REPORT

Ratification of data produced by the UK Ambient Hydrocarbon Automatic Air Quality Network, 1 July 2003 to 30 September 2003

A report produced for the Department for Environment, Food and Rural Affairs, the Scottish Executive, the Welsh Assembly Government and the Department of the Environment in Northern Ireland

AEAT/ENV/R/1633 Issue 1
December 2003

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1 Introduction

This report contains information on the quality and statistical parameters associated with ratified data from the UK Ambient Hydrocarbon Automatic Air Quality Network (The UK Hydrocarbon Network). The presented information and data cover the period 1 July 2003 to 30 September 2003. The ratified data have been made available on the World Wide Web at http://www.airquality.co.uk/archive/data_and_statistics_home.php

This report contains:

- The definition of a Data Quality Code for each reported hydrocarbon.
- The Data Quality Codes assigned to the data presented on the web.
- A list of periods of data loss, reasons for data loss and descriptions of the most significant causes of data loss.
- Statistical information for each measured hydrocarbon for each individual month.

In this report the unit used for expressing concentrations of gases is micrograms per cubic metre ($\mu g/m^3$), where some earlier reports have used parts per billion (ppb). This allows comparison to the relevant Air Quality Standards that are now expressed in micrograms per cubic metre ($\mu g/m^3$).

2 Hydrocarbon Data Quality

All hydrocarbon data are assigned a quality value. In general ratified hourly data have an uncertainty (at 95% confidence) of ±10% for values above 0.5 $\mu g/m^3$ and ±0.05 $\mu g/m^3$ for values below 0.5 $\mu g/m^3$. These data are termed 'good quality'.

In some cases, because of instrument problems, data cannot be described as 'good' quality, but the data may still be of use to modellers and is therefore included in the archive. This is termed 'acceptable' quality data, and has an uncertainty (at 95% confidence) of ± 25% above 0.5 $\mu g/m^3$ and ± 0.1 $\mu g/m^3$ below 0.5 $\mu g/m^3$.

Data that do not meet either the ‘good’ or ‘acceptable’ criteria do not appear in the archive.

Each month's data are assigned a Data Quality Code for each species as follows:

A. all 'good' quality data
B. most (> 75%) data points 'good', remainder 'acceptable' quality
C. roughly equal numbers of 'good' and 'acceptable' quality data
D. some (< 25%) data points 'good' quality; remainder 'acceptable' quality
E. all points 'acceptable' quality

3 Monthly Data Reports

The following sections give details of issues affecting data on a month by month basis.
Data quality codes have been assigned for each monthly set of data.

3.1 CARDIFF

3.1.1 July

3.1.1.1 Data Quality Codes

Data quality code A for all data for all of the month.

3.1.1.2 Missing Data – All hydrocarbons

- Calibration 10/07/03 hours 11 to 12.
- Calibration 24/07/03 hours 15 to 17.

3.1.1.3 Missing Data – Specific hydrocarbons

None, except where the integration was unreliable due to very low concentrations or response.

3.1.2 August

3.1.2.1 Data Quality Codes

Data quality code A for all data for all of the month.

3.1.2.2 Missing Data - All hydrocarbons

- Calibration 11/08/03 hours 11 to 12.
- PC/GC communication problem 14/08/03 hours 02 to 07.
- Analyser removed to Harwell. Harwell analyser installed 14/08/03 hours 13 to 15.
- Calibration 14/08/03 hours 16 to 17.

3.1.2.3 Missing Data - Specific hydrocarbons

None, except where the integration was unreliable due to very low concentrations or response.

3.1.3 September

3.1.3.1 Data Quality Codes

Data quality code A for all data for all of the month.

3.1.3.2 Missing Data - All hydrocarbons

- Calibration 04/09/03 hours 13 to 14.
- Calibration 18/09/03 hours 10 to 12.
- Calibration 29/09/03 hours 14 to 16.

3.1.3.3 Missing Data - Specific hydrocarbons

None, except where the integration was unreliable due to very low concentrations.

3.2 GLASGOW

3.2.1 July

3.2.1.1 Data Quality Codes

Data quality code A for all data for all of the month except:
Data quality code E for 1,3-butadiene for all of the month.

3.2.1.2 Missing Data - All hydrocarbons

- Calibration 01/07/03 hours 11 to 14.
- Calibration 15/07/03 hours 11 to 14.
- Calibration 29/07/03 hours 11 to 15.

3.2.1.3 Missing Data - Specific hydrocarbons

None.

3.2.2 August

3.2.2.1 Data Quality Codes

Data quality code A for all data for all of the month except:
Data quality code E for 1,3-butadiene for all of the month.

3.2.2.2 Missing Data - All hydrocarbons

- PC/GC communication problem 01/08/03 hours 04 to 06.
- Calibration 12/08/03 hours 11 to 14.
- Carrier gas supply and GC circuit board fault 12/08/03 hour 15 to 31/08/03 hour 24.

3.2.2.3 Missing Data - Specific hydrocarbons

None.

3.2.3 September

3.2.3.1 Data Quality Codes

Data quality code A for all data for all of the month.

3.2.3.2 Missing Data - All hydrocarbons

- Carrier gas supply and GC circuit board fault 01/09/03 hour 01 to 29/09/03 hour 22.

3.2.3.3 Missing Data - Specific hydrocarbons

None.

3.3 HARWELL

3.3.1 July

3.3.1.1 Data Quality Codes

Data quality code A for all data for all of the month.

3.3.1.2 Missing Data - All hydrocarbons

- Calibration 03/07/03 hours 09 to 11.
- CMCU service visit 17/07/03 hours 09 to 13.
- Calibration 17/07/03 hours 14 to 15.
- Noisy data 17/07/03 hour 16 to 20/07/03 hour 19.
- Calibration 21/07/03 hours 14 to 17.
- Calibration 24/07/03 hours 08 to 13.
- Calibration 31/07/03 hours 09 to 13.

