REPORT

# Ratification of data produced by the UK Ambient Automatic Hydrocarbon Air Quality Network, 1 October 2004 to 31 December 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

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# Contents

# 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 October 2004 to 31 December 2004, with annual statistics for 2004 and comparison with air quality objectives. 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.
- Information on air quality objectives for benzene and 1,3-butadiene for 2004.
- Re-established of the Eltham monitoring site.

In this report the unit used for expressing concentrations of gases is micrograms per cubic metre ($\mu g/m^3$) at the standardised temperature of 293K and a pressure of 101.3KPa, 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 October

#### 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 18/10/04 hours 13 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 November

#### 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 16/11/04 hours 10 to 12.
- Calibration 25/11/04 hours 11 to 13.

#### 3.1.2.3 Missing Data - Specific hydrocarbons

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

### 3.1.3 December

#### 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 08/12/04 hours 15 to 16.
- Calibration 30/12/04 hours 14 to 15.

#### 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 October

### 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

- Calibration 05/10/04 hours 10 to 14.
- Calibration 19/10/04 hours 11 to 14.
- Carrier gas supply fault 27/10/04 hour 01 to 31/10/04 hour 24.

### 3.2.1.3 Missing Data - Specific hydrocarbons

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

## 3.2.2 November

### 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

- Carrier gas supply fault 01/11/04 hour 01 to 05/11/04 hour 13.
- Calibration 24/11/04 hours 11 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 December

### 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 14/12/04 hours 11 to 16.
- Calibration 29/12/04 hours 12 to 15.

### 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 October

### 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

- PC locked up 05/10/04 hours 03 to 11.
- Calibration 07/10/04 hours 10 to 11.
- PC locked up 10/10/04 hour 03 to 12/10/04 hour 17.
- PC locked up 18/10/04 hour 14 to 21/10/04 hour 06.
- Calibration 21/10/04 hours 09 to 10.
- PC locked up 26/10/04 hour 02 to 28/10/04 hour 14.
- PC locked up 29/10/04 hour 11 to 31/10/04 hour 24.

### 3.3.1.3 Missing Data - Specific hydrocarbons

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

## 3.3.2 November

### 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

- PC locked up 01/11/04 hour 01. New PC installed 02/10/04 hour 15.
- Calibration 05/11/04 hours 15 to 16.
- Calibration 18/11/04 hours 15 to 16.
- Analyser fault 29/11/04 hour 13 to 30/11/04 hour 24.

### 3.3.2.3 Missing Data - Specific hydrocarbons

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

## 3.3.3 December

### 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

- Analyser fault 01/12/04 hour 01 to 03/12/04 hour 13.
- Calibration 07/12/04 hours 14 to 16.
- Calibration 20/12/04 hours 15 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 October

### 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 14/10/04 hours 07 to 10.
- Calibration 20/10/04 hours 13 to 16.

### 3.4.1.3 Missing Data - Specific hydrocarbons

None.

## 3.4.2 November

### 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 04/11/04 hours 05 to 08.
- Calibration 10/11/04 hours 13 to 16.
- Calibration 25/11/04 hours 06 to 09.

### 3.4.2.3 Missing Data - Specific hydrocarbons

None.

## 3.4.3 December

### 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 01/12/04 hours 17 to 20.
- Calibration 16/12/04 hours 08 to 11.
- Calibration 22/12/04 hours 15 to 18.

### 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 October 2004 to 31 December 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 99% and for 1,3-butadiene was 99%.

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 88% and for 1,3-butadiene was 88%.

On 27th October a fault occurred with the nitrogen carrier gas supply. The carrier gas supply was restored on the 5th November.

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 81% and for 1,3-butadiene was 81%.

During October the PC locked up on several occasions and was manually restarted by the LSO. The PC was replaced during a CMCU visit on 2nd November. At the end of November a fuse was blown on an internal power supply, the analyser was repaired by the CMCU on 3rd December.

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 98% and for 1,3-butadiene was 97%.

There have been no 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 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 $\mu g/m^3$ on a number of occasions see Figure 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. Cardiff experienced a high level of 1,3-butadiene in early October that may be attributed to a non motor vehicle source.

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 October to December 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 RUNNING ANNUAL MEANS

The running annual means (RAMs) for benzene and 1,3-butadiene for 2004 are plotted in figures 1 to 5, Appendix 3. There is a decreasing trend for benzene at all sites and a decreasing trend for 1,3-butadiene at Harwell and Marylebone Road. The running annual mean of 1,3-butadiene at Cardiff shows a step increase during August, this is the effect of higher concentrations during episodes in August 2004. The running annual mean for 1,3-butadiene at Glasgow does not follow the benzene trend; this is attributed to 1,3-butadiene not being measured at the site between 21$^{st}$ March 2004 and 28$^{th}$ July 2004.

# 4.5 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 quarterly means for benzene and 1,3-butadiene for 2004 together with the annual means for 2000, 2001, 2002, 2003 and 2004 and the rolling annual means for 2004 are given in Tables 1, 2, 3, 4, 5 and 6, Appendix 4.

The means for both benzene and 1,3-butadiene for quarter 1, 2004 were slightly lower than the annual means for 2003. The means for both benzene and 1,3-butadiene for quarters 2 and 3, 2004 were also lower than the annual means for 2003 and lower than the mean for quarter 1, 2004. The means for quarter 4, 2004 were approximately the same as the means for quarter 1, 2004. The observed trends in concentrations are probably due to seasonal variation.

For benzene the annual means for 2000, 2001, 2002, 2003 and 2004 were well below the relevant Air Quality Objective of 16.25 $\mu g/m^3$ to be met by the end of 2003. The annual means and maximum rolling annual means for 2004 were also below the Air Quality Objective to be met by 2010 for the respective region.

For 1,3-butadiene the maximum running annual means for 2004 for all sites were well below the Air Quality Objective of 2.25 $\mu g/m^3$ to be met by the end of 2003.

Hence, the 2003 Air Quality Objectives for both benzene and 1,3-butadiene was achieved at all sites in the UK Ambient Automatic Hydrocarbon Automatic Air Quality Network.

The annual means for benzene and 1,3-butadiene for 1994 to 2004 are plotted in figures 1 to 3, Appendix 5. The plots show the significant decrease of the concentration of these hydrocarbons over the last 10 years. In figure 2 the y-axis scale has been expanded to show this trend at the sites with lower concentrations.

# 4.6 ANALYSIS OF TRENDS OF MEASURED HYDROCARBONS

## 4.6.1 Long term Trends

Figures 1 to 4, Appendix 6 are plots of the long-term trends of the monthly mean concentrations of benzene, toluene and 1,3-butadiene at the four sites that comprised the UK Automatic Hydrocarbon Network at the end of December 2004.

Figure 1, the plot for the Marylebone Road site shows a significant decrease of the concentration of all three hydrocarbons. Figure 2, the plot for the Harwell site, shows a decrease of the benzene and 1,3-butadiene concentrations and a greater decrease in toluene during 2004.

Figures 3 and 4, the plots for the Cardiff Centre and Glasgow sites, cover a much shorter time period due to the fact the sites were established during autumn 2002. Cardiff Centre shows slight decreases in benzene and toluene concentrations but apparently less for the 1,3-butadiene. Glasgow shows a decrease in benzene and a significant decrease in 1,3-butadiene and toluene during 2004.

### 4.6.2 Ratios of the concentrations of the measured hydrocarbons

Figure 5 to 8, Appendix 6 are the plots of the monthly mean concentrations of the benzene, 1,3-butadiene and the benzene:1,3-butadiene ratios at hydrocarbon network sites. The measured concentrations are expressed as monthly means.

For the Marylebone Road site, figure 5, the decrease in the concentrations is apparent, however there does not appear to be a consistent trend in the benzene:1,3-butadiene ratio. A step change in the ratio of the concentrations at the Marylebone Road site occurred between late 1999 to early 2000. This change coincides with change in the legislative maximum concentration of benzene in petrol. Prior to the change the maximum benzene concentration in petrol was 5% in 'super' unleaded petrol and 2% in 'standard' unleaded petrol. After the change in legislation the maximum concentration of benzene was specified as 1% for all petrol.

The corresponding plot for the Harwell site, figure 6, shows some significant differences. The benzene and 1,3-butadiene exhibit a reduction in concentration, being similar to that at Marylebone road but lower in concentration. The plot of the ratio of the concentrations is significantly different with an apparent change during early 2002. The change corresponds to the time when the type of instrument at the site was changed. Up to the end of 2001 the instrument at the Harwell site was a Chrompack VOCAIR. From 2002 onward the type of instrument was changed to an Environnement VOC71M.

Initial inspection would suggest that the two instruments give significantly different results. An intercomparison of the two instruments at the Harwell site demonstrated that the results were quite comparable with very similar time series plots. Investigation of the data reveals that the elevated values for the benzene:1,3-butadien ratio occurs when the concentrations of 1,3-butadiene are low. Further investigation has revealed that the VOCAIR had a small but not significant 1,3-butadiene 'blank'. The level of the blank was such that the chromatographic peak was below the integration threshold so did not appear as a 'blank' value. Analysis of the ambient air samples collected by the VOCAIR included additional 1,3-butadiene sufficient to increase the peak areas above the integration threshold. The reported concentrations therefore, included the 'blank' due to the VOCAIR system. The level of the 'blank' was quite low, equivalent to about 0.07 to 0.11 $\mu g/m^3$, not significant relative to the 2.25 $\mu g/m^3$ Air Quality Standard. The level of the blank is therefore, only significant at very low ambient concentrations

Very low concentrations are usually measured when the air mass is clean, usually when the air mass has 'aged'. It appears unfortunate that the magnitude of the 'blank' has compensated for the decreasing 1,3-butadiene concentration due to it's removal by photo chemical reaction in the atmosphere.

The VOC71M appears to have no detectable 'blank'. When clean nitrogen is sampled by the VOC71M the chromatogram shows no evidence of a peak. It is likely that the VOC71M gives a more representative measure of the concentration of 1,3-butadiene at low concentrations and hence the benzene:1,3-butadiene ratio may well be more accurate after the installation of the VOC71M. During periods of increased photochemical activity i.e. the summertime, the concentration of 1,3-butadiene would be expected to decrease more rapidly in percentage terms than that of benzene. The second order rate constants for the reaction of OH with 1,3-butadiene is about 10 times greater than the corresponding value for benzene. The value of the ratio when expressed as a monthly average would be expected to be higher in summer than in winter. This is observed in figure 6 where the value of the ratio is lowest during November, December and January.

Figures 7 and 8, the plots for the Cardiff Centre and Glasgow sites, cover a much shorter time period due to the fact the sites were established during autumn 2002.

# 4.7 ELTHAM

The Hydrocarbon network has seen the re-introduction of a monitoring station at the Eltham site. This site was part of the network from 1993 to 2000 using a Chrompack VOCAIR analyser, but monitoring ceased as changes to the network occurred. A new Perkin Elmer ozone-precursor analyser has been introduced, and monitoring commenced on 17th October 2003. This ozone-precursor analyser is a development of the ATD400 analyser used at Marylebone Road since 1997.

This analyser has been installed and will be operated to fulfil the UK's obligation under the 3rd daughter directive of the EU Framework Directive 96/62/EC for ambient air quality assessment and management.

The data output files of the new analyser differed from those produced by the older ATD400 analyser installed at Marylebone Road. New software and data handling processes were developed for the integration of this data into the ratification process.

