

# REPORT

## **Ratification of data produced by the UK Ambient Automatic Hydrocarbon Air Quality Network, 1 January 2004 to 31 March 2004**

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/1866 Issue 1  
December 2004



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<b>Customer</b>	Department for Environment, Food and Rural Affairs, the Scottish Executive, the Welsh Assembly Government and the Department of the Environment in Northern Ireland
<b>Customer reference</b>	RMP 2423
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<b>File reference</b>	ED48202
<b>Report number</b>	AEAT/ENV/R/1866
<b>Report status</b>	Issue 1

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# 1 Introduction

This report contains information on the quality and statistical parameters associated with ratified data from the UK Ambient Automatic Hydrocarbon Air Quality Network (The UK Hydrocarbon Network). The presented information and data cover the period 1 January 2004 to 31 March 2004. The ratified data have been made available on the World Wide Web at [http://www.airquality.co.uk/archive/data\\_and\\_statistics\\_home.php](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 ( $\mu\text{g}/\text{m}^3$ ), 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 ( $\mu\text{g}/\text{m}^3$ ).

## 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  $0.5 \mu\text{g}/\text{m}^3$  and  $\pm 0.05 \mu\text{g}/\text{m}^3$  for values below  $0.5 \mu\text{g}/\text{m}^3$ . 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  $0.5 \mu\text{g}/\text{m}^3$  and  $\pm 0.1 \mu\text{g}/\text{m}^3$  below  $0.5 \mu\text{g}/\text{m}^3$ .

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

#### 3.1.1.2 Missing Data – All hydrocarbons

- Calibration 08/01/04 hours 12 to 14.
- Calibration 22/01/04 hours 09 to 14.

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

#### 3.1.2.2 Missing Data - All hydrocarbons

- Calibration 05/02/04 hours 11 to 12.
- Calibration 19/02/04 hours 12 to 14.

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

#### 3.1.3.2 Missing Data - All hydrocarbons

- Calibration 03/03/04 hours 12 to 13.
- PC/GC communication problem 12/03/04 hours 06 to 07.
- Calibration 16/03/04 hours 12 to 13.
- Calibration 26/03/04 hours 16 to 17.
- Power supply fault 28/03/04 hours 18 to 20

#### 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 January**

#### **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, toluene, ethylbenzene, (m+p)-xylene and o-xylene for all of the month.

#### **3.2.1.2 Missing Data - All hydrocarbons**

- Calibration 13/01/04 hours 12 to 16.
- PC/GC communication problem 16/01/04 hours 03 to 05.
- Calibration 27/01/04 hours 16 to 17.

#### **3.2.1.3 Missing Data - Specific hydrocarbons**

None, except where the integration was unreliable due to very low concentrations or very high peak width.

### **3.2.2 February**

#### **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.  
Data quality code E for toluene, ethylbenzene, (m+p)-xylene and o-xylene from 01/02/04 to 08/02/04.

#### **3.2.2.2 Missing Data - All hydrocarbons**

- Analyser removed for repair 08/02/04 hour 10. New analyser installed 19/02/04 hour 18.
- Calibration 24/02/04 hours 13 to 16.
- Carrier gas supply fault 26/02/04 hour 13 to 27/02/04 hour 17.

#### **3.2.2.3 Missing Data - Specific hydrocarbons**

None, except where the integration was unreliable due to very low concentrations or very high peak width.

### **3.2.3 March**

#### **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 09/03/04 hours 12 to 15.
- Analyser removed for repair 21/03/04 hour 09 to 31/03/04 hour 24.

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

#### **3.3.1.2 Missing Data - All hydrocarbons**

- Calibration 05/01/04 hours 15 to 17.
- Calibration 15/01/04 hours 09 to 11.

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

#### **3.3.2.2 Missing Data - All hydrocarbons**

- Calibration 03/02/04 hours 10 to 12.
- Calibration 12/02/04 hours 10 to 12.
- Calibration 18/02/04 hours 15 to 17.
- PC/GC communication problem 27/02/04 hours 09 to 11.

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

#### **3.3.3.2 Missing Data - All hydrocarbons**

- Calibration 05/03/04 hours 08 to 14.
- CMCU service visit 05/03/04 hours 15 to 06/03/04 hour 06.
- Calibration 11/03/04 hours 09 to 11.
- Power supply fault 22/03/04 hours 12 to 15
- Calibration 25/03/04 hours 11 to 13.

