Air Quality Consultants

Analysis of Factors Influencing Diffusion Tube Performance

Document Control

Client	Defra and the Devolved Administrations	Principal Contact	Janet Dixon (Defra)

Job Number	J504

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Document Status and Review Schedule

Issue No.	Report No.	Date	Status	Reviewed by
1	504/2/F1	13th June 2008	Final Report	Prof. Duncan Laxen
2				
3				

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Contents

1 Introduction

1.1 In early 2006, AEA Energy & Environment[1], on behalf of Defra and the Devolved Administrations (DAs), conducted a questionnaire survey of procedures used by commercial UK laboratories for the preparation and analysis of nitrogen dioxide diffusion tubes. The findings of this survey have been combined with the results of an ongoing survey being carried out by AQC to collate the results from diffusion tube co-location studies being carried out by Local Authorities across the UK (the results are published regularly on the Review and Assessment website: www.uwe.ac.uk/review). The aim has been to establish whether the collocation results can help identify those diffusion tube preparation and analysis techniques that improve diffusion tube performance in terms of both bias and precision. The findings have contributed to the formulation of the advice contained in the Practical Guidance for Laboratories and Users of Diffusion Tubes for Ambient NO_2 Monitoring[2].

1.2 Results from a total of 161 annual collocation studies involving 21 laboratories have been analysed using five different measures of diffusion tube performance. All analyses have been performed on annual mean datasets[3], and cover nine different aspects of the tube preparation and analysis.

1.3 In the absence of a standardised methodology for preparing and analysing diffusion tubes, laboratories have adopted a wide variety of techniques for each of the steps in their preparation and analysis. The wide range of procedures used complicates the analysis being carried out in this report, as comparisons of one set of techniques, e.g. dipping or pipetting to coat the grids with TEA, may be confounded by other techniques that correlate with those being examined, e.g. dipping is confined to the use of acetone solutions. It is thus very difficult to isolate the effect of one preparation / analysis technique from another. Those comparisons where confounding is more likely are highlighted in the discussion of the results. The aim is to highlight possible factors that might affect tube performance, which then deserve examination in a more controlled way. It is important to treat the findings of this study as indicative and not definitive.

1 Formerley known as netcen.
2 February, 2008. Available at www.laqmsupport.org.uk.
3 A minimum of 9 monthly results is required to give a valid annual mean.

2 Methodology

2.1 The responses from the AEA Energy & Environment laboratory questionnaire have been integrated with the results from the AQC Local Authority co-location study questionnaires. For each co-location study there is thus information on which laboratory prepared and analysed the tubes, the extraction method used, how the tubes were cleaned etc.. The analysis was carried out during 2006 and thus co-location studies reported after 2006 are not included. A summary of the 161 co-location studies included in the analysis is provided in Appendix 1.

2.2 All analyses are based on annual datasets. They cover 9 aspects of the diffusion tube preparation and analysis. The categories selected for analysis, and the questions from which they are derived, are summarised in Table 1. The choice of these 9 aspects takes account of the need to have a reasonable number of results for a particular category to make the analysis meaningful.

Table 1 Summary of Categories used in the Analyses[a]

<table>
<tr><th>Laboratory Survey Question</th><th colspan="2">Category 1</th><th colspan="2">Category 2</th></tr>
<tr><td>What type of plastic are the coloured end caps made of?</td><td colspan="2">Soft Opaque</td><td colspan="2">Hard Opaque</td></tr>
<tr><td>Is a surfactant added?</td><td colspan="2">With Brij-35</td><td colspan="2">No Brij-35</td></tr>
<tr><td>How is the solution applied to the grids?</td><td colspan="2">Dipping</td><td colspan="2">Pipetting</td></tr>
<tr><td>Where are the tubes prepared and/or assembled?</td><td colspan="2">Clean Air
Clean air room
Under a clean air hood</td><td colspan="2">Not Clean Air</td></tr>
<tr><td>If dipping, how long are grids left in the solution?</td><td colspan="2"><1 min
None, removed straight away
Stirred in solution for 10-12 seconds</td><td colspan="2">>10 min
10 minutes
Soaked until needed (up to 1 month)</td></tr>
<tr><td>How do you assemble the tubes?</td><td colspan="2">Wet grid
Pipetting
Wet dipped mesh</td><td colspan="2">Dry grid
Dry dipped mesh</td></tr>
<tr><td>What method is used for analysis?</td><td colspan="2">Manual
Manual colorimetric</td><td colspan="2">Automated
Automatic colorimetric</td></tr>
<tr><td>What method is used to agitate the grids and reagent?</td><td colspan="2">Shake by Hand</td><td colspan="2">Vibrating Tray</td></tr>
<tr><td rowspan="2">What type of TEA solution is used to prepare the tubes</td><td>Category 1</td><td>Category 2</td><td>Category 3</td><td>Category 4</td></tr>
<tr><td>10% TEA in Water</td><td>20% TEA in Water</td><td>50% TEA in Water</td><td>50% TEA in Acetone</td></tr>
</table>

[a] Text in bold is the summary term used in subsequent tables; text not in bold covers specific questionnaire responses included under a particular category heading

2.3 The results are presented in two ways, firstly, as x-y scatter plots, with the annual mean nitrogen dioxide concentration from the automatic monitor on the x-axis and the annual mean nitrogen dioxide concentration from the co-located diffusion tubes on the y-axis. Each symbol thus represents the result from a single annual mean co-location study. The position of each symbol in relation to the 1:1 line shows the study-specific bias.

2.4 In order to illustrate the potential influence of study-specific precision, the data in the x-y plots have been separated into "good precision" and "poor precision". A study is assumed to have "good precision" where the coefficient of variation (CV) (i.e the standard deviation of the triplicate monthly results normalised to the monthly mean) of eight or more monthly exposure periods is less than 20%, and the average CV of all monitoring periods is less than 10%. A study is assumed to have "poor precision" if four or more monthly exposure periods have a CV greater than 20% and/or the average CV is greater than 10%.

2.5 These scatter plots thus show how different techniques may have influenced bias; how they may have affected precision; and also whether good and poor precision tubes tend to result in different bias.

2.6 Secondly, the results are presented as box plots summarising the study-specific precision, as defined above. The mean across all of the technique-specific studies is shown as a thick red line. The boxes show the data quartiles (so that 50% of the results lie within the box). The "whiskers" show the full range of the data, with the exception of outliers[4] which are shown individually in the plots.

2.7 Five different quantitative tests have been applied to the datasets to identify whether a particular technique might produce 'better' results. The five tests and the basis for the decision that a particular technique is 'better' or 'much better' are as follows:

A) ***A bias that is closer to the pattern expected.*** In this context the measure of 'better' is a smaller proportion of result where the diffusion tube is under-predicting, i.e. the bias is less than 1.0, or in the context of the x-y plots, the value falls below the line. This is because theoretical understanding of the performance of diffusion tubes leads to the conclusion that they should over-predict. This analysis was carried out separately for the whole data set and the dataset with only good precision.

B) ***A smaller uncertainty in the bias.*** The measure is the correlation coefficient (r) of the diffusion tube versus automatic data; with a larger coefficient indicating less variation about the relationship between diffusion tubes and automatic monitors, and thus being 'better'. This

4 Outliers are defined as those values that exceed 1.5 times the inter-quartile range.

analysis was carried out separately for the whole dataset and the dataset with only good precision.

C) ***More results evaluated to have a 'good' precision.*** The measures of 'good' or 'poor' precision are as defined in paragraph 2.4 above. A larger number of results with 'good' precision indicates a 'better' performance.

D) ***Fewer results with a large coefficient of variation.*** The AEA Energy & Environment spreadsheet for recording the results of triplicate diffusion tube analyses includes an overall measure of precision, which is the average of the individual monthly precision results. The measure used is the number of annual collocation results with an overall diffusion tube precision >15%. A smaller number of results indicates a 'better' performance.

E) ***A significant difference in the average precision.*** This relies on a 2-tailed Students t-test to determine whether there is a significant difference between the mean of the two sets of average precision results, i.e. whether the two datasets shown in the box plots are significantly different. A technique is judged 'better' if it is different at the 5-10% significance level, and 'much better' if different at the 5% or less significance level.

2.8 In respect of test B, the term 'better' is only applied if the difference between the numerical values is more than 0.02; e.g. for test B, 0.92 is not described as better than 0.90, but is described as better than 0.89. For tests A, C and D, the term 'better' is only applied if the difference between the numerical values is more than 2. e.g. for test D, 6% is not described as better than 8%, but is described as better than 9%. The term 'much better' is applied if the difference is more than 0.10 for tests B and more than 10% for tests A, C and D. These distinctions are somewhat arbitrary, but provide a reasonable means of summarising the findings[5].

2.9 These five tests have been applied to 9 sets of differences in the techniques. As a large number of results were obtained from one laboratory, the tests were (where appropriate) applied with and without this laboratory (Gradko). This was done to ensure that the results from one laboratory were not determining the outcome. For many of the analyses (for example dipped vs pipetted), Gradko tubes only account for results in one of the two datasets being compared (in this case, pipetted). Thus, removing Gradko tubes depletes the pipetted dataset, but not the dipped dataset.

[5] For the analysis of different TEA solutions, for which there are four separate categories, the results for each category are judged to be 'better' or 'much better' if they fulfil these criteria in relation to at least 2 of the other categories.

3 Results and Discussion

3.1 The outcomes of the 5 tests applied to each of the 9 sets of comparisons being carried out are summarised below, with the full set of results presented in Appendix 2 (including the sample size of each dataset). A result that indicates a 'better' performance is summarised with a +, while one with a 'much better' performance is summarised with ++. In the case of tests A and B, only the results for the full dataset are included. Separate analyses have been performed for collocation results with diffusion tubes having 'good' performance, but in most cases the outcome is the same as for the full dataset. The results summarised in this section are those for the full datasets.

Influence of Soft and Hard Caps

3.2 The questionnaire distinguished between the use of soft or hard caps on the diffusion tubes to retain the grids and to seal the tube prior to and following exposure. There is no clear pattern to suggest that tubes prepared with soft caps perform better than those with a hard cap or vice versa (Table 1).

Table 1 Summary of tests applied to soft and hard diffusion tube caps.

Test		All Data		Gradko Excluded	
		Soft Opaque Caps	Hard Opaque Caps	Soft Opaque Caps	Hard Opaque Caps
A	Bias		++		
B	Uncertainty in bias	+		+	
C	Proportion with 'good' precision	++			
D	Proportion with large coefficients of variation				+
E	Average precision	++			

Influence of Addition of Brij-35 Surfactant

3.3 The questionnaire distinguished between tubes to which Brij-35 surfactant had been added and those with no surfactant added (Brij-35 was the only surfactant used). Since Brij-35 is only used in combination with the pipetting method, dipped tubes were removed from this analysis. There is some evidence to suggest that the addition of Brij-35 surfactant solution improves the performance of pipetted tubes, particularly when results for Gradko are excluded (Table 2).

Table 2 Summary of tests applied to diffusion tubes with or without Brij-35 surfactant solution added.

Test		All Data		Gradko Excluded	
		With Brij	No Brij	With Brij	No Brij
A	Bias	++		++	
B	Uncertainty in bias		+		
C	Proportion with ‘good’ precision		+	++	
D	Proportion with large coefficients of variation	+		++	
E	Average precision				

Influence of Pipetting or Dipping Grids

3.4 The questionnaire distinguished between grids prepared by dipping of grids in TEA solution or pipetting of TEA solution onto the grid. There is some evidence that tubes prepared by dipping the grids in TEA perform better. This evidence is not considered to be strong, as there is no statistically significant difference in the precision of the results for the two techniques (Table 3). Confounding factors are likely to be particularly strong in this comparison, as all dipped tubes are acetone based, while the majority of pipetted tubes are water based.

Table 3 Summary of tests applied to diffusion tubes with TEA added by dipping grids or pipetting onto grids already in tubes.

Test		All Data		Gradko Excluded	
		Dipping	Pipetting	Dipping	Pipetting
A	Bias	++		+	
B	Uncertainty in bias	+		++	
C	Proportion with ‘good’ precision		+	+	
D	Proportion with large coefficients of variation			+	
E	Average precision				

Influence of a Clean Air Environment

3.5 The questionnaire distinguished between tubes prepared in a clean air environment, or not. There is no clear pattern to suggest that tubes prepared in a clean air environment perform better (Table 4).

Table 4 Summary of tests applied to diffusion tubes prepared or not prepared in a clean air environment.

Test		All Data		Gradko Excluded	
		Clean Air	Not Clean Air	Clean Air	Not Clean Air
A	Bias	++		++	
B	Uncertainty in bias		+		+
C	Proportion with 'good' precision		++		+
D	Proportion with large coefficients of variation			+	
E	Average precision				

Influence of Dipping only Briefly or Soaking Grids in TEA Solution

3.6 The questionnaire distinguished between dipped grids exposed to the TEA solution for a short period: less than 1 minute, and a longer period: >10 minutes. In this case there is no exclusion of Gradko tubes, as they are prepared by pipetting, not dipping. There is a clear pattern that tubes prepared with grids that had been soaked for more than 10 minutes performed better than tubes prepared with grids with a short exposure to TEA solution (Table 5).

Table 5 Summary of tests applied to diffusion tube grids prepared by dipping briefly or soaking for some time in TEA solution.

Test		All Data	
		<1 min	>10 min
A	Bias	+	
B	Uncertainty in bias		+
C	Proportion with 'good' precision		++
D	Proportion with large coefficients of variation		++
E	Average precision		++

Influence of Use of Wet or Dry Grids when Tube is Assembled

3.7 The questionnaire distinguished between tubes prepared with wet grids and those prepared with dry grids. There is a clear pattern that tubes prepared with grids that have been dried before assembly perform better than those with grids that are wet when the tube is assembled (Table 6).

Table 6 Summary of tests applied to diffusion tubes prepared with grids dried or not before assembly.

Test		All Data		Gradko Excluded	
		Wet grid	Dry grid	Wet grid	Dry grid
A	Bias		++		+
B	Uncertainty in bias		+		++
C	Proportion with 'good' precision		+		++
D	Proportion with large coefficients of variation		+		++
E	Average precision				++

Influence of Automated or Manual Analysis

3.8 The questionnaire distinguished between tubes analysed with manual or automatic colorimetry. There is some evidence that tubes analysed with an auto-analyser perform better. This evidence is not considered to be strong, as there is no statistically significant difference in the precision of the results for the two techniques (Table 7).

Table 7 Summary of tests applied to diffusion tubes analysed using automated or manual techniques.

Test		All Data		Gradko Excluded	
		Manual	Automated	Manual	Automated
A	Bias		++		+
B	Uncertainty in bias				
C	Proportion with 'good' precision		+		++
D	Proportion with large coefficients of variation		+		+
E	Average precision				

Influence of Extraction Mixing

3.9 The questionnaire distinguished between tubes in which the extraction solution was mixed in the tube by manual shaking, and those mixed using a vibrating tray. There is some evidence that tubes shaken by hand perform better. This becomes more apparent when the Gradko results are excluded. Gradko use a vibrating tray. The number of results involving use of a vibrating tray becomes fairly small when Gradko is excluded (Table 8).

