## **REPORT**

# Annual summary of data produced by the UK Ambient Automatic Hydrocarbon Air Quality Network, 2006

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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#### 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 2006 to 31 December 2006. The ratified data have been made available on the World Wide Web at <a href="http://www.airquality.co.uk/archive/data">http://www.airquality.co.uk/archive/data</a> 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.

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 ( $\mu g/m^3$ ).

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### 2 Summary of network changes and related activity

The following section provides a summary of changes to the network during the reported year.

#### 2.1 AUCHENCORTH MOSS

The Auchencorth Moss site was commissioned during the reporting year. The site operates a Perkin Elmer ozone pre-cursor analyser, as installed at the London Eltham monitoring site. This will be used for reporting within the hydrocarbon monitoring network, and also to fulfil the UK's obligations to the EMEP monitoring network. Auchencorth Moss is one of the two EMEP designated 'supersites' for the UK, the other being Harwell in Oxfordshire. Data are reported for this site from 4 September 2006.

#### 2.2 HARWELL

During the reporting period the monitoring site was relocated within the Harwell campus. The existing monitoring cabin was decommissioned and the equipment moved to a nearby building where it was co-located with the AURN (inorganic) monitoring apparatus. As the new location was only approximately 200 meters from the original location and there was no change to the distance from nearest sources, a new site name or code was not deemed necessary.

### 3 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  $\mu$ g/m³ and  $\pm$  0.1  $\mu$ g/m³ below 0.5  $\mu$ g/m³.

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

Previous reports have used five separate data quality codes to describe the data. The separate quality codes are derived on the basis of the proportion of monthly data that is deemed either 'good' or 'acceptable'. These codes are shown below:-

- 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

On examination of data reported since 2002, predominantly data codes A and E have been used. On this basis a decision has been made to rationalise on the data codes used and all future data will be reported according to the following data codes: -

- A. all 'good' quality data
- B. all points 'acceptable' quality

### 4 Data Capture and Ratified Data

#### **4.1 DATA CAPTURE TARGETS**

The 3<sup>rd</sup> Daughter Directive relating to ozone in ambient air, states that volatile organic compounds (VOCs) should be monitored to assess their concentrations as ozone precursors. A data capture target is not specified for ozone precursor VOCs, however, it is important to achieve high data capture for all measured VOCs. The 2<sup>nd</sup> daughter directive relating to limit values for benzene and carbon monoxide in ambient air, sets the benzene minimum data capture target at 90%. The UK Air Quality Strategy suggests 1,3-butadiene data capture also be set to 90%. Defra have specified that all other VOC compounds have a minimum data capture target of 50%.

Tables 1 to 5, Appendix 1 contain statistical information relating to the ratified data, for each measured hydrocarbon, over the period 1 January 2006 to 31 December 2006. The tables list the percentage data capture, maximum concentration, mean concentration and minimum concentration of each hydrocarbon.

#### 4.2 THE RATIFIED DATA

The data capture and data quality codes for each site for benzene and 1,3-butadiene are summarised in table 2 below.

Table 2. Data capture summary

Site	Pollutant	Data capture %	Data Quality Code
Condiff	Benzene	89.3	Α
Cardiff	1,3-Butadiene	89.4	В
Classow	Benzene	92.3	Α
Glasgow	1,3-Butadiene	92.4	В
Harwell	Benzene	87.1	Α
пагмен	1,3-Butadiene	87.1	В
Marylebone	Benzene	77.1	Α
Road	1,3-Butadiene	70.7	Α
Auchencorth	Benzene	-	-
Moss	1,3-Butadiene	7.8	Α
Eltham	Benzene	80.5	Α
Eltham	1,3-Butadiene	79.7	Α

#### 4.2.1 Cardiff

For the Cardiff site data capture for benzene was 89.3% and for 1,3-butadiene was 89.4%. Data quality code B is applied to 1,3-butadiene and quality code A for all other compounds.

The major cause of data loss at the Cardiff site during the reporting period was due to a failure of the analyser column heater. This resulted in over 330 hours of lost data.

