REPORT

Ratification of data produced by the UK Ambient Hydrocarbon Automatic Air Quality Network, 1 April 2003 to 30 June 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/1571 Issue 1 September 2003

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 Customer
 Department for Environment, Food and Rural Affairs, the Scottish

Executive, the Welsh Assembly Government and the Department of the

Environment in Northern Ireland

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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 April 2003 to 30 June 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 $\pm 10\%$ for values above 0.5 $\mu g/m^3$ and $\pm 0.05~\mu g/m^3$ 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 \pm 25% above 0.5 μ g/m³ and \pm 0.1 μ g/m³ below 0.5 μ g/m³.

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 April

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 03/04/03 hours 10 to 11.
- Air conditioning failure 04/04/03 hour 13 to 30/04/03 hour 24.

3.1.1.3 Missing Data - Specific hydrocarbons

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

3.1.2 May

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

- Air conditioning failure 01/05/03 hours 01 to 10.
- Calibration 02/05/03 hours 10 to 11.
- Calibration 14/05/03 hours 09 to 11.
- Carrier gas supply problem 30/05/03 hour 09 to 31/05/03 hour 24.

3.1.2.3 Missing Data - Specific hydrocarbons

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

3.1.3 June

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

- Carrier gas supply problem 01/06/03 hour 01 to 05/06/03 hour 05.
- Calibration 05/06/03 hours 06 to 07.
- Calibration 12/06/03 hours 10 to 11.
- Calibration 26/06/03 hours 13 to 14.

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 April

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 08/04/03 hours 11 to 14.
- Calibration 22/04/03 hours 11 to 14.

3.2.1.3 Missing Data - Specific hydrocarbons

None, except where the integration was unreliable due to peak truncation.

3.2.2 May

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

- Calibration 06/05/03 hours 10 to 14.
- Calibration 20/05/03 hours 11 to 13.
- PC/GC communication problem 27/05/03 hours 04 to 06.

3.2.2.3 Missing Data - Specific hydrocarbons

None, except where the integration was unreliable due to peak truncation.

3.2.3 June

3.2.3.1 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.

3.2.3.2 Missing Data - All hydrocarbons

- Calibration 03/06/03 hours 11 to 15.
- Calibration 19/06/03 hours 08 to 11.

3.2.3.3 Missing Data - Specific hydrocarbons

None, except where the integration was unreliable due to peak truncation.

3.3 HARWELL

3.3.1 April

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 09/04/03 hours 09 to 11.
- Calibration 24/04/03 hours 09 to 17.
- PC/GC communication problem 25/05/03 hours 14 to 15.

3.3.1.3 Missing Data - Specific hydrocarbons

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

3.3.2 May

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

- Calibration 08/05/03 hours 09 to 11.
- Calibration 22/05/03 hours 09 to 10.

3.3.2.3 Missing Data - Specific hydrocarbons

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

3.3.3 June

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 05/06/03 hours 09 to 11.
- Calibration 19/06/03 hours 12 to 15.
- CMCU service visit 24/06/03 hours 16 to 17.

3.3.3.3 Missing Data - Specific hydrocarbons

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

3.4 MARYLEBONE ROAD

3.4.1 April

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 02/04/03 hours 14 to 17.
- Calibration 17/04/03 hours 05 to 08.
- Calibration 23/04/03 hours 13 to 16.

3.4.1.3 Missing Data - Specific hydrocarbons

None.

3.4.2 May

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

- Calibration 08/05/03 hours 04 to 07.
- Calibration 14/05/03 hours 16 to 19.
- ESU service visit 15/05/03 hours 06 to 15.
- Calibration 15/05/03 hours 17 to 20.
- Power supply fault 16/05/03 hour 09 to 19/05/03 hour 09.
- Calibration 19/05/03 hours 12 to 15.
- Hydrogen generator supply fault 31/05/03 hours 01 to 24.

3.4.2.3 Missing Data - Specific hydrocarbons

None.

3.4.3 June

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

- Hydrogen generator supply fault 01/06/03 hour 01 to 02/06/03 hour 15.
- Calibration 03/06/03 hours 04 to 07.
- Hydrogen generator supply fault 08/06/03 hour 13 to 09/06/03 hour 16.
- Calibration 11/06/03 hours 12 to 15.
- Hydrogen generator supply fault 16/06/03 hours 12 to 16.
- Hydrogen generator supply fault 17/06/03 hour 04 to 18/06/03 hour 13.
- Hydrogen generator supply fault 24/06/03 hours 12 to 14.
- Hydrogen generator supply fault 25/06/03 hour 05 to 26/06/03 hour 10.
- Calibration 26/06/03 hours 13 to 16.