Table 8 Summary of tests applied to diffusion tubes extracted by manual shaking or vibrating tray.

Test		All Data		Gradko Excluded	
		Shake By Hand	Vibrating Tray	Shake By Hand	Vibrating Tray
A	Bias	+		++	
B	Uncertainty in bias	++		++	
C	Proportion with 'good' precision		+	++	
D	Proportion with large coefficients of variation	+		++	
E	Average precision			+	

Influence of TEA Solution

3.10 Four different TEA solutions have been used to prepare the tubes. The results of comparing one technique against each of the others are set out in Table 9. The basis for a preparation technique performing "better" or "much better" in this four-way comparison is explained in paragraph 2.8, and also in the footnote to the Table. As with all of the analyses presented in this report, these tests will be affected by confounding factors. For instance, there is a strong link between the solution used and the method of application; dipping or pipetting. Furthermore, limited attention should be paid to the results for 10% and 50% TEA in water, as only one and two laboratories respectively used these techniques. The results show a clear pattern that tubes prepared using 20% TEA in water perform better than those using 50% TEA in acetone. Interestingly, this is despite there being some evidence (see para 3.4 above) that tubes prepared by dipping, and hence involving 50% TEA in acetone, perform better.

Table 9 Summary of tests applied to different tube preparation methods [a].

Test		All Data				Gradko Excluded			
		10% TEA/ Water	20% TEA/ Water	50% TEA/ Water	50% TEA/ Acet.	10% TEA/ Water	20% TEA/ Water	50% TEA/ Water	50% TEA/ Acet.
A	Bias	++	++			++	++		
B	Uncertainty in bias			+			+	+	
C	Proportion with 'good' precision	+	++			++	++		
D	Proportion with large coefficients of variation	++	+			++	+		
E	Average precision [b]		++						

[a] Because there are four categories, a method is judged to be 'better' or 'much better' if it fulfils the criteria given in section 2, when compared to at least TWO other methods. For example, Test C (all data): 10% TEA in water gives a result (69%), which is more than 2% greater than either 50% TEA in water (50%) or 50% TEA in acetone (61%) and is thus described at 'better'. 20% TEA in water (at 82%) is more than 10% greater than the worst two methods and is described as 'much better'.

[b] As assessed against all of the other categories on aggregate.

4 Summary and Conclusions

4.1 Results from 161 annual collocation studies involving 21 laboratories have been analysed to help establish whether specific diffusion tube preparation and analysis techniques improve diffusion tube performance.

4.2 Nine different sets of comparisons have been carried out, using five bias and precision related tests, to identify whether a particular technique might produce a 'better' performance. The results indicate:

- **no clear pattern** that a soft cap on a diffusion tube is better than a hard cap or vice versa;
- **some evidence** to suggest that the addition of Brij solution improves the performance of tubes prepared by pipetting;
- **some evidence** that the dipping of grids in TEA solution provides a better performance than pipetting of TEA solution into the tubes;
- **no clear pattern** that tubes prepared in a clean air environment perform better;
- **a clear pattern** that tubes prepared with grids that had been soaked for more than 10 minutes performed better than tubes prepared with grids with a short exposure to TEA solution of less than 1 minute;
- **a clear pattern** that tubes prepared with grids that have been dried before assembly perform better than those with grids that are wet when the tube is assembled;
- **some evidence** that tubes analysed with an auto-analyser perform better;
- **some evidence** that tubes shaken by hand during the analysis perform better than those in which the extraction solution was mixed using a vibrating tray.
- **a clear pattern** that tubes prepared using 20% TEA in water (and possibly 10% TEA in water) perform better than those using 50% TEA in acetone (and possibly 50% TEA in water).

4.3 The outcomes of this analysis have helped formulate advice on improvements in current practices in order to provide a more standardised approach to diffusion tube preparation and analysis.

Appendix 1 - Co-location Data Used in Analysis

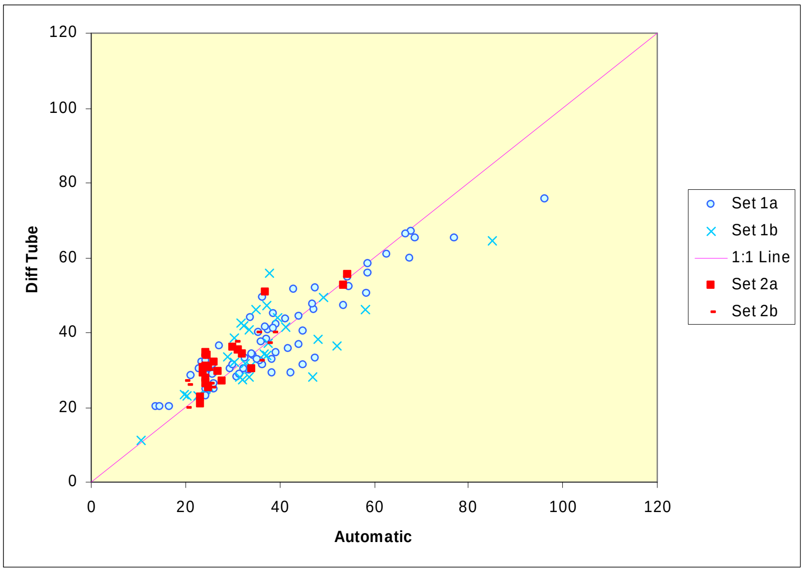
Analysed By	Method	Year of Study	Site Type	Local Authority	Length of Study (months)	Diffusion Tube Mean ($\mu g/m^3$)	Automatic Monitor Mean ($\mu g/m^3$)	Tube Precision	Mean CV
Gradko	50% TEA in Acetone	2003	UB	Sheffield CC	9	36	42	GOOD	7
Gradko	50% TEA in Acetone	2004	UC	Sheffield CC	12	30	34	GOOD	7
Gradko	50% TEA in Acetone	2004	UB	Sheffield CC	11	29	42	GOOD	10
Harwell Scientific Services	50% TEA in Acetone	2004	R	Gravesham BC	11	53	54	GOOD	9
Gradko	20% TEA in Water	2004	R	LB Ealing	10	55	54	GOOD	8
Gradko	20% TEA in Water	2004	UB	LB Ealing	12	44	41	GOOD	5
Gradko	20% TEA in Water	2004	R	Exeter CC	12	35	39	GOOD	3
Gradko	50% TEA in Acetone	2004	B	Sandwell MBC	10	30	29	GOOD	10
West Yorkshire Analytical Services	50% TEA in Acetone	2004	UB	Leeds CC	12	25	26	GOOD	8
Gradko	20% TEA in Water	2004	UB	Dudley MBC	11	29	26	GOOD	5
Harwell Scientific Services	50% TEA in Acetone	2004	I	Gravesham BC	11	35	31	GOOD	6
Gradko	20% TEA in Water	2004	R	Macclesfield BC	12	33	38	GOOD	7
West Yorkshire Analytical Services	50% TEA in Acetone	2004	Int	Leeds CC	10	40	45	GOOD	5
Jesmond Dene Laboratory	50% TEA in Acetone	2004	UC	Gateshead Council	10	36	36	GOOD	8
Gradko	20% TEA in Water	2004	R	Dudley MBC	12	46	47	GOOD	8
Casella Seal / GMSS / Casella CRE	10% TEA in Water	2004	UB	Warrington BC	9	29	26	GOOD	9
Gradko	20% TEA in Water	2004	R	South Lakeland DC	12	36	27	GOOD	9
Gradko	50% TEA in Water	2004	R	Mid Devon DC	11	47	53	GOOD	8
Gradko	50% TEA in Acetone	2004	UB	LB Hounslow	10	33	48	GOOD	8
Gradko	50% TEA in Acetone	2004	R	LB Hounslow	11	65	69	GOOD	8
Gradko	50% TEA in Acetone	2004	R	LB Hounslow	12	52	48	GOOD	9
Gradko	50% TEA in Acetone	2004	UC	Slough BC	12	34	34	GOOD	6
Gradko	50% TEA in Acetone	2004	Su	Slough BC	12	28	31	GOOD	9
Gradko	50% TEA in Acetone	2004	Su	Telford & Wrekin BC	11	29	38	GOOD	9
Gradko	50% TEA in Acetone	2004	R	LB Southwark	12	56	59	GOOD	8
Edinburgh Scientific Services	50% TEA in Acetone	2004	R	Edinburgh CC	12	41	37	GOOD	8
Edinburgh Scientific Services	50% TEA in Acetone	2004	R	Edinburgh CC	12	42	37	GOOD	7
Dundee CC	20% TEA in Water	2004	R	Fife Council	12	37	31	GOOD	5
Cardiff Scientific Services	50% TEA in Acetone	2002	UC	Cardiff CC	11	34	32	GOOD	9
Bristol Scientific Services	20% TEA in Water	2004	B	Cheltenham BC	12	23	23	GOOD	9
Glasgow Scientific Services	20% TEA in Water	2004	R	North Lanarkshire Council	10	29	24	GOOD	9
Bristol Scientific Services	20% TEA in Water	2004	R	West Wiltshire DC	10	32	26	GOOD	4
Milton Keynes Council	20% TEA in Water	2004	UB	Milton Keynes Council	12	28	21	GOOD	5
Casella Seal / GMSS / Casella CRE	10% TEA in Water	2004	R	Dumfries and Galloway Council	12	38	37	GOOD	8
Gradko	50% TEA in Acetone	2004	UB	AEA Tech Intercomparison	11	24	25	GOOD	8
Harwell Scientific Services	50% TEA in Acetone	2004	UB	AEA Tech Intercomparison	11	34	25	GOOD	7
Jesmond Dene Laboratory	50% TEA in Acetone	2004	UB	AEA Tech Intercomparison	12	28	24	GOOD	8
Milton Keynes Council	20% TEA in Water	2004	UB	AEA Tech Intercomparison	11	31	25	GOOD	6
Rotherham MBC / South Yorks	50% TEA in Acetone	2004	UB	AEA Tech Intercomparison	12	34	24	GOOD	1
Glasgow Scientific Services	20% TEA in Water	2004	UB	AEA Tech Intercomparison	10	32	25	GOOD	6

Analysed By	Method	Year of Study	Site Type	Local Authority	Length of Study (months)	Diffusion Tube Mean (mg/m3)	Automatic Monitor Mean (mg/m3)	Tube Precision	Mean CV
Clyde Analytical Laboratories	20% TEA in Water	2004	UB	AEA Tech Intercomparison	12	35	24	GOOD	7
Casella Seal / GMSS / Casella CRE	10% TEA in Water	2004	UB	AEA Tech Intercomparison	12	31	24	GOOD	8
Bristol Scientific Services	20% TEA in Water	2004	UB	AEA Tech Intercomparison	12	28	24	GOOD	6
Gradko	20% TEA in Water	2004	UB	AEA Tech Intercomparison	12	30	24	GOOD	4
Gradko	50% TEA in Water	2004	UB	AEA Tech Intercomparison	12	25	24	GOOD	7
Gradko	50% TEA in Acetone	2004	B	LB Barnet	11	32	36	GOOD	8
Rotherham MBC / South Yorks	50% TEA in Acetone	2004	R	Barnsley MBC	10	48	47	GOOD	6
Rotherham MBC / South Yorks	50% TEA in Acetone	2004	R	Oxford CC	10	67	68	GOOD	3
Gradko	20% TEA in Water	2005	R	Exeter CC	10	37	44	GOOD	3
Gradko	50% TEA in Acetone	2005	UB	Sheffield CC	12	30	32	GOOD	7
Gradko	50% TEA in Acetone	2005	UC	Sheffield CC	12	31	45	GOOD	6
Gradko	20% TEA in Water	2005	R	South Lakeland DC	12	31	26	GOOD	5
Harwell Scientific Services	50% TEA in Acetone	2005	R	Swale BC	10	30	27	GOOD	7
Casella Seal / GMSS / Casella CRE	10% TEA in Water	2005	UB	Wigan MBC	10	32	23	GOOD	8
Gradko	20% TEA in Water	2004	UB	Worcester CC	12	20	14	GOOD	6
Jesmond Dene Laboratory	50% TEA in Acetone	2005	UC	Newcastle upon Tyne CC	12	29	30	GOOD	9
Rotherham MBC / South Yorks	50% TEA in Acetone	2005	R	Barnsley MBC	12	44	44	GOOD	9
Casella Seal / GMSS / Casella CRE	10% TEA in Water	2005	R	Dumfries and Galloway Council	12	37	36	GOOD	7
Gradko	50% TEA in Acetone	2005	UB	Darlington BC	12	23	24	GOOD	6
Harwell Scientific Services	50% TEA in Acetone	2005	UC	Vale of White Horse DC	9	25	25	GOOD	5
Gradko	50% TEA in Acetone	2004	R	LB Hounslow	11	52	55	GOOD	6
Gradko	50% TEA in Acetone	2004	R	LB Hounslow	11	65	77	GOOD	6
Gradko	50% TEA in Acetone	2004	UB	LB Hounslow	11	33	36	GOOD	8
Harwell Scientific Services	50% TEA in Acetone	2005	B	Newport CC	12	31	25	GOOD	7
Gradko	20% TEA in Water	2005	UB	LB Ealing	12	42	39	GOOD	8
Gradko	20% TEA in Water	2005	R	LB Ealing	12	58	59	GOOD	7
Gradko	20% TEA in Water	2005	R	LB Ealing	10	76	96	GOOD	6
Gradko	20% TEA in Water	2005	R	Dartford Council	9	61	63	GOOD	7
Cardiff Scientific Services	50% TEA in Acetone	2005	R	Monmouthshire DC	12	51	37	GOOD	7
Cardiff Scientific Services	50% TEA in Acetone	2003	I	Monmouthshire DC	12	30	34	GOOD	9
Harwell Scientific Services	50% TEA in Acetone	2005	I	Huntingdon DC	10	27	28	GOOD	10
Gradko	50% TEA in Acetone	2005	R	LB Southwark	11	51	59	GOOD	10
Rotherham MBC / South Yorks	50% TEA in Acetone	2004	R	Oxford CC	11	66	67	GOOD	3
Rotherham MBC / South Yorks	50% TEA in Acetone	2005	R	Oxford CC	12	60	68	GOOD	4
Harwell Scientific Services	50% TEA in Acetone	2005	R	Gravesham BC	11	56	54	GOOD	7
Harwell Scientific Services	50% TEA in Acetone	2005	B	Gravesham BC	12	36	30	GOOD	7
Gradko	20% TEA in Water	2005	R	North Warwickshire BC	9	52	43	GOOD	5
Bristol Scientific Services	20% TEA in Water	2005	UB	Cheltenham BC	12	21	23	GOOD	8
Casella Seal / GMSS / Casella CRE	10% TEA in Water	2005	O	Flintshire CC	12	20	17	GOOD	6
Staffordshire CC Scientific Services	50% TEA in Water	2005	O	South Staffordshire DC	12	33	35	GOOD	8
Gradko	20% TEA in Water	2005	B	St Albans DC	10	26	26	GOOD	7
Casella Seal / GMSS / Casella CRE	10% TEA in Water	2005	R	Nottingham CC	12	49	36	GOOD	8
Casella Seal / GMSS / Casella CRE	10% TEA in Water	2005	UC	Nottingham CC	10	44	34	GOOD	6
Casella Seal / GMSS / Casella CRE	10% TEA in Water	2005	O	Nottingham CC	12	40	35	GOOD	8
Glasgow Scientific Services	20% TEA in	2005	K	Glasgow CC	12	87	64	GOOD	8