#### 4.2.2 Glasgow

For the Glasgow site the data capture for benzene was 92.3% and for 1,3-butadiene was 92.4%. Data quality code A is applied to all compounds.

The major cause of data loss at the Glasgow site during the reporting period was due to an ingress of water into the sample inlet. This caused a failure of the analyser and required the sample inlet to be removed, dried, re-sealed and re-installed. This resulted in over 220 hours of lost data.

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.

#### 4.2.3 Harwell

For the Harwell site the data capture for benzene was 87.1% and for 1,3-butadiene was 87.1%. Data quality code B is applied to 1,3-butadiene and quality code A for all other compounds.

The major cause of data loss at the Harwell site during the reporting period was the relocation of the site into the new monitoring point. This resulted in over 330 hours of lost data.

#### 4.2.4 Marylebone Road

For the Marylebone Road site the data capture for benzene was 77.1% and for 1,3-butadiene was 70.7%. Data quality code A is applied to all compounds.

Following routine Portable Electrical Appliance Testing in March, the site modem and PC were damaged and the repair was not completed until mid May. This resulted in over 1000 hours of lost data. Other periods of data loss are attributed to the PC controlling the analyser locking up and requiring a manual re-start.

#### 4.2.5 Eltham

For the Eltham site the data capture for benzene was 80.5% and for 1,3-butadiene was 79.7%. Data quality code A is applied to all compounds.

Significant data gaps at the Eltham site were the result of compressor failures; carrier gas failures, with the carrier gas being vented by the analyser; failures of the FID's and power cuts at the monitoring site.

#### 4.2.6 Auchencorth Moss

For the Auchencorth Moss site the data capture for 1,3-butadiene was 7.8%. Data quality code A is applied to all reported compounds. Benzene data are not reported for 2006 due to problems related to the column used for the measurement of the heavier ( $C_6$  and onwards) compounds. Both Perkin Elmer and AEA have investigated the issues surrounding this at great length. The analyser appeared to measure and report calibration data but all ambient data were rejected at ratification.

The low data capture is a function of the data not starting until 4 September. The data capture from the start date to the end of the calendar year is 24.2%. Data from this site have not been included in any comparative statistics as the results are not representative of a calendar year.

Because of the remote nature of the monitoring site and the access requirements, any issues that develop with the instrument take longer to rectify than if the site were located within a city centre. Other issues which have effected data capture during this period have been related to the power supply, communications links and failure of the carrier gas supply.

#### 4.3 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 Harwell and Cardiff has been assigned data quality code B.

#### 4.4 CONCENTRATION TRENDS

The periods when data for benzene and 1,3-butadiene were available 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, Harwell and Eltham 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 three 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, and they will have had little time to mix and react in the atmosphere. 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.

A comparison between Marylebone Road and Eltham has been made for 2006 to look at the relationship between a roadside site and an urban background site, measuring the same air mass. Figure 4, Appendix 3, shows that the ratio between the compounds measured is very similar at both sites, with levels at Eltham approximately half of those at Marylebone Road.

#### 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 2006 together with the annual means since 2000 are given in tables 1, 2, 4 and 5, Appendix 5. The maximum running annual means for 2006 are given in Tables 3 and 6, Appendix 5.

For benzene the annual means for 2002 to 2006 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 running annual means for 2006 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 2006 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 1993 to 2006 are plotted in figures 1 to 3, Appendix 3. 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 RUNNING ANNUAL MEANS**

The running annual means (RAMs) for benzene and 1,3-butadiene for 2006 are plotted in figures 1 to 5, Appendix 4.

For 1,3-butadiene the RAM concentration at the end of the year is less than that at the beginning of the year at all sites with the exception of Harwell. The Harwell 1,3 butadiene

RAM concentration undergoes a step change in early February. This occurs before the site relocation to the new monitoring site and is therefore not connected to that event. The Harwell site shows little change in the benzene RAM concentration.

The running annual mean of 1,3-butadiene, but to a greater degree benzene at Cardiff also shows various changes during 2006. These changes are to some extent attributable to the large data gap during 2005 when the site was off-line for an extended period.