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 April 2003 to 30 June 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 46.57% and for 1,3-butadiene was 47.30.%. On the 4^{th} April a fault developed with the air conditioning unit at the site. It was decided to switch off the VOC71M analyser to avoid possible overheating. The air conditioning unit was repaired on the 1^{st} May and the analyser was then switched back on. This accounted for a 30% loss to the total data capture for this quarter.

On the 30^{th} May a problem occurred with the nitrogen carrier gas supply. The problem was fixed on a CMCU visit on the 5^{th} June. This accounted for a 10% loss to the total data capture for this quarter.

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 98.72% and for 1,3-butadiene was 98.72%.

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 overstimation 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. 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 92.40% and for 1,3-butadiene was 92.90%. There have been no 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 86.54% and for 1,3-butadiene was 86.86%.

During May a fault developed with part of the system that supplies hydrogen to the GC FID. Approximately 160 hours of data (7%) was lost before the system was repaired. There have been no other 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 April to June 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 30 June 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 and second 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. This is probably due to seasonal variation.

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

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

^{\$} 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	2001	2002	Quarter 1	Quarter 2
	Annual Mean	Annual Mean	Annual Mean	2003	2003
				Mean	Mean
Cardiff Centre	\$\$	\$\$	0.15\$	0.16	0.07
Glasgow	\$\$\$	\$\$\$	0.36\$	0.38	0.34
Harwell	0.09	0.11	0.04	0.04	0.02
Marylebone Road	1.63	1.12	0.95	0.70	0.61

^{\$} 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.

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Appendix 1 Summary Statistical Information

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- 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 April 2003 to 30 June 2003
- 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 April 2003 to 30 June 2003

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 April 2003 to 30 June 2003

Compound	%Data	Maximum	Mean	Minimum
	capture	concentration	concentration	concentration
		$(\mu g/m^3)$	(μg/m³)	(μg/m³)
1,3-Butadiene	47.30	5.50	0.07	0.00
Benzene	46.57	4.09	0.58	0.00
Toluene	63.10	12.13	2.45	0.38
Ethylbenzene	19.96	4.76	0.57	0.13
(m+p)-Xylene *	53.85	20.67	1.32	0.09
o-Xylene	27.84	11.90	1.01	0.13

^{* (}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 April 2003 to 30 June 2003

Compound	%data	Maximum	Mean	Minimum
	capture	concentration	concentration	concentration
		$(\mu g/m^3)$	$(\mu g/m^3)$	$(\mu g/m^3)$
1,3-Butadiene	98.72	12.66	0.34	0.00
Benzene	98.72	5.84	1.36	0.16
Toluene	98.72	24.33	5.01	0.31
Ethylbenzene	98.53	16.97	0.84	0.04
(m+p)-Xylene *	98.35	34.73	3.09	0.18
o-Xylene	98.35	31.33	1.50	0.18

^{* (}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 April 2003 to 30 June 2003

Compound	%data	Maximum	Mean	Minimum
	capture	concentration	concentration	concentration
		(μg/m³)	(μg/m³)	$(\mu g/m^3)$
1,3-Butadiene	92.90	0.43	0.02	0.00
Benzene	92.40	1.82	0.36	0.00
Toluene	95.88	10.98	1.11	0.08
Ethylbenzene	50.09	1.50	0.26	0.09
(m+p)-Xylene *	86.17	4.67	0.62	0.09
o-Xylene	57.33	1.59	0.31	0.09

^{* (}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 April 2003 to 30 June 2003

Compound	%data	Maximum	Mean	Minimum
-	capture	concentration	concentration	concentration
		(μg/m³)	(μg/m³)	$(\mu g/m^3)$
Ethane	86.90	44.17	8.57	2.10
Ethene	86.90	25.98	5.88	0.42
Propane	86.90	54.77	4.98	0.90
Propene	86.90	12.40	2.95	0.23
Ethyne	86.90	22.88	4.81	0.40
2-Methylpropane	86.90	39.57	4.77	0.68
n-Butane	86.86	55.29	8.44	1.13
trans-2-Butene	86.90	2.37	0.65	0.19
1-Butene	86.90	2.79	0.68	0.07
cis-2-Butene	86.86	2.07	0.47	0.07
2-Methylbutane	86.90	77.77	12.48	0.87
n-Pentane	86.90	19.88	3.11	0.36
1,3-Butadiene	86.86	1.71	0.61	0.07
trans-2-Pentene	86.86	6.96	0.70	0.03
cis-2-Pentene	86.31	3.90	0.41	0.03
2-Methylpentane	86.90	30.36	3.93	0.21
3-Methylpentane	86.90	19.77	2.40	0.14
Isoprene	86.63	1.95	0.37	0.03
n-Hexane	86.81	12.23	1.36	0.07
n-Heptane	86.63	10.19	0.71	0.00
Benzene	86.54	15.05	3.08	0.13
Toluene	86.86	98.92	12.97	0.46
Ethylbenzene	86.54	16.09	2.34	0.09
(m+p)-Xylene *	79.49	63.02	8.73	0.62
o-Xylene	86.86	19.48	2.95	0.09
1,3,5-Trimethylbenzene	84.98	7.58	1.05	0.05
1,2,4-Trimethylbenzene	86.86	20.06	3.09	0.15

