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UK Automatic Rural Network: Ratification Report for July to December 2001

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by

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1. INTRODUCTION

This report has been prepared for the Department for the Environment, Food and Rural Affairs by NPL under contract EPG 1/3/123. It covers the ratification of data in the Rural Network relating to the period July to December 2001. There were no major changes made to the Network during this period.

The ratified data capture percentages and specific problems at sites are presented. An inventory of Department equipment held by NPL, and a list of recommendations for items to be purchased are also given.

Additionally, this report contains a provisional assessment of measurement uncertainty on a site-by-site basis, along the lines required by EC directives.

2. RATIFICATION PROCEDURE

The data received by NPL from the CMCU were processed and scaled according to calibrations carried out by the Local Site Operators every two weeks, and by NPL on a three monthly basis. The results of these NPL field calibrations are reported to the Department separately.

During an NPL intercomparison ozone analyser accuracy is quantified with a transfer standard photometer certified against the NPL primary photometer, while NO_x, CO and SO_2 analyser calibration responses are measured with gas mixtures certified against primary standard gases at NPL. Analyser linearities are determined by multi-point dilution of a high concentration mixture with zero air. Particulate analysers are calibrated with traceable pre-weighed masses, and sample and bypass flow rates are measured.

The data ratification process takes account of all relevant data from LSO, NPL and Equipment Service Unit calibrations. The optimum time-varying set of analyser response functions are determined and then applied to raw data to produce the ratified data set. The causes of gaps in the new data set are identified and periods for which analyser responses are seen to be unstable or changing rapidly are deleted.

3. DATA CAPTURE

The percentage data capture at each site for each pollutant is given in Table 1. For the period covered by this report the overall Network Mean data capture is 87%.

Table 1. Data capture for January to June 2001

	Percentage Data Capture by Pollutant					
Site Name	**O_3**	**NO_x**	**SO_2**	**CO**	**PM_{10}**	**Mean**
Aston Hill	**70**					70
Bottesford	99					99
Bush	97					97
Eskdalemuir	100					100
Glazebury	96					96
Great Dun Fell	99					99
Harwell	96	**77**	95			89
High Muffles	99					99
Ladybower	**82**	**82**	99			88
Lough Navar	99				99	99
Lullington Heath	98	91	92			94
Narberth	93	**59**	**0**		91	61
Rochester	97	92	**69**		95	88
Sibton	99					99
Somerton	96					96
Strath Vaich	**37**					37
Teddington	98	**89**	98			95
Weybourne	99					99
Wicken Fen	**86**	**80**	**86**			84
Yarner Wood	93					93
Mean	92	81	77	---	95	

Percentages below 90% are highlighted.

4. GENERIC REASONS FOR ABSENT RATIFIED DATA

Two general categories for ratified data loss are distinguished:

4.1 ABSENT UNRATIFIED DATA

During periods of power failure, telecommunications failure, instrument calibration and repair, or other similar circumstances, clearly there are no "raw" data to ratify, and this will be reflected directly in the data capture. Such instances are described below as periods for which data were not received by the QA/QC Unit. Typically the reasons are not investigated, as this is more of a matter for the CMCU.

4.2 UNRATIFIABLE DATA

From time to time most sites will produce data that cannot be ratified with sufficient confidence due to an analyser malfunction or a peripheral problem such as leaking pipe work. Most problems are apparent to the CMCU as they carry out regular remote checks, and they can initiate repairs promptly, preventing large amounts of data loss. The speed of repair will of course depend on the organisation responsible for maintaining the instrument, which will not necessarily be the CMCU for affiliated sites.

The instances described in this Report are those where either the repair took a significant time, or the problem was not readily apparent remotely. In these cases the problem is usually noticed at a visit by the LSO or QA/QC Unit, then reported and remedied. As LSO visits on the Rural Network are fortnightly (monthly for ozone-only sites), and QA/QC Unit visits are quarterly, this can lead to periods of data lasting several weeks being deleted. The crucial elements in minimising data loss are experience in recognising the problems, clear communication of the problem to the CMCU, and prompt remedial action. To a limited extent the experience of these problems can be used to modify LSO, CMCU, ESU or QA/QC Unit procedures, or extend the training of LSOs.