The running annual means of both benzene and 1,3 butadiene show a relatively flat profile at Glasgow and Marylebone Road, with an overall decrease in concentrations across the year.

#### 4.7 ANALYSIS OF TRENDS OF MEASURED HYDROCARBONS

#### 4.7.1 Long term Trends

Figures 1 to 5, Appendix 6 are plots of the long-term trends of the monthly mean concentrations of benzene, toluene and 1,3-butadiene at the five sites that comprised the UK Automatic Hydrocarbon Network at the beginning of 2006.

Figures 1 and 2, the plots for the Cardiff Centre and Glasgow sites, cover a shorter time period due to the fact the sites were established during autumn 2002. Both sites show that during 2006 concentrations have generally reached a stable state with some evidence of seasonal variations.

Figure 3, the plot for the Harwell site, shows an overall decrease of the benzene, 1,3-butadiene concentrations since measurements began.

Figure 4, the plot for the Marylebone Road site shows a significant decrease of the concentration of all three hydrocarbons.

Figure 5, the plot for the Eltham site shows little in terms of a definitive trend since measurements started in 2004.

#### 4.7.2 Ratios of the concentrations of the measured hydrocarbons

Figure 6, Appendix 6 shows a plot of the monthly mean benzene: 1,3-butadiene ratios at hydrocarbon network sites. The measured concentrations are expressed as monthly means.

For the Marylebone Road site, data reported above have shown a decrease in the concentrations of both benzene and 1,3 butadiene, however there does not appear to be a consistent trend in the benzene:1,3-butadiene ratio.

The corresponding data for the Harwell site 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.

## **Appendices**

Appendix 1	Summary Statistical Information
Appendix 2	Time Series Plots of Hydrocarbon Concentrations
Appendix 3	Annual Mean Plots
Appendix 4	Rolling Annual Mean Plots
Appendix 5	Quarterly, annual and maximum running means
Annendix 6	Trend Analysis Plots

# Appendix 1 Summary Statistical Information

- 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 2006 to 31 December 2006
- 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 2006 to 31 December 2006
- 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 2006 to 31 December 2006
- Table 4. Percentage data capture, maximum, mean and minimum values of ratified data from the Marylebone Road site of the UK Hydrocarbon Network, for the period; 1 January 2006 to 31 December 2006
- Table 5. Percentage data capture, maximum, mean and minimum values of ratified data from the Eltham site of the UK Hydrocarbon Network, for the period; 1 January 2006 to 31 December 2006
- Table 6. Percentage data capture, maximum, mean and minimum values of ratified data from the Auchencorth Moss site of the UK Hydrocarbon Network, for the period; 1 January 2006 to 31 December 2006

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 2006 to 31 December 2006

Compound	% Data	Maximum	Mean	Minimum
	capture	hourly	concentration	hourly
		concentration	(μg/m³)	concentration
		(μg/m³)		(μg/m³)
1,3-Butadiene	89.4	6.06	0.09	0.00
Benzene	89.3	24.10	0.78	0.00
Toluene	89.4	232.72	2.48	0.15
Ethylbenzene	87.5	6.65	0.34	0.00
(m+p)-Xylene *	89.4	23.58	1.32	0.00
o-Xylene	85.7	12.65	0.88	0.00

 $<sup>^{*}</sup>$  (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 2006 to 31 December 2006

Compound	% Data	Maximum	Mean	Minimum
	capture	hourly	concentration	hourly
		concentration	(μg/m³)	concentration
		(μg/m³)		(μg/m³)
1,3-Butadiene	92.4	4.33	0.17	0.00
Benzene	92.3	14.27	1.07	0.00
Toluene	93.2	128.48	3.88	0.15
Ethylbenzene	76.0	68.62	0.78	0.04
(m+p)-Xylene *	92.5	109.21	2.58	0.09
o-Xylene	85.6	29.48	2.54	0.04

 $<sup>^*</sup>$  (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 2006 to 31 December 2006

