Ratification of data produced by the UK Ambient Hydrocarbon Automatic Air Quality Network, 1 January 2002 to 31 March 2002

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1 Introduction

1.1 DATA RATIFICATION AND STATISTICS

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 January 2002 to 31 March 2002. The ratified data have been made available on the World Wide Web at http://www.airquality.co.uk/archive/data_and_statistics.php?f_group_id=7&action=step1&go=Step+1

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 previous reports have used parts per billion (ppb).

1.2 MONITORING INSTRUMENTATION AT THE CARDIFF, EDINBURGH AND HARWELL SITES

The Environnement VOC71M replaced the Chrompack VOCAIR at the Cardiff, Edinburgh and Harwell sites for the period covered by this report. The number of reported hydrocarbons was reduced from 26 to 6. The reported hydrocarbons being 1,3-butadiene, benzene, toluene, ethylbenzene, (m+p)-xylene and o-xylene. The instrument at the Marylebone Road site, the Perkin Elmer ATD400, has remained unchanged.

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 January

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

Carrier gas supply problem 07/02/02 hour 16 to 08/02/02 hour 16.

3.1.1.3 Missing Data – Specific hydrocarbons

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

3.1.2 February

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 07/02/02 hours 12 to 15.
Calibration 20/02/02 hours 13 to 15.

3.1.2.3 Missing Data - Specific hydrocarbons

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

3.1.3 March

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 08/03/02 hours 10 to 12.
Calibration 21/03/02 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 EDINBURGH

3.2.1 January

3.2.1.1 Data Quality Codes

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

3.2.1.2 Missing Data - All hydrocarbons

PC/GC communication problem 04/01/02 hours 06 to 23.
Calibration 17/01/02 hours 15 to 19.
Calibration 17/01/02 hours 12 to 17.

3.2.1.3 Missing Data - Specific hydrocarbons

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

3.2.2 February

3.2.2.1 Data Quality Codes

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

3.2.2.2 Missing Data - All hydrocarbons

Calibration 12/02/02 hours 12 to 14.
Calibration 28/02/02 hours 12 to 15.

3.2.2.3 Missing Data - Specific hydrocarbons

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

3.2.3 March

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

Calibration 12/03/02 hours 12 to 16.
Calibration 26/03/02 hours 12 to 17.

3.2.3.3 Missing Data - Specific hydrocarbons

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

3.3 HARWELL

3.3.1 January

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

GC commissioning tests 01/01/02 hour 01 to 03/01/02 hour 18.
Calibration 04/01/02 hours 13 to 16.
Calibration 10/01/02 hours 09 to 12.
Calibration 31/01/02 hours 12 to 14.

3.3.1.3 Missing Data - Specific hydrocarbons

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

3.3.2 February

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 14/02/02 hours 10 to 12.
Zero and Calibration tests 18/02/02 hour 15 to 19/02/02 hour 08.
Calibration 28/02/02 hours 12 to 13.

3.3.2.3 Missing Data - Specific hydrocarbons

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

3.3.3 March

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

PC/GC communication problem 04/03/02 hour 13 to 06/03/02 hour 13.
Zero tests 12/03/02 hour 20 to 13/03/02 hour 07.
Calibration 14/03/02 hours 13 to 15.
Calibration 26/03/02 hours 13 to 15.

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 January

3.4.1.1 Data Quality Codes

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

3.4.1.2 Missing Data - All hydrocarbons

Calibration 03/01/02 hours 06 to 09.
Calibration 09/01/02 hours 15 to 18.
PC problem / no data files 19/01/02 hours 09 to 10.
Calibration 24/01/02 hours 06 to 09.
Calibration 30/01/02 hours 18 to 21.

3.4.1.3 Missing Data - Specific hydrocarbons

None.

3.4.2 February

3.4.2.1 Data Quality Codes

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

3.4.2.2 Missing Data - All hydrocarbons

Calibration tests 11/02/02 hour 13 to 12/02/02 hour 16.
Calibration 12/02/02 hours 17 to 20.
Calibration tests 15/02/02 hours 12 to 17.
Calibration tests 20/02/02 hours 12 to 20.
Calibration 20/02/02 hours 21 to 24.
Calibration 27/02/02 hours 15 to 18.

3.4.2.3 Missing Data - Specific hydrocarbons

None.

3.4.3 March

3.4.3.1 Data Quality Codes

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

3.4.3.2 Missing Data - All hydrocarbons

Calibration 13/03/02 hours 14 to 17.
Calibration 27/03/02 hours 15 to 18.