#### **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.

#### **3.4.1.2 Missing Data - All hydrocarbons**

- Calibration 15/01/04 hours 07 to 10.
- Calibration 21/01/04 hours 14 to 17.
- CMCU service visit 22/01/04 hours 15 to 17.
- Calibration 22/01/04 hours 20 to 23.

#### **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.

#### **3.4.2.2 Missing Data - All hydrocarbons**

- Power supply fault 25/02/04 hour 08 to 26/02/04 hour 13.
- Compressed air supply problem 03/02/04 hour 01 to 05/02/04 hour 14.
- Calibration 05/02/04 hours 17 to 20.
- Compressed air supply problem 06/02/04 hour 05 to 11/02/04 hour 12.
- Calibration 18/02/04 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.

#### **3.4.3.2 Missing Data - All hydrocarbons**

- Calibration 04/03/04 hours 06 to 09.
- Calibration 10/03/04 hours 14 to 17.
- Calibration 24/03/04 hours 14 to 17.

#### **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 January 2004 to 31 March 2004. 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 98.86% and for 1,3-butadiene was 98.86%.

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

### 4.1.2 Glasgow

For the Glasgow site the data capture for benzene was 73.26% and for 1,3-butadiene was 73.26%.

During December 2003 it was observed in some chromatograms that the peak width of toluene, ethylbenzene, (m+p)-xylene and o-xylene had increased. At very wide peak widths the integration of the reported peak areas becomes unreliable and these data have been removed. Approximately 68% of toluene, 91% of ethylbenzene, 91% of (m+p)-xylene and 95% of o-xylene have been removed from the 1<sup>st</sup> January to 8<sup>th</sup> February, 2004.

It was also observed that the calibration samples for these compounds were affected by increased peak width. The response factor for these compounds has been derived from the relative response to benzene using an approach similar to that used for 1,3-butadiene, described in section 4.2. Because of the increased uncertainty of this method all data for toluene, ethylbenzene, (m+p)-xylene and o-xylene have been assigned data quality code E from the 1<sup>st</sup> January to 8<sup>th</sup> February, 2004.

This problem was caused by a breakdown of the sorbent packing in the focussing tube, which was replaced after the analyser was returned to the CMCU on the 8<sup>th</sup> February, 2004. The analyser was returned to the Glasgow site on the 19<sup>th</sup> February. Benzene and 1,3-butadiene were not affected by this problem.

On the 21<sup>st</sup> March, 2004 a problem occurred with the power supply of the analyser. It was not possible to repair this at the site or at the CMCU, so the analyser had to be returned to the manufacturer. This resulted in no data to the end of the quarter.

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 97.66% and for 1,3-butadiene was 97.66%.

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 82.1% and for 1,3-butadiene was 88.00%.

During February a fault developed with part of the system that supplies compressed air to the GC FID. Approximately 200 hours of data was lost before the system was repaired.

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

### 4.2 1,3-BUTADIENE DATA FOR THE VOC71M

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 the 1,3-butadiene data at Cardiff, Glasgow and Harwell has been assigned data quality code E.

### 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  $0.02 \mu\text{g}/\text{m}^3$  on a number of occasions see Figures 2, 4 and 6, Appendix 2. Where concentrations fell below  $0.02 \mu\text{g}/\text{m}^3$  the ratified concentrations have been reported as  $0.00 \mu\text{g}/\text{m}^3$ .

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 January to March 2004 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.

## 4.4 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  $16.25 \mu\text{g}/\text{m}^3$  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  $5 \mu\text{g}/\text{m}^3$  expressed as an annual mean to be met by end of 2010. In Scotland an additional objective has been set for benzene of  $3.25 \mu\text{g}/\text{m}^3$  to be met by the end of 2010. The Air Quality Objective for 1,3-butadiene is specified as a running annual mean of  $2.25 \mu\text{g}/\text{m}^3$  to be met by the end of 2003.

The annual means for benzene and 1,3-butadiene for 2000, 2001, 2002 and 2003 together with the quarterly mean for the first quarter of 2004 are given in Tables 1 and 2 below. For benzene the annual means for 2000, 2001, 2002 and 2003 were well below the respective Air Quality Objective of  $16.25 \mu\text{g}/\text{m}^3$  to be met by the end of 2003. The annual means for 2003 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, 2004 were slightly lower than the annual means for 2003.

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

Monitoring Site	2000 Annual Mean	2001 Annual Mean	2002 Annual Mean	2003 Annual Mean	Quarter 1 2004 Mean
Cardiff Centre	\$\$	\$\$	1.22\$	1.17	1.17
Glasgow	\$\$\$	\$\$\$	2.33 \$	1.82	1.65
Harwell	0.53	0.62	0.60	0.59	0.52
Marylebone Road	6.29	4.55	3.91	3.32	2.92

\$ Annual means calculated from significantly less than 12 months data

\$\$ The Cardiff Centre site was installed on 5<sup>th</sup> September 2002.