Compound	% Data capture	Maximum hourly concentration (µg/m³)	Mean concentration (μg/m³)	Minimum hourly concentration (µg/m³)
1,3-Butadiene	87.1	7.27	0.02	0.00
Benzene	87.1	6.62	0.40	0.00
Toluene	84.3	34.69	0.73	0.00
Ethylbenzene	54.6	6.30	0.16	0.00
(m+p)-Xylene *	74.3	16.92	0.41	0.00
o-Xylene	53.3	6.08	0.24	0.00

<sup>\* (</sup>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 2006 to 31 December 2006

Compound	% Data	Maximum	Mean	Minimum
P 1 1	capture	hourly	concentration	hourly
	•	concentration	(μg/m <sup>3</sup> )	concentration
		$(\mu g/m^3)$	, ,	$(\mu g/m^3)$
Ethane	71.6	122.95	10.04	0.00
Ethene	71.5	25.08	3.91	0.00
Propane	70.6	120.57	6.25	0.00
Propene	67.1	24.99	2.03	0.00
Ethyne	68.8	16.28	2.53	0.00
2-Methylpropane	70.6	36.34	4.82	0.00
n-Butane	71.1	75.41	8.32	0.00
trans-2-Butene	63.1	8.92	0.58	0.00
1-Butene	65.8	8.68	0.53	0.00
cis-2-Butene	68.8	8.75	0.42	0.00
2-Methylbutane	71.2	108.16	8.96	0.00
n-Pentane	71.6	34.78	2.79	0.00
1,3-Butadiene	70.7	8.73	0.40	0.00
trans-2-Pentene	68.6	10.62	0.56	0.00
1-Pentene	68.7	10.74	0.32	0.00
2-Methylpentane	71.4	30.50	2.72	0.00
n-Hexane	71.4	16.27	1.14	0.00
Isoprene	29.4	0.99	0.20	0.03
Benzene	77.1	14.53	1.92	0.00
2,2,4-trimethylpentane	74.8	13.70	1.47	0.00
n-Heptane	75.4	30.77	0.63	0.00
n-Octane	71.0	18.96	0.23	0.00
Toluene	77.9	98.80	7.89	0.00
Ethylbenzene	78.0	18.07	1.20	0.00
(m+p)-Xylene *	77.9	62.27	4.53	0.00
o-Xylene	77.9	22.83	1.68	0.00
1,3,5-Trimethylbenzene	77.4	17.01	0.52	0.00
1,2,4-Trimethylbenzene	77.8	24.20	1.69	0.00
1,2,3-Trimethylbenzene	76.8	15.02	0.75	0.00

<sup>\*</sup> (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.

Table 5. 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 2006 to 31 December 2006

Compound	% Data capture	Maximum hourly	Mean concentration	Minimum hourly
		concentration	(μg/m³)	concentration
		(μg/m³)	(, 5, ,	(μg/m³)
Ethane	79.1	84.39	6.04	0.00
Ethene	78.7	19.93	1.17	0.00
Propane	81.8	33.51	3.00	0.00
Propene	80.7	9.74	0.48	0.00
Ethyne	80.5	8.05	0.64	0.00
2-Methylpropane	81.8	42.25	1.85	0.00
n-Butane	81.6	51.17	3.15	0.00
trans-2-Butene	77.9	2.82	0.15	0.00
1-Butene	77.1	2.35	0.12	0.00
cis-2-Butene	78.4	2.44	0.09	0.00
2-Methylbutane	81.7	73.31	2.02	0.00
n-Pentane	81.7	16.91	0.72	0.00
1,3-Butadiene	79.7	1.30	0.08	0.00
trans-2-Pentene	73.6	2.62	0.07	0.00
1-Pentene	73.1	2.39	0.07	0.00
2-Methylpentane	81.8	8.90	0.51	0.00
n-Hexane	81.3	25.07	0.37	0.00
Isoprene	74.7	6.14	0.25	0.00
Benzene	80.5	9.27	0.96	0.03
2,2,4-trimethylpentane	58.1	7.68	0.51	0.05
n-Heptane	75.5	4.86	0.28	0.04
n-Octane	68.2	1.66	0.09	0.00
Toluene	81.4	49.65	2.06	0.08
Ethylbenzene	81.1	5.51	0.35	0.04
(m+p)-Xylene *	80.8	35.57	1.05	0.04
o-Xylene	80.7	8.24	0.38	0.04
1,3,5-Trimethylbenzene	72.1	10.73	0.16	0.00
1,2,4-Trimethylbenzene	74.6	12.77	0.39	0.00
1,2,3-Trimethylbenzene	71.5	6.09	0.29	0.00

<sup>\* (</sup>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.