Analysed By	Method	Year of Study	Site Type	Local Authority	Length of Study (months)	Diffusion Tube Mean (μg/m^3)	Automatic Monitor Mean (μg/m^3)	Tube Precision	Mean CV
	Water								
Casella Seal / GMSS / Casella CRE	10% TEA in Water	2004	O	Flintshire CC	12	20	15	GOOD	7
Milton Keynes Council	20% TEA in Water	2005	UC	Milton Keynes Council	12	30	23	GOOD	6
Milton Keynes Council	20% TEA in Water	2005	R	Milton Keynes Council	11	45	39	GOOD	5
Gradko	20% TEA in Water	2005	R	Rushmoor BC	10	41	39	GOOD	7
Harwell Scientific Services	50% TEA in Acetone	2005	R	Babergh DC	12	29	24	GOOD	10
Harwell Scientific Services	50% TEA in Acetone	2004	R	Babergh DC	12	31	24	GOOD	7
Gradko	50% TEA in Acetone	2005	S	Slough BC	12	29	31	GOOD	6
Gradko	20% TEA in Water	2005	R	Macclesfield BC	12	34	34	GOOD	6
Gradko	50% TEA in Acetone	2005	UC	Slough BC	12	33	33	GOOD	8
Aberdeen CC	50% TEA in Acetone	2005	UB	Netcen Liverpool Speke Intercomparison	10	30	25	GOOD	6
Clyde Analytical Laboratories	20% TEA in Water	2005	UB	Netcen Liverpool Speke Intercomparison	12	31	24	GOOD	10
Bristol Scientific Services	20% TEA in Water	2005	UB	Netcen Liverpool Speke Intercomparison	12	26	24	GOOD	9
Casella Seal / GMSS / Casella CRE	10% TEA in Water	2005	UB	Netcen Liverpool Speke Intercomparison	12	32	24	GOOD	6
Glasgow Scientific Services	20% TEA in Water	2005	UB	Netcen Liverpool Speke Intercomparison	12	31	24	GOOD	7
Gradko	20% TEA in Water	2005	UB	Netcen Liverpool Speke Intercomparison	12	31	24	GOOD	6
Gradko	50% TEA in Acetone	2005	UB	Netcen Liverpool Speke Intercomparison	12	29	24	GOOD	7
Gradko	50% TEA in Water	2005	UB	Netcen Liverpool Speke Intercomparison	12	28	24	GOOD	4
Jesmond Dene Laboratory	50% TEA in Acetone	2005	UB	Netcen Liverpool Speke Intercomparison	12	25	24	GOOD	6
Milton Keynes Council	20% TEA in Water	2005	UB	Netcen Liverpool Speke Intercomparison	11	30	24	GOOD	5
Rotherham MBC / South Yorks	50% TEA in Acetone	2005	UB	Netcen Liverpool Speke Intercomparison	12	34	24	GOOD	1
Staffordshire CC Scientific Services	50% TEA in Water	2005	UB	Netcen Liverpool Speke Intercomparison	11	25	25	GOOD	10
Gradko	50% TEA in Acetone	2003	UC	Sheffield CC	12	37	38	POOR	12
Northampton BC	20% TEA in Water	2004	B	Northampton BC	9	20	20	POOR	13
Kent Scientific Services	50% TEA in Acetone	2004	R	Eastleigh BC	12	41	55	POOR	12
Kent Scientific Services	50% TEA in Acetone	2004	R	Eastleigh BC	12	30	40	POOR	11
Gradko	50% TEA in Acetone	2003	B	Sandwell MBC	11	34	37	POOR	11
Jesmond Dene Laboratory	50% TEA in Acetone	2004	R	Gateshead Council	11	36	41	POOR	14
Staffordshire CC Scientific Services	50% TEA in Water	2004	R	East Staffordshire BC	11	32	33	POOR	12
Gradko	50% TEA in Acetone	2004	UC	LB Camden	12	49	49	POOR	12
Casella Seal / GMSS / Casella CRE	10% TEA in Water	2004	R	Wrexham CBC	12	23	20	POOR	11
Gradko	20% TEA in Water	2004	R	Rushmoor BC	11	39	30	POOR	10
West Yorkshire Analytical Services	50% TEA in Acetone	2004	UC	Leeds CC	11	41	34	POOR	12
Casella Seal / GMSS / Casella CRE	10% TEA in Water	2004	0	Stockport MBC	10	47	37	POOR	14
Gradko	50% TEA in Acetone	2003	UB	LB Hounslow	11	36	52	POOR	13
Gradko	50% TEA in Acetone	2003	R	LB Hounslow	9	64	85	POOR	13
Edinburgh Scientific Services	50% TEA in Acetone	2004	B	Edinburgh CC	10	11	11	POOR	14
Gradko	50% TEA in Water	2004	R	Thurrock Council	12	44	40	POOR	12
Bristol Scientific Services	20% TEA in Water	2004	R	Brighton and Hove CC	12	37	37	POOR	11
Bristol Scientific Services	20% TEA in Water	2003	R	Brighton and Hove CC	12	40	39	POOR	12
Cardiff Scientific Services	50% TEA in Acetone	2003	UC	Cardiff CC	11	40	35	POOR	11
Cardiff Scientific Services	50% TEA in Acetone	2004	UC	Cardiff CC	12	37	31	POOR	10
Jesmond Dene Laboratory	50% TEA in Acetone	2004	UC	Newcastle upon Tyne CC	10	28	28	POOR	13
Harwell Scientific Services	50% TEA in Acetone	2004	UB	Rugby BC	9	26	21	POOR	11
Casella Seal / GMSS / Casella CRE	10% TEA in Water	2003	R	Dumfries and Galloway Council	10	34	37	POOR	11

Analysed By	Method	Year of Study	Site Type	Local Authority	Length of Study (months)	Diffusion Tube Mean (μg/m^3)	Automatic Monitor Mean (μg/m^3)	Tube Precision	Mean CV
Northampton BC	20% TEA in Water	2004	UB	AEA Tech Intercomparison	10	26	25	POOR	27
Staffordshire CC Scientific Services	50% TEA in Water	2004	UB	AEA Tech Intercomparison	11	26	25	POOR	10
Edinburgh Scientific Services	50% TEA in Acetone	2004	UB	AEA Tech Intercomparison	12	25	24	POOR	13
Lancashire CC	50% TEA in Acetone	2003	UC	Lancaster CC	12	27	32	POOR	19
Lancashire CC	50% TEA in Acetone	2004	UC	Lancaster CC	12	28	31	POOR	17
Staffordshire CC Scientific Services	50% TEA in Water	2004	0	Stoke-on-Trent City Council	12	32	30	POOR	10
West Yorkshire Analytical Services	50% TEA in Acetone	2005	R	Calderdale MBC	11	56	38	POOR	20
Kent Scientific Services	50% TEA in Acetone	2005	R	Eastleigh BC	12	52	50	POOR	12
Kent Scientific Services	50% TEA in Acetone	2005	O	Eastleigh BC	9	33	37	POOR	12
Gradko	50% TEA in Acetone	2003	R	LB Richmond	11	38	48	POOR	17
Gradko	50% TEA in Acetone	2003	B	LB Richmond	12	28	47	POOR	20
Harwell Scientific Services	50% TEA in Acetone	2005	B	Swale BC	10	26	25	POOR	11
West Yorkshire Analytical Services	50% TEA in Acetone	2005	UB	Wakefield MDC	9	33	29	POOR	16
West Yorkshire Analytical Services	50% TEA in Acetone	2005	UC	Wakefield MDC	12	46	35	POOR	15
Casella Seal / GMSS / Casella CRE	10% TEA in Water	2005	UB	Stockport MBC	11	42	32	POOR	10
Gradko	50% TEA in Acetone	2005	B	LB Richmond	10	28	34	POOR	11
West Yorkshire Analytical Services	50% TEA in Acetone	2005	B	Leeds CC	11	41	41	POOR	12
Harwell Scientific Services	50% TEA in Acetone	2005	UB	Rugby BC	12	27	20	POOR	24
University of Essex	50% TEA in Acetone	2005	S	Colchester BC	11	46	58	POOR	10
Bristol Scientific Services	20% TEA in Water	2005	R	Brighton and Hove CC	12	32	36	POOR	11
Harwell Scientific Services	50% TEA in Acetone	2005	R	Hambleton DC	12	26	25	POOR	12
Staffordshire CC Scientific Services	50% TEA in Water	2005	UC	Stoke-on-Trent City Council	12	31	34	POOR	16
Casella Seal / GMSS / Casella CRE	10% TEA in Water	2005	R	Wrexham CBC	12	23	20	POOR	10
Glasgow Scientific Services	20% TEA in Water	2005	UB	Glasgow CC	11	47	34	POOR	10
West Yorkshire Analytical Services	50% TEA in Acetone	2005	UC	Leeds CC	10	42	32	POOR	15
Edinburgh Scientific Services	50% TEA in Acetone	2005	UB	Netcen Liverpool Speke Intercomparison	10	23	23	POOR	11
Harwell Scientific Services	50% TEA in Acetone	2005	UB	Netcen Liverpool Speke Intercomparison	11	34	23	POOR	10
Kirklees Council Scientific Services	50% TEA in Acetone	2005	UB	Netcen Liverpool Speke Intercomparison	11	30	25	POOR	12
Northampton BC	20% TEA in Water	2005	UB	Netcen Liverpool Speke Intercomparison	10	25	26	POOR	30

Appendix 2 – Detailed Results: Plots and Tables



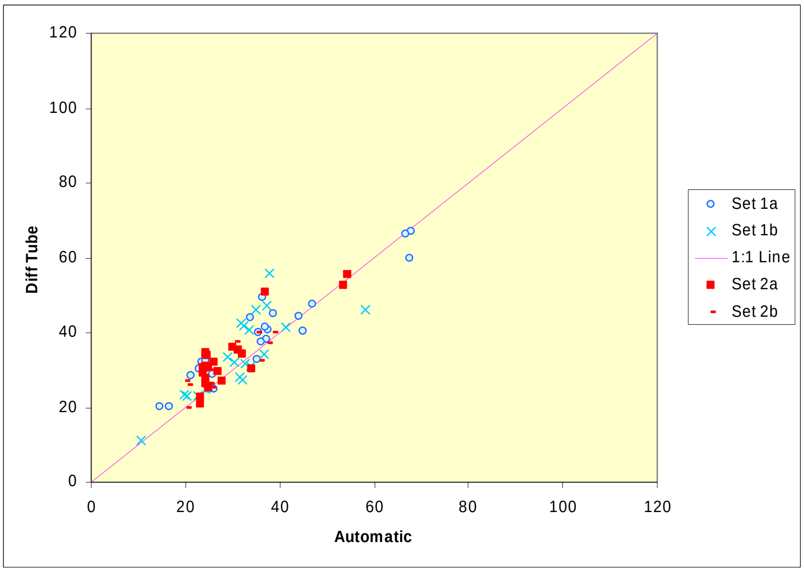
All values are annual mean concentrations of nitrogen dioxide in µg/m^3

Figure 1a Influence of Soft and Hard Opaque Tube Caps

Set 1 Soft opaque caps (9 Labs)

Set 2 Hard opaque caps (6 Labs)

(a) good precision, (b) poor precision



All values are annual mean concentrations of nitrogen dioxide in µg/m^3

Figure 1b Influence of Soft and Hard Opaque Tube Caps Gradko excluded

Set 1 Soft opaque caps (8 Labs)

Set 2 Hard opaque caps (6 Labs)

(a) good precision, (b) poor precision

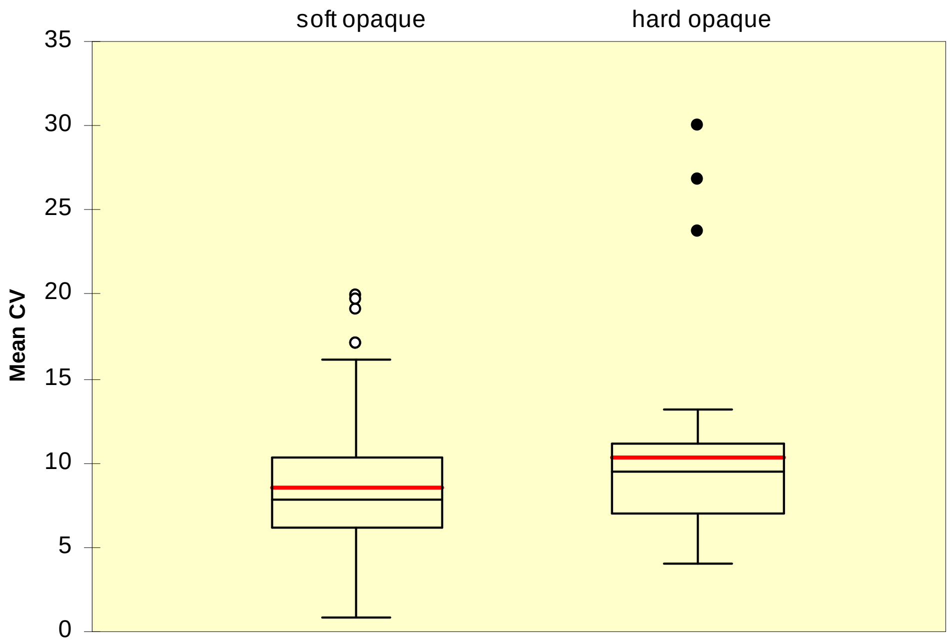


Figure 1c Influence of Soft and Hard Opaque Tube Cap

Soft opaque caps (9 labs)

Hard opaque caps (6 labs)

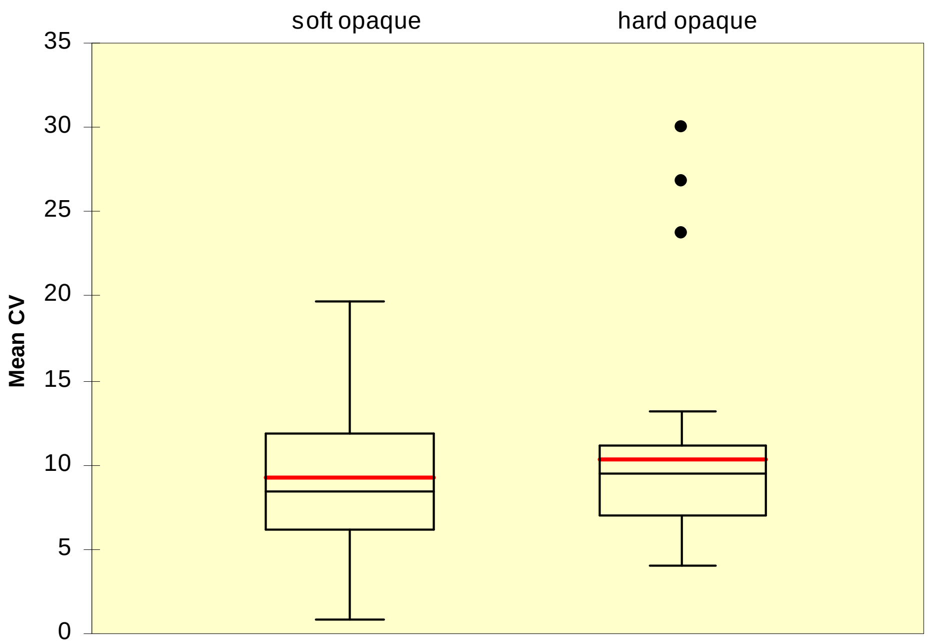


Figure 1d Influence of Soft and Hard Opaque Tube Cap Gradko excluded

Soft opaque caps (8 labs)