\$\$\$ The Glasgow site was installed on 1<sup>st</sup> August 2002.

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

Monitoring Site	2000 Annual Mean	2001 Annual Mean	2002 Annual Mean	2003 Annual Mean	Quarter 1 2004 Mean
Cardiff Centre	\$\$	\$\$	0.15\$	0.15	0.13
Glasgow	\$\$\$	\$\$\$	0.36\$	0.42	0.31
Harwell	0.09	0.11	0.04	0.03	0.02
Marylebone Road	1.63	1.12	0.95	0.64	0.56

\$ Annual means calculated from significantly less than 12 months data

\$\$ The Cardiff Centre site was installed on 5<sup>th</sup> September 2002.

\$\$\$ The Glasgow site was installed on 1<sup>st</sup> August 2002.

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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 January 2004 to 31 March 2004

Compound	%Data capture	Maximum hourly concentration ( $\mu\text{g}/\text{m}^3$ )	Mean concentration ( $\mu\text{g}/\text{m}^3$ )	Minimum hourly concentration ( $\mu\text{g}/\text{m}^3$ )
1,3-Butadiene	98.86	1.86	0.13	0.00
Benzene	98.86	13.04	1.17	0.06
Toluene	98.86	92.72	3.63	0.04
Ethylbenzene	94.18	23.89	0.62	0.00
(m+p)-Xylene *	98.35	64.52	2.03	0.00
o-Xylene	92.4	32.22	1.10	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 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 January 2004 to 31 March 2004

Compound	%data capture	Maximum hourly concentration ( $\mu\text{g}/\text{m}^3$ )	Mean concentration ( $\mu\text{g}/\text{m}^3$ )	Minimum hourly concentration ( $\mu\text{g}/\text{m}^3$ )
1,3-Butadiene	73.26	3.23	0.31	0.00
Benzene	73.26	10.99	1.65	0.00
Toluene	45.1	46.67	6.01	0.11
Ethylbenzene	34.62	8.86	1.01	0.00
(m+p)-Xylene *	35.53	34.73	3.79	0.04
o-Xylene	33.47	12.16	1.32	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 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 2004 to 31 March 2004

Compound	%data capture	Maximum hourly concentration ( $\mu\text{g}/\text{m}^3$ )	Mean concentration ( $\mu\text{g}/\text{m}^3$ )	Minimum hourly concentration ( $\mu\text{g}/\text{m}^3$ )
1,3-Butadiene	97.66	0.31	0.02	0.00
Benzene	97.66	2.17	0.52	0.00
Toluene	80.17	20.77	0.88	0.04
Ethylbenzene	26.69	1.01	0.13	0.04
(m+p)-Xylene *	37.18	3.44	0.31	0.04
o-Xylene	25.69	1.32	0.13	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 affiliated to the UK Hydrocarbon Network for the period; 1 January 2004 to 31 March 2004

Compound	%data capture	Maximum hourly concentration ( $\mu\text{g}/\text{m}^3$ )	Mean concentration ( $\mu\text{g}/\text{m}^3$ )	Minimum hourly concentration ( $\mu\text{g}/\text{m}^3$ )
Ethane	88.19	77.38	10.86	1.75
Ethene	88.19	24.31	5.40	0.29
Propane	88.19	32.97	6.13	1.70
Propene	88.14	12.14	2.64	0.21
Ethyne	88.14	25.60	4.65	0.57
2-Methylpropane	88.19	28.55	5.47	0.75
n-Butane	88.19	55.80	9.77	1.06
trans-2-Butene	88.10	3.61	0.68	0.09
1-Butene	88.14	3.61	0.65	0.02
cis-2-Butene	88.00	2.84	0.51	0.05
2-Methylbutane	88.19	51.49	8.56	0.63
n-Pentane	88.19	11.53	2.42	0.39
1,3-Butadiene	88.00	4.63	0.56	0.07
trans-2-Pentene	87.41	3.49	0.67	0.03
cis-2-Pentene	85.44	1.95	0.38	0.03
2-Methylpentane	88.14	16.66	2.90	0.21
3-Methylpentane	87.96	9.98	1.75	0.11
Isoprene	85.44	1.10	0.25	0.03
n-Hexane	88.42	5.51	1.14	0.00
n-Heptane	88.23	3.58	0.71	0.00
Benzene	82.10	14.53	2.92	0.10
Toluene	88.19	64.64	10.14	0.08
Ethylbenzene	87.23	20.54	1.81	0.00
(m+p)-Xylene *	64.61	52.58	8.02	0.22
o-Xylene	87.64	158.17	2.38	0.04
1,3,5-Trimethylbenzene	87.59	12.82	1.00	0.00
1,2,4-Trimethylbenzene	88.32	71.20	2.64	0.05

