. Are they based on local factors?
>   c. A combination and national and local factors?
>   d. Can you please list any changes to your approach and when they were introduced?
> 5. Do you operate co-location sites (where tubes are run alongside automatic monitors)?
> 6.
>   a. If so do you report all the results to the National Database?
>
> Please provide as much detail as possible.

A2 Summary of Local Authority Responses

A2.1 The following is a summary of the responses from the questions put to the local authorities.

Table A1: Summary of Local Authority Responses

Local Authority	Laboratory [a]	Change in Laboratory Used	Carry out Co-location	Reported to National Database
Aberdeen	Aberdeen SS	No	Yes	Yes
Aberdeenshire	Aberdeen SS	No	No	n/a
Angus	Tayside SS	No	No	n/a
Argyll & Bute	Glasgow SS	No	No	n/a
Clackmannanshire	Glasgow SS	No	Yes	No
Dumfries & Galloway	Socotec (formerly ESG)	No	Yes	Yes
Dundee	Tayside SS	No	Yes	Yes
East Ayrshire	Glasgow SS	No	Yes	Not always
East Dunbartonshire	Glasgow SS	No	Yes	Yes
East Lothian	Edinburgh SS	No	Yes	No
East Renfrewshire	Glasgow SS	No	No	n/a
Edinburgh	Edinburgh SS	No	Yes	Yes
Eilean Siar	Glasgow SS	No	No	n/a
Falkirk	Gradko (50% TEA acetone)	Socotec until 2015	Yes	Yes
Fife	Tayside SS	Socotec from 2018	Yes	Yes
Glasgow	Glasgow SS	No	Yes	Yes
Highland	Gradko (20% TEA water)	No	Yes	No
Inverclyde	Glasgow SS	Clyde Analytical until 2006	Yes	No
Midlothian	Edinburgh SS	No	No	n/a
Moray	Aberdeen SS	No	No	n/a
North Ayrshire	Glasgow SS	Gradko up to 2013	Yes	Yes
North Lanarkshire	Glasgow SS	No	Yes	Sometimes
Orkney	Edinburgh SS	No	No	n/a
Perth & Kinross	Tayside SS	No	Yes	Yes
Renfrewshire	Glasgow SS	No	Yes	No

Local Authority	Laboratory [a]	Change in Laboratory Used	Carry out Co-location	Reported to National Database
Scottish Borders	Edinburgh SS	Changed from Yorkshire Lab – date unknown	No	n/a
Shetland	n/a	n/a	n/a	n/a
South Ayrshire	Glasgow SS	No	Yes	No
South Lanarkshire	Edinburgh SS	Changed from Glasgow SS in 2007	No	n/a
Stirling	Edinburgh SS	No	Yes	Yes
West Dunbartonshire	Glasgow SS	No	Yes	No
West Lothian	Edinburgh SS	No	Yes	Most years

[a] the tube types are set out in Table 1.

Table A2: Summary of Local Authority Responses [a]

Local Authority	National Database	Local Factor	Combination	Changes
Aberdeen	-	Yes	-	None apparent
Aberdeenshire	Yes	No	-	Asked what colleagues in Aberdeen City Council are using – if deemed appropriate would use that. However, to date, national factors are most appropriate
Angus	Yes	No	-	None
Argyll & Bute	Yes	No	No	No changes
Clackmannanshire	Yes	-	-	Not since 2008
Dumfries & Galloway	No	Yes	No	None
Dundee	-	-	Yes	Normally considered appropriate to use an overall factor derived from roadside and kerbside sites. A manual approximate orthogonal regression calculation using Bias B figures is carried out for the local roadside sites separately and incorporating the national inter-comparison kerbside site at Marylebone Road. The factor obtained using only local roadside sites is compared with the factor obtained when the kerbside site at Marylebone Road is included and the most conservative one is chosen. When there is insufficient data capture available for local sites then the figure from the National Co-location Spreadsheet is used. Quite often the kerbside site at Marylebone Road is the only result showing on the National Colocation Spreadsheet when we come to consider the bias.
East Ayrshire	Yes	No	No	-