In some instances, the cause of ratified data loss is an underlying problem that can be predicted to recur, and preventative action can therefore be recommended.

5. SPECIFIC PROBLEMS AT SITES

The sites with data capture of less than 90% for any pollutant are listed here and reasons are given for the absence of the data.

5.1 Aston Hill (O_3 70% data capture)

Absent Unratified Data

8th November to 31st December (1291 hours). The data were lost as a result of a malfunction on the site data logger. The logger was replaced on 8th February 2002 by the ESU.

5.2 Harwell (NO_x 77% data capture)

Absent Unratified Data

6th – 15th July (204 hours). These data were lost as a result of site power problems.

15th - 16th December (37 hours). No data were received from the CMCU.

Unratifiable Data

2nd – 9th August (158 hours). An analyser malfunction caused the loss of these data. No ESU visit records were received but data appeared normal following an LSO visit on 8th August, and were re-instated following the next consistent overnight auto-calibration.

16th – 19th August (62 hours). The analyser zero could not be determined satisfactorily for the two days following an LSO site visit. Data therefore had to be deleted for this period.

13th –26th September (302 hours). The analyser zero was unstable following the LSO calibration on 13th September - this necessitated deletion of the data because a satisfactory value could not be assigned.

11th – 16th October (108 hours). The analyser zero was again unstable following an LSO calibration on 11th October. The data were deleted.

29th October to 1st November (61 hours). Data were deleted owing to an unstable analyser zero point.

5.3 Ladybower (Ozone 82%, NO_x 82% data capture)

Absent Unratified Data

11th December. Two hours of SO_2 data were deleted as a result of a significant pollution episode causing the SO_2 analyser to over-range. The LSO has been informed of this problem and has changed the analyser running range. The DDU have been informed that although the data cannot be quantified accurately, they should still count towards exceedence totals since the concentrations measured during the missing five 15-minute averages are all in excess of 150 ppb.

14th – 19th August (110 hours of NO_x data). No data from CMCU for 14th – 17th August. A power problem was suspected and so data were additionally deleted 17th -19th to allow analyser stabilisation.

Unratifiable Data

1st – 13th July (300 hours of Ozone data). A replacement analyser installed in March 2001 by the ESU had been malfunctioning since that time. The QA/QC unit reported a fault at the following quarterly visit, on 21st June, but the replacement analyser that was installed by the ESU on 5th July itself developed a fault and was replaced on 13th July. No service records were received from the ESU for any of the work that they carried out.

13th – 31st August (441 hours of Ozone data). The site analyser developed a fault - which it was not possible to repair on site - and was replaced by the ESU. No ESU service records were received.

13th November – 12th December (672 hours of NO_x data). Data were lost initially due to an analyser malfunction. The ESU attended the site to repair the instrument although no associated calibration information was received. The LSO calibrations immediately following the repair were inconsistent and - since no further information could be obtained from the site auto-calibrations - data were deleted until a consistent LSO calibration was obtained.

5.4 Narberth (NO_x 59%, SO_2 0% data capture)

Absent Unratified Data

1st July – 31st December. Approx 183 hours (around one hour per day) were lost throughout the period owing to a malfunction that caused the daily NO_x auto-calibration to over-run into the subsequent day's data. This was evident from inspection of the data.

Unratifiable Data

1st July – 31st December. 4416 hours of SO_2 data were deleted because of diurnal variation patterns in the data. The problem was immediately obvious upon inspection of the dataset but no cause could be attributed. The data were not realistic and so had to be removed.

1st –31st July. 744 hours of NO_x data were deleted because the analyser showed a continuation of the diurnal variation discussed in the previous ratification report. The cyclical nature of the dataset was obviously suspect upon inspection.

1st – 11th August. 242 hours of NO_x data were deleted following a routine instrument service by the ESU. No service records were received for this work. The data were removed owing to an unstable analyser zero point.