The same compounds that are monitored at the Marylebone Road site are monitored at the Eltham site. The Eltham data was processed as an annual batch, and these data are presented in annual form. The ratified data from 2003 has not been included in this report but can be viewed on the World Wide Web at http://www.airquality.co.uk/archive/data_and_statistics_home.php

During the ratification process 1,3-butadiene and benzene have been assigned a Data Quality Code A; all other compounds ratified are assigned Data Quality Code E. Table 1, Appendix 7, shows the percentage data capture, maximum, mean and minimum values of ratified data from the Eltham site for 2004. Annual concentrations of benzene and 1,3-butadiene are plotted graphically in Figures 1 to 2, Appendix 7. There are two periods of missing data, the first from 11th May 2004 to 27th May 2004, was due to excessive noise on the FID detectors. The second period of missing data was attributed to a GC oven door failure on 1st July 2004, this was repaired and monitoring commenced on 14th July 2004.

The 2004 running annual mean (RAM) for benzene and 1,3-butadiene at Eltham is plotted in figure 5, Appendix 3. As monitoring commenced in October 2003 it is not possible to calculate a running annual mean for the whole of 2004, therefore a clear trend cannot yet be determined.

For benzene the annual mean in 2004 was well below the Air Quality Objective of 16.25 $\mu g/m^3$ to be met by the end of 2003. The annual mean is also below the Air Quality Objective to be met by 2010 for this region. For 1,3-butadiene the annual mean for 2004 was well below the Air Quality Objective of 2.25 $\mu g/m^3$ to be met by the end of 2003. The annual means for benzene and 1,3-butadiene together with the rolling annual means for 2004 are given in Tables 2, 3, 5 and 6, Appendix 4. The tables show the annual mean at Eltham is well below that at Marylebone Road, which is consistent with an urban background site.

The annual means for benzene and 1,3-butadiene for 1994 to 2004 are plotted in figures 1 to 3, Appendix 5. The plots show the significant decrease of the concentration of these hydrocarbons over the last 10 years. In figure 2 the y-axis scale has been expanded to show this trend at the sites with lower concentrations. The plots show that concentrations at the Eltham site have continued to decline.

# Appendices

## CONTENTS

# Appendix 1
# Summary Statistical Information

## CONTENTS

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 October 2004 to 31 December 2004

| 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 | 99.05 | 4.02 | 0.13 | 0.00 |
| Benzene | 98.78 | 8.92 | 0.91 | 0.00 |
| Toluene | 99.28 | 38.44 | 3.86 | 0.42 |
| Ethylbenzene | 83.29 | 6.13 | 0.57 | 0.09 |
| (m+p)-Xylene * | 97.51 | 20.85 | 1.76 | 0.04 |
| o-Xylene | 85.91 | 15.82 | 1.15 | 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 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 October 2004 to 31 December 2004

| 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 | 88.41 | 3.19 | 0.27 | 0.00 |
| Benzene | 88.41 | 9.99 | 1.65 | 0.00 |
| Toluene | 88.45 | 54.51 | 5.58 | 0.31 |
| Ethylbenzene | 77.17 | 15.91 | 1.06 | 0.13 |
| (m+p)-Xylene * | 88.18 | 36.36 | 3.48 | 0.13 |
| o-Xylene | 81.25 | 21.77 | 2.20 | 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 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 October 2004 to 31 December 2004

| 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 | 80.89 | 0.40 | 0.02 | 0.00 |
| Benzene | 80.89 | 2.89 | 0.45 | 0.00 |
| Toluene | 79.98 | 13.46 | 0.99 | 0.04 |
| Ethylbenzene | 35.51 | 1.76 | 0.26 | 0.04 |
| (m+p)-Xylene * | 68.80 | 5.86 | 0.57 | 0.04 |
| o-Xylene | 40.62 | 2.64 | 0.26 | 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 October 2004 to 31 December 2004

| Compound | %data capture | Maximum hourly concentration ($\mu g/m^3$) | Mean concentration ($\mu g/m^3$) | Minimum hourly concentration ($\mu g/m^3$) |
|---|---|---|---|---|
| Ethane | 98.32 | 113.94 | 12.44 | 2.88 |
| Ethene | 98.28 | 24.68 | 6.02 | 0.37 |
| Propane | 98.32 | 43.25 | 7.54 | 1.54 |
| Propene | 98.32 | 10.93 | 3.13 | 0.02 |
| Ethyne | 98.14 | 20.77 | 5.26 | 0.03 |
| 2-Methylpropane | 98.32 | 42.76 | 7.09 | 0.72 |
| n-Butane | 98.32 | 74.47 | 13.84 | 1.23 |
| trans-2-Butene | 98.32 | 3.68 | 0.84 | 0.16 |
| 1-Butene | 98.32 | 3.31 | 0.77 | 0.07 |
| cis-2-Butene | 98.32 | 2.70 | 0.58 | 0.07 |
| 2-Methylbutane | 98.28 | 62.68 | 11.97 | 0.75 |
| n-Pentane | 98.32 | 15.51 | 3.11 | 0.45 |
| 1,3-Butadiene | 97.19 | 2.11 | 0.63 | 0.04 |
| trans-2-Pentene | 98.32 | 4.80 | 0.87 | 0.03 |
| cis-2-Pentene | 97.55 | 2.74 | 0.49 | 0.03 |
| 2-Methylpentane | 98.28 | 23.10 | 3.79 | 0.21 |
| 3-Methylpentane | 98.23 | 14.77 | 2.29 | 0.11 |
| Isoprene | 97.60 | 1.27 | 0.37 | 0.03 |
| n-Hexane | 97.51 | 13.34 | 1.47 | 0.04 |
| n-Heptane | 98.19 | 6.82 | 0.87 | 0.00 |
| Benzene | 97.69 | 18.49 | 2.95 | 0.29 |
| Toluene | 98.32 | 94.29 | 12.81 | 0.54 |
| Ethylbenzene | 98.28 | 12.03 | 2.16 | 0.04 |
| (m+p)-Xylene * | 98.19 | 35.57 | 7.18 | 0.26 |
| o-Xylene | 98.28 | 15.51 | 2.82 | 0.13 |
| 1,3,5-Trimethylbenzene | 98.32 | 4.59 | 1.00 | 0.05 |
| 1,2,4-Trimethylbenzene | 98.32 | 14.32 | 3.24 | 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 2
# Time Series Plots of Hydrocarbon Concentrations

## CONTENTS

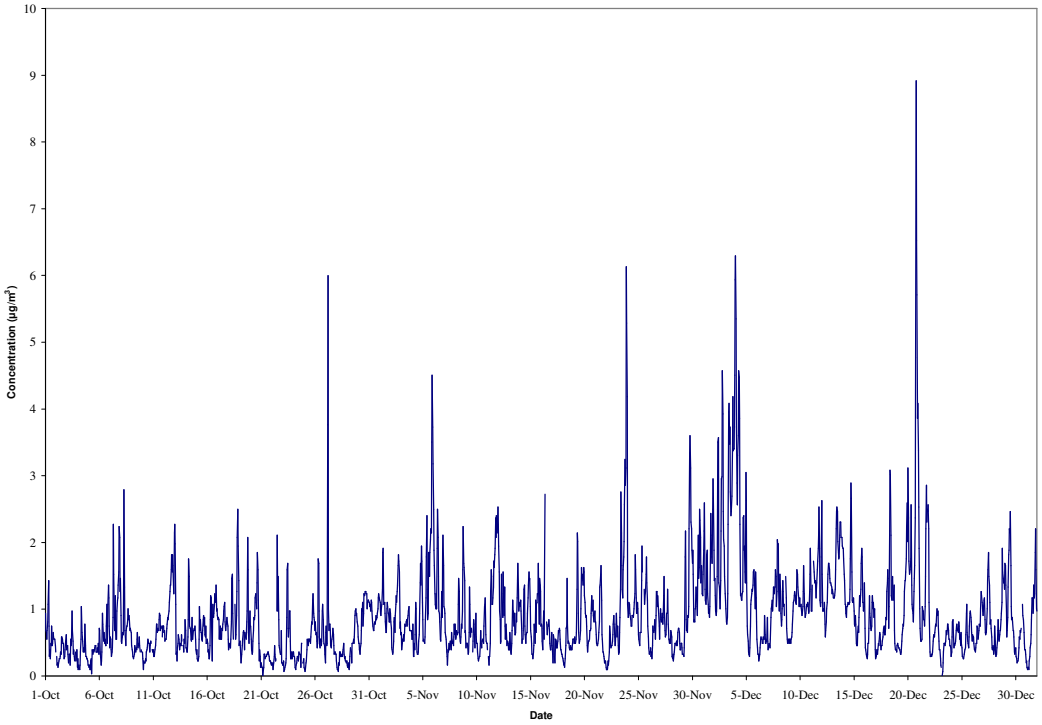


Figure 1. Time series plot of the ratified benzene data from the Cardiff site of the UK Hydrocarbon Network, for the period; 1 October 2004 to 31 December 2004

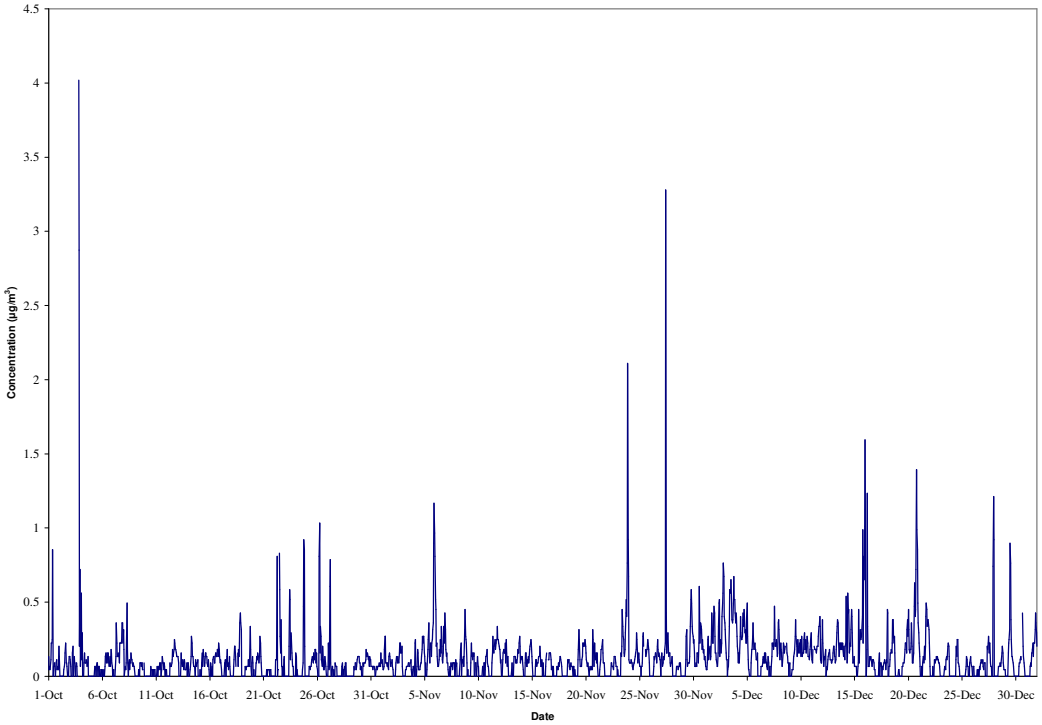


Figure 2. Time series plot of the ratified 1,3-butadiene data from the Cardiff site of the UK Hydrocarbon Network, for the period; 1 October 2004 to 31 December 2004