3.3.1.3 Missing Data - Specific hydrocarbons

None, except where the integration was unreliable due to very low concentrations or response.

3.3.2 August

3.3.2.1 Data Quality Codes

Data quality code A for all data for all of the month.

3.3.2.2 Missing Data - All hydrocarbons

- PC/GC communication problem 01/08/03 hours 01 to 03.
- Calibration 14/08/03 hours 10 to 12.
- Analyser removed to Cardiff. Cardiff analyser installed 14/08/03 hour 13 to 15/08/03 hour 11.
- Calibration 28/08/03 hours 09 to 11.

3.3.2.3 Missing Data - Specific hydrocarbons

None, except where the integration was unreliable due to very low concentrations or response.

3.3.3 September

3.3.3.1 Data Quality Codes

Data quality code A for all data for all of the month.

3.3.3.2 Missing Data - All hydrocarbons

- Calibration 11/09/03 hours 08 to 10.
- CMCU service visit 19/09/03 hours 19 to 20.
- Calibration 24/09/03 hours 10 to 15.

3.3.3.3 Missing Data - Specific hydrocarbons

None, except where the integration was unreliable due to very low concentrations or response.

3.4 MARYLEBONE ROAD

3.4.1 July

3.4.1.1 Data Quality Codes

Data quality code A for all data for all of the month.

3.4.1.2 Missing Data - All hydrocarbons

- Calibration 11/07/03 hours 04 to 07.
- Calibration 16/07/03 hours 17 to 20.
- Calibration 31/07/03 hours 08 to 11.

3.4.1.3 Missing Data - Specific hydrocarbons

None.

3.4.2 August

3.4.2.1 Data Quality Codes

Data quality code A for all data for all of the month.

3.4.2.2 Missing Data - All hydrocarbons

- PC/GC communication problem 06/08/03 hour 12 to 07/08/03 hour 17.
- Power cut 20/08/03 hours 01 to 15.
- Calibration 20/08/03 hours 18 to 21.

3.4.2.3 Missing Data - Specific hydrocarbons

None.

3.4.3 September

3.4.3.1 Data Quality Codes

Data quality code A for all data for all of the month.

3.4.3.2 Missing Data - All hydrocarbons

- Calibration 04/09/03 hours 09 to 12.
- Calibration 10/09/03 hours 14 to 17.
- Calibration 25/09/03 hours 06 to 09.

3.4.3.3 Missing Data - Specific hydrocarbons

None.

4 Discussion

4.1 THE RATIFIED DATA

Tables 1 to 4, Appendix 1 contain statistical information relating to the ratified data, for each measured hydrocarbon, over the period 1 July 2003 to 30 September 2003. The tables list the percentage data capture, maximum concentration, mean concentration and minimum concentration of each hydrocarbon. The data capture is the number of ratified hourly data values expressed as a percentage of the number of hours in the specified period.

4.1.1 Cardiff

For the Cardiff site the data capture for benzene was 58.83% and for 1,3-butadiene was 59.19%.

During July it was observed that the peak areas were close to the limit of detection, indicating that the PID lamp was approaching the end of its useful life. This problem was more apparent due to the lower concentrations often observed during the summer and autumn seasons.
A replacement PID lamp was not immediately available from the manufacturer of the analyser and was therefore sourced directly from the manufacturer of the PID lamps.
The delay in aquiring a replacement lamp resulted in poor data capture during July and into August. On the 14th August the Harwell analyser was installed to prevent further data loss.

There have been no other significant problems for the period covered by this report.

4.1.2 Glasgow

For the Glasgow site the data capture for benzene was 46.56% and for 1,3-butadiene was 45.38%.

On the 12th August a problem in the carrier gas supply system led to a fault developing on the GC circuit board. It was not possible to repair this at the site so the analyser was returned to the CMCU. This resulted in no data from the 12th August to 29th September.

During the process of calculating response factors for the data covered in this report it was observed that the 1,3-butadiene peak had merged with a neighbouring peak, trans-2-butene, in the chromatograms of the calibration samples. The reported peak areas for 1,3-butadiene in the standards were therefore, overestimated. As a result an accurate response factor for 1,3-butadiene could not be generated as the degree of overestimation could not be accurately quantified.

An alternative approach was used to generate the response factor for 1,3-butadiene. The response factor for cis-2-butene, a well-resolved peak, was used to derive a response factor for 1,3-butadiene. The relative response factors for 1,3-butadiene and cis-2-butene are fairly constant over time when both peaks are well resolved. The cis-2-butene response factor and relative response factor were used to derive a response factor for 1,3-butadiene.

It is likely that this approach generates a relatively accurate response factor for 1,3-butadiene. However due to the increased uncertainty associated with this method, all the1,3-butadiene data has been assigned data quality code E.

There have been no other significant problems for the period covered by this report.

It should be noted that the hydrocarbon instrumentation at the Glasgow site samples air through a separate inlet from that used for the inorganic measurements. The inlet for the inorganic measurements is within one metre from the kerb and hence these are classed as kerbside measurements. The sample inlet for the hydrocarbon measurements is more than one metre from the kerb (but less than five metres) and hence these are classed as roadside measurements.

4.1.3 Harwell

For the Harwell site the data capture for benzene was 50.50% and for 1,3-butadiene was 50.68%.

During July it was noticed that the peak areas were close to the limit of detection, indicating that the PID lamp was approaching the end of its useful life. This problem was more noticeable with the lower concentrations due to seasonal variation. The PID lamp was changed on the 17th July.