24th – 25th August, 19th – 20th and 25th – 26th September. 75 hours of NO_x data in total were deleted due to an unknown zero point following an overnight step-change.

24th October – 21st November. 677 hours of NO_x data were deleted because the analyser span factor changed following a calibration. It was not possible to retrospectively assign a factor from the following calibration because of irregularities in the site daily auto-calibration data.

5.5 Rochester (SO_2 69% data capture)

Absent Unratified Data

4th - 8th October. 93 hours of data were deleted by the CMCU.

Unratifiable Data

5th July – 25th August. 1227 hours were deleted as a result of analyser malfunction caused by overheating. The site air conditioning was insufficiently able to regulate the site temperature and affected the SO_2 analyser performance. Although there is a temperature probe at the site the data does not appear to have been logged by the CMCU – these would have been of great assistance during data ratification.

5.6 Strath Vaich (Ozone 37% data capture)

Unratifiable Data

1st July – 7th August. 898 hours were deleted because of a leak in the analyser main valve, discovered at the QA/QC visit. This was repaired on 6th August but no calibration information was received from the ESU.

1st October to 5th December. 1604 hours of data were lost because of a further leak which was discovered at the QA/QC visit on 3rd December. The ESU attended the site but no maintenance or calibration records were forwarded.

5th – 18th December. 312 hours of data had to be deleted – it is suspected that during this period the manifold inlet had become blocked with ice.

5.7 Teddington (NO_x 89% data capture)

Absent Unratified Data

6th – 9th July. 55 hours of data were deleted by the CMCU.

Unratifiable Data

29th October – 14th November. 390 hours were deleted owing to an unexplained step-change in the analyser response between calibrations. Unfortunately the site auto-calibration data did not show when the change had occurred and so all data between calibrations had to be removed.

5.8 Wicken Fen (Ozone 86%, NO_x 80%, SO_2 86% data capture)

Absent Unratified Data

29th September – 3rd October. 100 hours of all data were either deleted or not received by the CMCU.

25th August - 10th September. 372 hours of data from all species were deleted because the sampling manifold fan ceased to function. CMCU became aware of the problem upon examining the data and issued an LSO callout, which was carried out on 31st August and confirmed the problem.

7th – 10th October. 32 hours of data for all species were either deleted or not received by the CMCU. Following this 94 hours of Ozone and SO_2 data were deleted because the relevant analyser factors could not be determined.

Unratifiable Data

23rd – 24th July. 25 hours of NO_x data were deleted because the analyser zero could not be determined.

13th – 25th August. 304 hours of NO_x data were deleted resulting from an analyser malfunction. This was caused by the analyser's susceptibility to temperature variation, which was exposed when the site air conditioning malfunctioned.

6. RATIFIED DATA UNCERTAINTY

The EC Daughter Directives for the pollutants monitored contain Data Quality Objectives for both data capture and measurement uncertainty, which in the case of NO_2, SO_2, CO and ozone is 15% at the 95% confidence level. A common method of evaluating the measurement uncertainty has been published in a CEN Report CR 14377, while the detailed procedures for acceptable measurements are being set out in individual CEN standards drafted by CEN TC 264 WG 12. These are not yet finalised, and these estimates of uncertainty are therefore provisional.

Overall measurement uncertainty may be calculated by the combination of a number of factors, each giving an insight into how a particular analyser system is capable of performing under a given set of circumstances. Thus quantities such as analyser drift uncertainty, zero and span noise, analyser linearity error and transfer standard uncertainty may be combined to give an overall standard uncertainty, calculated by accepted methodology, which for these purposes should be less than 15%. Table 2 gives results from the AURN sites based on actual or representative data. In a few cases assumptions have had to be made to simplify calculation, and the particulate data has not been included in this survey.