^{* (}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 2Time 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 April 2003 to 30 June 2003
Figure 2.	Time series plot of the ratified 1,3-butadiene data from the Cardiff

- 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 April 2003 to 30 June 2003
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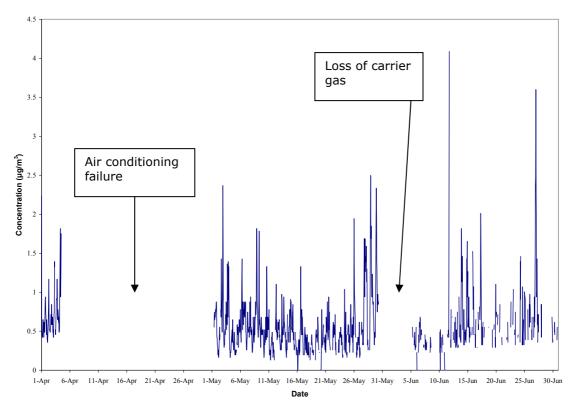


Figure 1. Time series plot of the ratified benzene data from the Cardiff site of the UK Hydrocarbon Network, for the period; 1 April 2003 to 30 June 2003

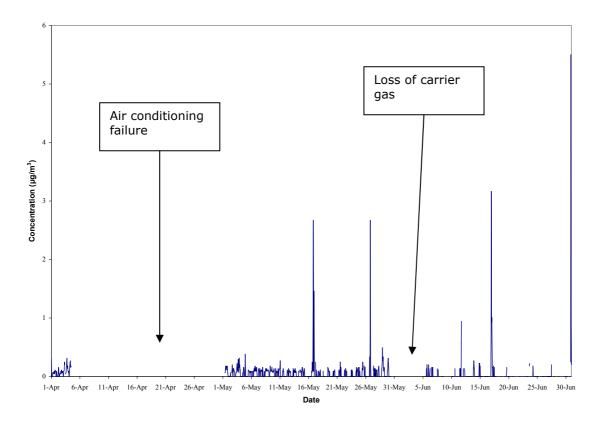


Figure 2. Time series plot of the ratified 1,3-butadiene data from the Cardiff site of the UK Hydrocarbon Network, for the period; 1 April 2003 to 30 June 2003

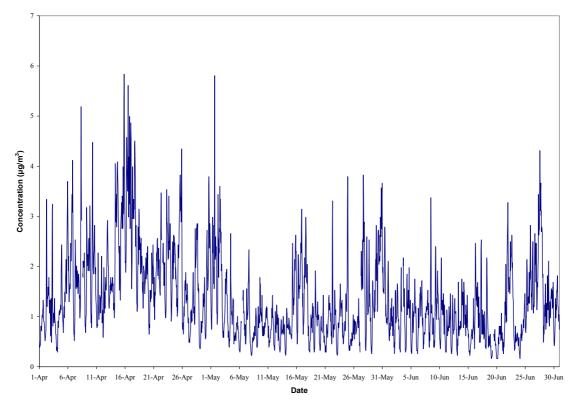


Figure 3. Time series plots for the ratified benzene data from the Glasgow site of the UK Hydrocarbon Network, for the period; 1 April 2003 to 30 June 2003