\* (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 3. Time series plot of the ratified benzene data from the Glasgow site of the UK Hydrocarbon Network, for the period; 1 January 2004 to 31 March 2004
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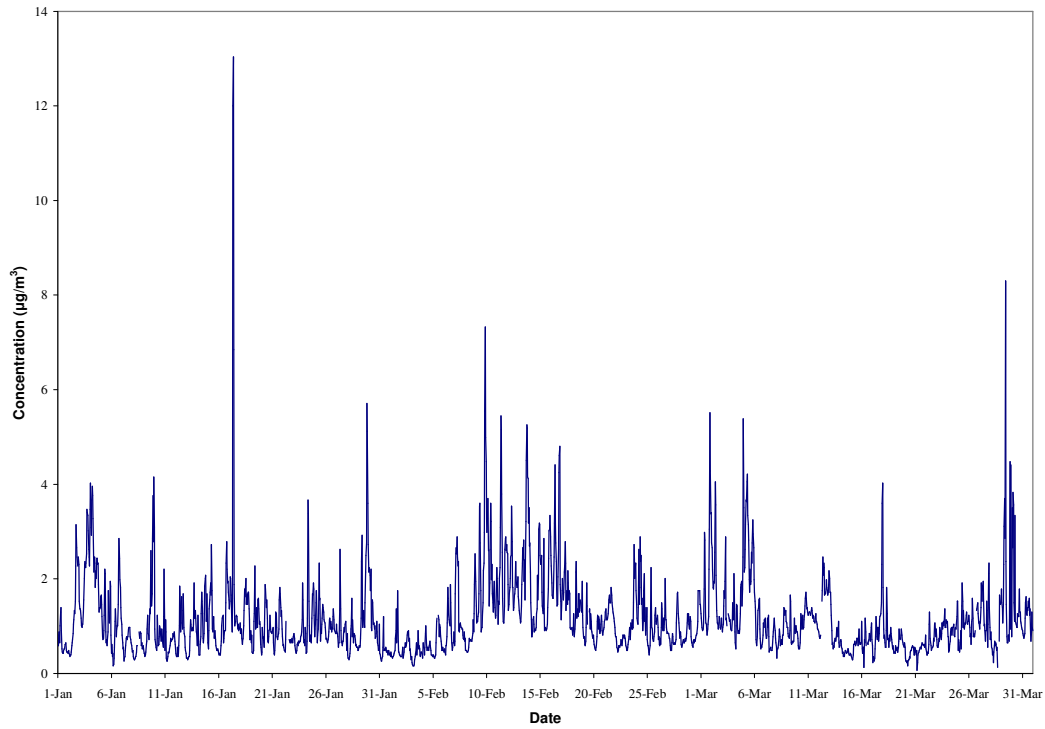


Figure 1. Time series plot of the ratified benzene data from the Cardiff site of the UK Hydrocarbon Network, for the period; 1 January 2004 to 31 March 2004