3.4.3.3 Missing Data - Specific hydrocarbons

None.

4 Discussion

4.1 REPLACEMENT OF THE CHROMPACK VOCAIR WITH THE ENVIRONNEMENT VOC71M ANALYSER

For the Cardiff, Edinburgh and Harwell sites this period has seen the introduction of a new analyser. The Chrompack VOCAIR was decommissioned and replaced with the Environnement VOC71M. There was no change at Marylebone Road, where the Perkin Elmer ATD400 continued to operate.

The VOC71M is a gas chromatograph (GC) fitted with a Photo Ionisation Detector (PID). It has the advantage of being cost effective to buy and operate, only requiring mains power and clean nitrogen for the carrier gas. It measures fewer compounds than the VOCAIR but includes 1,3-Butadiene and Benzene, the two VOC compounds that have air quality objectives in the UK. It also measures Toluene, Ethylbenzene, (m+p)-Xylene and o-Xylene.

The data output files are in an industry standard format. The data handling processes have been integrated into the ratification process, using Matchfinder and other software previously developed for the Hydrocarbon network. Analysis of the calibration data has shown that the sensitivity of the PID detector drops rapidly over the first few weeks of operation, but then settles to a more stable level. The software used to calculate the sensitivity has been modified to generate accurate sensitivities for the first few weeks when operating with a new detector.

Initially the analysers were set up to collect 15-minute samples but it was found that the peak areas, especially for 1,3-Butadiene, were close to the limit of detection. The Harwell analyser was set up to collect 30-minute samples and thus reduced the lower detection limits for each monitored hydrocarbon. The minimum peak area filter in the integration software was reduced with no significant increase in noise to improve the data capture considerably. Prior to the change to the minimum peak area filter, there were a number of occasions when the benzene peak area was reported but not the 1,3-butadiene peak area. As a result the data capture of 1,3-butadiene was less than that of benzene. After the reduction of the peak area filter the data capture of the 1,3-butadiene approached that of the benzene.

The adjustments to the sampling time and the minimum peak area filter were made to the Edinburgh analyser on the 17th January and to the Cardiff analyser on the 7th February. The data capture for all reported compounds improved at each site after the changes were undertaken.

4.2 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 January 2002 to 31 March 2002. 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.

4.2.1 Cardiff

For the Cardiff site the data capture for Benzene was 89.2% and for 1,3-Butadiene was 78.47%. There were no significant problems for the period covered by this report. Data capture is likely to be much higher due to the change of minimum area filter.

4.2.2 Edinburgh

For the Edinburgh site the data capture for Benzene was 97.5% and for 1,3-Butadiene was 86.1%. There were no significant problems for the period covered by this report.

4.2.3 Harwell

For the Harwell site the data capture for Benzene was 91.99% and for 1,3-Butadiene was 86.7%. There were no significant problems for the period covered by this report.

4.2.4 Marylebone Road

For the Marylebone Road site the data capture values for Benzene and 1,3-Butadiene were greater than 95%.

During the ratification of data collected during quarter 4 of 2001, an apparent increase of 70% in instrument sensitivity was observed. This increase coincided with a change of the cylinder used for the routine calibrations. A number of calibration tests were undertaken and it was concluded that the regulator outlet pressure had been set too high. This caused a loss of control over the calibration sample flow. When adjusted to the correct pressure the calculated sensitivity was in agreement with those produced by the old cylinder.

The instrument response to the calibration gas over the period of excessive pressure was stable indicating that the instrument sensitivity was stable. The instrument response to the calibration gas was consistent for both old and new cylinders when the calibration gas was supplied at the correct pressure. It was therefore, concluded that the sensitivity had remained stable over the period of excessive calibration gas pressure. This is consistent with the observation that the response of the FIDs remains relatively unchanged over periods of months.

It has been observed that occasionally the 3-methylpentane peak partially elutes on the 'B' column. This is due to a slow drift of retention times and the Deans Switch split time setting. When this has occurred the data has been removed and because of increased uncertainty the remaining data have been assigned data quality code E. No further problems have occurred.

4.3 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, 4 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, Edinburgh and Harwell the measured concentrations of hydrocarbons were low for most of the period covered by this report with no episodes of significantly elevated concentrations. 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. The seasonal trend may well be less pronounced for January to March 2002 due to the apparent lack of episodes of higher concentrations.