Local Authority	National Database	Local Factor	Combination	Changes
East Dunbartonshire	-	-	Yes	Usually opt to use whichever figure is higher – local or national (it is usually local)
East Lothian	No	Yes	No	
East Renfrewshire	Yes (from 2017 APR)	-	-	-
Edinburgh	-	-	Yes	Prior to 2011 a locally derived bias adjustment factor was calculated as a mean of all the local studies. Between 2011 and 2016 the factor was calculated using a combination of local factors and the factors for the Marylebone Road site and West Lothian sites
Eilean Siar	Yes	-	-	-
Falkirk	Yes	Yes	-	Used national factor for 2016 results but local bias adjustment factors for all other years since 2008
Fife	-	-	Yes	
Glasgow	Yes	No	No	None
Highland	Yes	Yes	Yes	Generally used the national factor until 2010 after which, on most occasions, used local factor, after direction to do so by the reporter to the SG on LAQM. Apart from: 2013 - used national factor as there had been significant variation in local factor compared to previous years (and the combined factor was more conservative) 2015 – combined factor used as insufficient data from AURN site to derive a local factor 2016 – local factors from AURN Inverness and SAQD Inverness Academy Street used to adjust all sites. Likely to use this local bias factor for adjustment of tubes in and around the AQMA.
Inverclyde	Yes	Not known	Not known	n/a
Midlothian	Yes	-	Yes	No recent changes
Moray	Yes	-	-	No recent changes
North Ayrshire	No	Yes	n/a	n/a
North Lanarkshire	Yes	-	-	-
Orkney	Yes	-	-	-
Perth & Kinross	-	Yes	-	No changes
Renfrewshire	-	-	-	Has been variable over the years
Scottish Borders	Yes	No	No	n/a
Shetland	n/a	n/a	n/a	n/a
South Ayrshire	Yes	No	No	n/a

Local Authority	National Database	Local Factor	Combination	Changes
South Lanarkshire	Yes	No	No	-
Stirling	Yes	Yes	Yes	n/a
West Dunbartonshire	Yes	No	No	None
West Lothian	-	Yes	-	-

[a] Responses have been paraphrased in places

A3 Questionnaire sent to Laboratories

A3.1 The following is the questionnaire sent to the six laboratories supplying and analysing tubes for Scottish local authorities (one laboratory supplies both 20% TEA in water and 50% TEA in acetone tubes:

Questions

All questions relate to the timeframe of 2000 to 2017. If you need to provide further detail for some of the questions, please do so in the space provided or in the allocated space at the end of the document. Please also provide details at the end of the document for the person completing the questionnaire and the date of completion.

The questionnaire is provided as a template. Please save with your Laboratory's name and then return it to: Prof. Duncan Laxen at AQC (DuncanLaxen@aqconsultants.co.uk).

			Y or N
1	This form is being completed for tubes prepared as (use separate form for both if necessary)	20% TEA in Water	
		50% TEA in Acetone	

		Y or N
3	The laboratory both prepares and analyses the tubes	
	If the laboratory analyses only, who provides the tubes and has this changed.	
(add response here)		

4	Did you make changes following the publication of the Defra guidance in 2008? *Please describe the changes you introduced and the date(s). See checklist 1 for prompts.*
(add response here)	

5	Have you made other changes in more recent years? *Please describe the changes you introduced and the date(s). See checklist 1 for prompts.*
(add response here)	

6	Have you made changes to the way you calculate the concentrations reported? *Please describe the changes you introduced and the date(s). See checklist 2 for prompts.*
(add response here)	

Checklist 1 - Procedures

- The nature of the grids used
- Changes to the way the grids are coated with TEA
- Changes in the tube material (polypropylene or acrylic) and/or the caps (including change in colour)
- Changes of supplier of tubes and/or caps
- Changes to the way the tubes are assembled
- Changes to the cleaning of tubes if reused – or change from reuse to new tubes every time
- Changes to the extraction procedure (in tube or grids removed, vortex mixer or vibrating tray)
- Changes to the nitrite analysis (manual or automated, preparation of reagents, calibration procedure, storage of reagents)
- Change in location of the laboratory and/or equipment used, including replacement instruments etc.

Checklist 2 – Reporting of results

- Changes to the calculation of mg nitrite per tube
- Changes to the calculation/precision of the exposure time
- Changes to the calculation of the ambient concentration (the temperature used for reporting (typical ambient mean of 10ºC or reference of 20ºC) and the diffusion coefficient used)
- Changes to any corrections for laboratory and/or travel blanks
- Changes to rounding of reported results (e.g. from no decimal place to one or more decimal place)

Additional information

6	Is there any additional information you would like to provide
(add response here)	

Respondent Details

7	*Please provide details of the person completing the form and the laboratory*		
Person			
Tel No		Email	
Laboratory			
Date completed			

A4 Summary of Laboratory Responses

A4.1 The following sets out the responses of the laboratories to questions 4 and 5 in the questionnaire (see Appendix A3). Further details about the tubes used by each laboratory are provided in Table 1. In response to question 6, *Have you made changes to the way you calculate the concentrations reported?* none of the laboratories reported any changes.