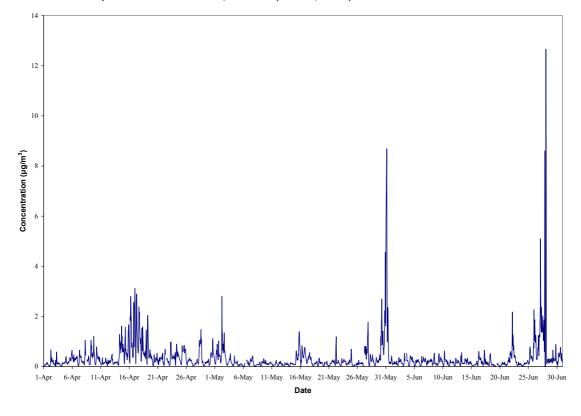


Figure 4. Time series plots for the ratified 1,3-butadiene data from the Glasgow site of the UK Hydrocarbon Network, for the period; 1 April 2003 to 30 June 2003

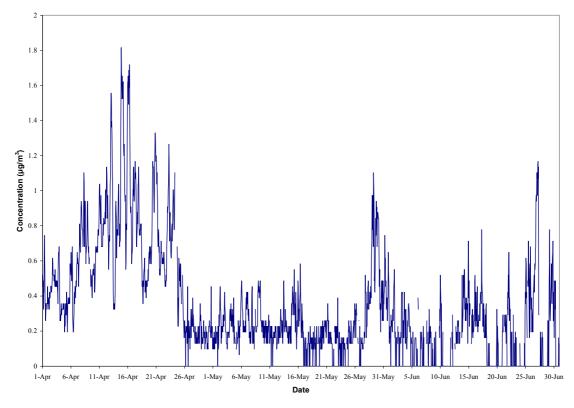


Figure 5. Time series plots for the ratified benzene data from the Harwell site of the UK Hydrocarbon Network, for the period; 1 April 2003 to 30 June 2003

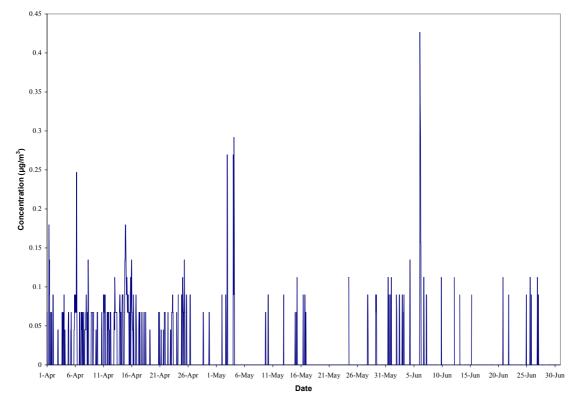


Figure 6. Time series plots for the ratified 1,3-butadiene data from the Harwell site of The UK Hydrocarbon Network, for the period; 1 April 2003 to 30 June 2003

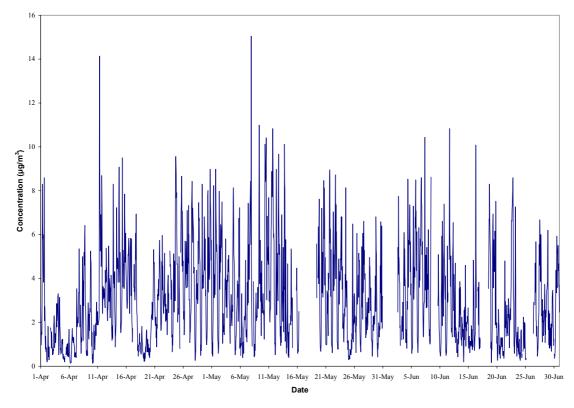


Figure 7. Time series plots for the ratified benzene data from the Marylebone Road site affiliated to the UK Hydrocarbon Network, for the period;1 April 2003 to 30 June 2003

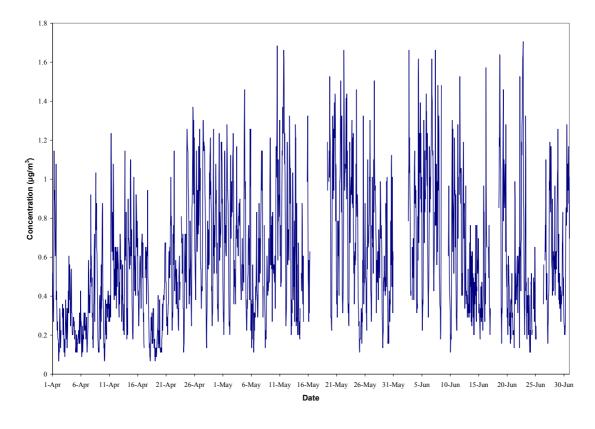


Figure 8. Time series plots for the ratified 1,3-butadiene data from the Marylebone Road site affiliated to the UK Hydrocarbon Network, for the period; 1 April 2003 to 30 June 2003