As described in section 4.1.1 above, the analyser at the Cardiff site had similar problems with the PID lamp. A replacement PID lamp was not immediately available therefore, on the 14th August the analyser installed at the Harwell site was moved and installed at Cardiff to prevent further loss at the Cardiff site. The analyser from Cardiff was installed at the Harwell site but no useful data were obtained until a replacement PID lamp was fitted on 19th September shortly after receipt of a new PID lamp.

There have been no other significant problems for the period covered by this report.

4.1.4 Marylebone Road

For the Marylebone Road site the data capture for benzene was 93.16% and for 1,3-butadiene was 96.47%.

There have been no significant problems for the period covered by this report.

4.2 CONCENTRATION TRENDS

The periods when data for benzene and 1,3-butadiene were available, for all the sites, are plotted graphically in Figures 1 to 8, Appendix 2. The measured concentrations of 1,3-butadiene fell below 0.02 $\mu g/m^3$ on a number of occasions see Figures 2 and 6, Appendix 2. Where concentrations fell below 0.02 $\mu g/m^3$ the ratified concentrations have been reported as 0.00 $\mu g/m^3$.

At Cardiff and Harwell the measured concentrations of hydrocarbons were low for most of the period covered by this report. At these urban background and rural sites there tends to be a pattern of seasonal variation with higher levels during the winter when dispersion is generally poorer and photochemical removal is at a minimum.

The Glasgow and Marylebone Road data tend to exhibit higher levels with less seasonal variation than is apparent in data from the other two sites. The measured concentrations and trends are typical of sites close to busy roads where the source of the measured hydrocarbons is close to the monitoring location. The emitted hydrocarbons will have had little time to mix and react in the atmosphere. The measured concentrations at Glasgow and Marylebone Road for July to September 2003 exhibited no significant episodes of elevated concentrations. There is insufficient information to provide an explanation of the observed difference in the trends from site to site, although spatial variations in meteorological conditions may well be the cause. The variation in trends from site to site is probably due to variations in atmospheric dispersion.

4.3 COMPARISON WITH AIR QUALITY OBJECTIVES

The Air Quality Strategy for the UK has set Air Quality Objectives for benzene and 1,3-butadiene. The Air Quality Objective for benzene in the UK is 16.25 $\mu g/m^3$ expressed as a running annual mean to be met by 31 December 2003. In England and Wales there is an additional objective for benzene of 5 $\mu g/m^3$ expressed as an annual mean to be met by end of 2010. In Scotland an additional objective has been set for benzene of 3.25 $\mu g/m^3$ to be met by the end of 2010. The Air Quality Objective for 1,3-butadiene is specified as a running annual mean of 2.25 $\mu g/m^3$ to be met by the end of 2003.

The annual means for benzene and 1,3-butadiene for 2000, 2001 and 2002 together with the quarterly means for the first, second and third quarter of 2003 are given in Tables 1 and 2 below. For benzene the annual means for 2000, 2001 and 2002 were well below the respective Air Quality Objective of 16.25 $\mu g/m^3$ to be met by the end of 2003. The annual means for 2002 were also below the Air Quality Objective to be met by 2010 for the respective region.

The means for both benzene and 1,3-butadiene for quarter 1, 2003 were slightly higher than the annual means for 2002. The means for both benzene and 1,3-butadiene for quarter 2, 2003 were lower than the annual means for 2002 and the means for quarter 1, 2003. The means for quarter 3, 2003 were approximately the same as the means for quarter 2, 2003. The observed trends in concentrations are probably due to seasonal variation.

Table 1. Means of measured benzene concentrations ($\mu g/m^3$) at each of the UK Automatic Hydrocarbon Sites.

Monitoring Site	2000 Annual Mean	2001 Annual Mean	2002 Annual Mean	Quarter 1 2003 Mean	Quarter 2 2003 Mean	Quarter 3 2003 Mean
Cardiff Centre	$$	$$	1.22$	1.36	0.58	0.94
Glasgow	$$$	$$$	2.33 $	2.43	1.36	1.30
Harwell	0.53	0.62	0.60	0.91	0.36	0.39
Marylebone Road	6.29	4.55	3.91	3.86	3.08	2.85

$ Annual means calculated from significantly less than 12 months data
$$ The Cardiff Centre site was installed on 5th September 2002.
$$$ The Glasgow site was installed on 1st August 2002.

Table 2. Means of measured 1,3-butadiene concentrations ($\mu g/m^3$) at each of the UK Automatic Hydrocarbon Sites.

Monitoring Site	2000 Annual Mean	2001 Annual Mean	2002 Annual Mean	Quarter 1 2003 Mean	Quarter 2 2003 Mean	Quarter 3 2003 Mean
Cardiff Centre	$$	$$	0.15$	0.16	0.07	0.11
Glasgow	$$$	$$$	0.36$	0.38	0.34	0.38
Harwell	0.09	0.11	0.04	0.04	0.02	0.02
Marylebone Road	1.63	1.12	0.95	0.70	0.61	0.58

$ Annual means calculated from significantly less than 12 months data
$$ The Cardiff Centre site was installed on 5th September 2002.
$$$ The Glasgow site was installed on 1st August 2002.

4.4 PID LAMP SENSITIVITY

The sensitivity of PID lamps often exhibit a short period of marked decrease in sensitivity after initial installation. The initial decrease in sensitivity is then followed by a much slower decrease in sensitivity over the lifetime of the lamp. After a number of months the sensitivity may exhibit no further change during the remaining life of the lamp.

The decrease in sensitivity coupled with the low concentration observed during the summer and autumn seasons resulted in periods when the concentrations fell below the limit of detection of the VOC71M. The limit of detection prior to the change of the lamps was of the order of 10% of the Air Quality Objective.

During future years it is intended that the PID lamps are changed on an annual basis even though the lamps remain operational for an average of 2 years. The lamps will be changed during mid to late spring, the time when the concentrations tend to be lower. The period of maximum sensitivity will then conincide with the period when ambient concentrations tend to be lowest.