Marylebone Road tends to exhibits higher levels with less seasonal variation than is apparent at the other sites. The measured concentrations and trends are typical of a roadside site 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 Marylebone Road for January to March 2002 exhibited no significant episodes of elevated concentrations.

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 ratified data from the Cardiff site of the UK Hydrocarbon Network, for the period 1 January 2002 to 31 March 2002

Compound	%data capture	Maximum concentration ($\mu g/m^3$)	Mean concentration ($\mu g/m^3$)	Minimum concentration ($\mu g/m^3$)
1,3-Butadiene	78.47	4.47	0.09	0.00
Benzene	89.26	10.25	1.01	0.00
Toluene	93.56	43.49	3.75	0.11
Ethylbenzene	69.68	4.72	0.40	0.04
(m+p)-Xylene *	91.44	19.13	1.63	0.00
o-Xylene	79.17	8.55	0.79	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 Edinburgh site of the UK Hydrocarbon Network, for the period 1 January 2002 to 31 March 2002

Compound	%data capture	Maximum concentration ($\mu g/m^3$)	Mean concentration ($\mu g/m^3$)	Minimum concentration ($\mu g/m^3$)
1,3-Butadiene	86.16	1.28	0.07	0.00
Benzene	97.50	19.23	0.88	0.00
Toluene	97.45	48.62	3.29	0.11
Ethylbenzene	72.36	6.21	0.62	0.09
(m+p)-Xylene *	95.42	25.25	2.12	0.09
o-Xylene	75.79	8.29	0.75	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 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 January 2002 to 31 March 2002

Compound	%data capture	Maximum concentration ($\mu g/m^3$)	Mean concentration ($\mu g/m^3$)	Minimum concentration ($\mu g/m^3$)
1,3-Butadiene	86.76	0.56	0.04	0.00
Benzene	91.99	4.09	0.68	0.16
Toluene	90.56	22.57	1.19	0.04
Ethylbenzene	45.69	2.16	0.26	0.04
(m+p)-Xylene *	78.10	7.76	0.62	0.04
o-Xylene	54.81	3.83	0.40	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 4. Percentage data capture, maximum, mean and minimum values of ratified data from the Marylebone Road site for the period; 1 January 2002 to 31 March 2002

Compound	%data capture	Maximum concentration ($\mu g/m^3$)	Mean concentration ($\mu g/m^3$)	Minimum concentration ($\mu g/m^3$)
Ethane	96.20	743.15	14.12	2.98
Ethene	96.20	35.56	9.27	0.48
Propane	96.11	279.90	7.67	1.48
Propene	96.11	17.31	4.78	0.33
Ethyne	96.16	20.84	5.57	0.64
2-Methylpropane	96.20	89.97	10.78	0.94
n-Butane	96.20	120.69	17.36	1.33
trans-2-Butene	96.20	4.28	1.02	0.07
1-Butene	96.20	4.42	1.12	0.09
cis-2-Butene	96.11	3.21	0.79	0.05
2-Methylbutane	96.20	79.33	16.79	0.87
n-Pentane	96.20	31.10	4.34	0.45
1,3-Butadiene	96.20	3.93	1.15	0.07
trans-2-Pentene	96.16	9.26	1.08	0.03
cis-2-Pentene	96.11	5.18	0.55	0.03
2-Methylpentane	96.11	31.18	5.29	0.11
3-Methylpentane	86.57	11.33	2.11	0.07
Isoprene	96.11	6.36	0.59	0.03
n-Hexane	95.74	12.26	2.00	0.04
n-Heptane	95.88	16.88	1.16	0.04
Benzene	96.11	24.00	4.64	0.13
Toluene	96.16	92.64	19.55	0.50
Ethylbenzene	96.11	16.79	3.61	0.13
(m+p)-Xylene *	96.11	58.22	12.82	0.18
o-Xylene	96.11	20.89	4.63	0.18
1,3,5-Trimethylbenzene	96.02	6.59	1.35	0.05
1,2,4-Trimethylbenzene	96.06	19.31	4.49	0.10