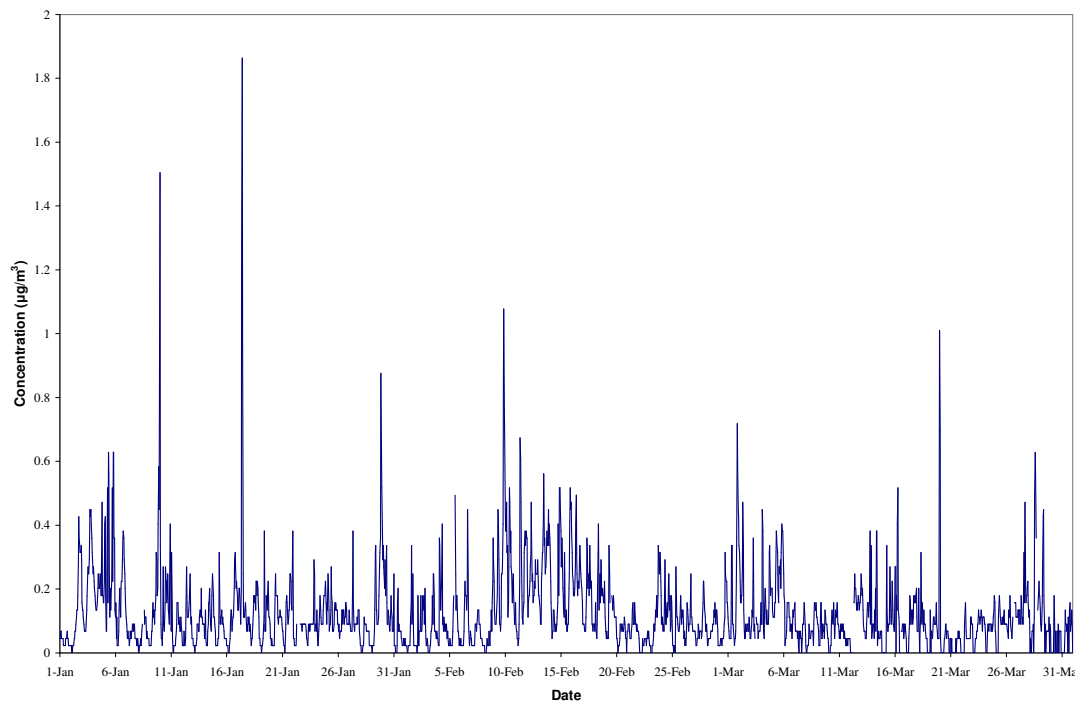


Figure 2. Time series plot of the ratified 1,3-butadiene data from the Cardiff site of the UK Hydrocarbon Network, for the period; 1 January 2004 to 31 March 2004

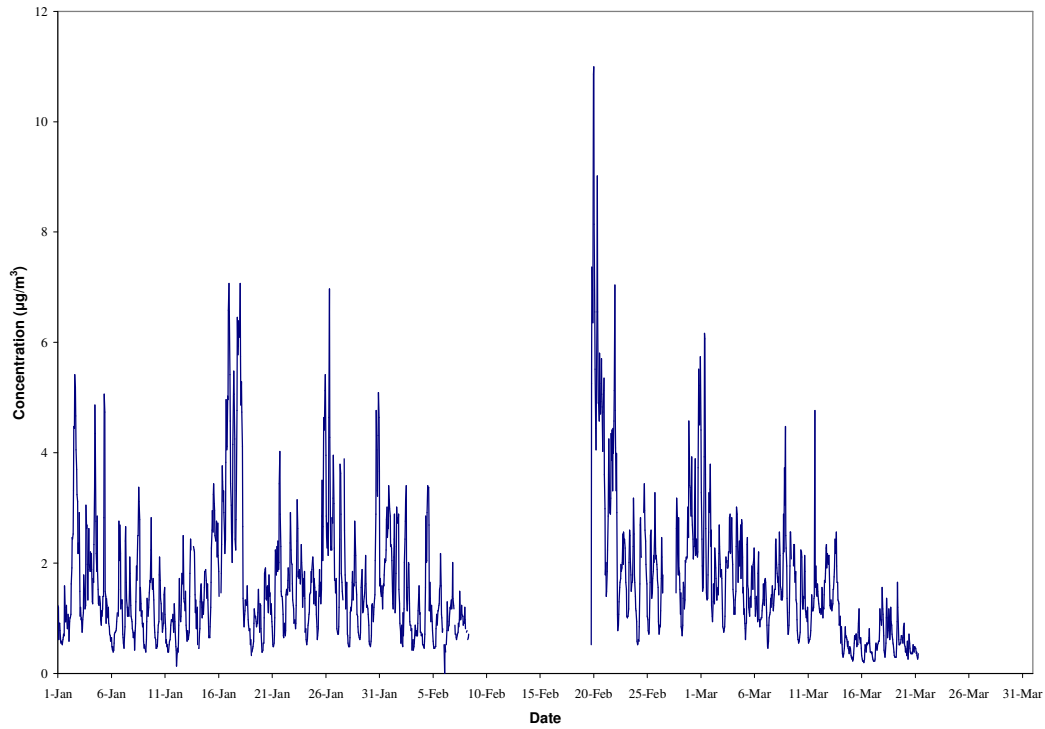


Figure 3. Time series plots for the ratified benzene data from the Glasgow site of the UK Hydrocarbon Network, for the period; 1 January 2004 to 31 March 2004