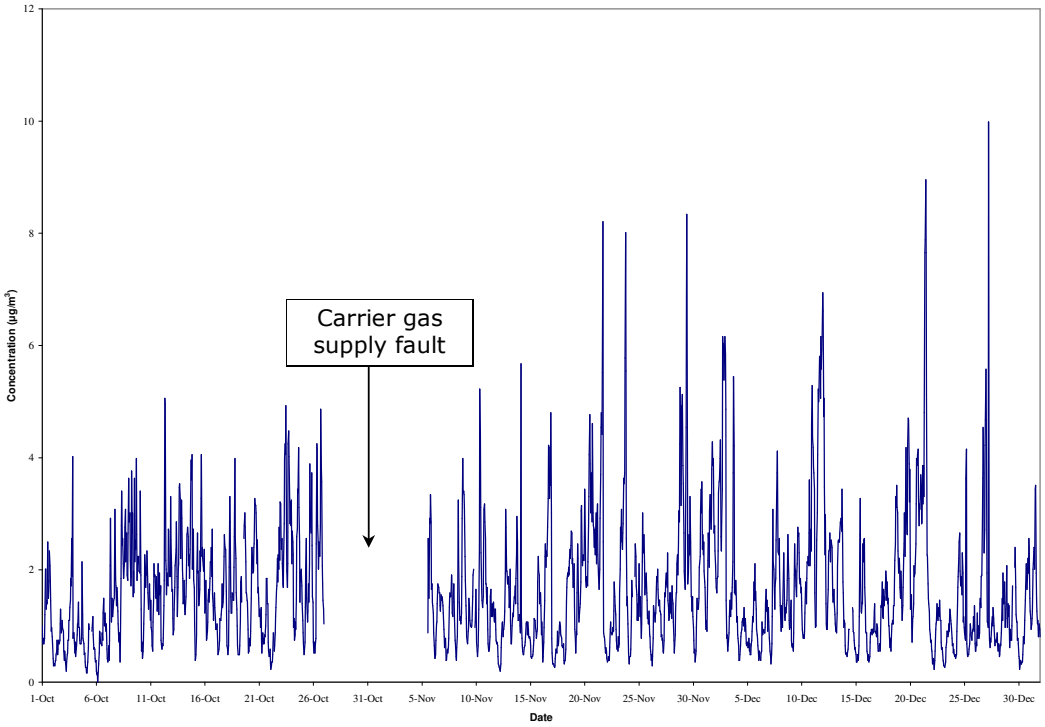


Figure 3. Time series plots for the ratified benzene data from the Glasgow site of the UK Hydrocarbon Network, for the period; 1 October 2004 to 31 December 2004

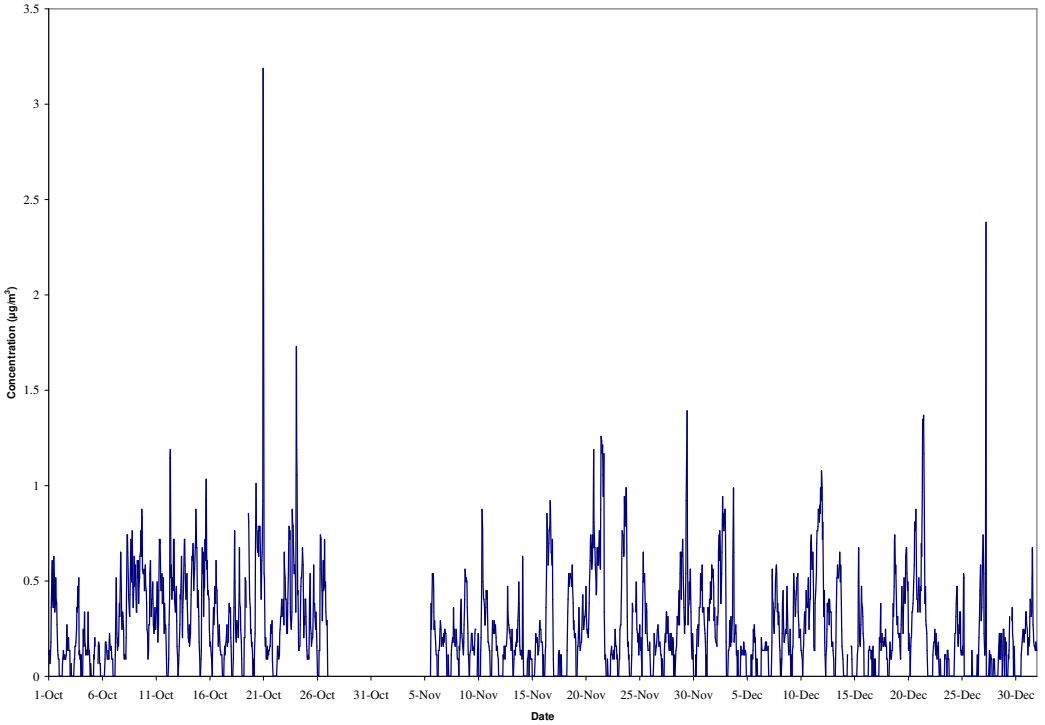


Figure 4. Time series plots for the ratified 1,3-butadiene data from the Glasgow site of the UK Hydrocarbon Network, for the period; 1 October 2004 to 31 December 2004

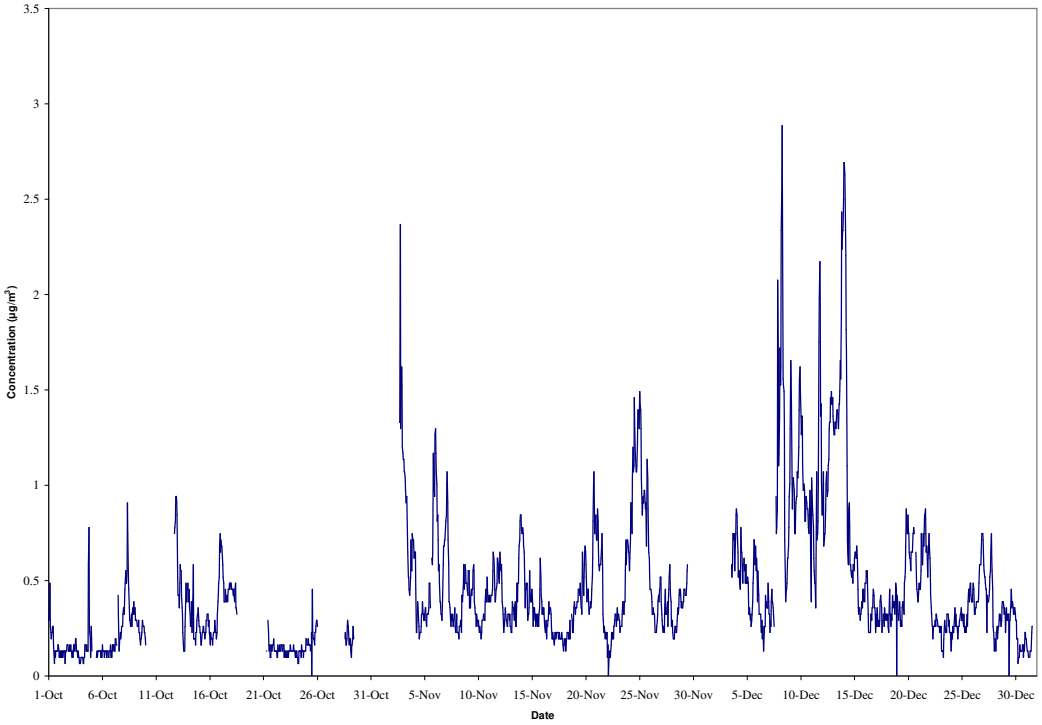


Figure 5. Time series plots for the ratified benzene data from the Harwell site of the UK Hydrocarbon Network, for the period; 1 October 2004 to 31 December 2004

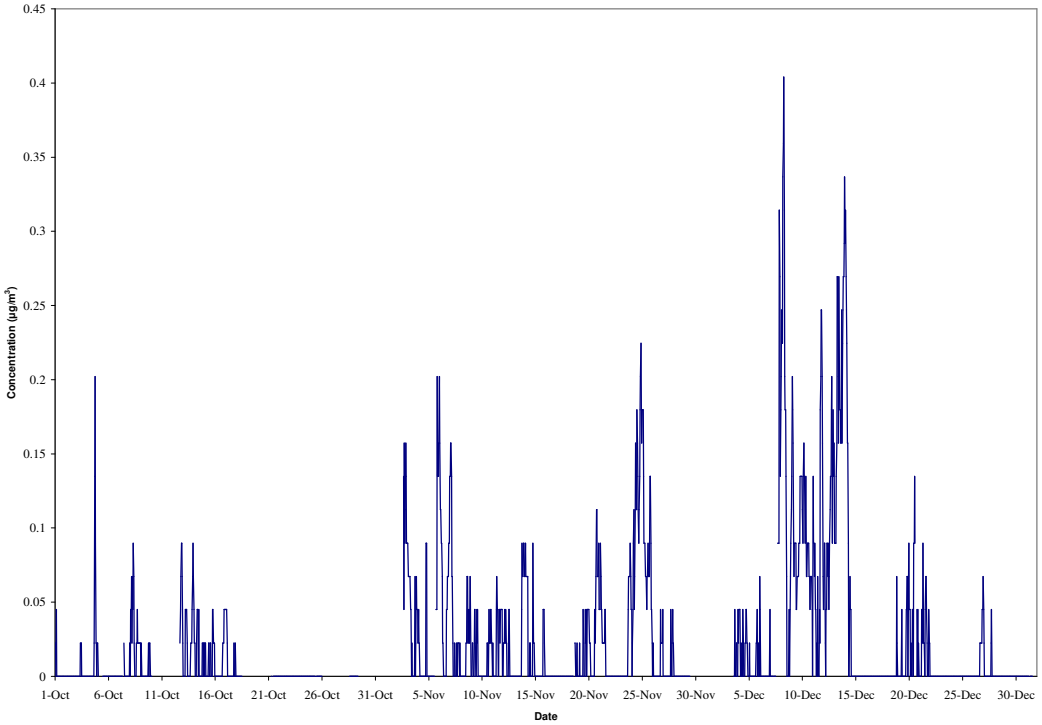


Figure 6. Time series plots for the ratified 1,3-butadiene data from the Harwell site of The UK Hydrocarbon Network, for the period; 1 October 2004 to 31 December 2004