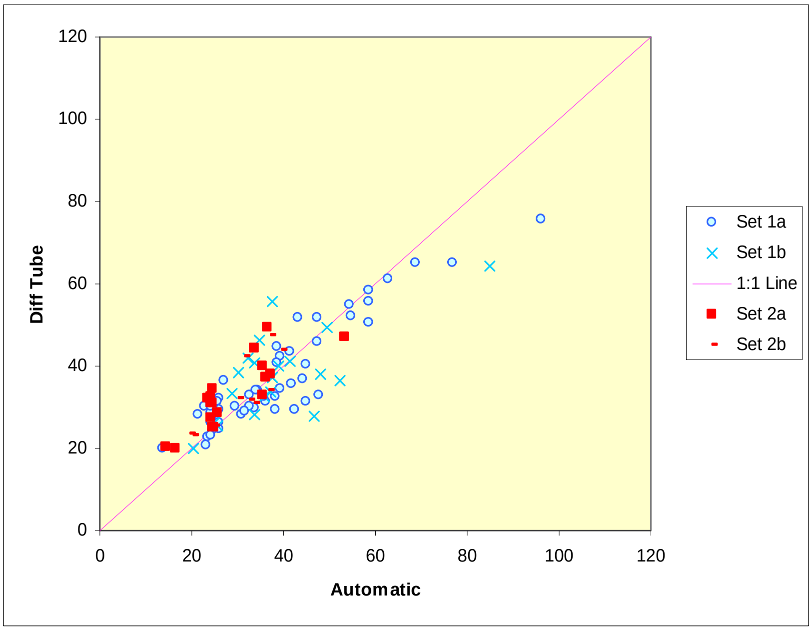
Hard opaque caps (6 labs)

Table 1a Influence of Soft and Hard Opaque Tube Cap

Test			Soft Opaque Caps	Hard Opaque Caps
Number of studies		All Results	108	35
		Good Precision only	77	21
A	% of studies under-predicting	All Results	44%	**26%**
		Good Precision only	44%	**24%**
B	Correlation coefficient (r)	All Results	0.88	0.87
		Good Precision only	**0.92**	0.89
C	% of results giving good precision		**71%**	60%
D	% of results with annual mean CV > 15%		8%	9%
E	Probability (p) associated with 2-tailed students t-test that the means shown in the box plots differ because of random chance		3% - significant	

Table 1b Influence of Soft and Hard Opaque Tube Cap Gradko Excluded

Test			Soft Opaque Caps	Hard Opaque Caps
Number of studies		All Results	50	35
		Good Precision only	29	21
A	% of studies under-predicting	All Results	26%	26%
		Good Precision only	24%	24%
B	Correlation coefficient (r)	All Results	0.89	0.87
		Good Precision only	**0.95**	0.89
C	% of results giving good precision		58%	60%
D	% of results with annual mean CV > 15%		14%	**9%**
E	Probability (p) associated with 2-tailed students t-test that the means shown in the box plots differ because of random chance		30% - not significant	



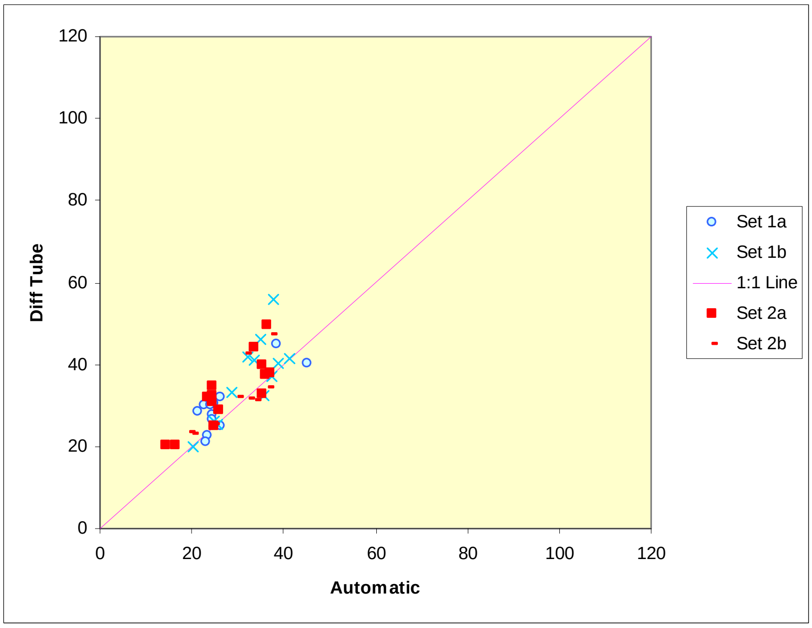
All values are annual mean concentrations of nitrogen dioxide in µg/m^3

Figure 2a Influence of Addition of Brij Solution to Tubes

Set 1 No Brij (5 Labs)

Set 2 Brij added (4 Labs)

(a) good precision, (b) poor precision



All values are annual mean concentrations of nitrogen dioxide in µg/m^3

Figure 2b Influence of Addition of Brij Solution to Tubes Gradko excluded

Set 1 No Brij (4 Labs)

Set 2 Brij added (3 Labs)

(a) good precision, (b) poor precision

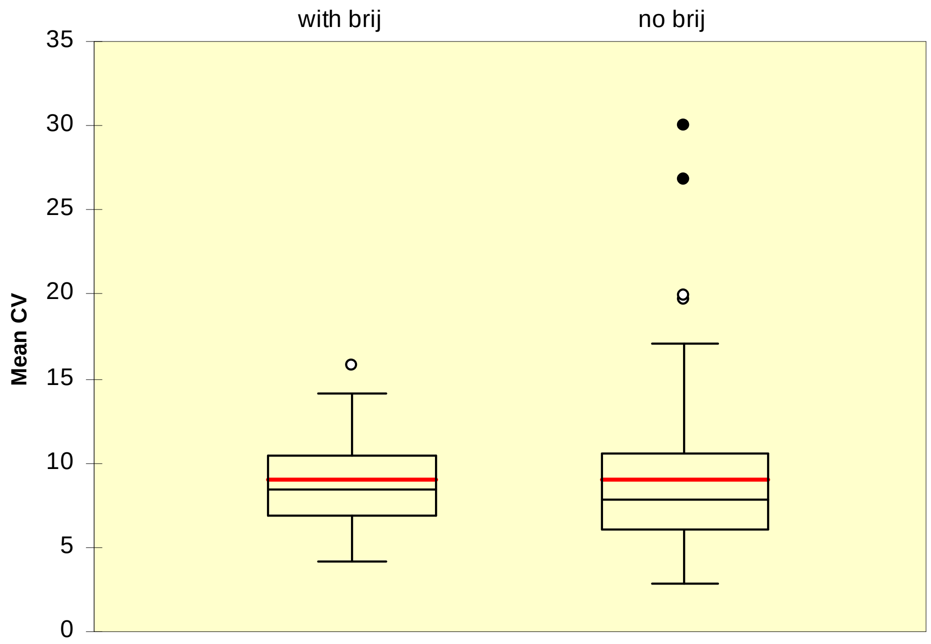


Figure 2c **Influence of Addition of Brij Solution to Tubes (dipped tubes only)**

No Brij (5 labs)

Brij added (4 labs)

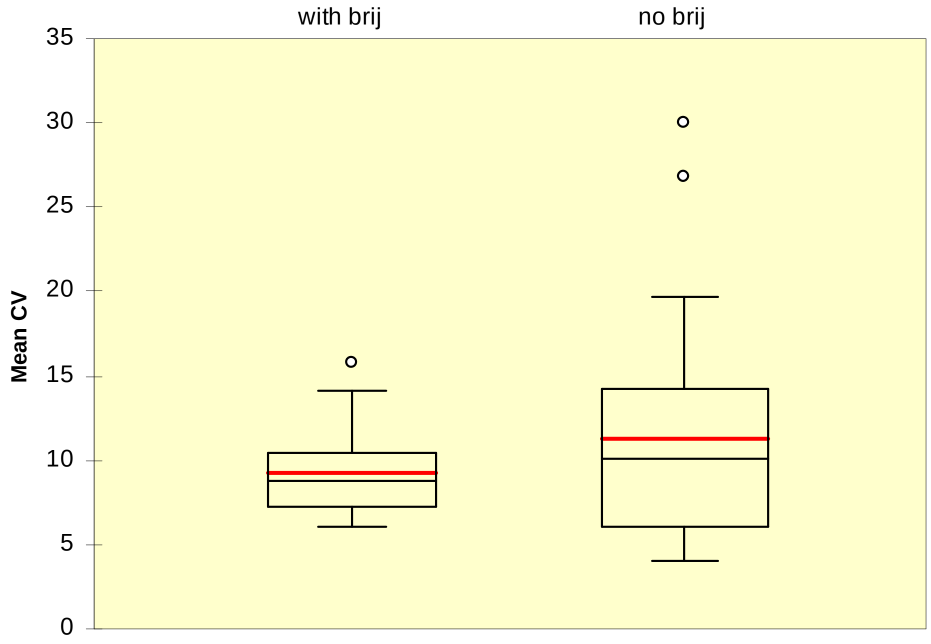


Figure 2d **Influence of Addition of Brij Solution to Tubes Gradko Excluded (dipped tubes only)**

No Brij (4 labs)

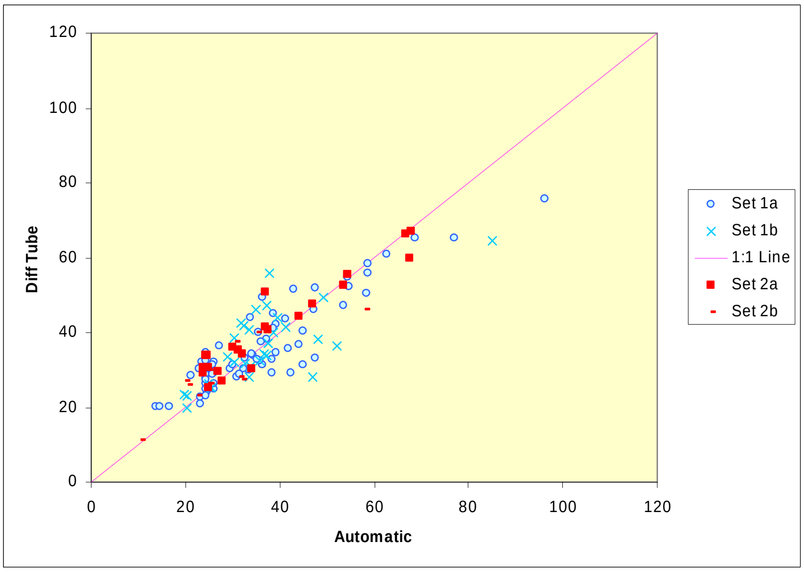
Brij added (3 labs)

Table 2a Influence of Addition of Brij Solution to Tubes (dipped tubes only)

	Test		With Brij	No Brij
Number of studies		All Results	28	76
		Good Precision only	18	55
A	% of studies under-predicting	All Results	**21%**	55%
		Good Precision only	**17%**	55%
B	Correlation coefficient (r)	All Results	0.83	**0.87**
		Good Precision only	0.85	**0.92**
C	% of results giving good precision		64%	**72%**
D	% of results with annual mean CV > 15%		**4%**	11%
E	Probability (p) associated with 2-tailed students t-test that the means shown in the box plots differ because of random chance		98% - not significant	

Table 2b Influence Influence of Addition of Brij Solution to Tubes Gradko Excluded (dipped tubes only)

	Test		With Brij	No Brij
Number of studies		All Results	24	24
		Good Precision only	15	12
A	% of studies under-predicting	All Results	**21%**	33%
		Good Precision only	**13%**	33%
B	Correlation coefficient (r)	All Results	0.81	0.81
		Good Precision only	0.84	0.82
C	% of results giving good precision		**63%**	50%
D	% of results with annual mean CV > 15%		**4%**	25%
E	Probability (p) associated with 2-tailed students t-test that the means shown in the box plots differ because of random chance		17% - not significant	



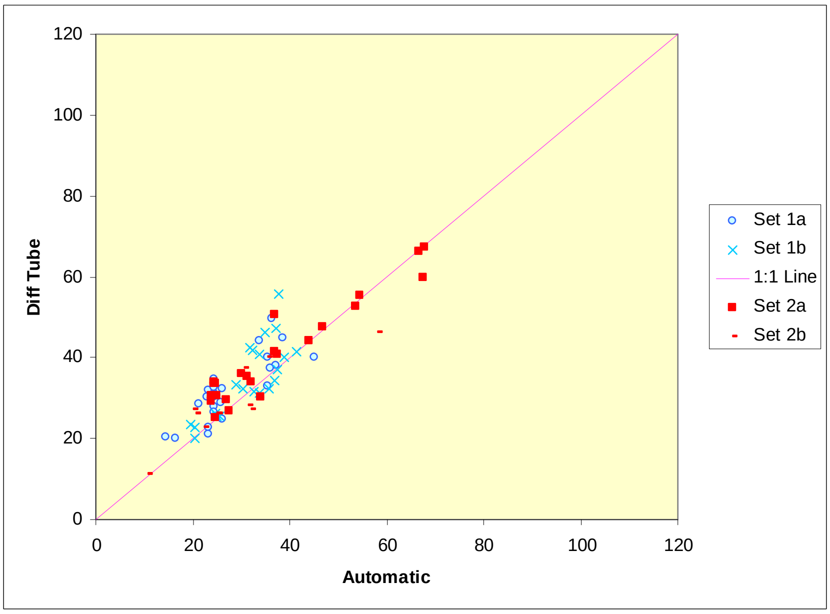
All values are annual mean concentrations of nitrogen dioxide in µg/m^3

Figure 3a Influence of Pipetting or Dipping Grids

Set 1 Pipetting (8 Labs)

Set 2 Dipping (7 Labs)

(a) good precision, (b) poor precision



All values are annual mean concentrations of nitrogen dioxide in µg/m^3

Figure 3b Influence of Pipetting or Dipping Grids Gradko Excluded

Set 1 Pipetting (7 Labs)

Set 2 Dipping (7 Labs)