Table 6. Percentage data capture, maximum, mean and minimum values of ratified data from the Auchencorth Moss site of the UK Hydrocarbon Network for the period; 1 January 2006 to 31 December 2006

Compound	% Data capture	Maximum hourly	Mean concentration	Minimum hourly
	•	concentration	$(\mu g/m^3)$	concentration
		(μg/m³)		(μg/m³)
Ethane	12.8	1.06	0.35	0
Ethene	8.9	0.65	0.05	0
Propane	8.9	0.75	0.26	0
Propene	6.6	0.12	0.03	0
Ethyne	5.2	0.1	0.02	0
2-Methylpropane	4.2	0.41	0.07	0
n-Butane	7.6	0.7	0.13	0
trans-2-Butene	12.6	0.05	0.02	0
1-Butene	9.8	0.07	0.01	0
cis-2-Butene	12.5	0.07	0.00	0
2-Methylbutane	7.5	0.39	0.06	0
n-Pentane	7.0	0.24	0.05	0
1,3-Butadiene	7.8	0.16	0.02	0
trans-2-Pentene				
1-Pentene				
2-Methylpentane				
n-Hexane				
Isoprene	5.1	0.9	0.05	0
Benzene				
2,2,4-trimethylpentane				
n-Heptane				
n-Octane				
Toluene				
Ethylbenzene				
(m+p)-Xylene *				
o-Xylene				
1,3,5-Trimethylbenzene				
1,2,4-Trimethylbenzene				
1,2,3-Trimethylbenzene				

<sup>\* (</sup>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.

The data capture figures quoted above are for the calendar year, although the analyser system was not installed until 4 September.

# Appendix 2 Time Series Plots of Hydrocarbon Concentrations

- Figure 1. Time series plot of the ratified benzene data from the Cardiff site of the UK Hydrocarbon Network, for the period; 1 January 2006 to 31 December 2006
- 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 2006 to 31 December 2006
- Figure 3. Time series plot of the ratified benzene data from the Glasgow site of the UK Hydrocarbon Network, for the period; 1 January 2006 to 31 December 2006
- Figure 4. Time series plot of the ratified 1,3-butadiene data from the Glasgow site of the UK Hydrocarbon Network, for the period; 1 January 2006 to 31 December 2006
- Figure 5. Time series plot of the ratified benzene data from the Harwell site of the UK Hydrocarbon Network, for the period; 1 January 2006 to 31 December 2006
- Figure 6. Time series plot of the ratified 1,3-butadiene data from the Harwell site of the UK Hydrocarbon Network, for the period; 1 January 2006 to 31 December 2006
- Figure 7. Time series plot of the ratified benzene data from the Marylebone Road site affiliated to the UK Hydrocarbon Network, for the period; 1 January 2006 to 31 December 2006
- Figure 8. Time series plot of the ratified 1,3-butadiene data from the Marylebone Road site affiliated to the UK Hydrocarbon Network, for the period; 1 January 2006 to 31 December 2006
- Figure 9. Time series plot of the ratified benzene data from the Eltham site of the UK Hydrocarbon Network, for the period; 1 January 2006 to 31 December 2006

- Figure 10. Time series plot of the ratified 1,3-butadiene data from the Eltham site of the UK Hydrocarbon Network, for the period; 1 January 2006 to 31 December 2006
- Figure 11. Time series plot of the ratified 1,3-butadiene data from the Auchencorth Moss site of the UK Hydrocarbon Network, for the period; 1 January 2006 to 31 December 2006