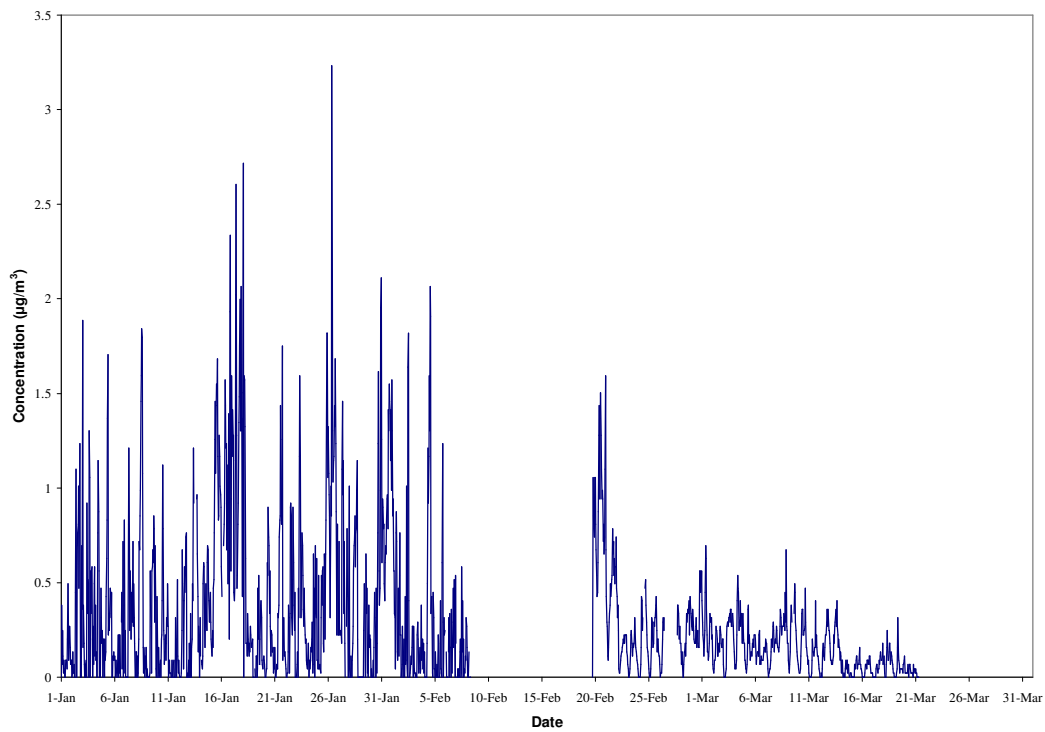


Figure 4. Time series plots for the ratified 1,3-butadiene data from the Glasgow site of the UK Hydrocarbon Network, for the period; 1 January 2004 to 31 March 2004