(a) good precision, (b) poor precision

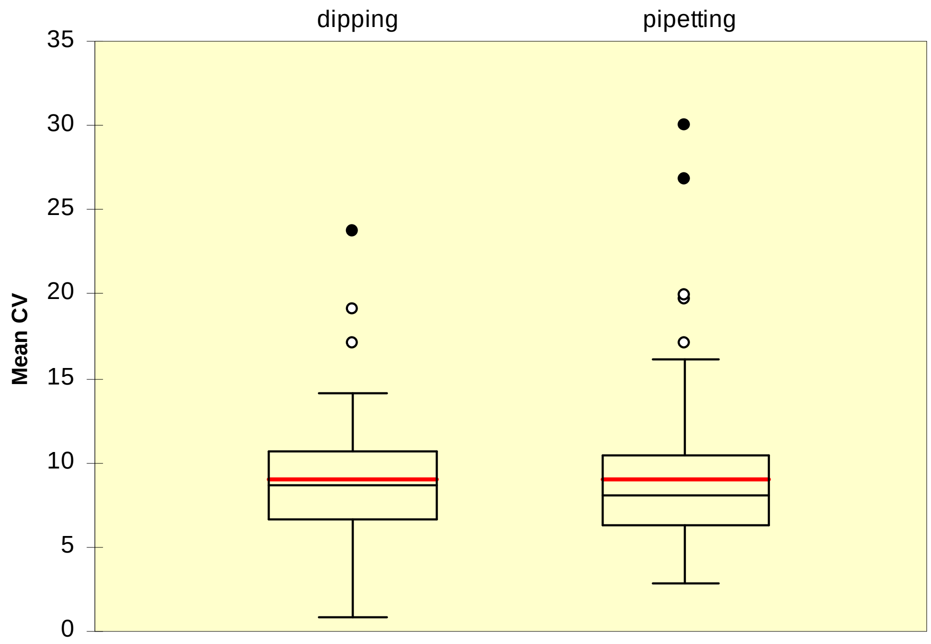


Figure 3c Influence of Pipetting or Dipping Grids

Pipetting (8 labs)

Dipping (7 labs)

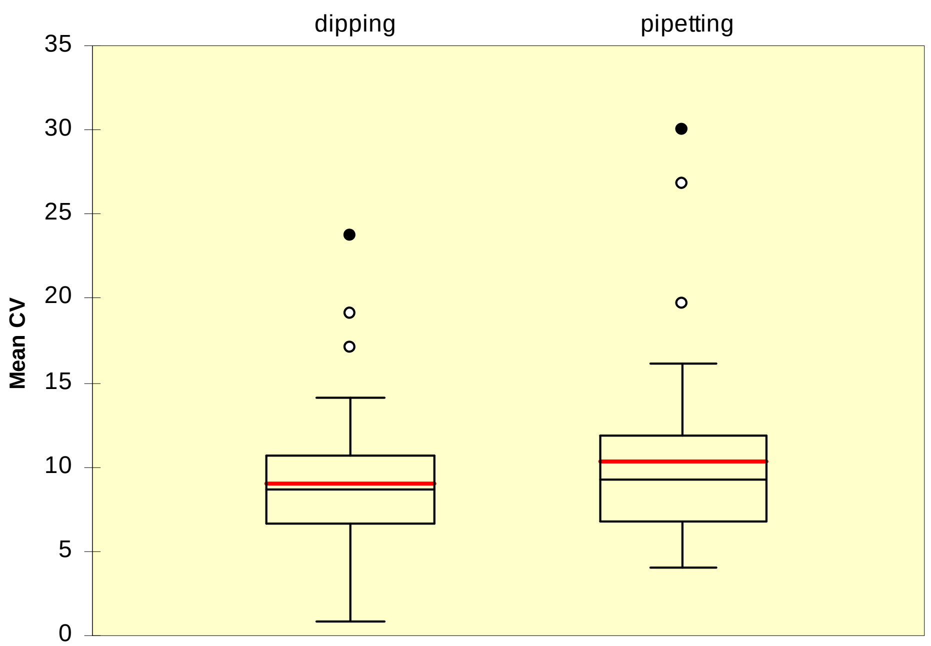


Figure 3d Influence of Pipetting or Dipping Grids Gradko Excluded

Pipetting (7 labs)

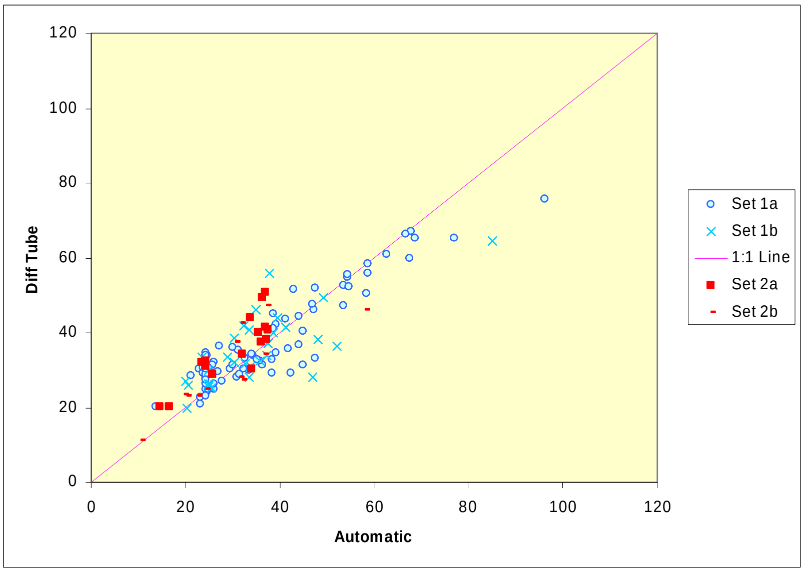
Dipping (7 labs)

Table 3a Influence of Pipetting or Dipping Grids

Test			Dipping	Pipetting
Number of studies		All Results	37	104
		Good Precision only	23	73
A	% of studies under-predicting	All Results	**24%**	46%
		Good Precision only	**26%**	45%
B	Correlation coefficient (r)	All Results	**0.94**	0.87
		Good Precision only	**0.95**	0.91
C	% of results giving good precision		62%	**70%**
D	% of results with annual mean CV > 15%		8%	9%
E	Probability (p) associated with 2-tailed students t-test that the means shown in the box plots differ because of random chance		94% - not significant	

Table 3b Influence of Pipetting or Dipping Grids Gradko Excluded

Test			Dipping	Pipetting
Number of studies		All Results	37	48
		Good Precision only	23	27
A	% of studies under-predicting	All Results	**24%**	27%
		Good Precision only	26%	**22%**
B	Correlation coefficient (r)	All Results	**0.94**	0.81
		Good Precision only	**0.95**	0.83
C	% of results giving good precision		**62%**	56%
D	% of results with annual mean CV > 15%		**8%**	15%
E	Probability (p) associated with 2-tailed students t-test that the means shown in the box plots differ because of random chance		23% - not significant	



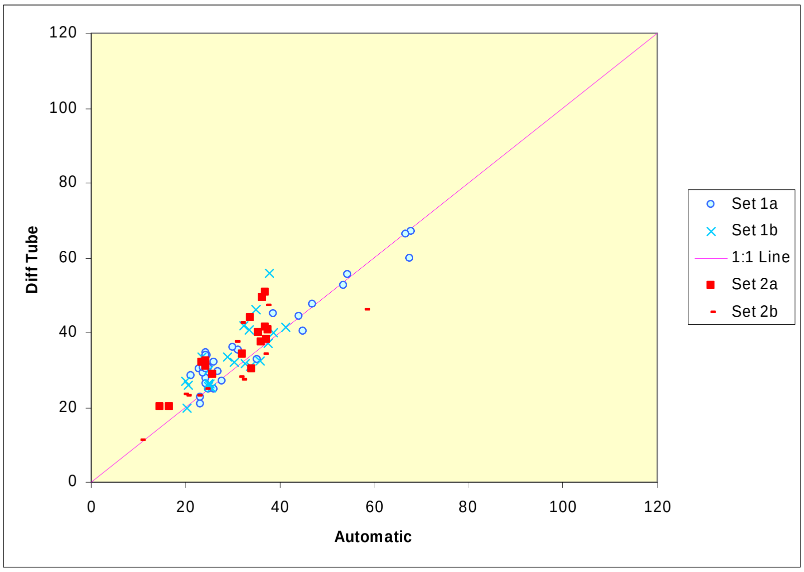
All values are annual mean concentrations of nitrogen dioxide in μg/m^3

Figure 4a Influence of Use of Clean Air Environment

Set 1 Not Clean Air (10 Labs)

Set 2 Clean Air Environment (5 Labs)

(a) good precision, (b) poor precision



All values are annual mean concentrations of nitrogen dioxide in μg/m^3

Figure 4b Influence of Use of Clean Air Environment Gradko excluded

Set 1 Not Clean Air (9 Labs)

Set 2 Clean Air Environment (5 Labs)

(a) good precision, (b) poor precision

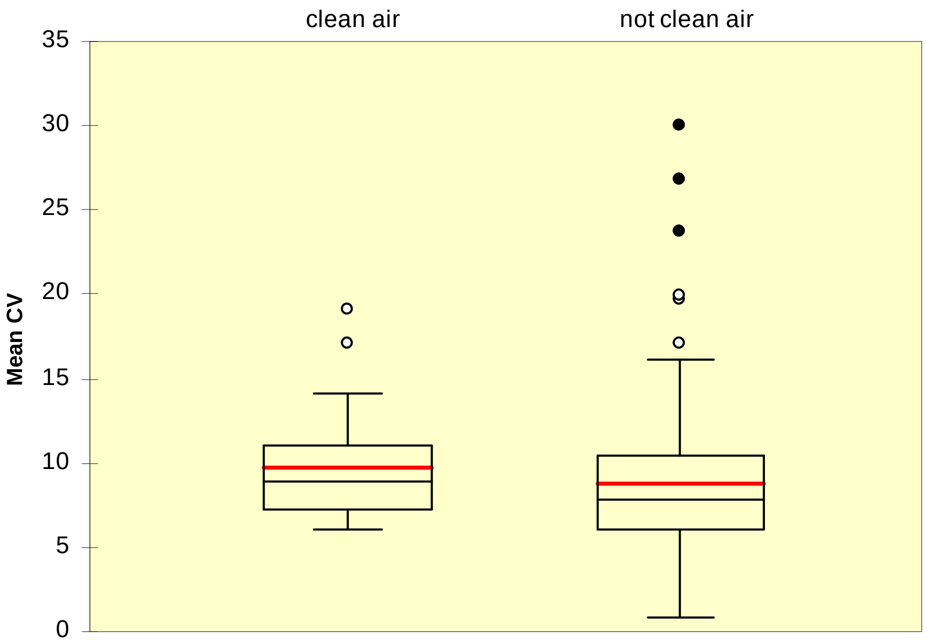


Figure 4c Influence of Use of Clean Air Environment

Not Clean Air (10 labs)

Clean Air Environment (5 labs)

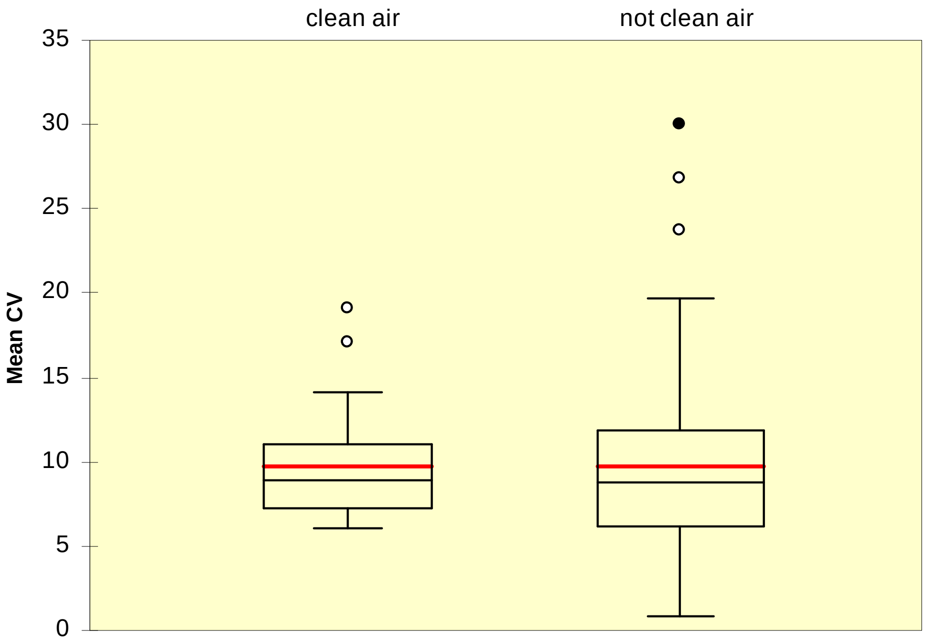


Figure 4d Influence of Use of Clean Air Environment Gradko Excluded

Not Clean Air (9 labs)

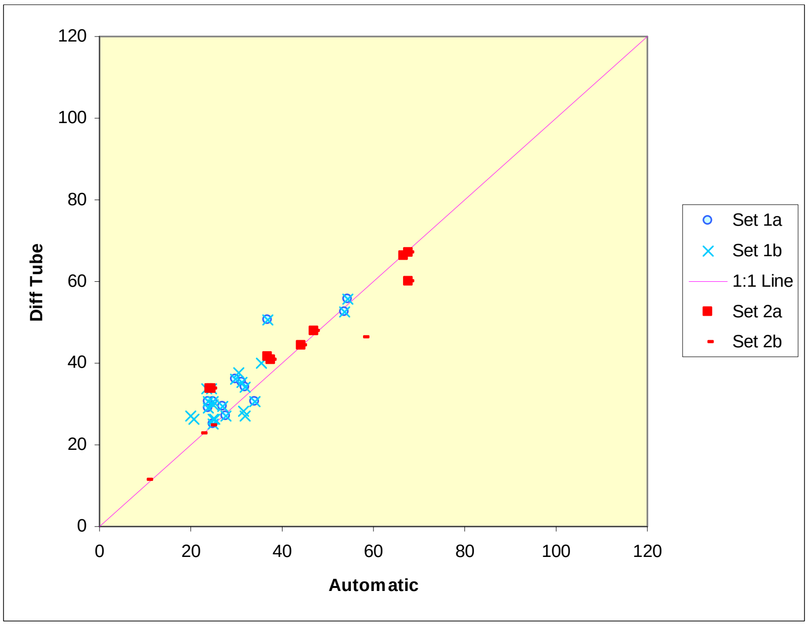
Clean Air Environment (5 labs)

Table 4a Influence of Use of Clean Air Environment

Test			Clean Air	Not Clean Air
Number of studies		All Results	29	112
		Good Precision only	16	80
A	% of studies under-predicting	All Results	**17%**	46%
		Good Precision only	**6%**	48%
B	Correlation coefficient (r)	All Results	0.83	**0.89**
		Good Precision only	0.86	**0.93**
C	% of results giving good precision		55%	**71%**
D	% of results with annual mean CV > 15%		7%	9%
E	Probability (p) associated with 2-tailed students t-test that the means shown in the box plots differ because of random chance		30% - not significant	