* (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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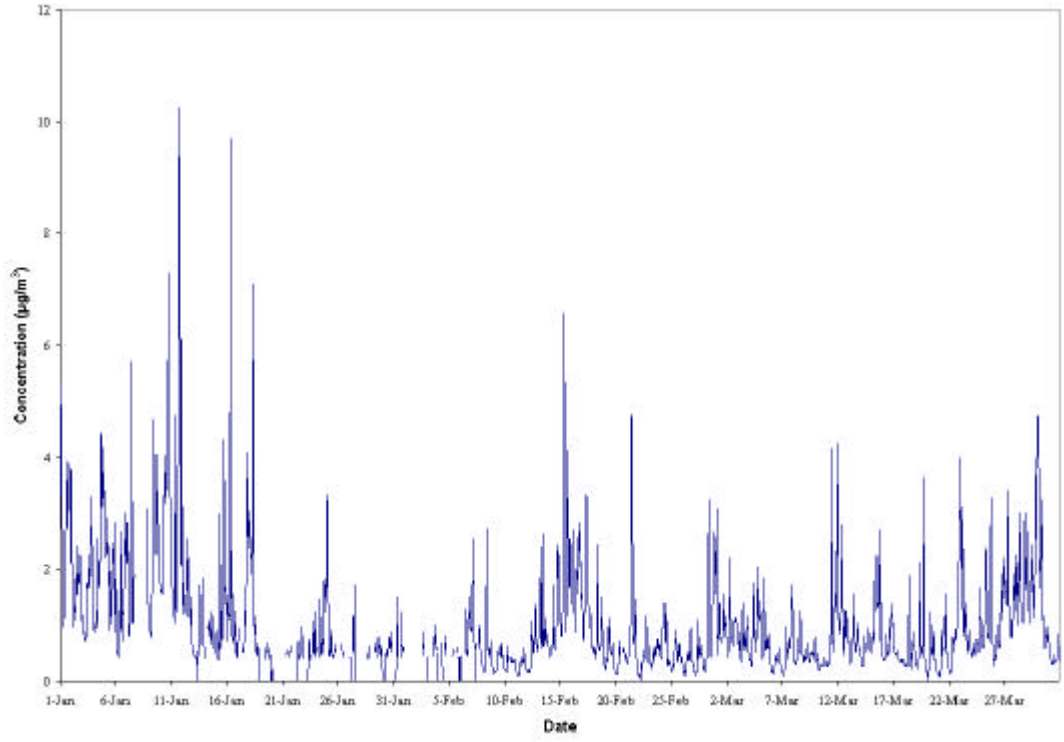

Figure 1. Time series plot of the ratified Benzene data from the Cardiff site of the UK Hydrocarbon Network, for the period; 1 January 2002 to 31 March 2002