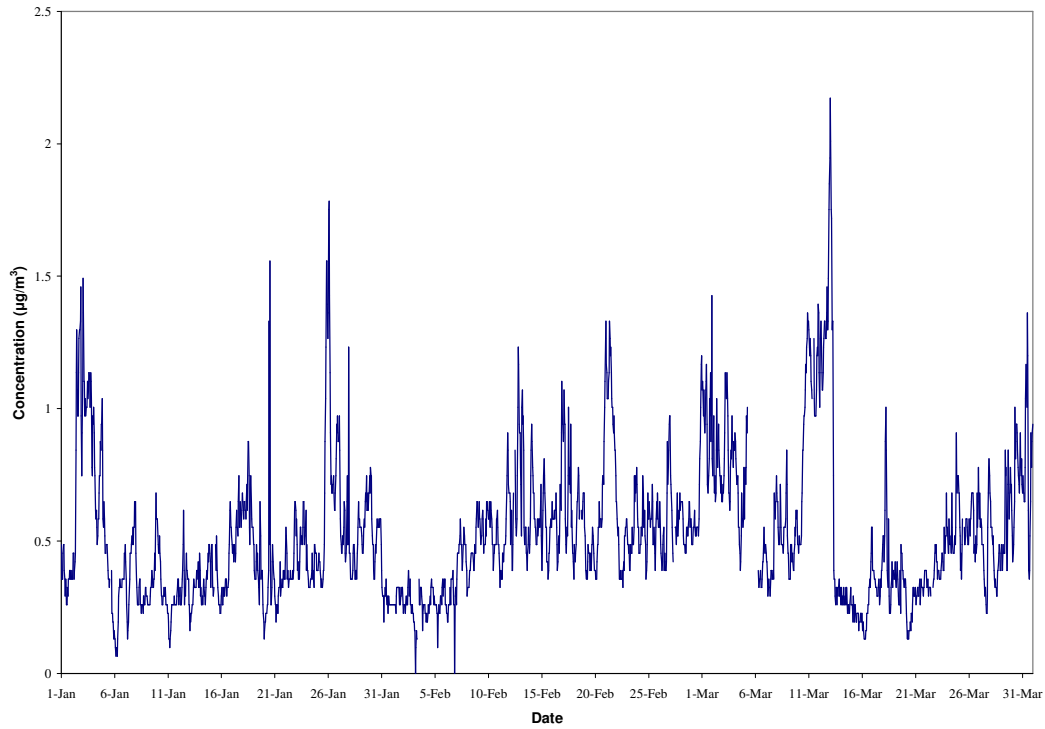


Figure 5. Time series plots for the ratified benzene data from the Harwell site of the UK Hydrocarbon Network, for the period; 1 January 2004 to 31 March 2004

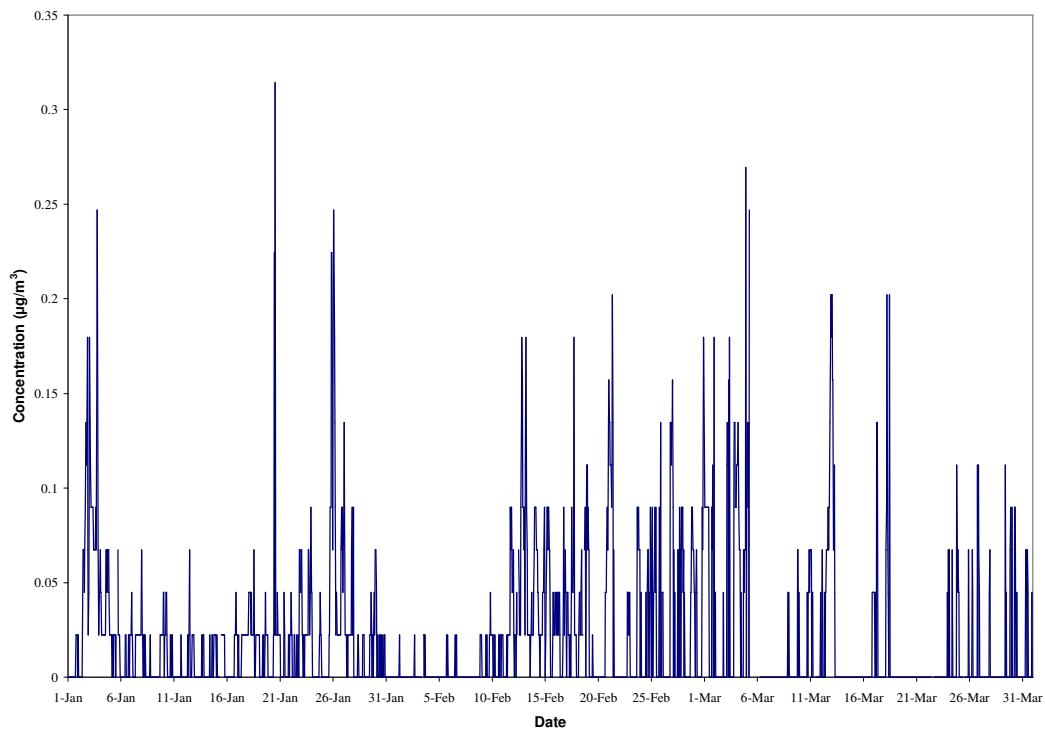


Figure 6. Time series plots for the ratified 1,3-butadiene data from the Harwell site of The UK Hydrocarbon Network, for the period; 1 January 2004 to 31 March 2004