Appendices

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Appendix 1
Summary Statistical Information

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Table 1. Percentage data capture, maximum, mean and minimum values of the ratified data from the Cardiff site of the UK Hydrocarbon Network, for the period 1 July 2003 to 30 September 2003

Compound	%Data capture	Maximum hourly concentration ($\mu g/m^3$)	Mean concentration ($\mu g/m^3$)	Minimum hourly concentration ($\mu g/m^3$)
1,3-Butadiene	59.19	3.39	0.11	0.00
Benzene	58.83	5.74	0.94	0.00
Toluene	92.39	68.66	3.29	0.57
Ethylbenzene	55.62	6.61	0.71	0.00
(m+p)-Xylene *	71.38	86.78	2.07	0.13
o-Xylene	62.36	14.85	1.23	0.04

* (m+p)-Xylene data are reported as the sum of the 2 individual components due to the fact that they are not sufficiently well resolved in the chromatogram.

Table 2. Percentage data capture maximum, mean and minimum values of ratified data from the Glasgow site of the UK Hydrocarbon Network, for the period 1 July 2003 to 30 September 2003

Compound	%data capture	Maximum hourly concentration ($\mu g/m^3$)	Mean concentration ($\mu g/m^3$)	Minimum hourly concentration ($\mu g/m^3$)
1,3-Butadiene	45.38	5.57	0.38	0.00
Benzene	46.56	5.64	1.30	0.16
Toluene	46.56	32.67	5.43	0.65
Ethylbenzene	46.56	7.67	0.93	0.13
(m+p)-Xylene *	46.56	29.48	3.53	0.44
o-Xylene	46.56	20.10	3.83	0.62

* (m+p)-Xylene data are reported as the sum of the 2 individual components due to the fact that they are not sufficiently well resolved in the chromatogram.

Table 3. Percentage data capture, maximum, mean and minimum values of ratified data from the Harwell site of the UK Hydrocarbon Network, for the period; 1 July 2003 to 30 September 2003

Compound	%data capture	Maximum hourly concentration ($\mu g/m^3$)	Mean concentration ($\mu g/m^3$)	Minimum hourly concentration ($\mu g/m^3$)
1,3-Butadiene	50.68	0.22	0.02	0.00
Benzene	50.5	1.59	0.39	0.00
Toluene	58.92	7.42	1.49	0.11
Ethylbenzene	35.42	1.01	0.22	0.00
(m+p)-Xylene *	45.56	3.09	0.57	0.00
o-Xylene	35.69	1.28	0.31	0.00

* (m+p)-Xylene data are reported as the sum of the 2 individual components due to the fact that they are not sufficiently well resolved in the chromatogram.

Table 4. Percentage data capture, maximum, mean and minimum values of ratified data from the Marylebone Road site affiliated to the UK Hydrocarbon Network for the period; 1 July 2003 to 30 September 2003

Compound	%data capture	Maximum hourly concentration ($\mu g/m^3$)	Mean concentration ($\mu g/m^3$)	Minimum hourly concentration ($\mu g/m^3$)
Ethane	96.60	65.78	8.53	1.87
Ethene	96.60	21.28	5.27	0.28
Propane	96.60	33.50	4.98	0.57
Propene	96.60	11.47	2.71	0.30
Ethyne	96.60	21.49	4.14	0.38
2-Methylpropane	96.60	102.51	5.50	0.39
n-Butane	96.60	183.80	10.97	0.82
trans-2-Butene	96.60	7.33	0.70	0.23
1-Butene	96.42	5.77	0.65	0.07
cis-2-Butene	96.56	6.12	0.51	0.09
2-Methylbutane	96.60	168.36	14.64	0.84
n-Pentane	96.60	33.35	3.80	0.27
1,3-Butadiene	96.47	2.02	0.58	0.04
trans-2-Pentene	96.38	7.51	0.79	0.03
cis-2-Pentene	95.34	3.96	0.47	0.03
2-Methylpentane	96.60	29.07	4.15	0.29
3-Methylpentane	96.60	16.84	2.50	0.18
Isoprene	95.88	4.83	0.62	0.06
n-Hexane	96.60	8.55	1.50	0.04
n-Heptane	96.47	6.49	0.79	0.00
Benzene	93.16	13.65	2.85	0.13
Toluene	96.65	64.18	12.24	0.57
Ethylbenzene	96.65	10.14	2.16	0.04
(m+p)-Xylene *	81.30	36.84	8.42	0.79
o-Xylene	96.65	14.19	2.78	0.09
1,3,5-Trimethylbenzene	96.47	5.49	1.00	0.00
1,2,4-Trimethylbenzene	96.51	16.56	3.04	0.25

* (m+p)-Xylene are reported as the sum of the 2 individual components due to the fact that they are not sufficiently well resolved in the chromatogram.