Laboratory	Changes following Guidance	Changes in Recent Years
Aberdeen Scientific Services	Changed in Jan 2009 to reflect Guidance: *a)* Introduction of mixed reagent which replaced the separate sulphanilamide and NEDD reagents that were in use. *b)* Method of preparation of standards changed to that specified in the Guidance. The previous method involved the use of micro-pipettes. *c)* Vortex mixing of the tubes added to the method. *d)* Daily pipette calibrations introduced.	No further changes made
Edinburgh Scientific Services	Yes, there was a change to the Nitrite analysis. 4mls of colour reagent is put into the tube (excess). Previously 2.5mls was added.	Yes, there was a change to the extraction procedure in May 2009. A vibrating tray is now specified in the extraction procedure
Glasgow Scientific Services	Pre 2008 1 mL of water was added to tubes plus 1 Ml of each reagent. Mixing was carried out between each addition. Also pre 2008 tubes were purchased from Gradko each month, however, around 2003 the lab started to clean and re-use tubes each month carrying our appropriate QC checks. Since 2008 the lab has carried out NO2 tube analysis in line with the DEFRA guidance.	The tubes are analysed by a UV spectrophotometer. 6 years ago an autosampler was purchased that was compatible with the instrument to free up analyst time. However, the autosampler only introduces the coloured solution to the spectrophotometer. The reagents are all still prepared and added to the tube by the analyst. • Changes to the extraction procedure (in tube or grids removed, vortex mixer or vibrating tray): A vibrating was introduced April 2018. A vortex mixer was used exclusively up until this point. • Change in location of the laboratory and/or equipment used, including replacement instruments: A more up to date UV spectrophotometer was purchased in November 2012. The lab where the tube analysis has been carried out has been relocated on the following dates 2012 (month not available), February 2018. The change in location has been a change of room within the same building
Tayside Scientific Services		Depending on the spectrometer used we have modified the calibration range. Cheaper spectrometers have lesser range; better ones more range. With more range there is less need to dilute samples from urban tubes.
Socotec [a]	No	Relocated laboratory in 2011. No other changes

Laboratory	Changes following Guidance	Changes in Recent Years
Gradko	Did not respond to questionnaire	Did not respond to questionnaire

[a] Socotec was formerly ESG Didcot and before that Harwell

A4.2 Only one laboratory provided further information. Aberdeen Scientific Services said:

"The laboratory does not correct sample results to compensate for any blank results as these are generally very low.

Although the need to harmonise the methods used by laboratories was understood, the main observation that I would make is that the Guidance method was more time consuming and laborious than the original in-house procedure used by ASSL and although the laboratory performance has remained good throughout the last 10 years, the original in-house procedure did seem to produce more consistent results."

A5 Sites used in Trend Analyses

A5.1 The following sites have valid data for use in the trend analyses of automatic monitor data ins Scotland (see paragraph 4.1 for discussion on valid data sets).

Table A3: Sites with Valid Data for Trend Analyses, 2008-2017

Site	Type [a]
Aberdeen Anderson Dr	Roadside
Aberdeen Errol Place	Urban Background
Aberdeen Union Street Roadside	Roadside
Aberdeen Wellington Road	Roadside
Auchencorth Moss	Rural
Bush Estate	Rural
Dumfries	Roadside
Dundee Lochee Road	Roadside
Dundee Seagate	Roadside
Dundee Whitehall Street	Roadside
East Dunbartonshire Bearsden	Roadside
East Dunbartonshire Bishopbriggs	Roadside
East Dunbartonshire Kirkintilloch	Roadside
Edinburgh Gorgie Road	Roadside
Edinburgh St John's Road	Roadside
Edinburgh St Leonards	Urban Background
Eskdalemuir	Rural
Falkirk Grangemouth MC	Urban Background
Falkirk Haggs	Roadside
Falkirk Hope St	Roadside
Fife Cupar	Roadside
Fife Dunfermline	Roadside
Fife Rosyth	Roadside
Fort William	Urban Background
Glasgow Anderston	Urban Background
Glasgow Byres Road	Roadside
Glasgow Kerbside	Roadside