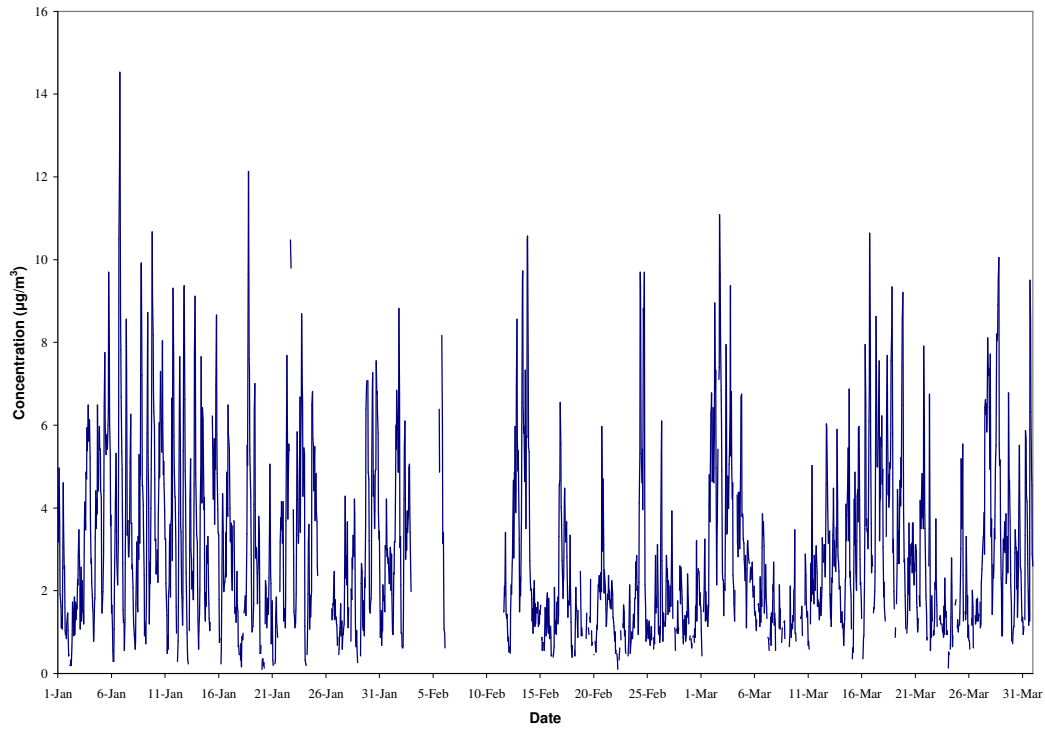


Figure 7. Time series plots for the ratified benzene data from the Marylebone Road site affiliated to the UK Hydrocarbon Network, for the period; 1 January 2004 to 31 March 2004

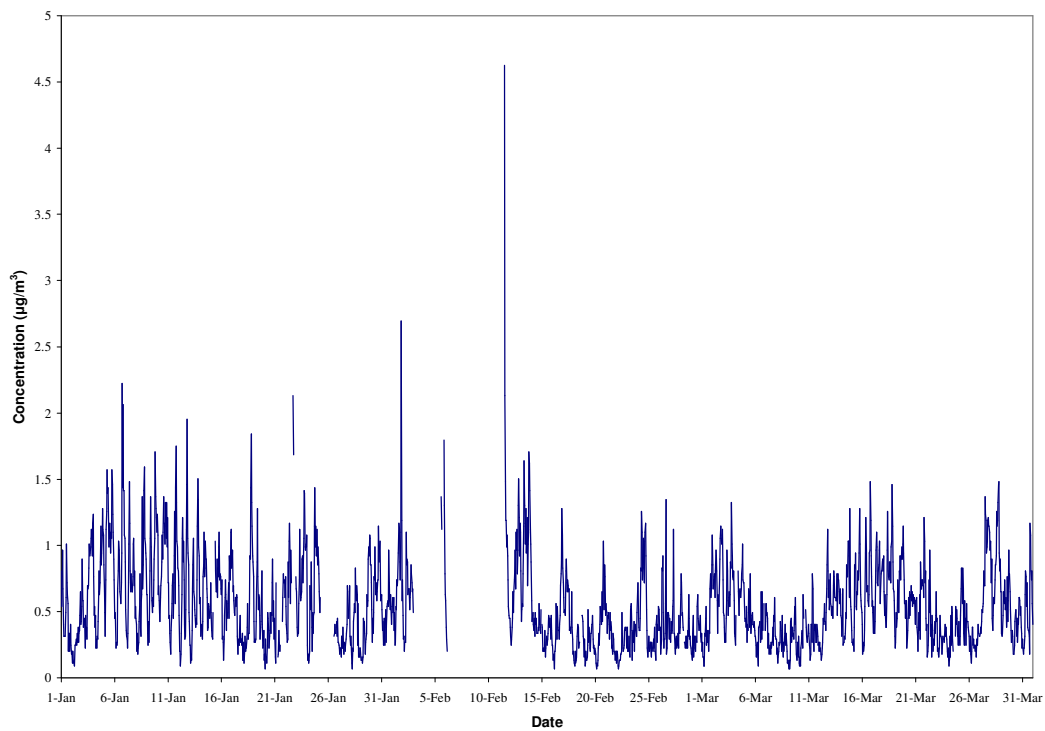


Figure 8. Time series plots for the ratified 1,3-butadiene data from the Marylebone Road site affiliated to the UK Hydrocarbon Network, for the period; 1 January 2004 to 31 March 2004