Appendix 2
Time Series Plots of Hydrocarbon Concentrations

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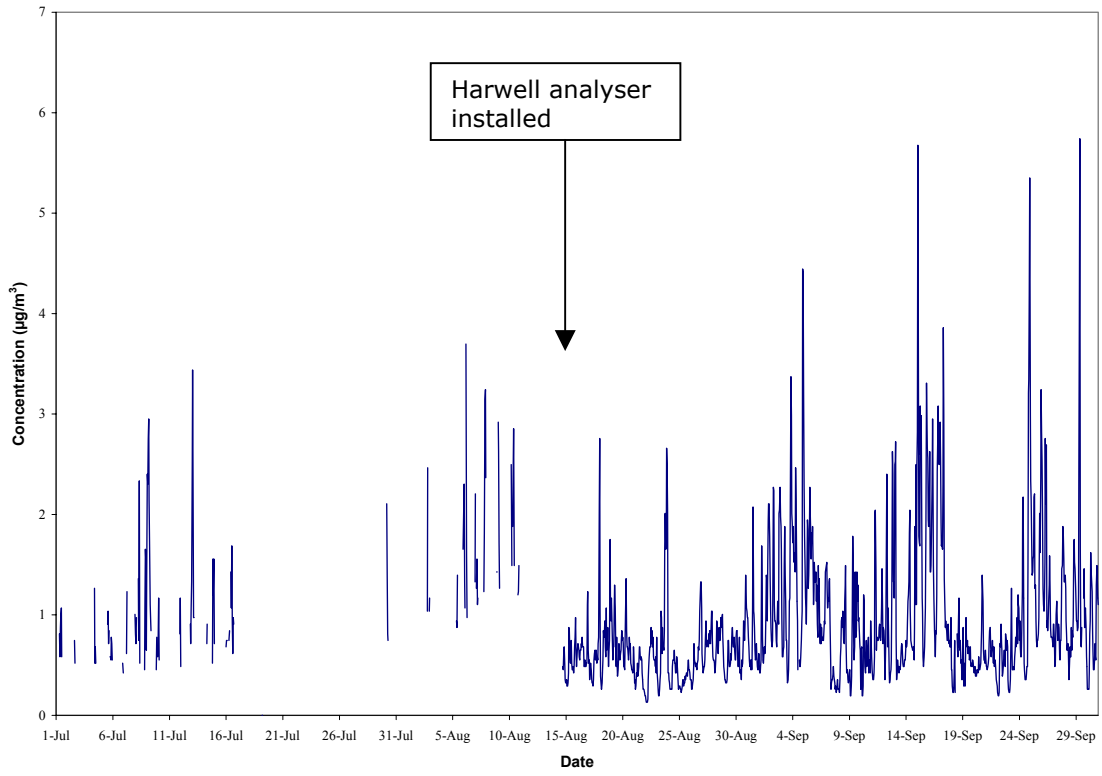

Figure 1. Time series plot of the ratified benzene data from the Cardiff site of the UK Hydrocarbon Network, for the period; 1 July 2003 to 30 September 2003

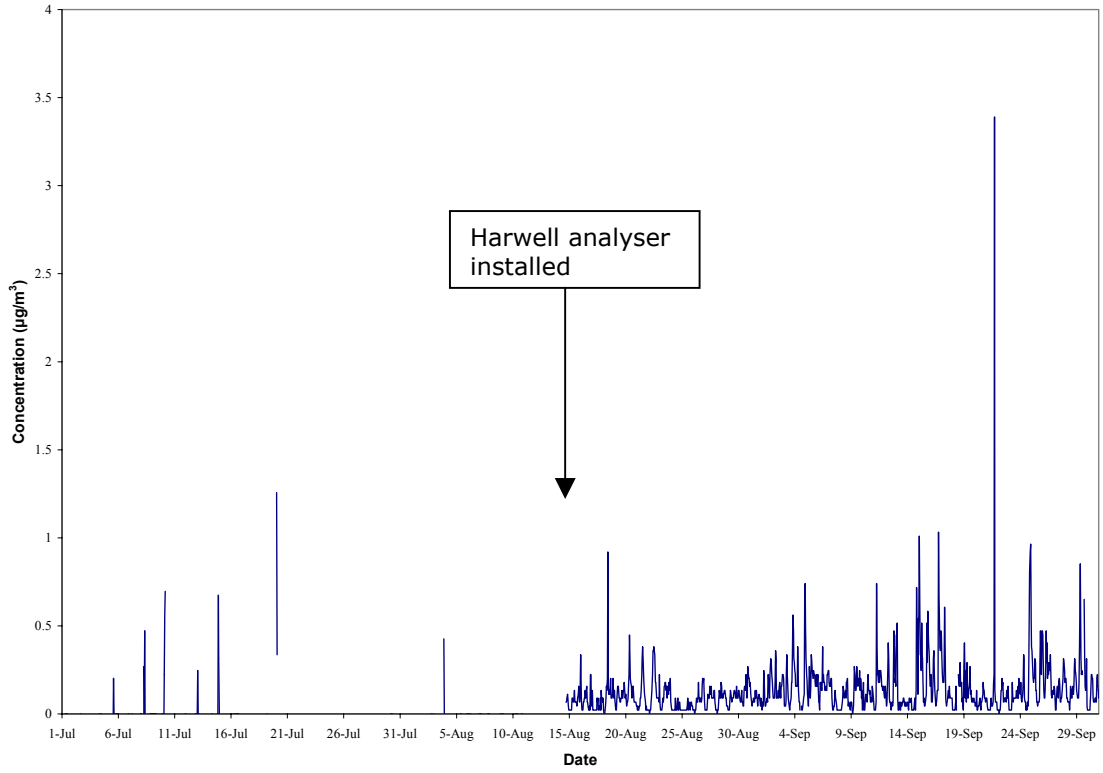

Figure 2. Time series plot of the ratified 1,3-butadiene data from the Cardiff site of the UK Hydrocarbon Network, for the period; 1 July 2003 to 30 September 2003