Table 2. Uncertainty Calculation for Ratified Datasets (95% confidence)

	Percentage Uncertainty		
Site Name	**O_3**	**NO_2**	**SO_2**
Aston Hill	8		
Bottesford	7		
Bush	8		
Eskdalemuir	8		
Glazebury	9		
Great Dun Fell	9		
Harwell	7	16	8
High Muffles	8		
Ladybower	8	14	10
Lough Navar	8		
Lullington Heath	10	24	8
Narberth	8	16	-
Rochester	8	14	10
Sibton	8		
Somerton	7		
Strath Vaich	10		
Teddington	8	12	7
Weybourne	7		
Wicken Fen	10	17	8
Yarner Wood	9		

It can be seen from these results that the large majority of measurements fall within the 15% uncertainty limit. Four of the sites measuring NO_2 - namely Harwell, Lullington Heath, Narberth and Wicken Fen - exceed the 15% criterion. This is a result of the large uncertainties related to the determination of analyser linearities at the most recent inter-calibration visit, combined in most cases with the significant sources of error from assigning a satisfactory calibration factor. This investigation supports the recent decision to replace the NO_x analyser at Lullington Heath, and reinforces the recommendations to consider replacement of the Wicken Fen and Harwell NO_x analysers in section 7.

This first attempt at quantifying the overall uncertainty has included certain sources where the typical errors are currently not well characterised, and therefore some assumptions have had to be made. These sources include interference from other gaseous species, analyser temperature dependency and uncertainty in the drift in concentration of calibration mixtures. When these terms are added in to future iterations of this procedure it may be possible to reduce their overall contribution if their effects can be better quantified. Sample degradation occurring in the sample manifold is not included in the calculation. The draft CEN standard requires regular checking and cleaning of the manifold as part of ongoing QA/QC and assumes that there is no contribution to the uncertainty budget.

7. RECOMMENDATIONS TO IMPROVE DATA QUALITY / CAPTURE

7.1 Site Sampling Manifolds

Recent tests have been carried out by NPL on-site sampling manifold arrangements. These tests have highlighted significant measurement losses at some sites, for certain pollutants. It may therefore be the case that some sites in the AURN are under-reporting measured pollutant concentrations as the pollutants are being in some removed by contact with the inner surfaces of the manifolds. As a result of these tests it is recommended that all Teflon-coated metal manifolds currently operating on the AURN should be changed. In addition, all other types of manifold should be routinely cleaned at the six-monthly service. NPL understands that this process is currently being co-ordinated by the CMCU.

7.2 Timing of internal zero and span

The CMCU should check that the same hour of data is not missing every day.

ESUs should also check for this fault at the bi-annual services.

7.3 Failure to calibrate replacement analysers

On a number of occasions the ESU has been unable to repair an analyser on site and has had to remove the faulty analyser for repair. There have been instances where the ESU installed a replacement analyser at the site, but failed to calibrate this analyser, or did not calibrate it before its subsequent removal. These events occur in between QA/QC visits, and so often no calibrations are performed on the analysers. This is a particular problem in the case of ozone instruments, as there is no on-site standard for use by the LSO and therefore no response factors may be calculated.

The ESU must perform a full calibration on an analyser when it is installed and removed from site. The ESU must also record the serial numbers of any artefacts used to calibrate analysers. These calibrations should always be forwarded to the CMCU and QA/QC units to enable data checking and ratification procedures to be satisfactorily carried out.

The CMCU should check that a replacement analyser has been calibrated at installation and removal.

8. INVENTORY

The DETR owned assets used for this work are as follows:

1 PC (486-66)
NPL-developed ratification software
Cylinders, regulators and measurement instruments with individual values of less than £1000

9. RECOMMENDATIONS FOR EQUIPMENT PURCHASES

NPL would recommend that the following items be installed:

1. A Permapure dryer for Harwell NO_x analyser.
2. A chart recorder at Dunslair Heights.
3. Consideration should be given to the installation of new analysers at Lullington Heath (currently scheduled to be carried out by the ESU), and a new NOx analyser for both Harwell and Wicken Fen.
4. New manifold sampling systems for Aston Hill, Eskdalemuir, Harwell, High Muffles Ladybower, Lullington Heath, Strath Vaich, Wicken Fen and Yarner Wood. Also, a replacement for the existing system at Bush should be considered as this system is currently impossible to verify due to its high sampling flow-rate. NPL understands that this process is currently being carried out by the ESU, in co-ordination with the CMCU.