Site	Type [a]
Glasgow Waulkmillglen Reservoir	Rural
Grangemouth	Urban Background
Inverness	Roadside
Lerwick	Rural
N Lanarkshire Chapelhall	Roadside
N Lanarkshire Croy	Roadside
N Lanarkshire Moodiesburn	Roadside
Paisley Gordon Street	Roadside
Perth Atholl Street	Roadside
Perth High Street	Roadside
South Ayrshire Ayr High St	Roadside
South Lanarkshire East Kilbride	Roadside
Strath Vaich	Rural
West Dunbartonshire Clydebank	Roadside
West Dunbartonshire Glasgow Road	Roadside
West Lothian Broxburn	Roadside

[a] The term roadside includes kerbside sites for the purpose of this report

A6 Trends in NO_2 and NOx Concentrations in Scotland 2008-2017 by Site Type

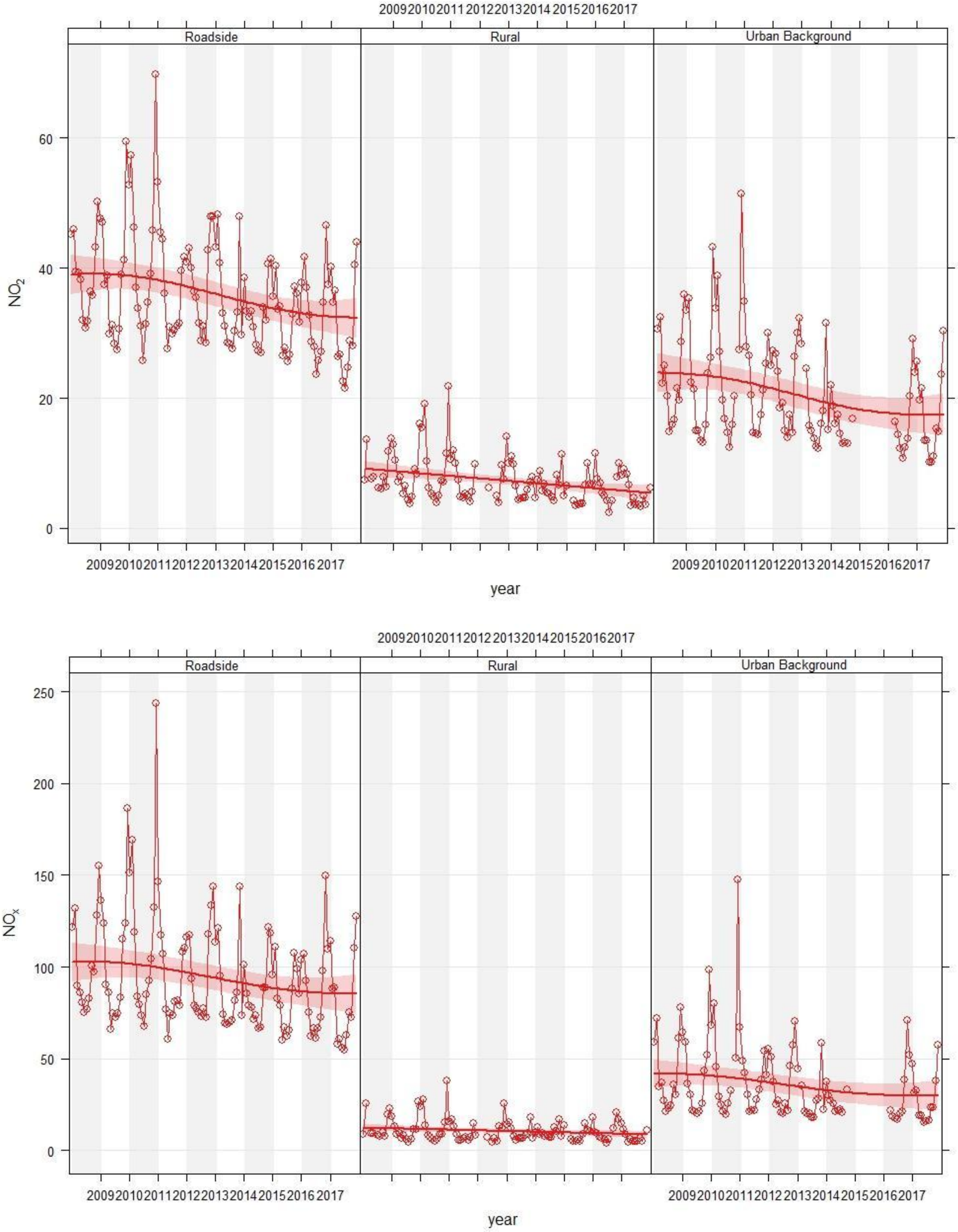

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Figure A1 SmoothTrend for NO_2 (top) and NOx (bottom) at 31 Roadside, 6 Rural and 6 Urban Background Sites (bottom), 2008-2017