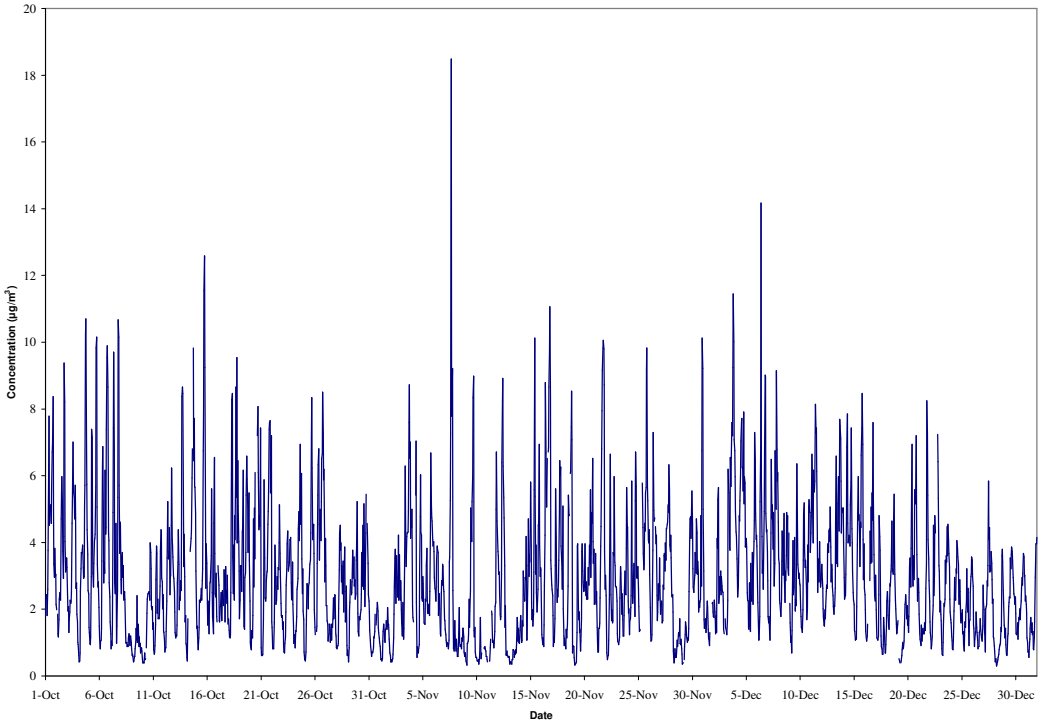


Figure 7. Time series plots for the ratified benzene data from the Marylebone Road site affiliated to the UK Hydrocarbon Network, for the period;1 October 2004 to 31 December 2004

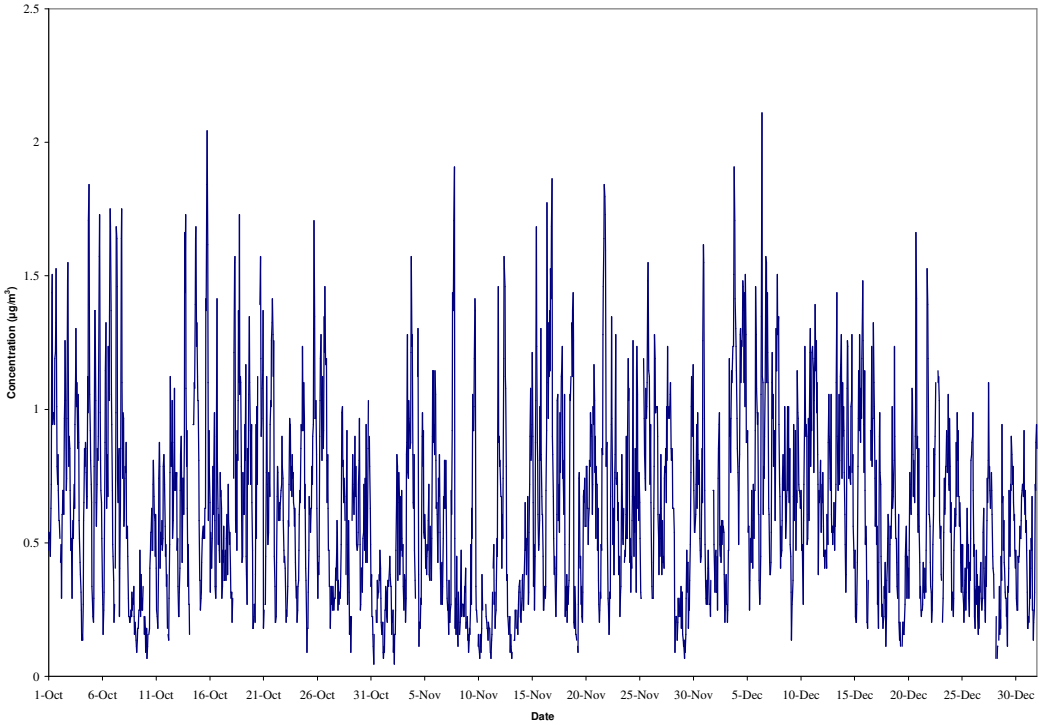


Figure 8. Time series plots for the ratified 1,3-butadiene data from the Marylebone Road site affiliated to the UK Hydrocarbon Network, for the period; 1 October 2004 to 31 December 2004

# Appendix 3
## Rolling Annual Mean Plots

## CONTENTS

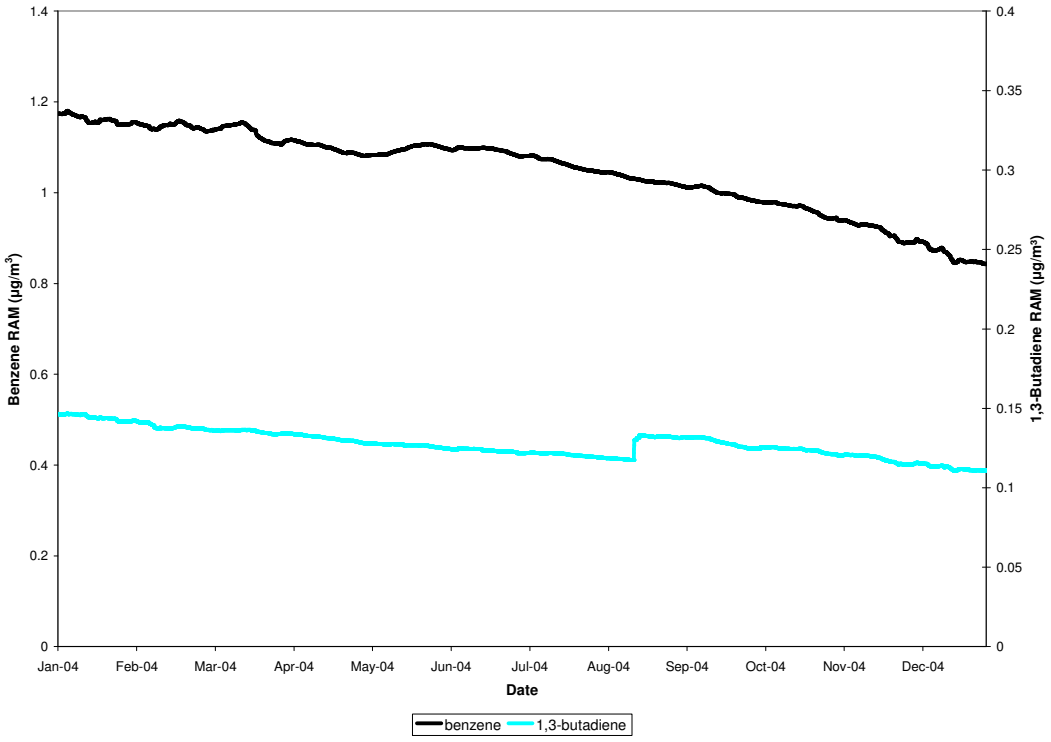


Figure 1. Time series plot of the rolling annual mean for benzene and 1,3-butadiene data from the Cardiff site of the UK Hydrocarbon Network, for the period; January 2004 to December 2004.

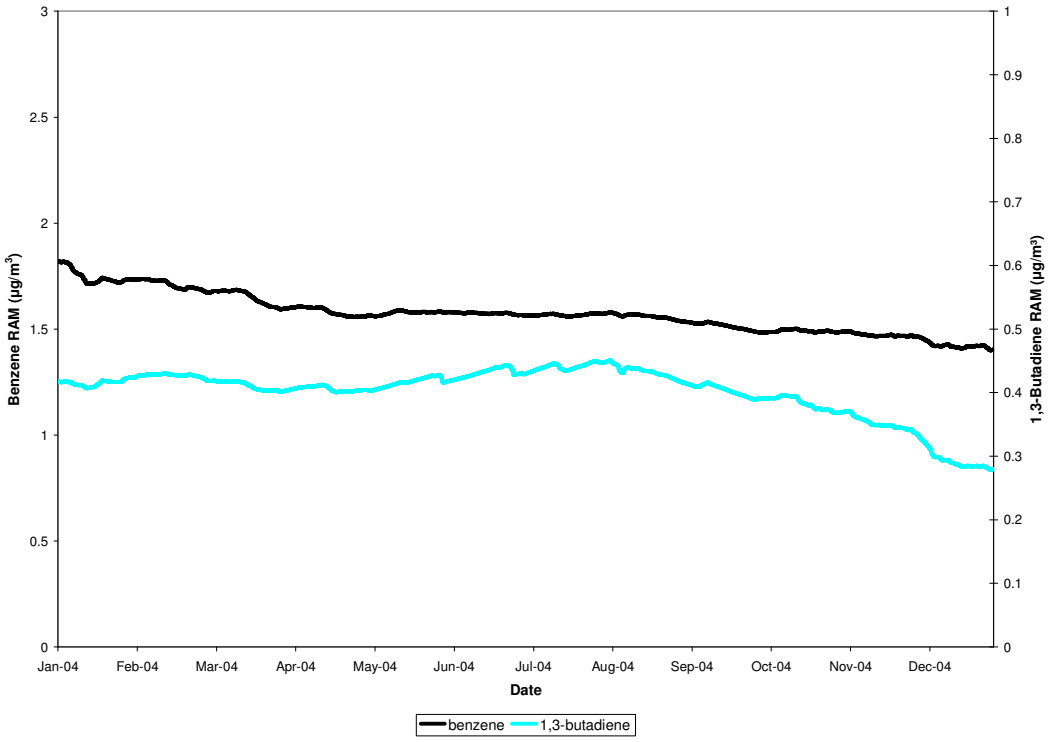


Figure 2. Time series plot of the rolling annual mean for benzene and 1,3-butadiene data from the Glasgow site of the UK Hydrocarbon Network, for the period; January 2004 to December 2004.

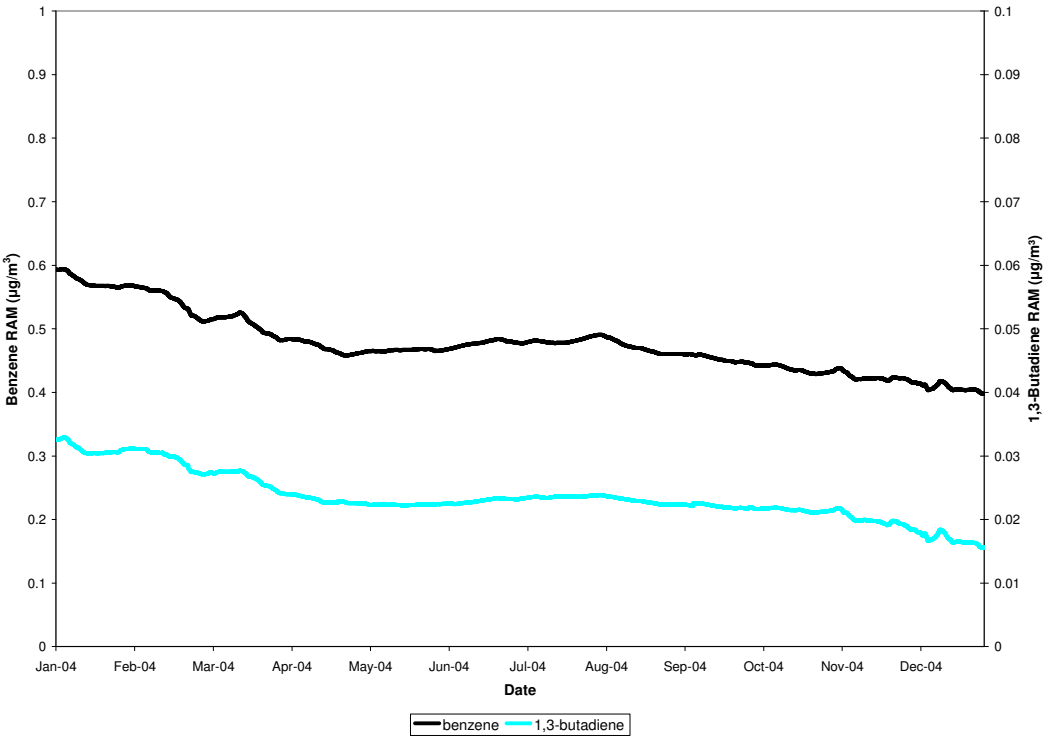


Figure 3. Time series plot of the rolling annual mean for benzene and 1,3-butadiene data from the Harwell site of the UK Hydrocarbon Network, for the period; January 2004 to December 2004.