Table 4b Influence of Use of Clean Air Environment Gradko Excluded

Test			Clean Air	Not Clean Air
Number of studies		All Results	29	56
		Good Precision only	16	34
A	% of studies under-predicting	All Results	**17%**	30%
		Good Precision only	**6%**	32%
B	Correlation coefficient (r)	All Results	0.83	**0.92**
		Good Precision only	0.86	**0.95**
C	% of results giving good precision		55%	**61%**
D	% of results with annual mean CV > 15%		**7%**	14%
E	Probability (p) associated with 2-tailed students t-test that the means shown in the box plots differ because of random chance		94% - not significant	



All values are annual mean concentrations of nitrogen dioxide in µg/m^3

Figure 5a Influence of Dipping of Grids

Set 1 Meshes dipped only briefly (<1min) in solution (4 Labs)

Set 2 Meshes soaked (for at least 10 mins) in solution (3 Labs)

(a) good precision, (b) poor precision

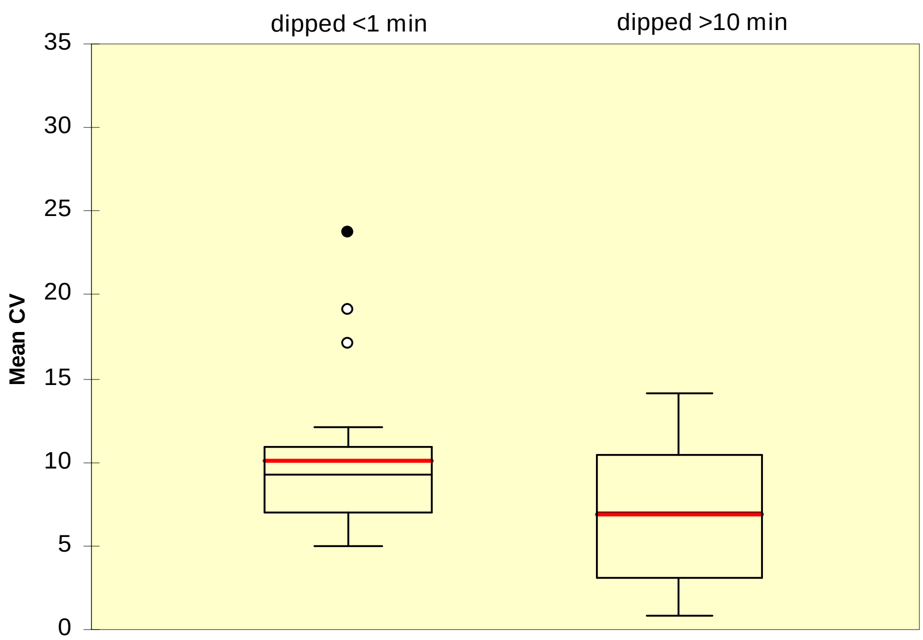


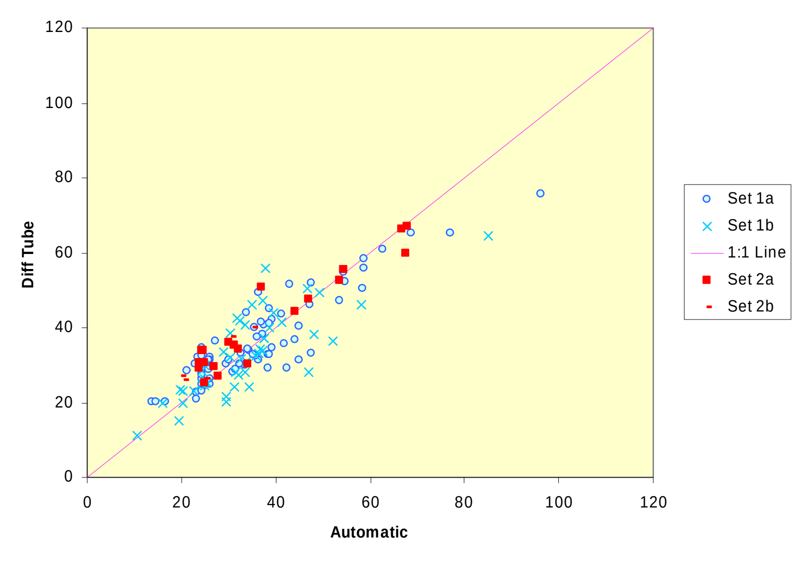
Figure 5b Influence of Dipping of Grids

Meshes dipped only briefly (<1min) in solution

Meshes soaked (for at least 10 mins) in solution

Table 5 Influence of Grid Dip Duration

		< 1 min	> 10 min
Number of studies	All Results	24	13
	Good Precision only	14	9
% of studies under-predicting	All Results	**21%**	31%
	Good Precision only	**21%**	33%
Correlation coefficient (r)	All Results	0.86	**0.96**
	Good Precision only	0.90	**0.98**
% of results giving good precision		58%	**69%**
% of results with annual mean CV > 15%		13%	**0%**
Probability (p) associated with 2-tailed students t-test that the means shown in the box plots differ because of random chance		**4% - significant**	



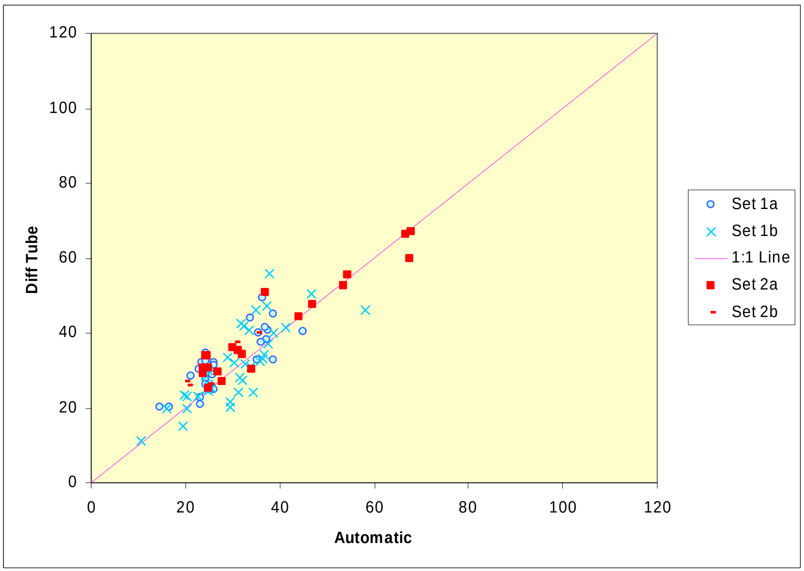
All values are annual mean concentrations of nitrogen dioxide in µg/m^3

Figure 6a Influence of Drying Grids

Set 1 Grids wet when tube assembled (12 Labs)

Set 2 Grids dried when tube assembled (3 Labs)

(a) good precision, (b) poor precision



All values are annual mean concentrations of nitrogen dioxide in µg/m^3

Figure 6b Influence of Drying Grids Gradko excluded

Set 1 Grids wet when tube assembled (11 Labs)

Set 2 Grids dried when tube assembled (3 Labs)

(a) good precision, (b) poor precision

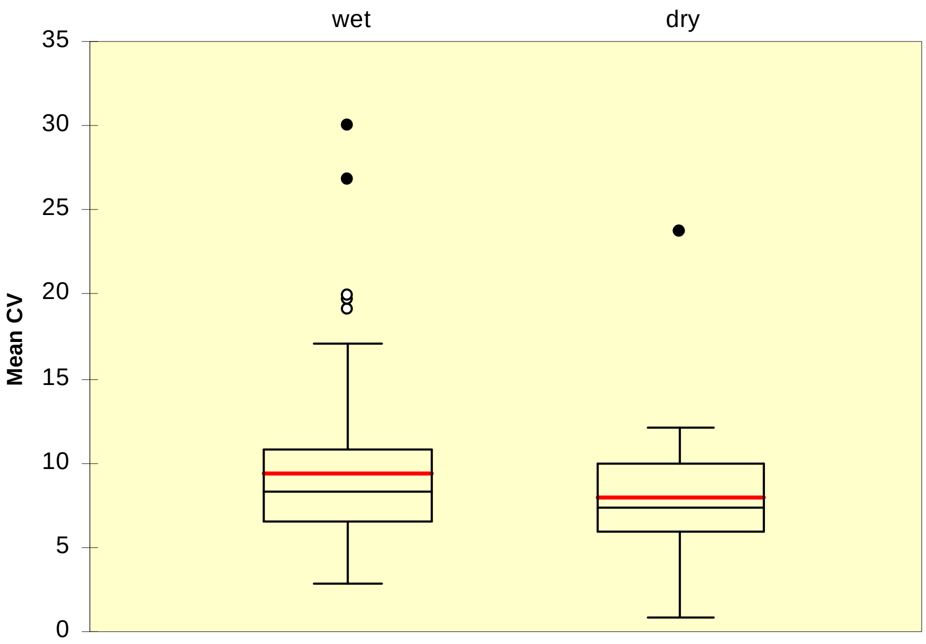


Figure 6c Influence of Drying Grids

Wet (12 labs)

Dry (3 labs)

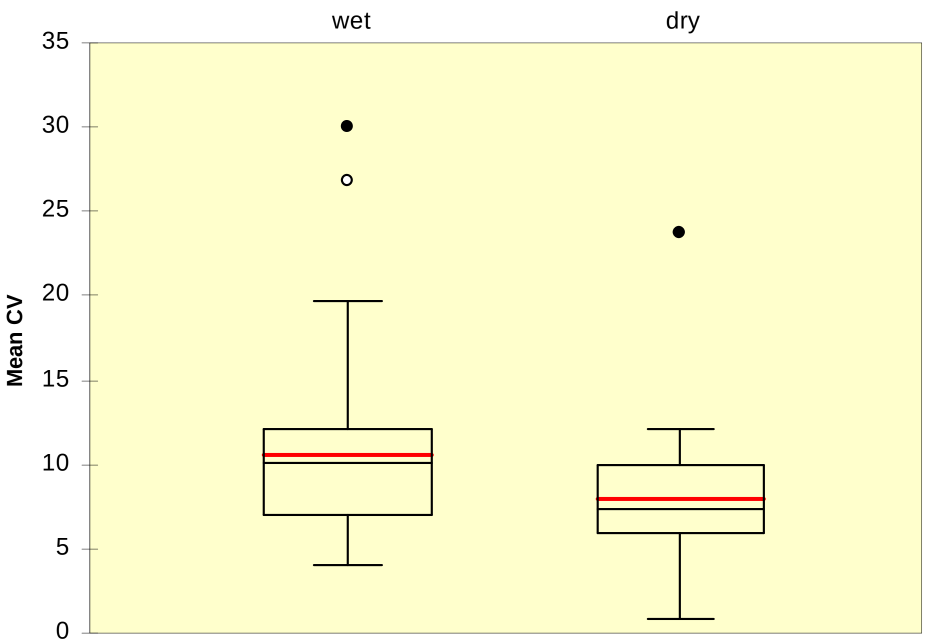


Figure 6d Influence of Drying Grids Gradko excluded

Wet (11 labs)

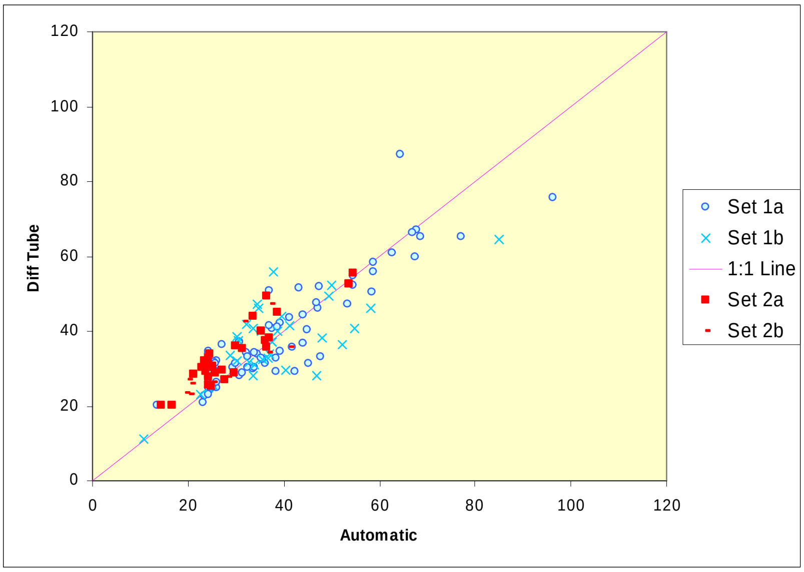
Dry (3 labs)

Table 6a Influence of Drying Grids

		Wet	Dry
Number of studies	All Results	114	28
	Good Precision only	75	21
% of studies under-predicting	All Results	45%	**21%**
	Good Precision only	44%	**29%**
Correlation coefficient (r)	All Results	0.87	**0.95**
	Good Precision only	0.91	**0.95**
% of results giving good precision		66%	**75%**
% of results with annual mean CV > 15%		10%	**4%**
Probability (p) associated with 2-tailed students t-test that the means shown in the box plots differ because of random chance		12% - not significant	

Table 6b Influence of Drying Grids Gradko excluded

		Wet	Dry
Number of studies	All Results	58	28
	Good Precision only	29	21
% of studies under-predicting	All Results	28%	**21%**
	Good Precision only	**21%**	29%
Correlation coefficient (r)	All Results	0.81	**0.95**
	Good Precision only	0.84	**0.95**
% of results giving good precision		50%	**75%**
% of results with annual mean CV > 15%		16%	**4%**
Probability (p) associated with 2-tailed students t-test that the means shown in the box plots differ because of random chance		**2% - significant**	



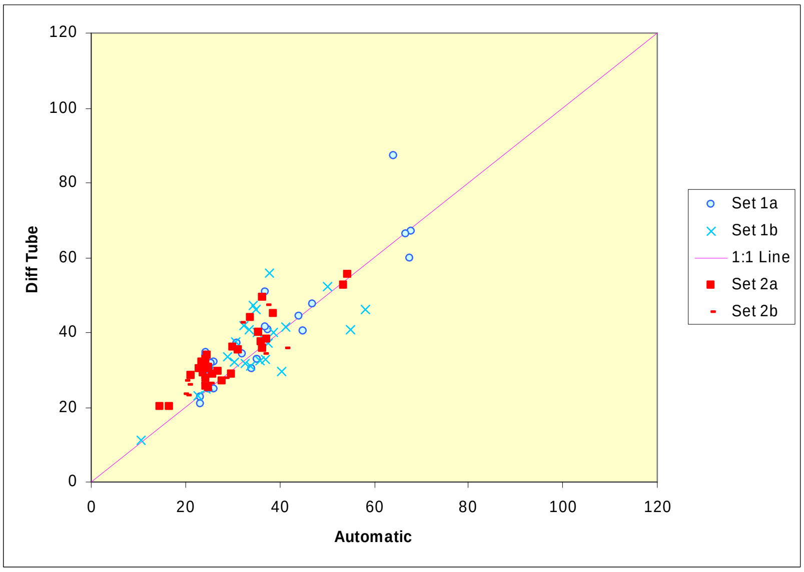
All values are annual mean concentrations of nitrogen dioxide in µg/m^3

Figure 7a Influence of Manual or Automated Analysis

Set 1 Manual Colorimetric (14 Labs)