A7 Trends in Temperature and Humidity in Scotland 2008-2017

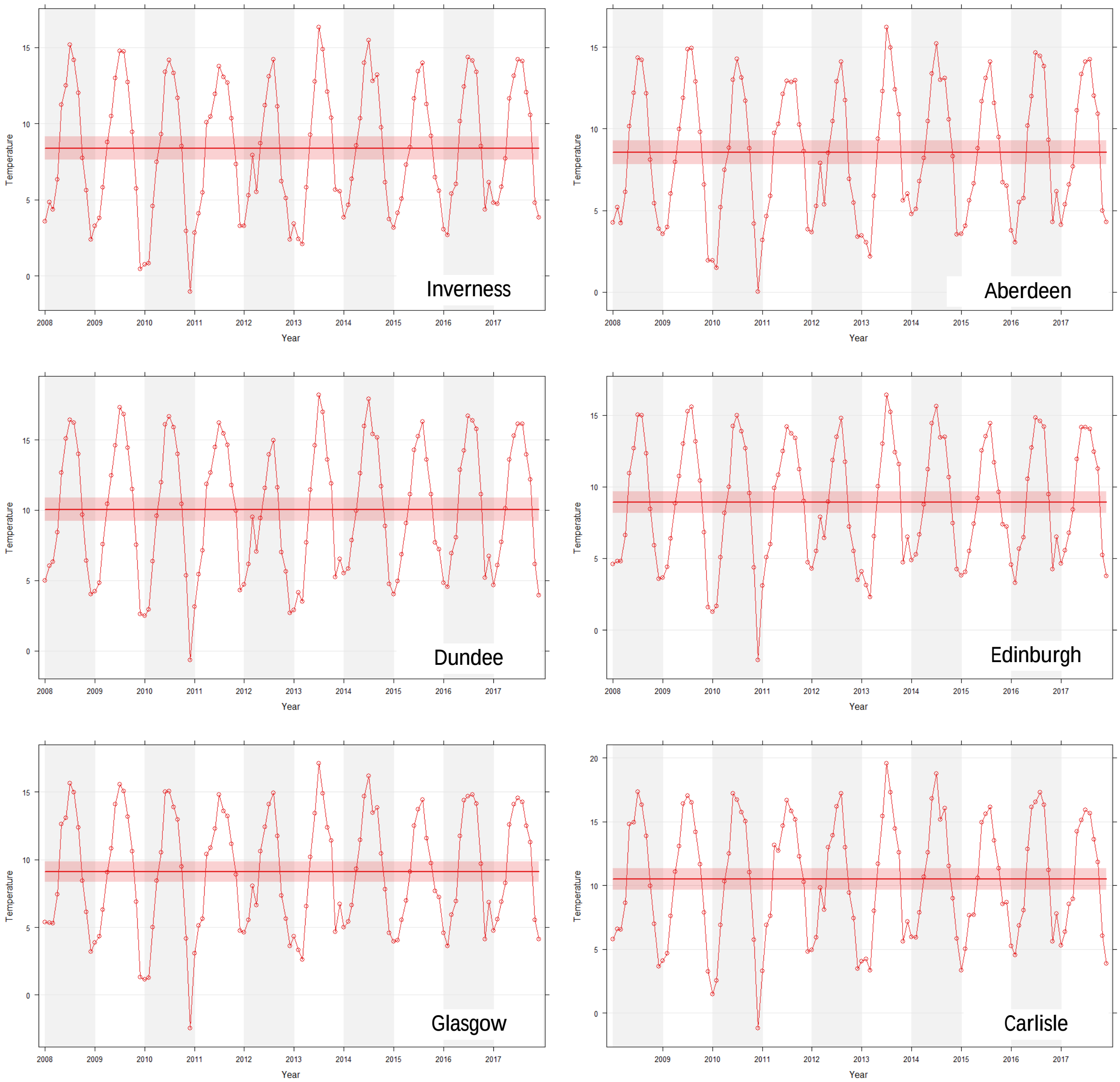

Figure A2 SmoothTrend for Temperature, 2008-2017 a) Inverness, b) Aberdeen, c) Dundee, d) Edinburgh, e) Glasgow and f) Carlisle