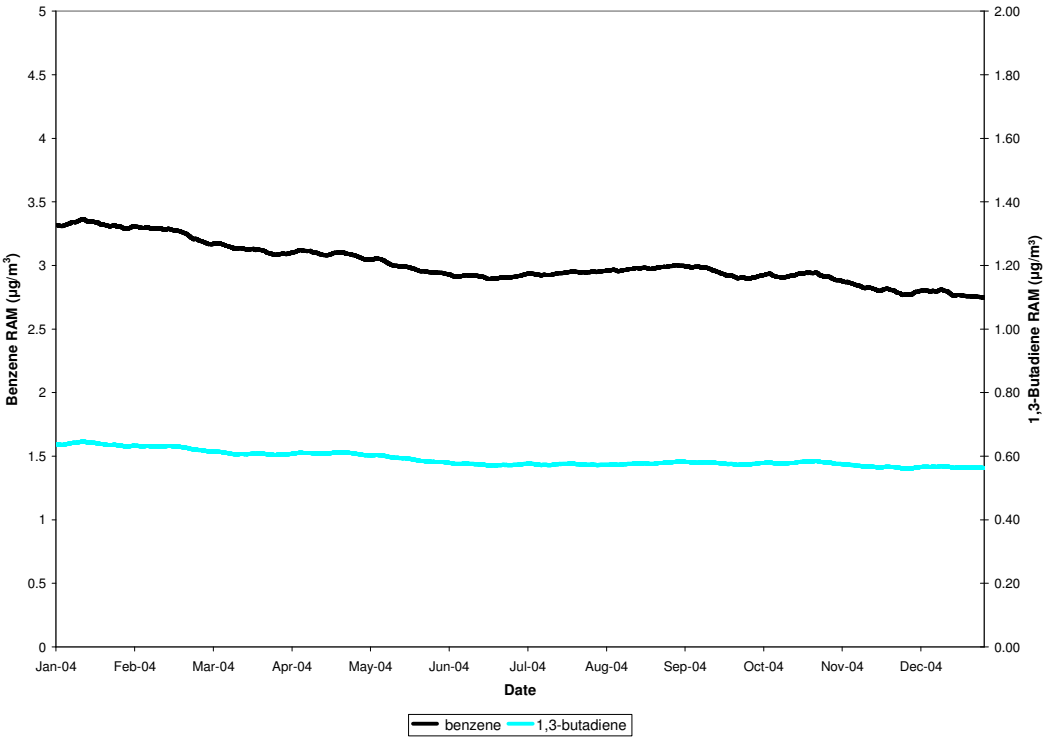


Figure 4. Time series plot of the rolling annual mean for benzene and 1,3-butadiene data from the Marylebone Road site affiliated to the UK Hydrocarbon Network, for the period; January 2004 to December 2004.

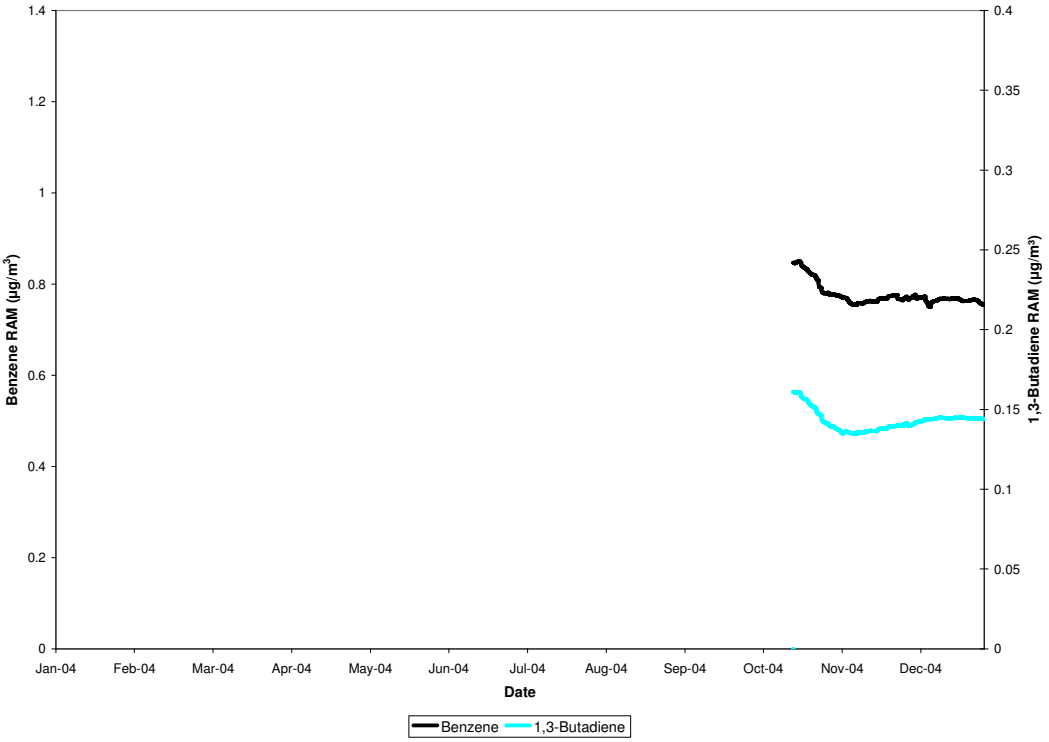


Figure 5. Time series plot of the rolling annual mean for benzene and 1,3-butadiene data from the Eltham site affiliated to the UK Hydrocarbon Network, for the period; January 2004 to December 2004.

# Appendix 4
# Quarterly, annual and maximum running means

## CONTENTS

Table 1. Quarterly means of measured benzene concentrations (μg/m$^3$) at each of the UK Automatic Hydrocarbon Sites.

| Monitoring Site | Quarter 1 2004 Mean | Quarter 2 2004 Mean | Quarter 3 2004 Mean | Quarter 4 2004 Mean |
|---|---|---|---|---|
| Cardiff Centre | 1.17 | 0.68 | 0.52 | 0.91 |
| Glasgow | 1.65 | 1.17 | 1.14 | 1.65 |
| Harwell | 0.52 | 0.29 | 0.23 | 0.45 |
| Marylebone Road | 2.92 | 2.33 | 2.76 | 2.95 |

Table 2. Annual means of measured benzene concentrations (μg/m$^3$) at each of the UK Automatic Hydrocarbon Sites.

| Monitoring Site | 2000 Annual Mean | 2001 Annual Mean | 2002 Annual Mean | 2003 Annual Mean | 2004 Annual Mean | 2004 Data Capture % |
|---|---|---|---|---|---|---|
| Cardiff Centre | $$ | $$ | 1.22$ | 1.17 | 0.84 | 91.38 |
| Glasgow | $$$ | $$$ | 2.33 $ | 1.82 | 1.40 | 82.47 |
| Harwell | 0.53 | 0.62 | 0.60 | 0.59 | 0.40 | 74.65 |
| Marylebone Road | 6.29 | 4.55 | 3.91 | 3.32 | 2.75 | 85.12 |
| Eltham | $$$$ | $$$$ | $$$$ | $$$$ | 0.76 | 82.29 |

$ 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
$$$$ The Eltham site was installed on 17th October 2003

Table 3. Maximum running annual means of measured benzene concentrations (μg/m$^3$) at each of the UK Automatic Hydrocarbon Sites.

| Monitoring Site | 2004 Maximum running annual mean | 2004 MRAM Data Capture % |
|---|---|---|
| Cardiff Centre | 1.18 | 75.86 |
| Glasgow | 1.82 | 84.92 |
| Harwell | 0.59 | 84.73 |
| Marylebone Road | 3.37 | 90.81 |
| Eltham * | 0.85 | 74.48 |

* MRAM calculated from data after 17th October 2004

Table 4. Quarterly means of measured 1,3-butadiene concentrations (μg/m$^3$) at each of the UK Automatic Hydrocarbon Sites.

| Monitoring Site | Quarter 1 2004 Mean | Quarter 2 2004 Mean | Quarter 3 2004 Mean | Quarter 4 2004 Mean |
|---|---|---|---|---|
| Cardiff Centre | 0.13 | 0.04 | 0.13 | 0.13 |
| Glasgow | 0.31 | $ | 0.25 | 0.27 |
| Harwell | 0.02 | 0.00 | 0.00 | 0.02 |
| Marylebone Road | 0.56 | 0.47 | 0.61 | 0.63 |

$ No 1,3-butadiene measured for the quarter.

Table 5. Annual Means of measured 1,3-butadiene concentrations (μg/m$^3$) at each of the UK Automatic Hydrocarbon Sites.

| Monitoring Site | 2000 Annual Mean | 2001 Annual Mean | 2002 Annual Mean | 2003 Annual Mean | 2004 Annual Mean | 2004 Data Capture % |
|---|---|---|---|---|---|---|
| Cardiff Centre | $$ | $$ | 0.15$ | 0.15 | 0.11 | 91.68 |
| Glasgow | $$$ | $$$ | 0.36$ | 0.42 | 0.28 | 57.22 |
| Harwell | 0.09 | 0.11 | 0.04 | 0.03 | 0.02 | 74.66 |
| Marylebone Road | 1.63 | 1.12 | 0.95 | 0.64 | 0.56 | 91.37 |
| Eltham | $$$$ | $$$$ | $$$$ | $$$$ | 0.15 | 80.81 |

$ 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
$$$$ The Eltham site was installed on 17th October 2003

Table 6. Maximum running annual means of measured 1,3-butadiene concentrations (μg/m$^3$) at each of the UK Automatic Hydrocarbon Sites.

| Monitoring Site | 2004 Maximum running annual mean | 2004 MRAM Data Capture % |
|---|---|---|
| Cardiff Centre | 0.15 | 76.13 |
| Glasgow | 0.45 | 46.15 |
| Harwell | 0.03 | 84.90 |
| Marylebone Road | 0.65 | 92.50 |
| Eltham * | 0.16 | 69.54 |