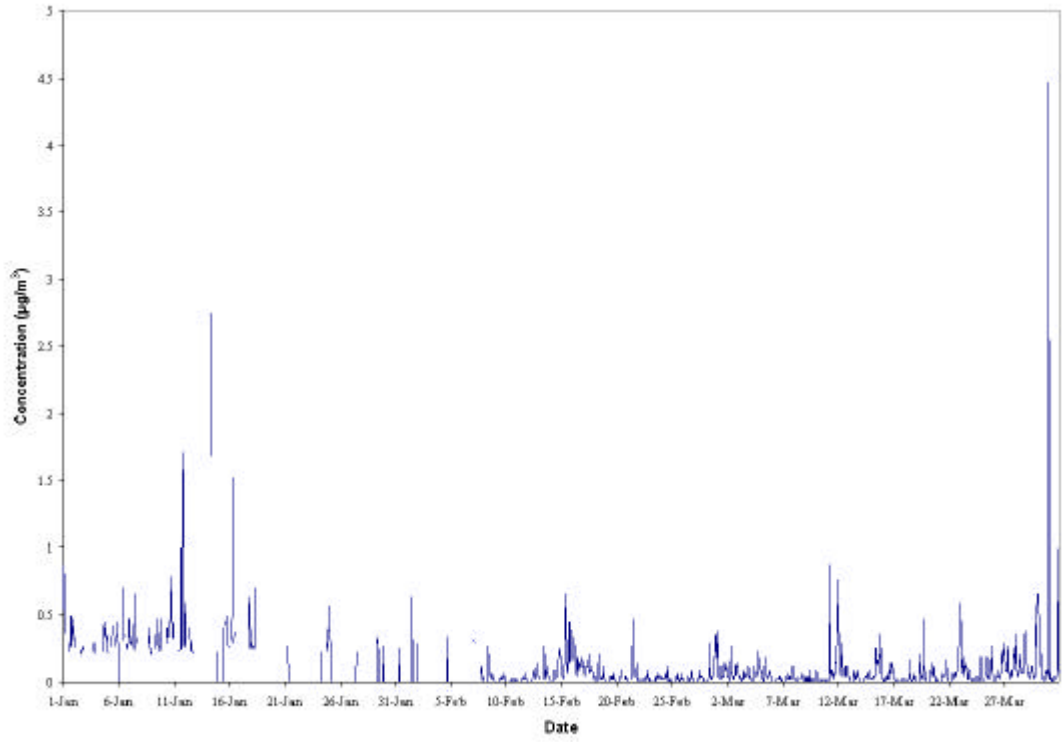

Figure 2. Time series plot of the ratified 1,3-Butadiene data from the Cardiff site of the UK Hydrocarbon Network, for the period; 1 January 2002 to 31 March 2002

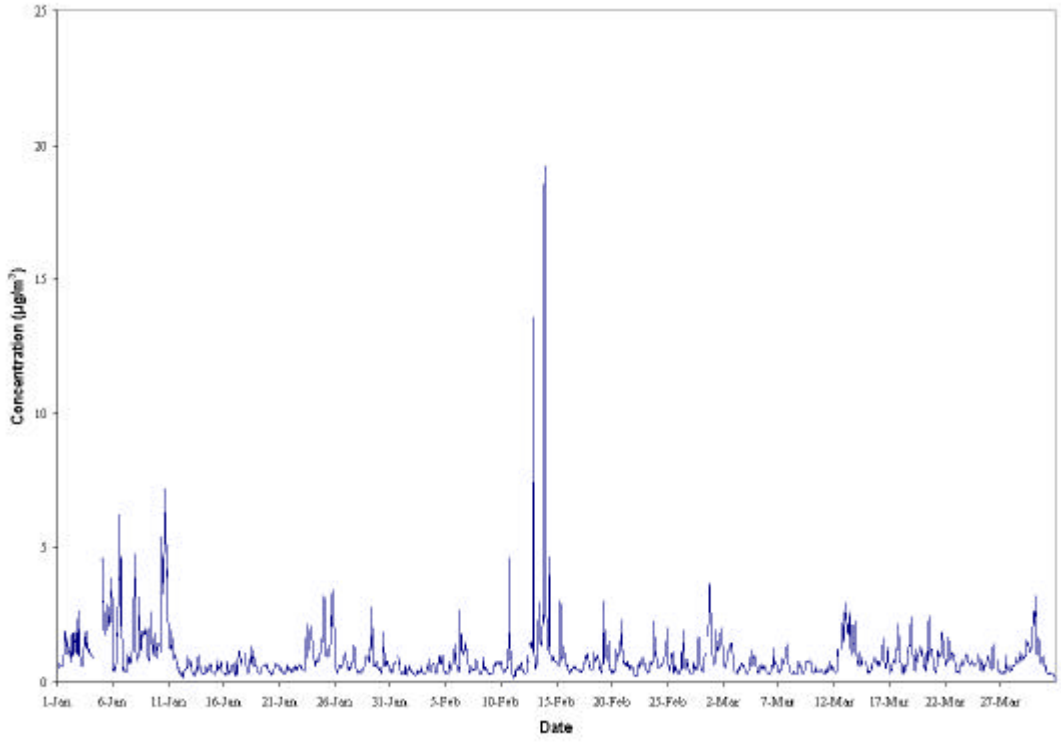

Figure 3. Time series plots for the ratified Benzene data from the Edinburgh site of the UK Hydrocarbon Network, for the period; 1 January 2002 to 31 March 2002