Set 2 Automated Colorimetric (4 Labs)

(a) good precision, (b) poor precision



All values are annual mean concentrations of nitrogen dioxide in µg/m^3

Figure 7b Influence of Manual or Automated Analysis Gradko excluded

Set 1 Manual Colorimetric (13 Labs)

Set 2 Automated Colorimetric (4 Labs)

(a) good precision, (b) poor precision

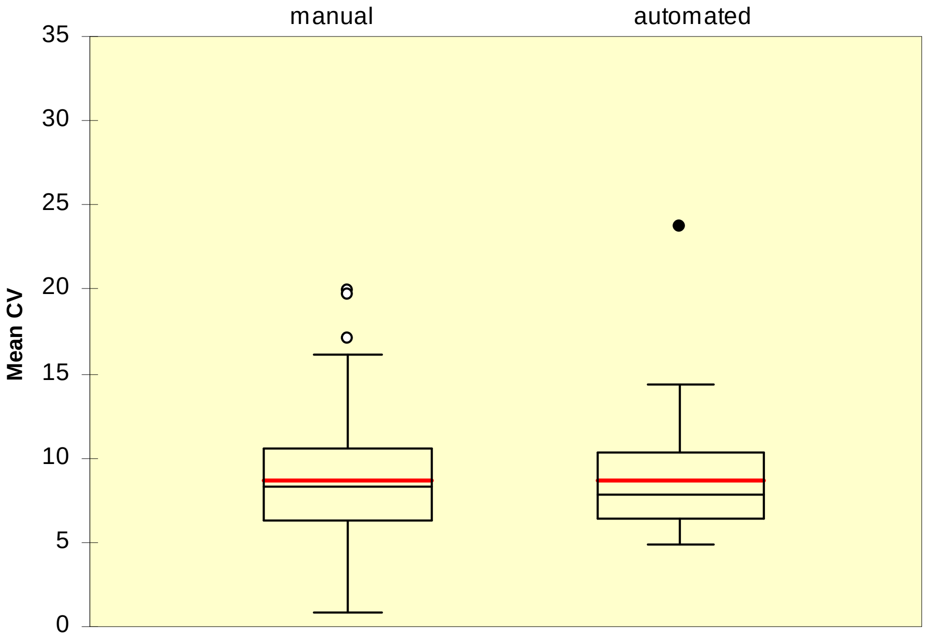


Figure 7c Influence of Manual or Automated Analysis

Manual Colorimetric (14 labs),

Automatic Colorimetric (4 labs)

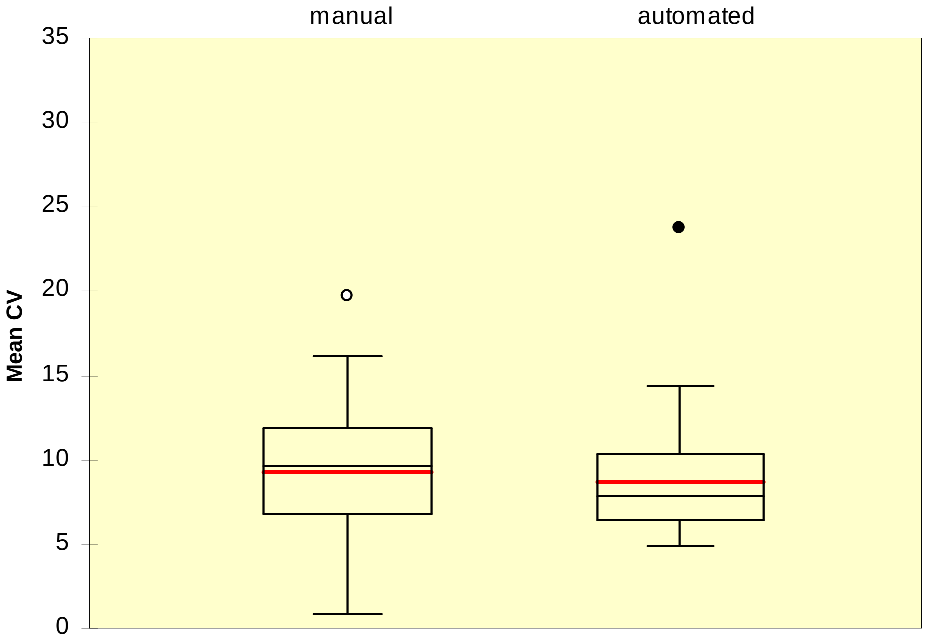


Figure 7d Influence of Manual or Automated Analysis Gradko Excluded

Manual Colorimetric (13 labs),

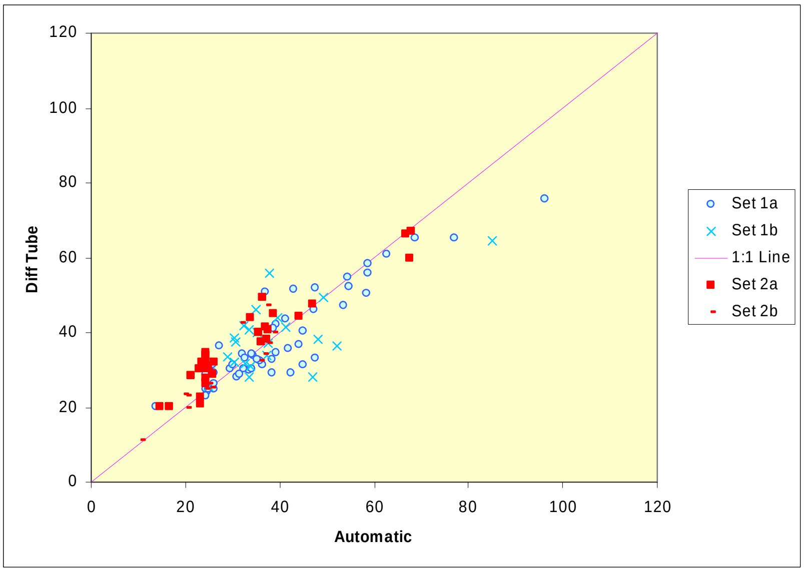
Automatic Colorimetric (4 labs)

Table 7a Influence of Manual or Automated Analysis

		Manual	Automated
Number of studies	All Results	110	43
	Good Precision only	75	31
% of studies under-predicting	All Results	48%	**16%**
	Good Precision only	49%	**13%**
Correlation coefficient (r)	All Results	0.86	0.88
	Good Precision only	0.90	0.92
% of results giving good precision		68%	**72%**
% of results with annual mean CV > 15%		6%	**2%**
Probability (p) associated with 2-tailed students t-test that the means shown in the box plots differ because of random chance		89% - not significant	

Table 7b Influence of Manual or Automated Analysis Gradko Excluded

		Manual	Automated
Number of studies	All Results	54	43
	Good Precision only	29	31
% of studies under-predicting	All Results	33%	**16%**
	Good Precision only	34%	**13%**
Correlation coefficient (r)	All Results	0.86	0.88
	Good Precision only	0.92	0.92
% of results giving good precision		54%	**72%**
% of results with annual mean CV > 15%		9%	**2%**
Probability (p) associated with 2-tailed students t-test that the means shown in the box plots differ because of random chance		44% - not significant	



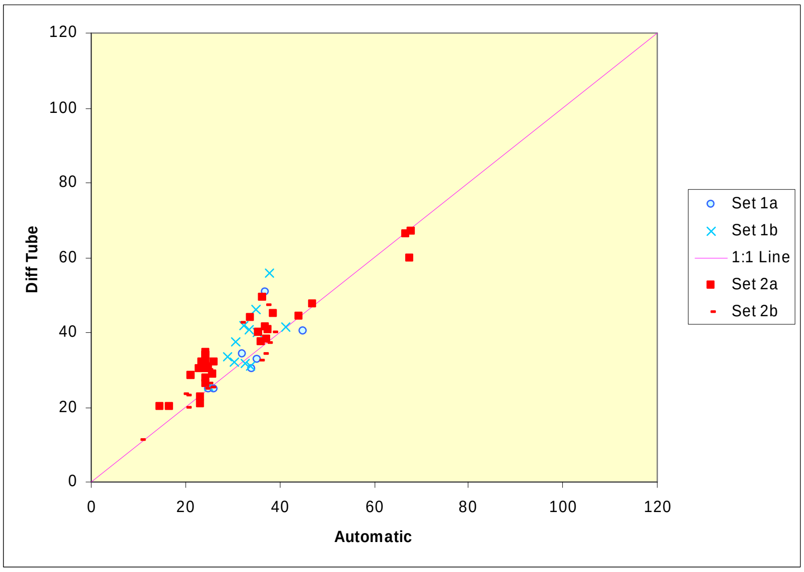
All values are annual mean concentrations of nitrogen dioxide in μg/m³

Figure 8a Influence of Extraction Mixing

Set 1 Vibrating Tray (4 Labs)

Set 2 Shake by Hand (8 Labs)

(a) good precision, (b) poor precision



All values are annual mean concentrations of nitrogen dioxide in μg/m³

Figure 8b Influence of Extraction Mixing Gradko Excluded

Set 1 Vibrating Tray (3 Labs)

Set 2 Shake by Hand (8 Labs)

(a) good precision, (b) poor precision

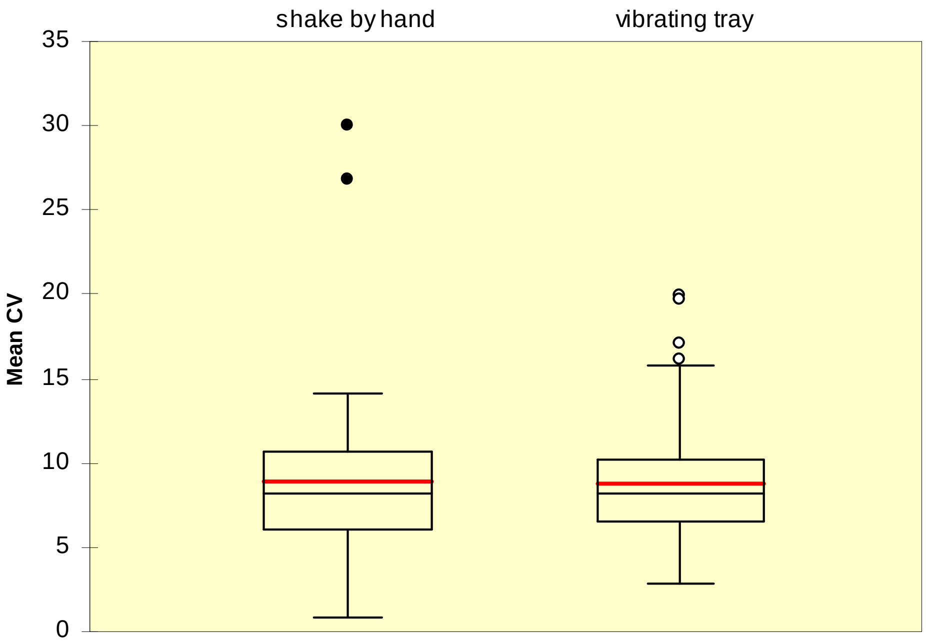


Figure 8c Influence of Extraction Mixing

Shake by Hand (8 labs)

Vibrating Tray (4 labs)

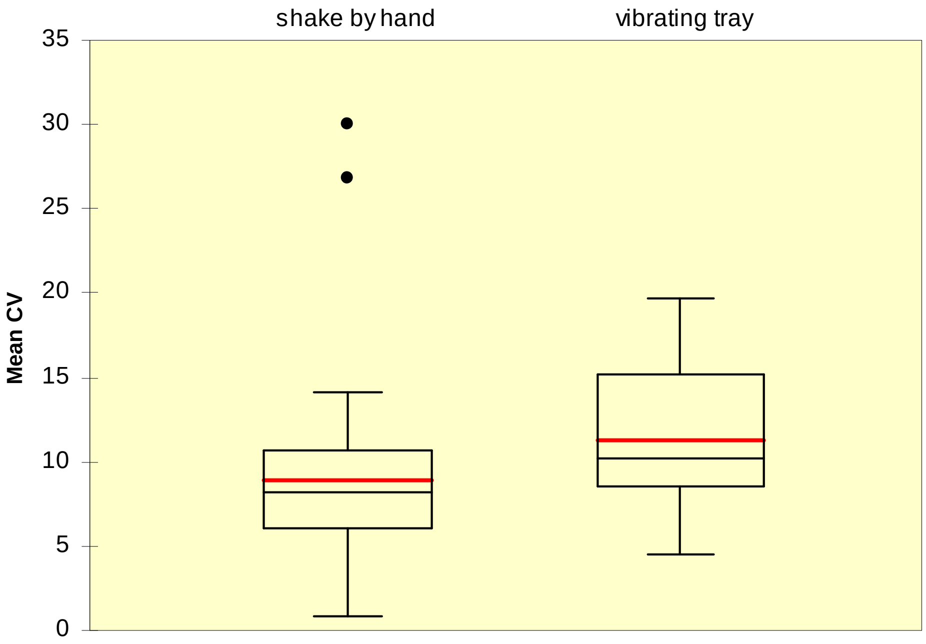


Figure 8d Influence of Extraction Mixing Gradko Excluded

Shake by Hand (8 labs)

Vibrating Tray (3 labs).