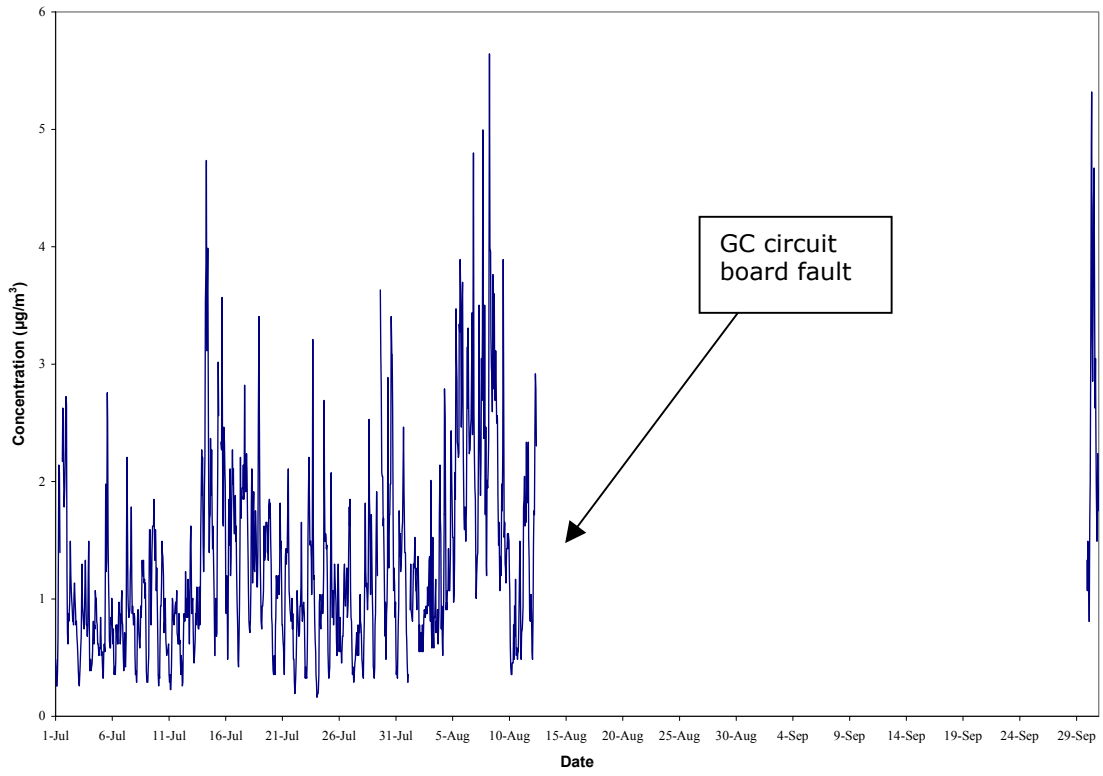

Figure 3. Time series plots for the ratified benzene data from the Glasgow site of the UK Hydrocarbon Network, for the period; 1 July 2003 to 30 September 2003

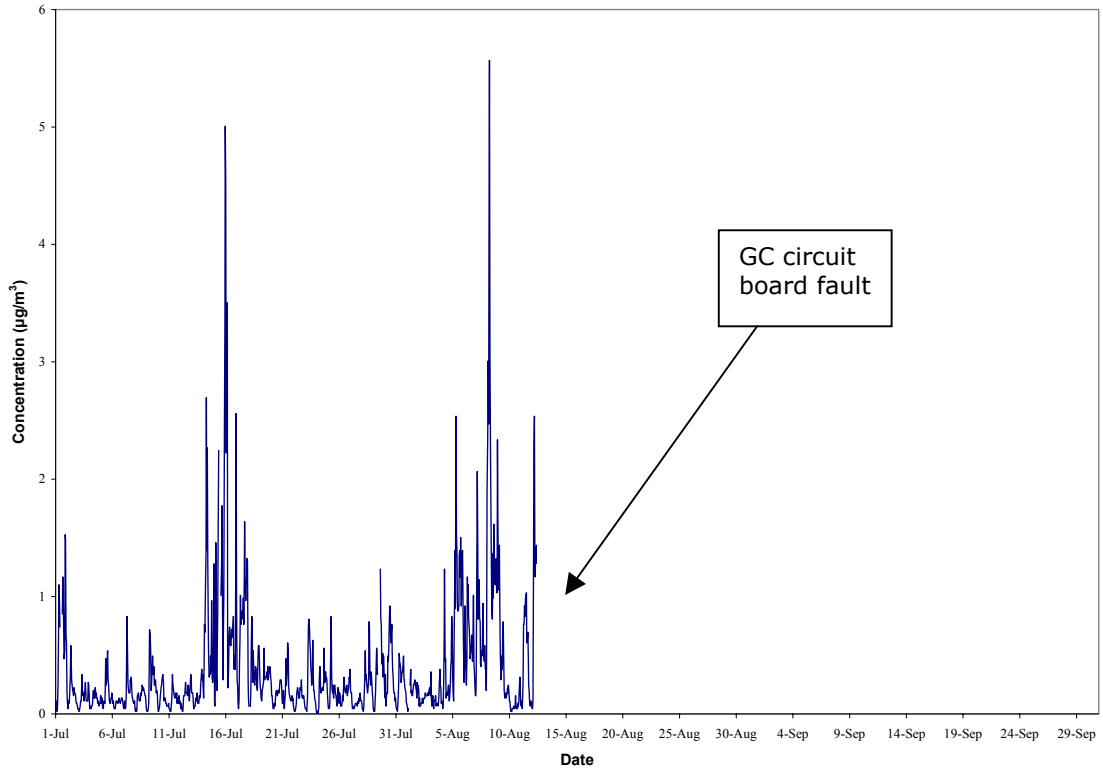

Figure 4. Time series plots for the ratified 1,3-butadiene data from the Glasgow site of the UK Hydrocarbon Network, for the period; 1 July 2003 to 30 September 2003