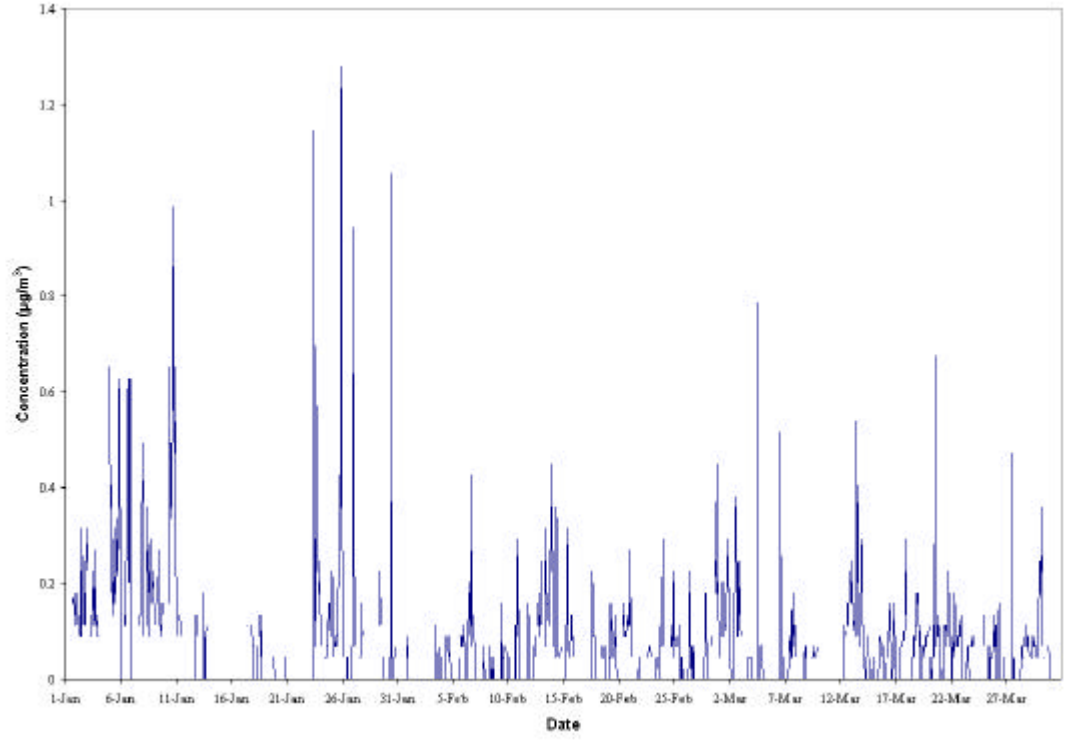

Figure 4. Time series plots for the ratified 1,3-Butadiene data from the Edinburgh site of the UK Hydrocarbon Network, for the period; 1 January 2002 to 31 March 2002

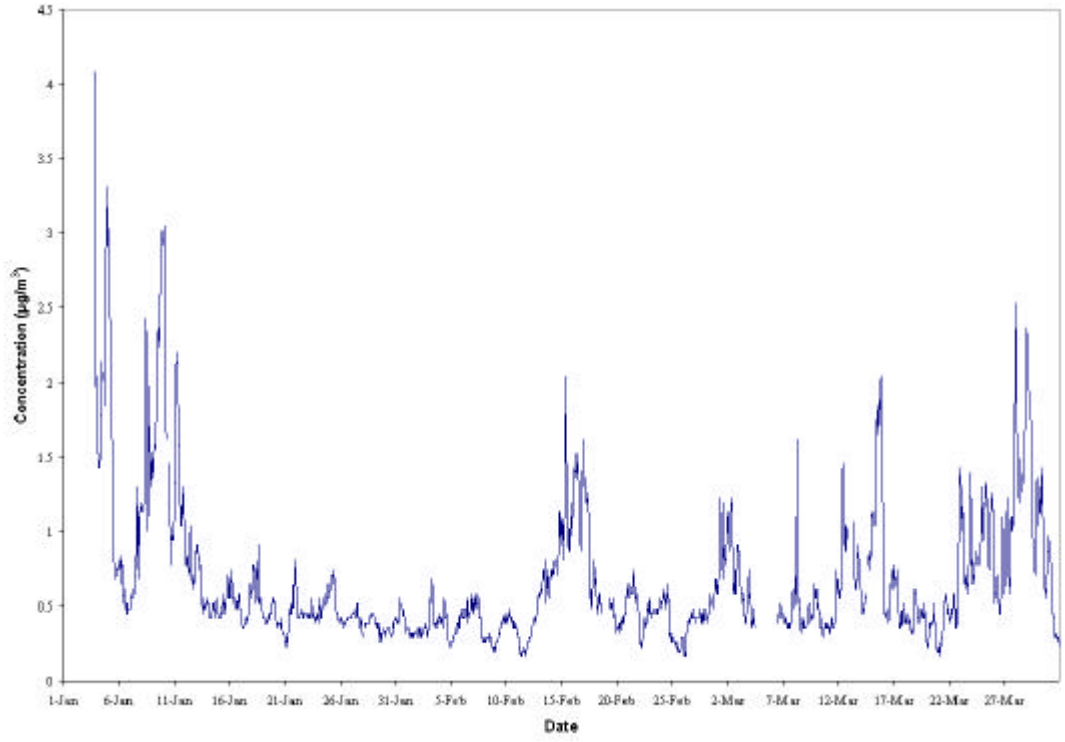

Figure 5. Time series plots for the ratified Benzene data from the Harwell site of the UK Hydrocarbon Network, for the period; 1 January 2002 to 31 March 2002