Table 8a Influence of Extraction Mixing

		Shake by Hand	Vibrating Tray
Number of studies	All Results	47	75
	Good Precision only	32	53
Correlation coefficient (r)	All Results	**0.94**	0.86
	Good Precision only	**0.95**	0.91
% of studies under-predicting	All Results	**21%**	56%
	Good Precision only	**16%**	60%
% of results giving good precision		68%	**71%**
% of results with annual mean CV > 15%		**4%**	9%
Probability (p) associated with 2-tailed students t-test that the means shown in the box plots differ because of random chance		98% - not significant	

Table 8b Influence of Extraction Mixing Gradko Excluded

		Shake by Hand	Vibrating Tray
Number of studies	All Results	47	19
	Good Precision only	32	7
Correlation coefficient (r)	All Results	**0.94**	0.67
	Good Precision only	**0.95**	0.73
% of studies under-predicting	All Results	**21%**	37%
	Good Precision only	**16%**	71%
% of results giving good precision		**68%**	37%
% of results with annual mean CV > 15%		**4%**	26%
Probability (p) associated with 2-tailed students t-test that the means shown in the box plots differ because of random chance		7% - not significant	

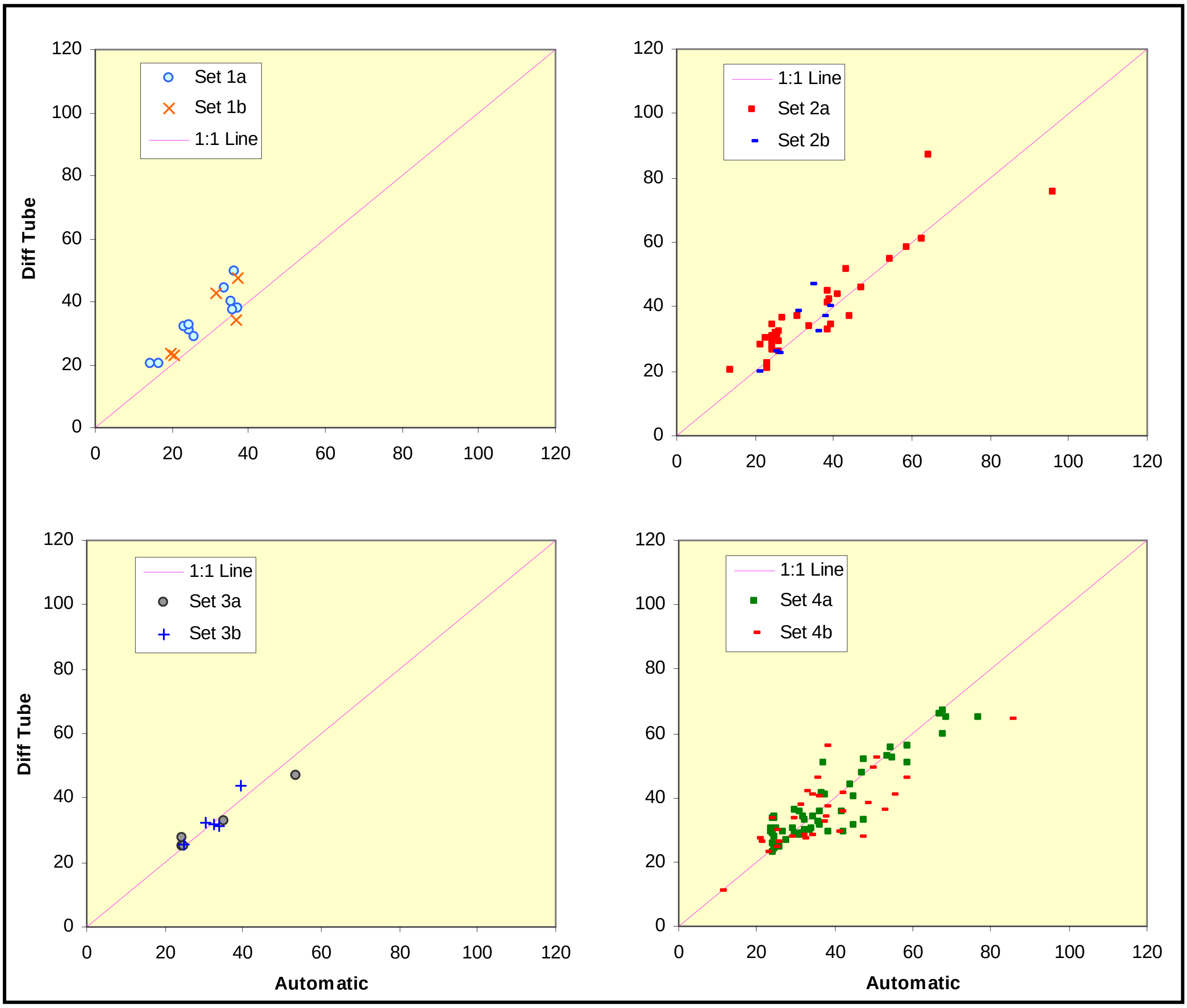


Figure 9a Influence of TEA Solution

Set 1 10% TEA in Water (1 Lab)

Set 2 20% TEA in Water (7 Labs)

Set 3 50% TEA in Water (2 Labs)

Set 4 50% TEA in Acetone (12 Labs)

(a) good precision, (b) poor precision

All values are annual mean concentrations of nitrogen dioxide in µg/m^3

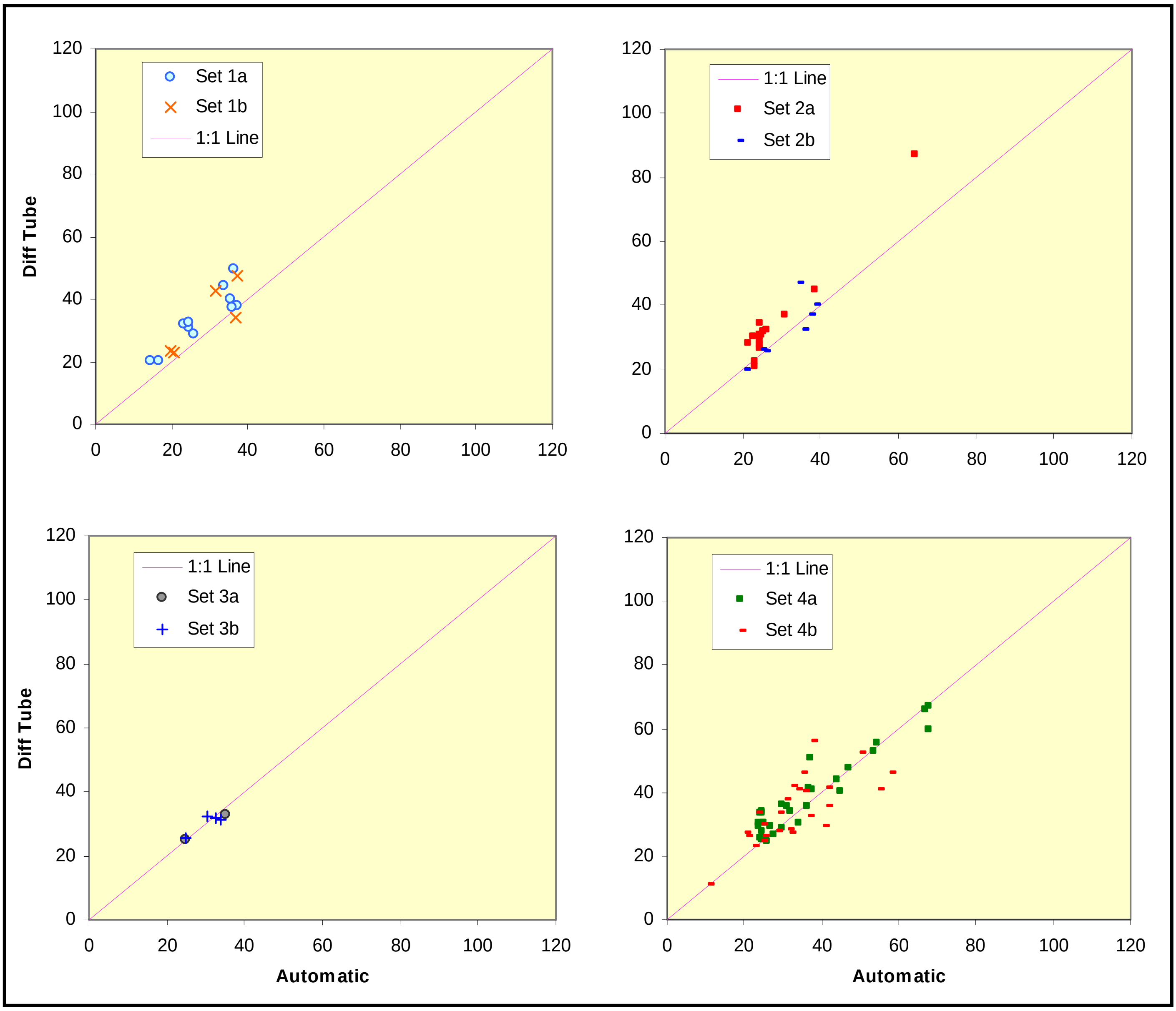


Figure 9b Influence of TEA Solution Gradko Excluded

Set 1 10% TEA in Water (1 Lab)

Set 2 20% TEA in Water (6 Labs)

Set 3 50% TEA in Water (1 Lab)

Set 4 50% TEA in Acetone (11 Labs)

(a) good precision, (b) poor precision

All values are annual mean concentrations of nitrogen dioxide in µg/m^3

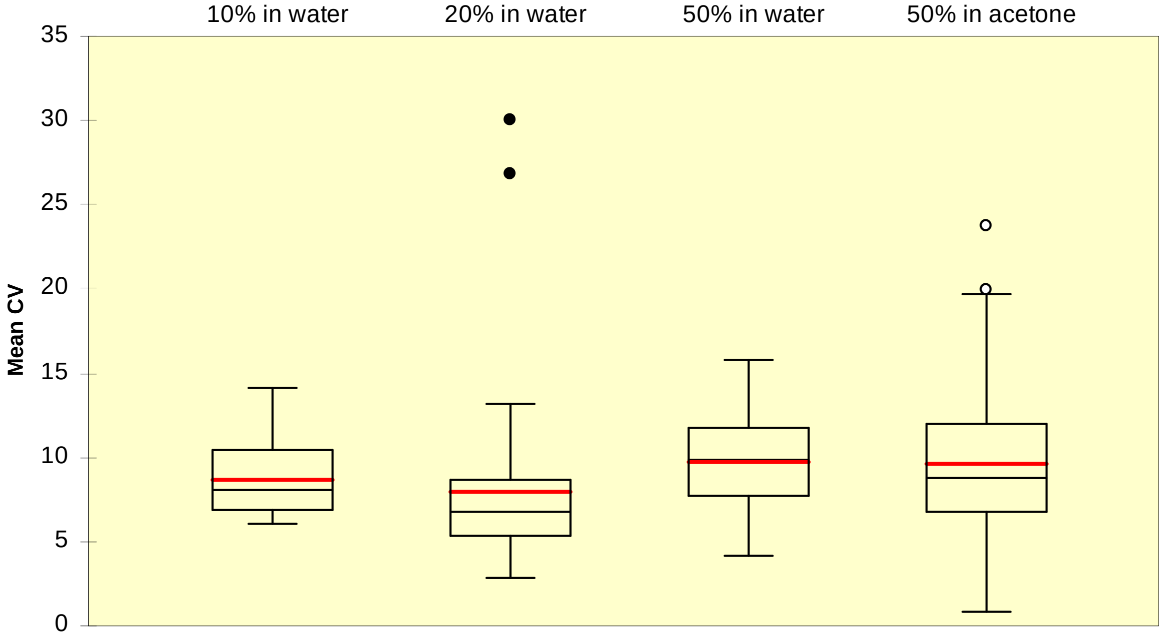


Figure 9c Influence of TEA Solution

10% TEA in Water (1 Lab); 20% TEA in Water (7 Labs); 50% TEA in Water (2 Labs)

50% TEA in Acetone (12 Labs)

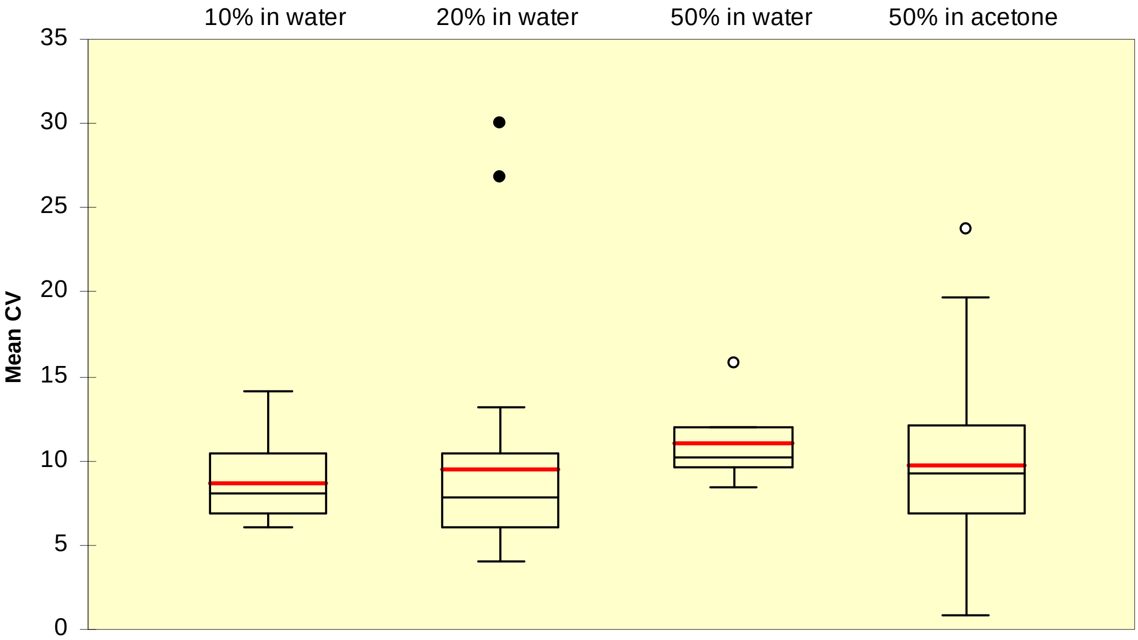


Figure 9d Influence of TEA Solution Gradko Excluded

10% TEA in Water (1 Lab); 20% TEA in Water (6 Labs); 50% TEA in Water (1 Labs)

50% TEA in Acetone (11 Labs)

Table 9a Influence of TEA Solution

Test			10% TEA in Water	20% TEA in Water	50% TEA in Water	50% TEA in Acetone
Number of studies		All Results	16	45	10	87
Number of studies		Good Precision only	11	37	5	53
A	% of studies under-predicting	All Results	**6%**	**29%**	50%	52%
A	% of studies under-predicting	Good Precision only	**0%**	**24%**	60%	55%
B	Correlation coefficient (r)	All Results	0.89	0.91	**0.95**	0.86
B	Correlation coefficient (r)	Good Precision only	0.91	0.91	**0.99**	0.91
C	% of results giving good precision		**69%**	**82%**	50%	61%
D	% of results with annual mean CV > 15%		**0%**	**4%**	10%	10%
E	Probability (p) associated with 2-tailed students t-test that the means shown in the box plots differ because of random chance [a]	20% W[a]	59%	-	-	-
E		50% W[a]	37%	32%	-	-
E		50% A[a]	40%	**5%**	94%	-
E		All[b]	73%	**5%**	62%	**8%**

[a] Presented as a matrix. 20% W = 20% TEA in water; 50%W = 50% TEA in water; 50% A = 50% TEA in Acetone.
[b] Comparing each individual subset with the aggregate of the other three subsets.

Table 9b Influence of TEA Solution Gradko Excluded

Test			10% TEA in Water	20% TEA in Water	50% TEA in Water	50% TEA in Acetone
Number of studies		All Results	16	24	6	18
Number of studies		Good Precision only	11	17	2	10
A	% of studies under-predicting	All Results	**6%**	**25%**	67%	32%
A	% of studies under-predicting	Good Precision only	**0%**	**12%**	100%	33%
B	Correlation coefficient (r)	All Results	0.89	**0.94**	**0.93**	0.88
B	Correlation coefficient (r)	Good Precision only	0.91	**0.98**	**na**	0.95
C	% of results giving good precision		**69%**	**71%**	33%	54%
D	% of results with annual mean CV > 15%		**0%**	**8%**	17%	13%
E	Probability (p) associated with 2-tailed students t-test that the means shown in the box plots differ because of random chance [a]	20% W[a]	62%	-	-	-
E		50% W[a]	**5%**	58%	-	-
E		50% A[a]	35%	85%	50%	-
E		All[b]	38%	91%	44%	72%

[a] Presented as a matrix. 20% W = 20% TEA in water; 50%W = 50% TEA in water; 50% A = 50% TEA in Acetone.
[b] Comparing each individual subset with the aggregate of the other three subsets.