* MRAM calculated from data after 17th October 2004

# Appendix 5
## Annual Mean Plots

## CONTENTS

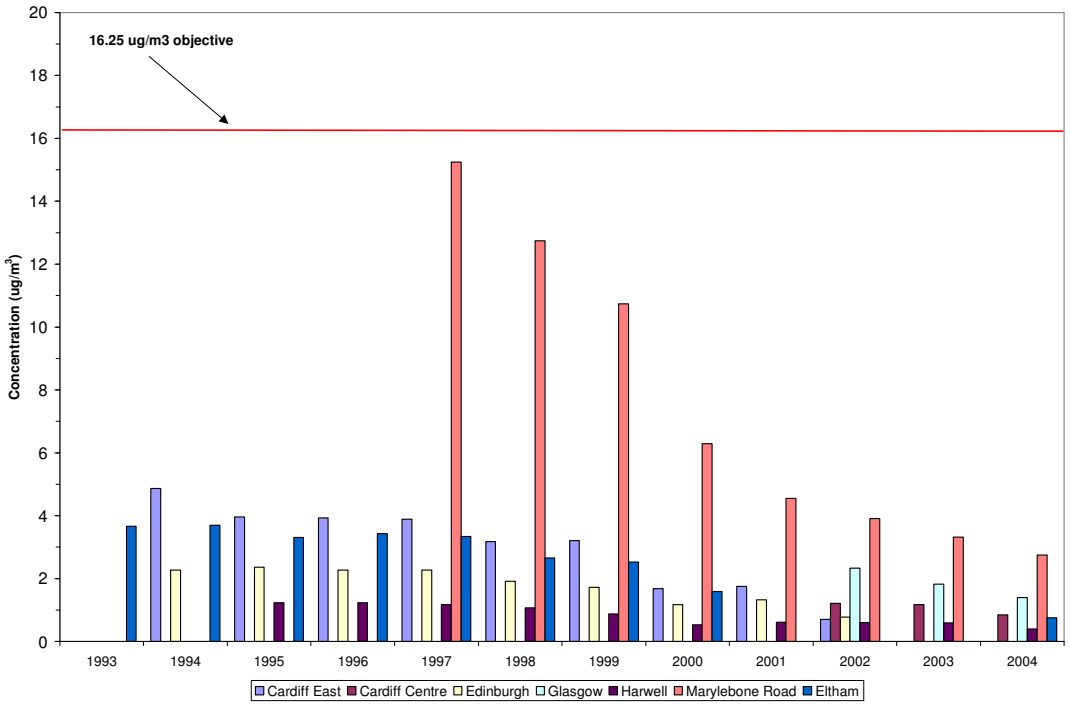


Figure 1. Mean benzene concentrations for the UK Automatic Hydrocarbon Network, 1993-2004

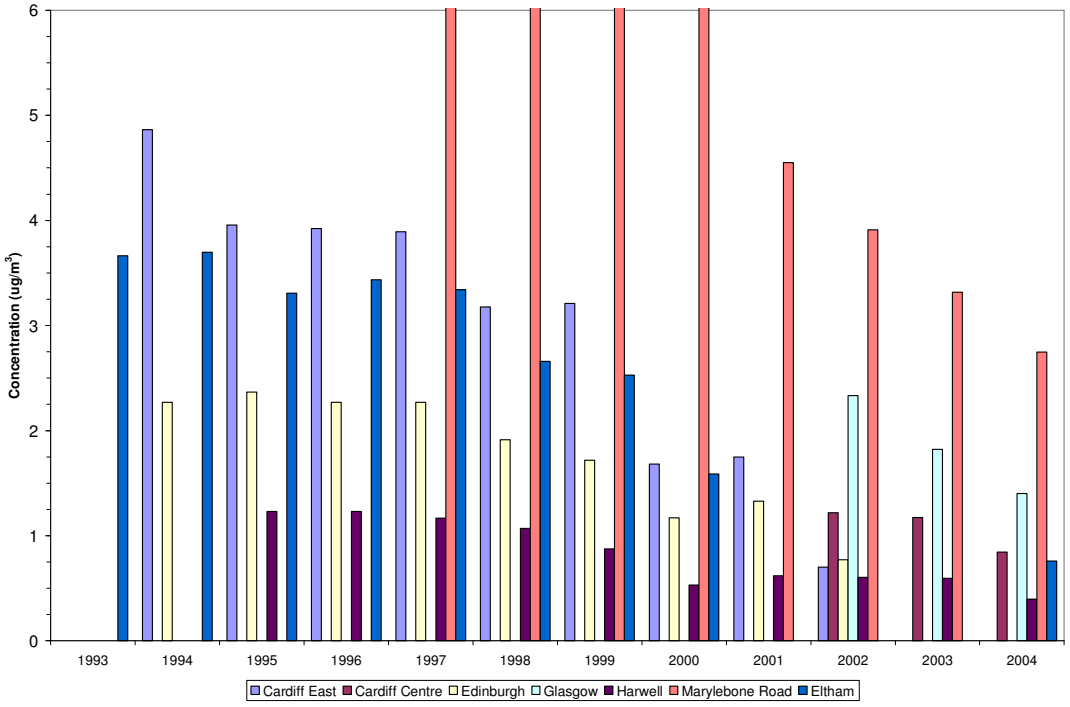


Figure 2. Mean benzene concentrations for the UK Automatic Hydrocarbon Network, 1993-2004 (magnified y-axis)

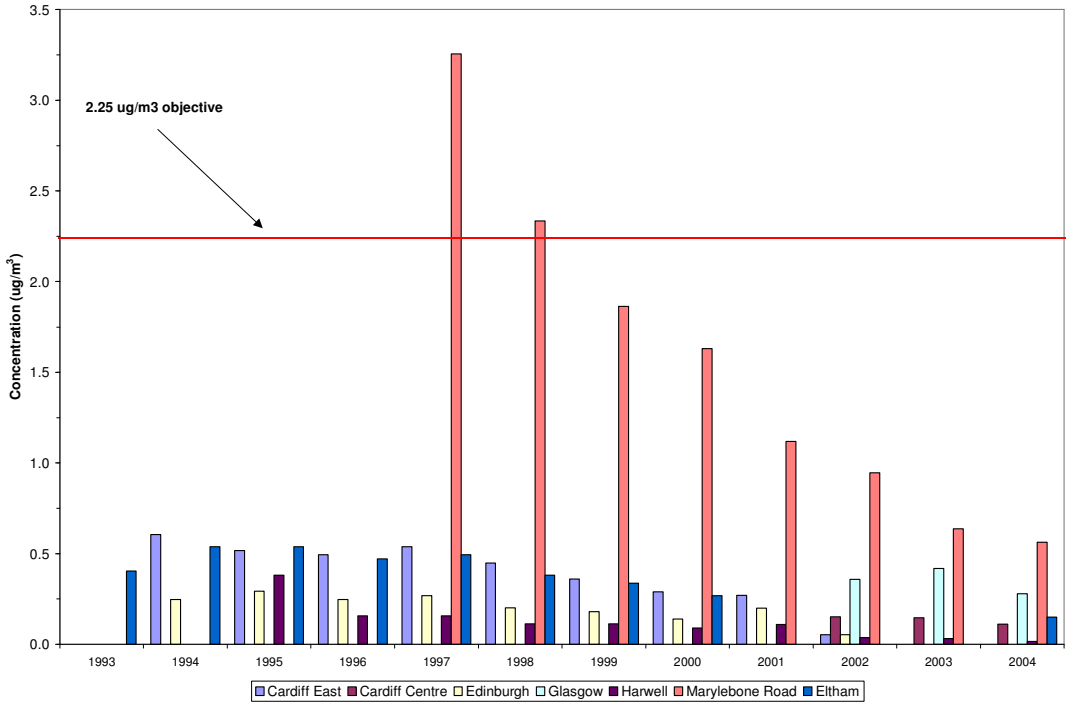


Figure 3. Mean 1,3-Butadiene concentrations for the UK Automatic Hydrocarbon Network, 1993-2004

# Appendix 6
# Trend Analysis Plots

## CONTENTS

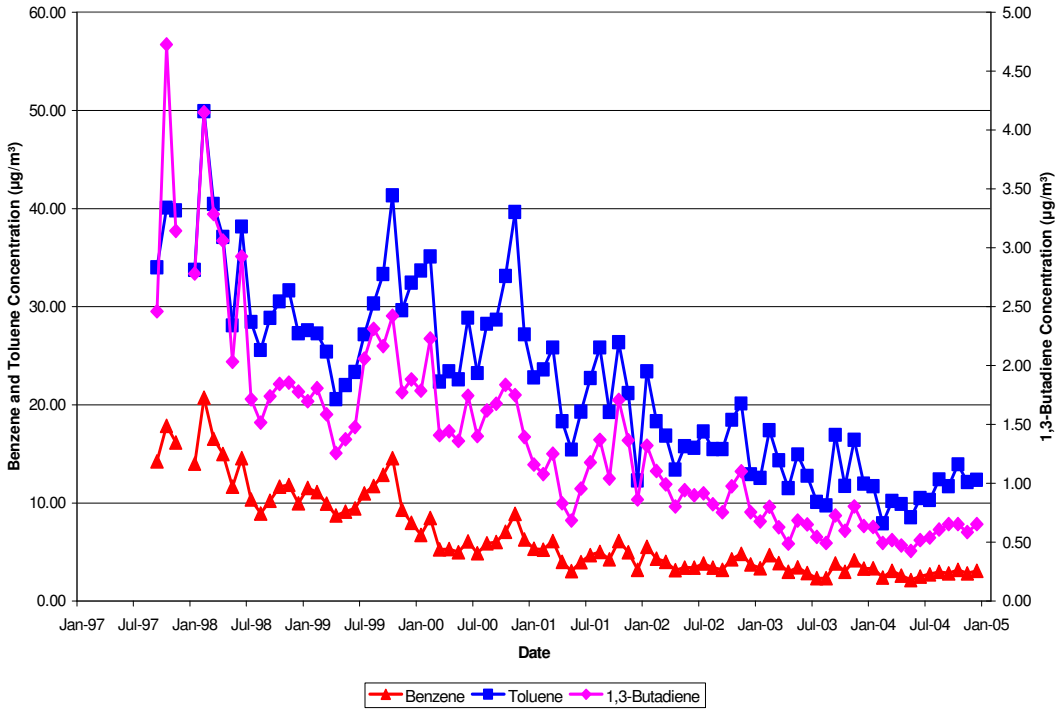


Figure 1. Plot of the monthly mean concentrations of benzene, toluene and 1,3-butadiene at the Marylebone Road site of the UK Hydrocarbon Network

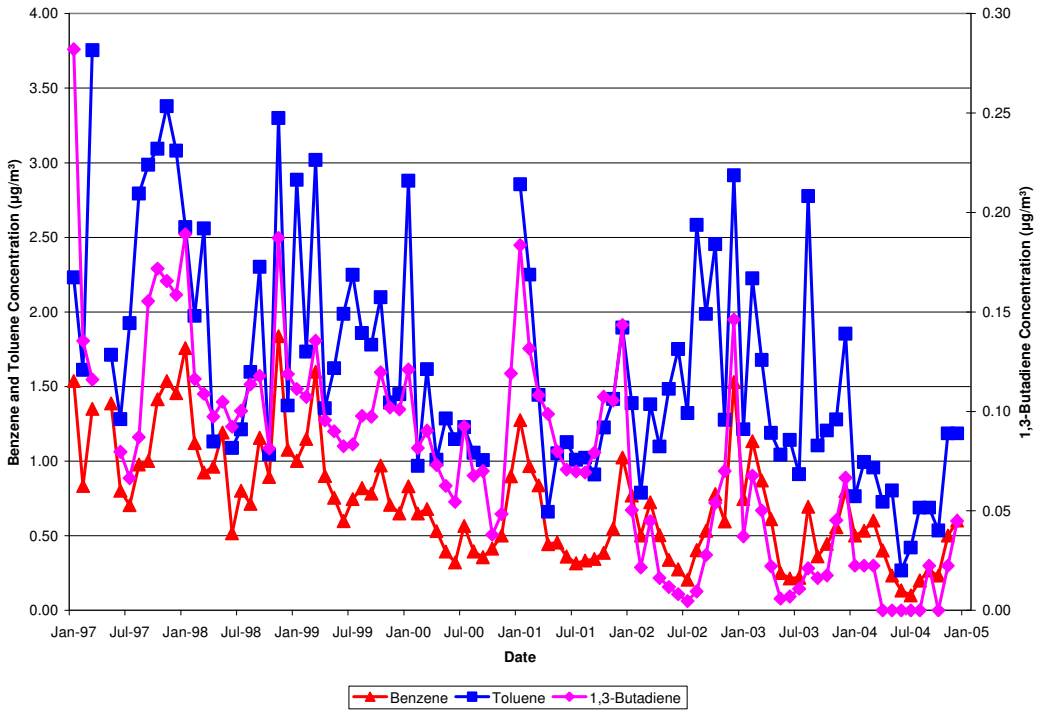


Figure 2. Plot of the monthly mean concentrations of benzene, toluene and 1,3-butadiene at the Harwell site of the UK Hydrocarbon Network