The data are all for meteorological monitoring sites at airports

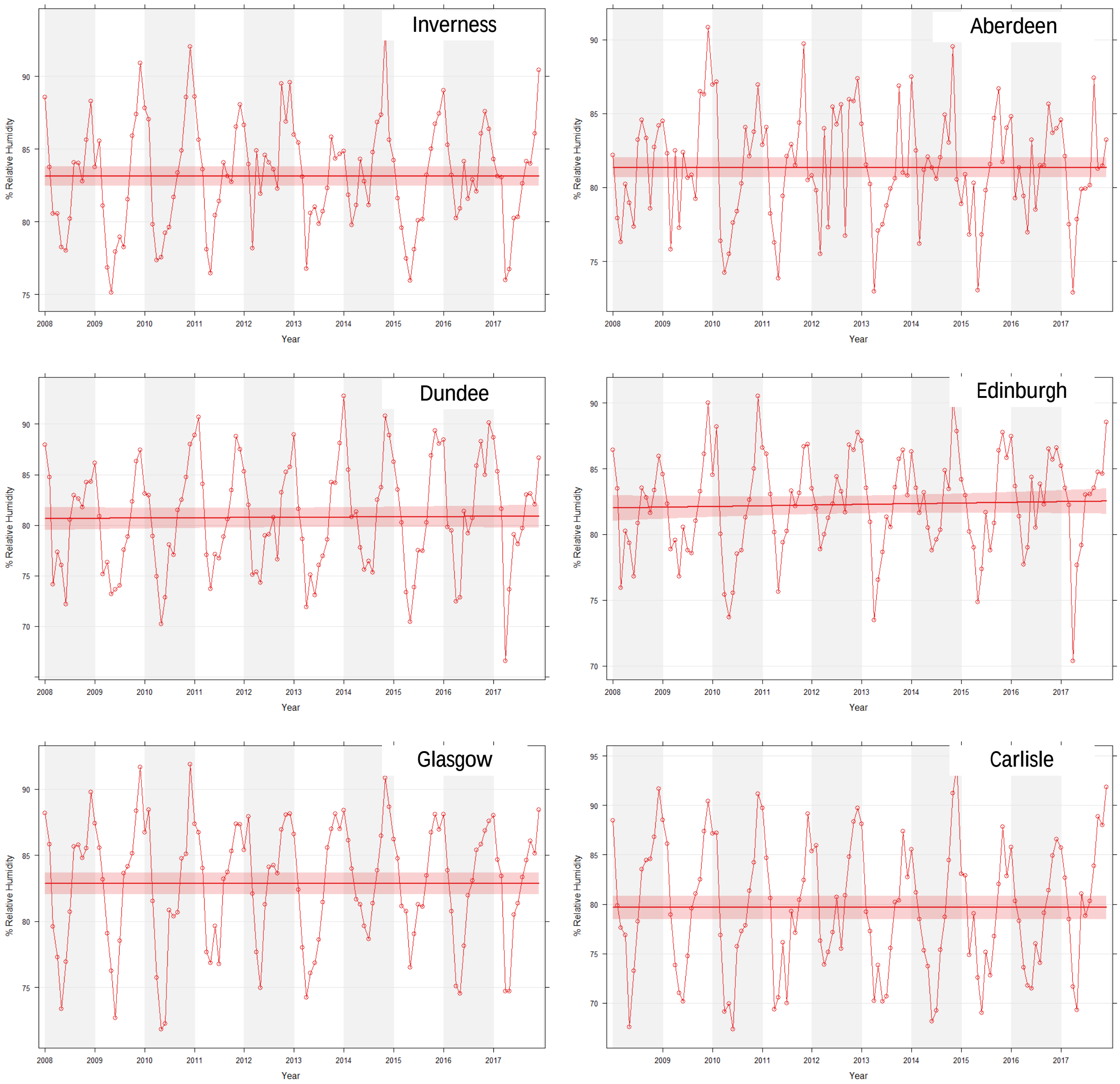

Figure A3 SmoothTrend for Relative Humidity, 2008-2017 a) Inverness, b) Aberdeen, c) Dundee, d) Edinburgh, e) Glasgow and f) Carlisle

The data are all for meteorological monitoring sites at airports