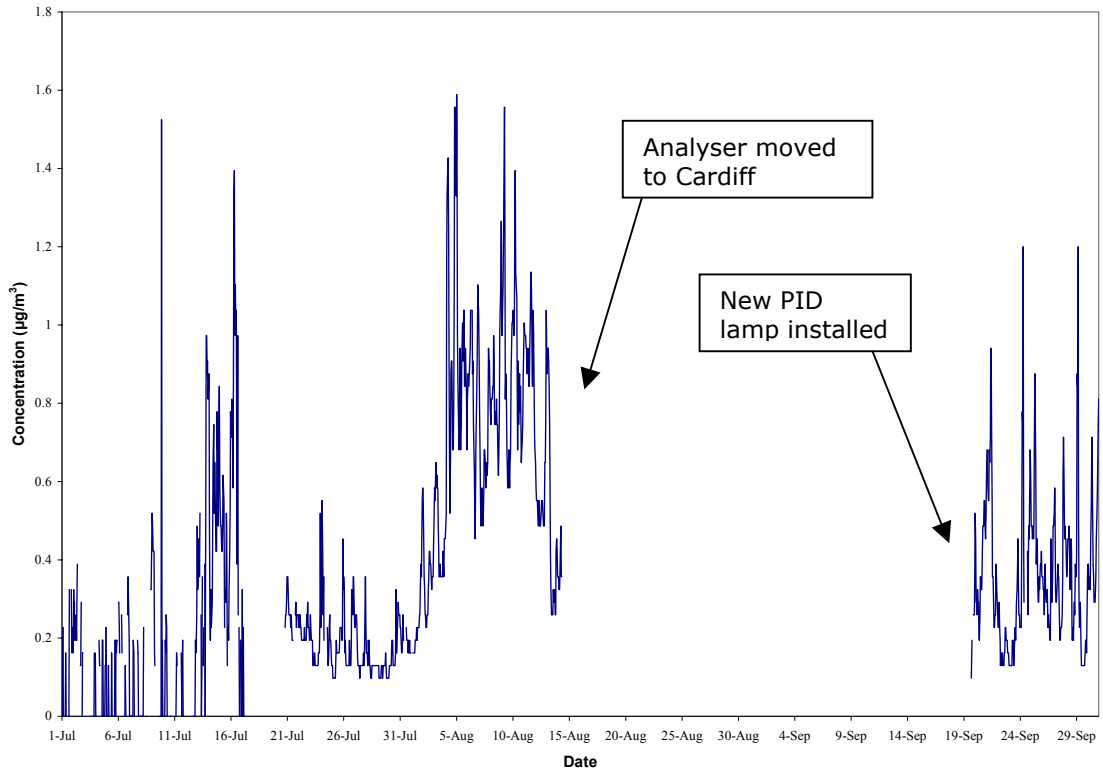

Figure 5. Time series plots for the ratified benzene data from the Harwell site of the UK Hydrocarbon Network, for the period; 1 July 2003 to 30 September 2003

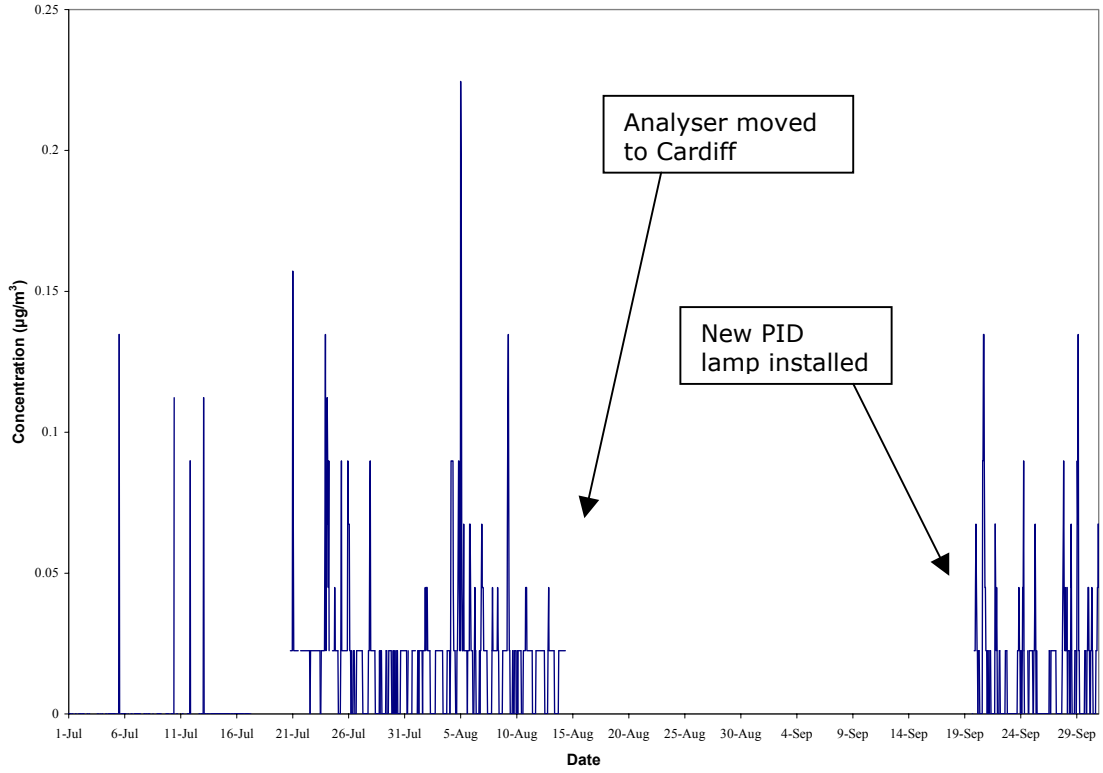

Figure 6. Time series plots for the ratified 1,3-butadiene data from the Harwell site of The UK Hydrocarbon Network, for the period; 1 July 2003 to 30 September 2003