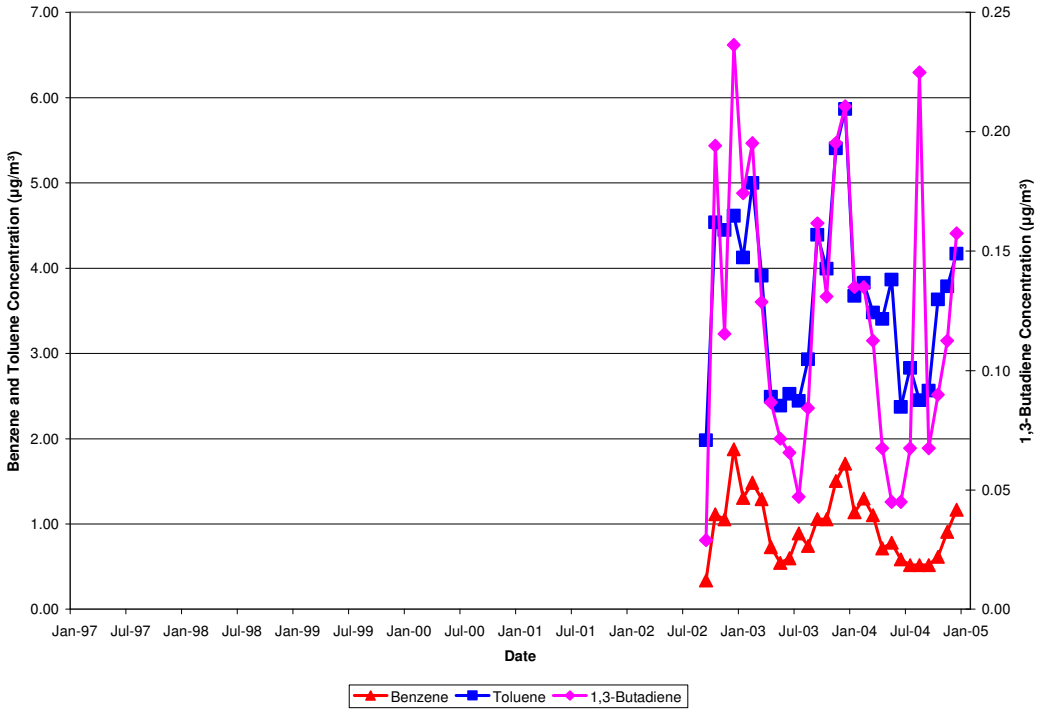


Figure 3. Plot of the monthly mean concentrations of benzene, toluene and 1,3-butadiene at the Cardiff Centre site of the UK Hydrocarbon Network

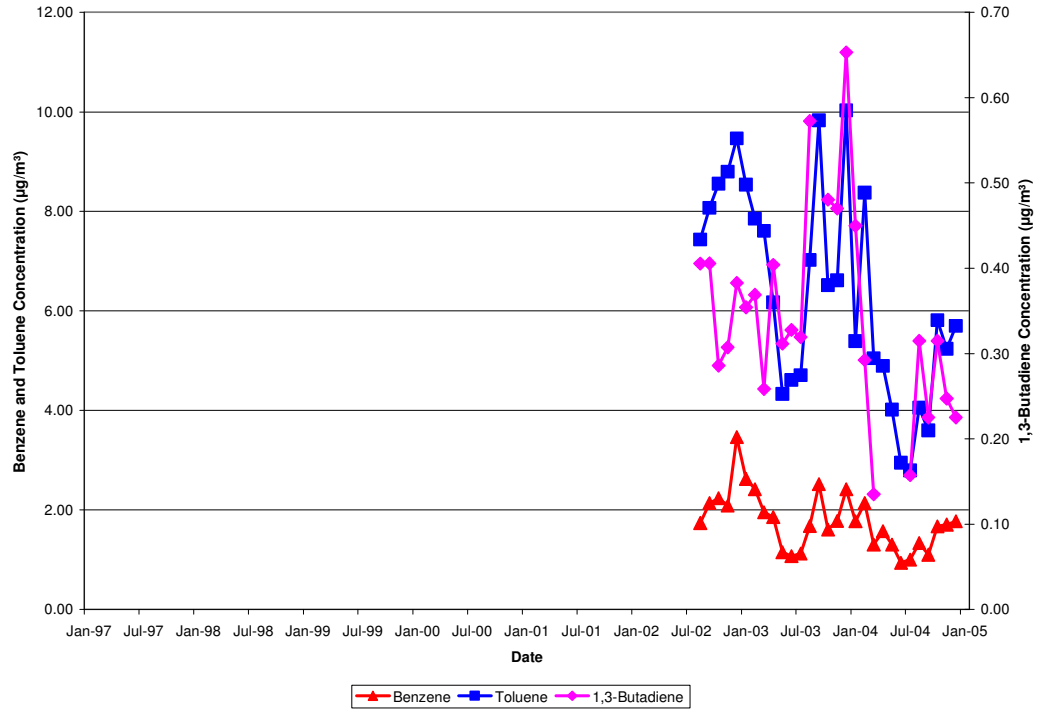


Figure 4. Plot of the monthly mean concentrations of benzene, toluene and 1,3-butadiene at the Glasgow site of the UK Hydrocarbon Network

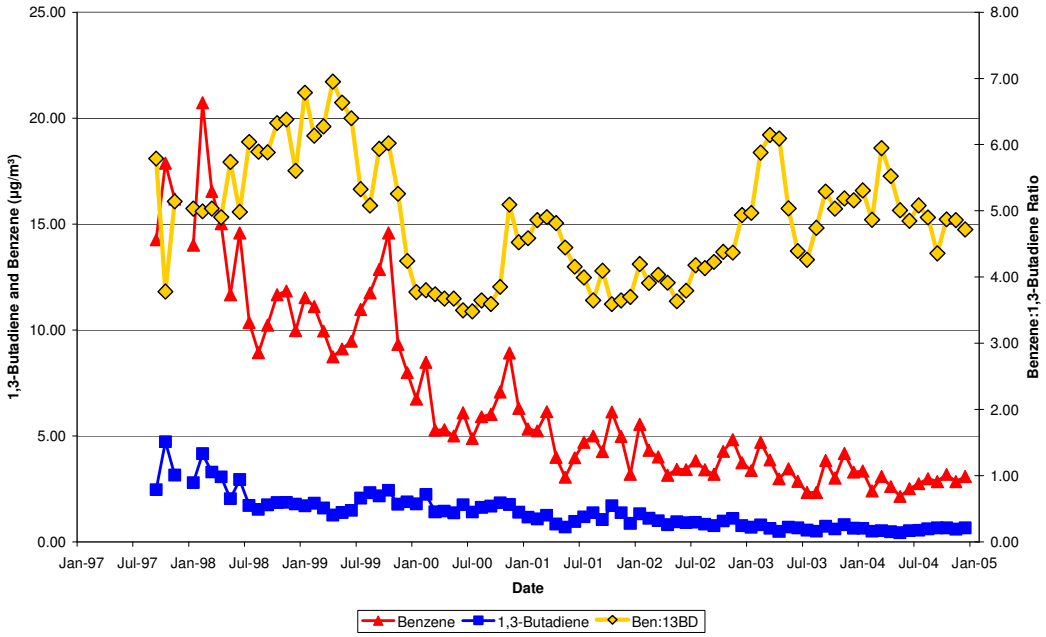


Figure 5. Plot of the monthly mean concentrations of benzene, 1,3-butadiene and the benzene: 1,3-butadiene ratio for the Marylebone Road site of the UK Hydrocarbon Network

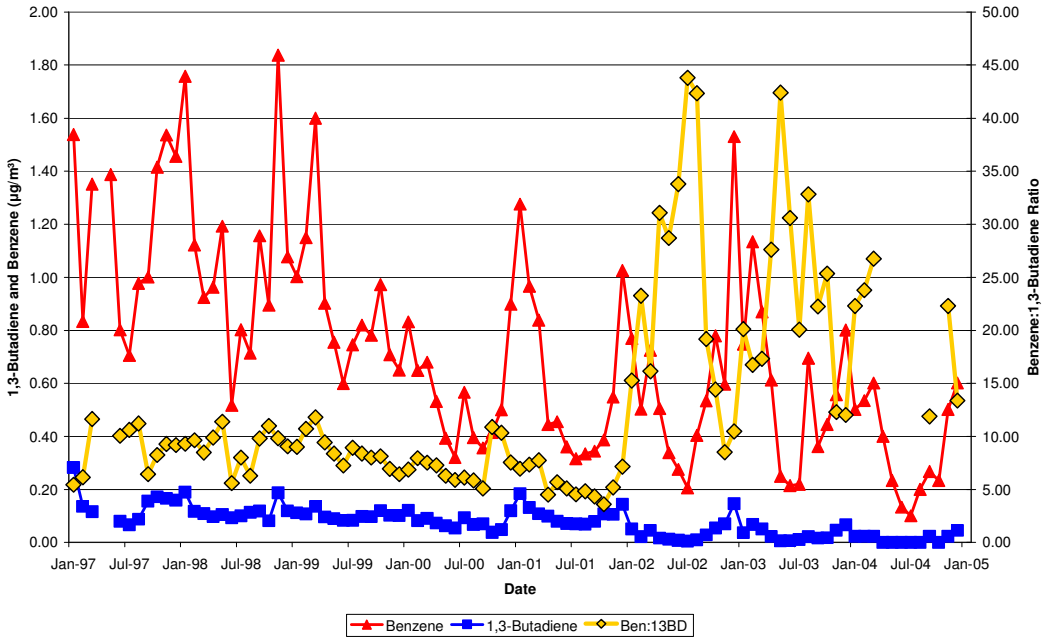


Figure 6. Plot of the monthly mean concentrations of benzene, 1,3-butadiene and the benzene: 1,3-butadiene ratio for the Harwell site of the UK Hydrocarbon Network