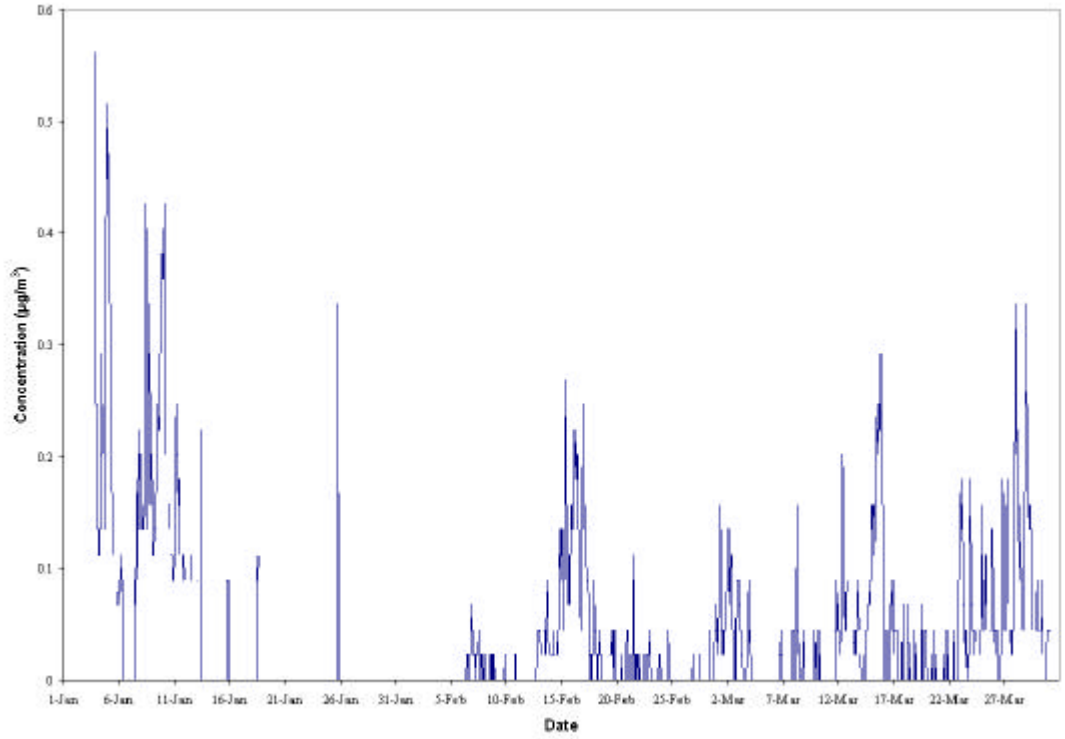

Figure 6. Time series plots for the ratified 1,3-Butadiene data from the Harwell site of The UK Hydrocarbon Network, for the period; 1 January 2002 to 31 March 2002