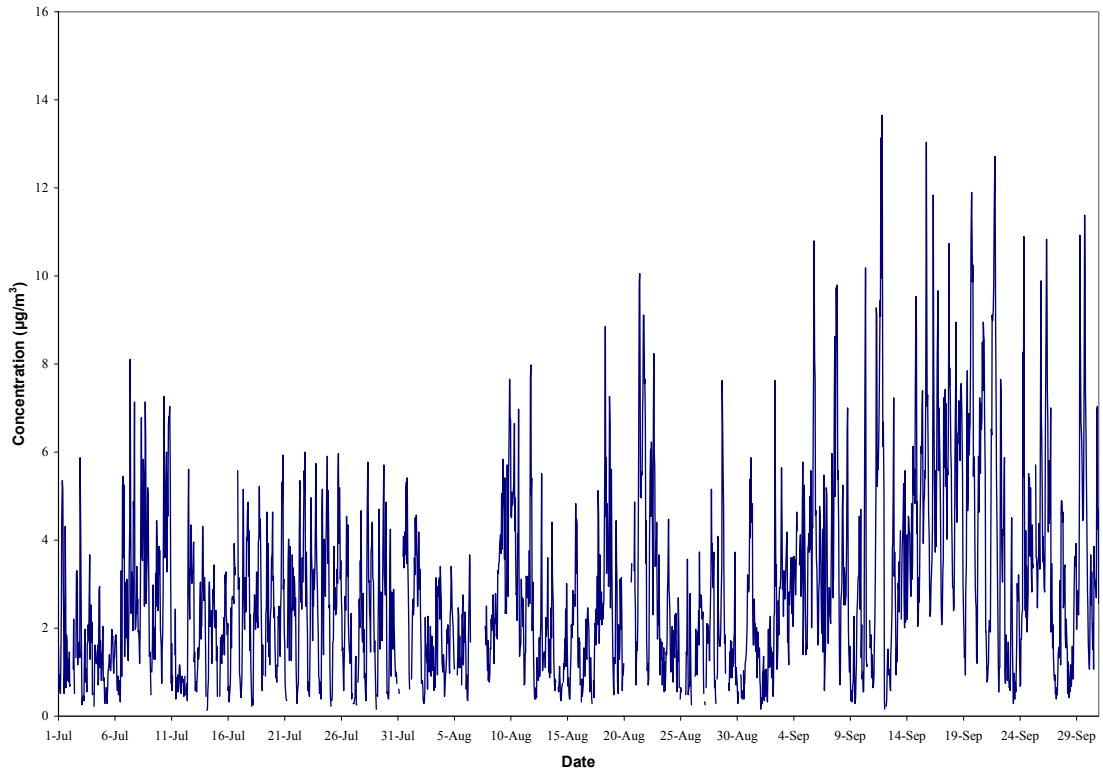

Figure 7. Time series plots for the ratified benzene data from the Marylebone Road site affiliated to the UK Hydrocarbon Network, for the period;1 July 2003 to 30 September 2003

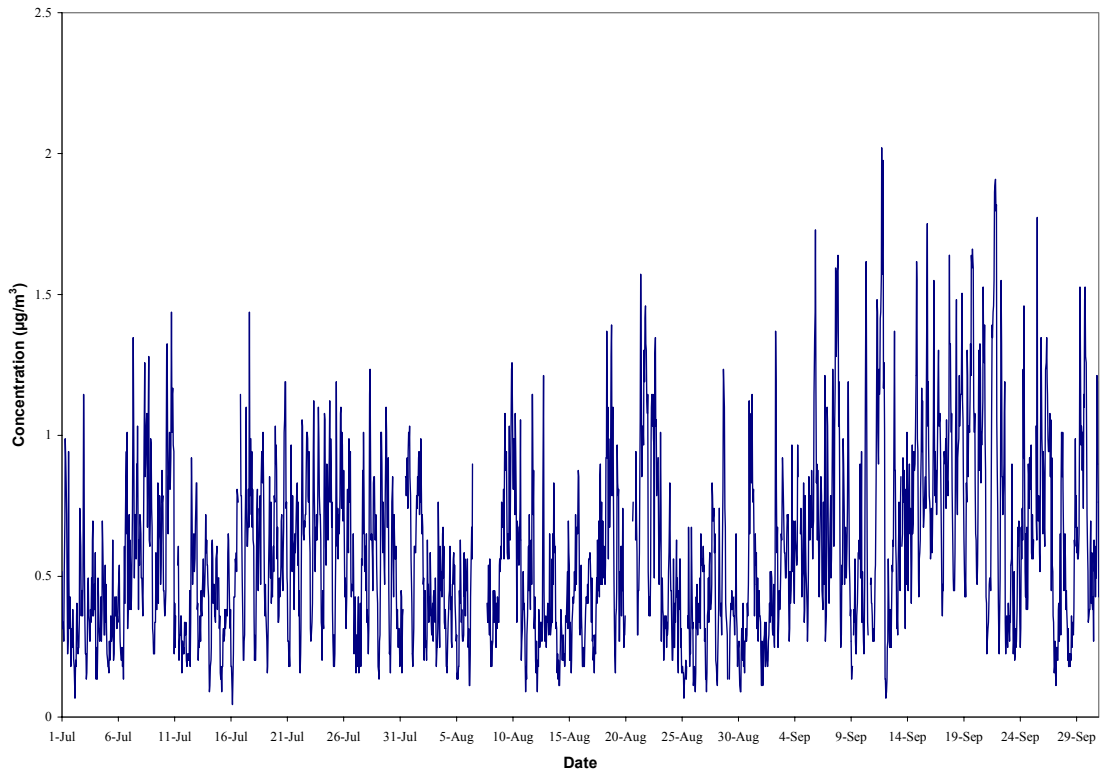

Figure 8. Time series plots for the ratified 1,3-butadiene data from the Marylebone Road site affiliated to the UK Hydrocarbon Network, for the period; 1 July 2003 to 30 September 2003