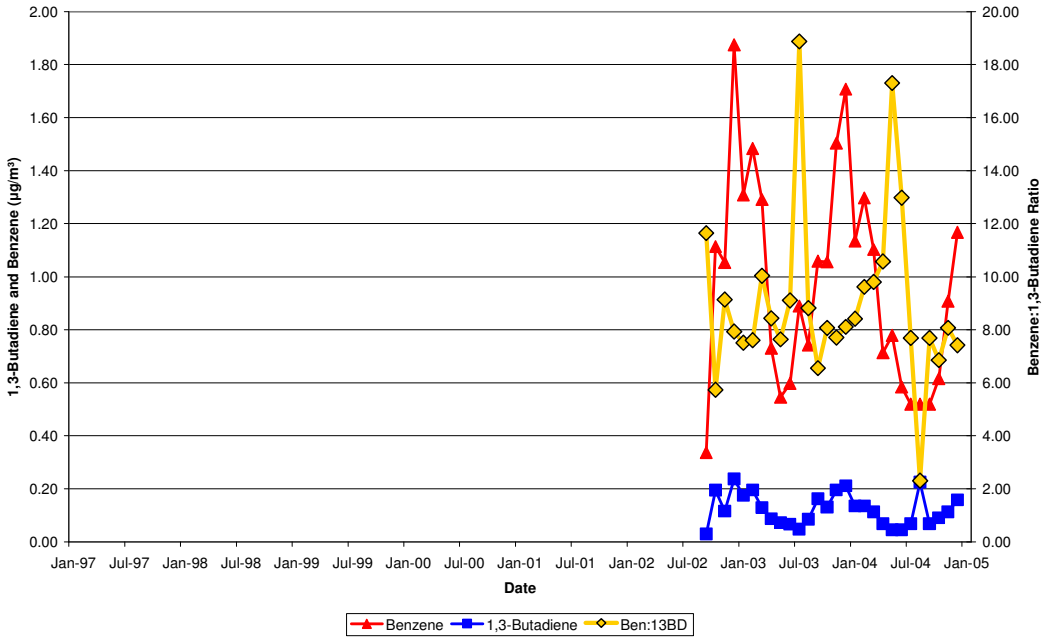


Figure 7. Plot of the monthly mean concentrations of benzene, 1,3-butadiene and the benzene: 1,3-butadiene ratio for the Cardiff Centre site of the UK Hydrocarbon Network

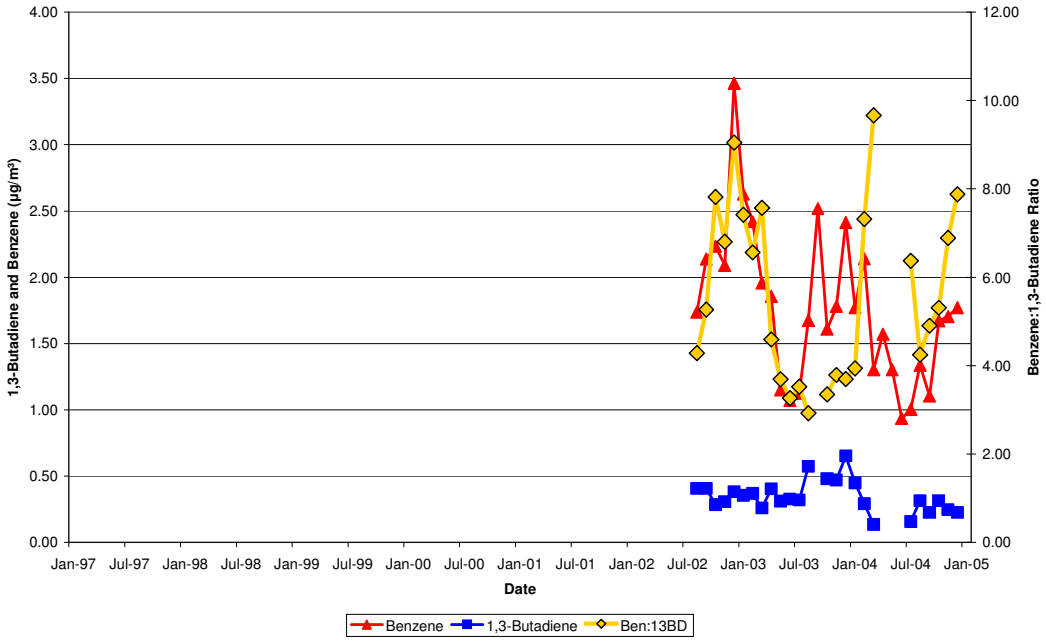


Figure 8. Plot of the monthly mean concentrations of benzene, 1,3-butadiene and the benzene: 1,3-butadiene ratio for the Glasgow site of the UK Hydrocarbon Network

# Appendix 7
# Eltham Annual Statistics and Time Series Plots

## CONTENTS

Table 1 Percentage data capture, maximum, mean and minimum values of ratified data from the Eltham site affiliated to the UK Hydrocarbon Network for the period; 1 January 2004 to 31 December 2004

| Compound | %data capture | Maximum hourly concentration ($\mu g/m^3$) | Mean concentration ($\mu g/m^3$) | Minimum hourly concentration ($\mu g/m^3$) |
|---|---|---|---|---|
| Ethane | 86.75 | 55.49 | 5.35 | 0.01 |
| Ethene | 85.31 | 14.83 | 0.96 | 0.01 |
| Propane | 76.95 | 44.20 | 3.18 | 0.00 |
| Propene | 63.44 | 7.33 | 0.57 | 0.00 |
| Ethyne | 70.63 | 8.08 | 0.65 | 0.01 |
| 2-Methylpropane | 80.11 | 44.61 | 2.18 | 0.00 |
| n-Butane | 81.23 | 59.01 | 3.90 | 0.02 |
| trans-2-Butene | 85.52 | 4.10 | 0.15 | 0.00 |
| 1-Butene | 84.67 | 3.14 | 0.17 | 0.00 |
| cis-2-Butene | 82.33 | 3.28 | 0.11 | 0.00 |
| 2-Methylbutane | 80.91 | 41.43 | 2.96 | 0.03 |
| n-Pentane | 83.44 | 12.81 | 0.93 | 0.03 |
| 1,3-Butadiene | 80.81 | 10.78 | 0.15 | 0.00 |
| trans-2-Pentene | 78.48 | 2.47 | 0.11 | 0.00 |
| cis-2-Pentene | 49.67 | 1.02 | 0.08 | 0.00 |
| 2-Methylpentane | 82.88 | 6.79 | 0.57 | 0.00 |
| 3-Methylpentane | 76.17 | 5.54 | 0.39 | 0.00 |
| Isoprene | 63.71 | 3.90 | 0.17 | 0.00 |
| n-Hexane | 79.27 | 28.35 | 0.08 | 0.00 |
| n-Heptane | 65.08 | 2.41 | 0.12 | 0.00 |
| Benzene | 82.29 | 15.18 | 0.76 | 0.00 |
| Toluene | 78.95 | 45.56 | 2.87 | 0.00 |
| Ethylbenzene | 58.34 | 5.69 | 0.21 | 0.00 |
| (m+p)-Xylene * | 64.88 | 23.23 | 0.84 | 0.00 |
| o-Xylene | 62.32 | 8.59 | 0.36 | 0.00 |
| 1,3,5-Trimethylbenzene | 31.85 | 4.59 | 0.16 | 0.00 |
| 1,2,4-Trimethylbenzene | 42.40 | 19.71 | 0.80 | 0.00 |

* (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.

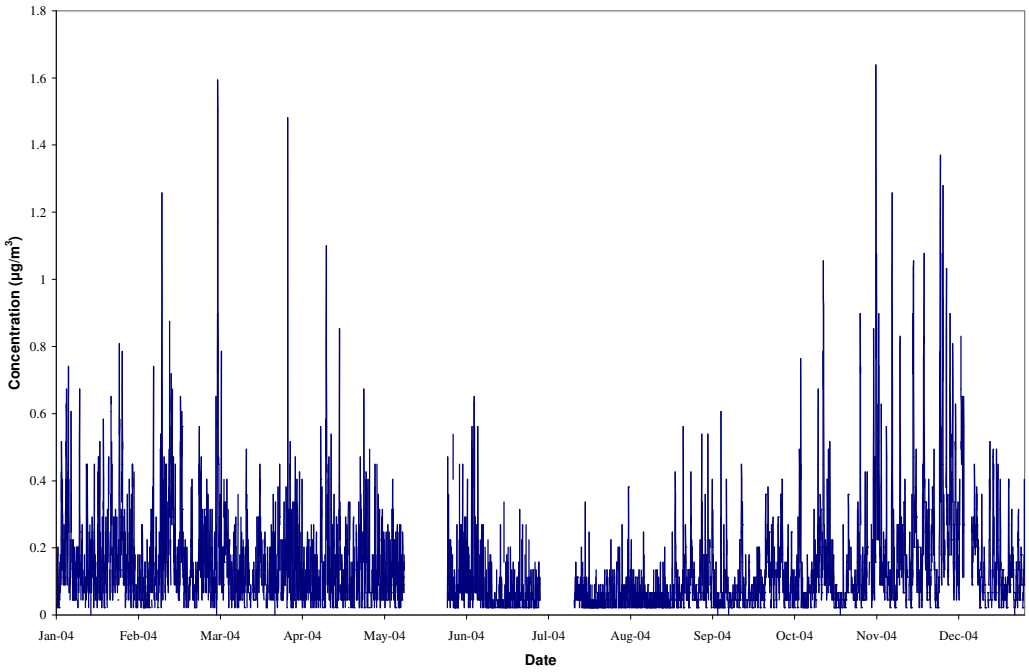


Figure 1. Time series plot of the ratified 1,3-butadiene data from the Eltham site of the UK Hydrocarbon Network, for the period; 1 January 2004 to 31 December 2004

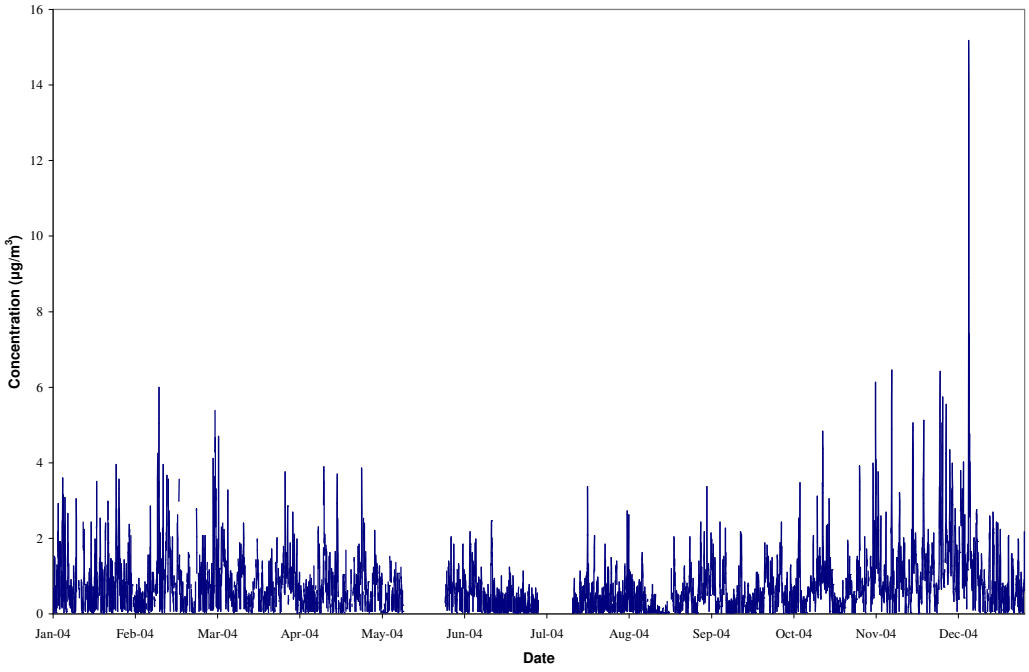


Figure 2. Time series plot of the ratified benzene data from the Eltham site of the UK Hydrocarbon Network, for the period; 1 January 2004 to 31 December 2004