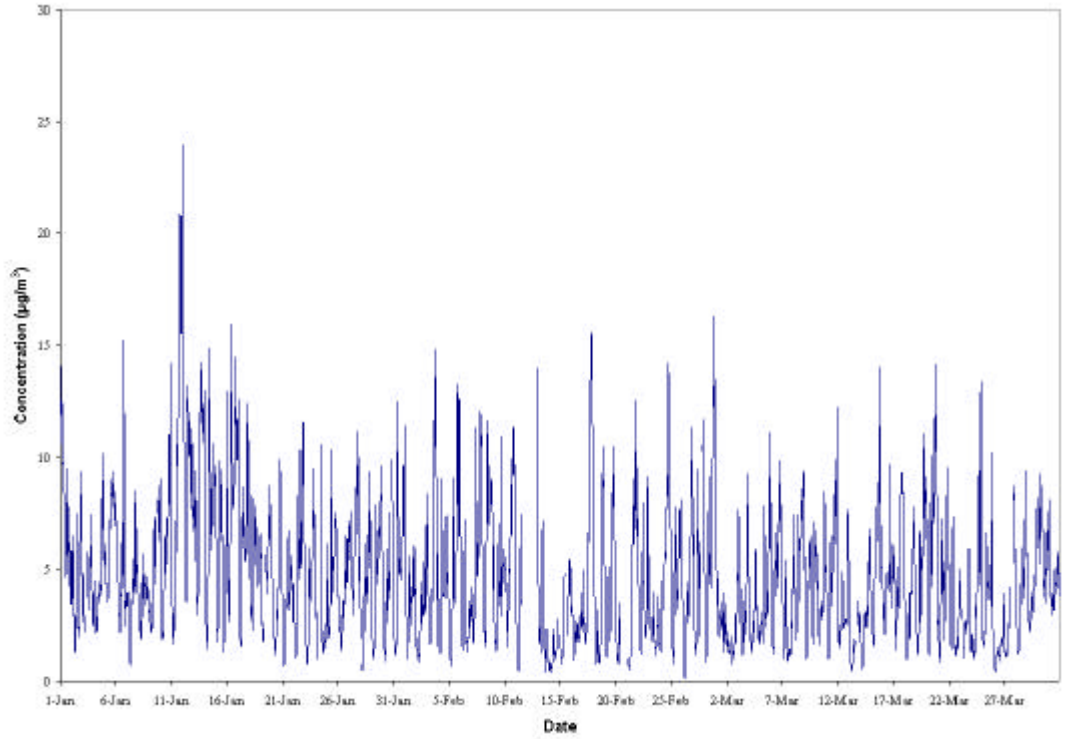

Figure 7. Time series plots for the ratified Benzene data from the Marylebone Road site affiliated to the UK Hydrocarbon Network, for the period;
1 January 2002 to 31 March 2002

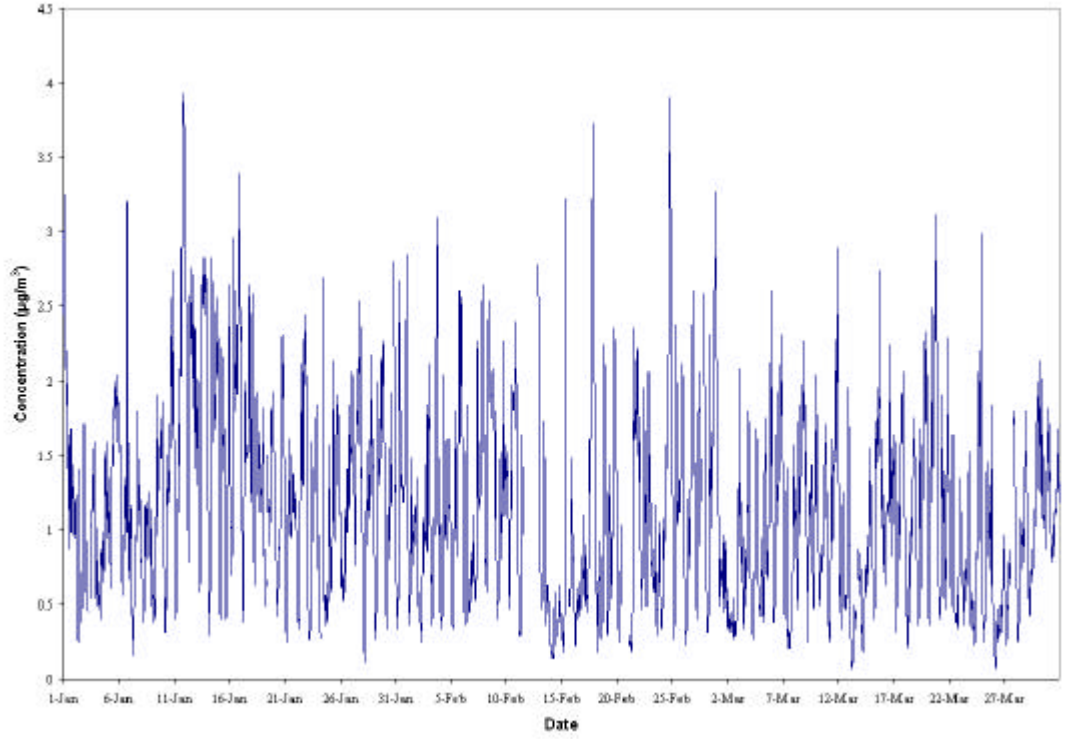

Figure 8. Time series plots for the ratified 1,3-Butadiene data from the Marylebone Road site affiliated to the UK Hydrocarbon Network, for the period;
1 January 2002 to 31 March 2002