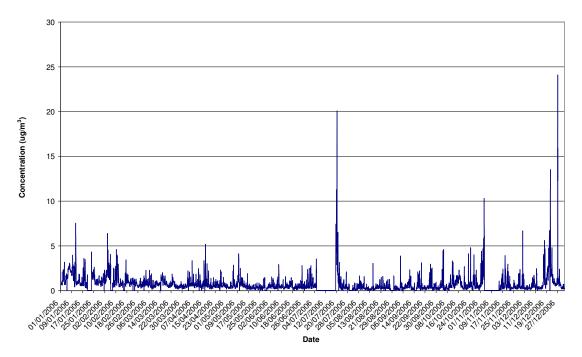


Figure 1. Time series plots for the ratified benzene data from the Cardiff site of the UK Hydrocarbon Network, for the period; 1 January 2006 to 31 December 2006

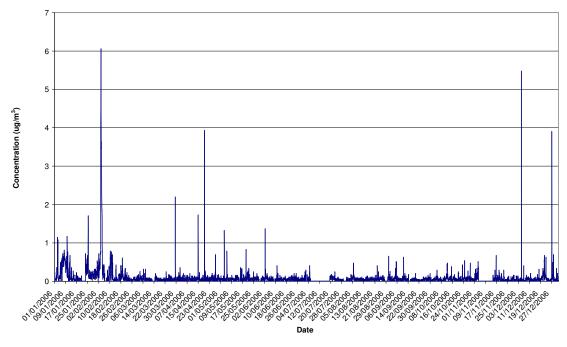


Figure 2. Time series plots for the ratified 1,3-butadiene data from the Cardiff site of the UK Hydrocarbon Network, for the period; 1 January 2006 to 31 December 2006

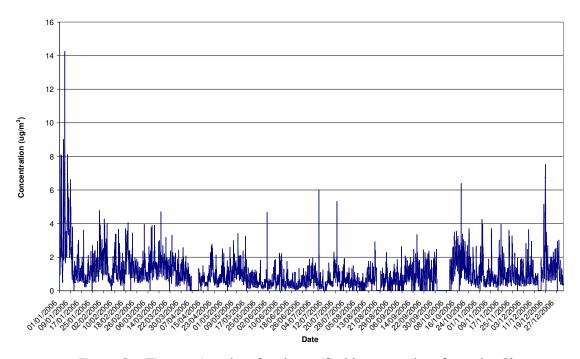


Figure 3. Time series plots for the ratified benzene data from the Glasgow site of the UK Hydrocarbon Network, for the period; 1 January 2006 to 31 December 2006

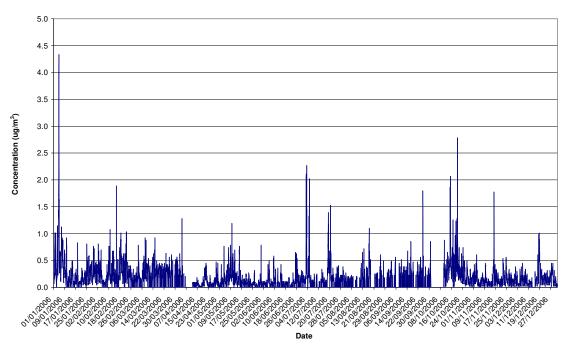


Figure 4. Time series plots for the ratified 1,3-butadiene data from the Glasgow site of the UK Hydrocarbon Network, for the period; 1 January 2006 to 31 December 2006

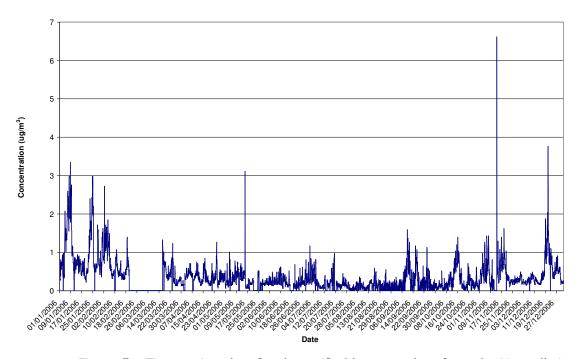


Figure 5. Time series plots for the ratified benzene data from the Harwell site of the UK Hydrocarbon Network, for the period; 1 January 2006 to 31 December 2006

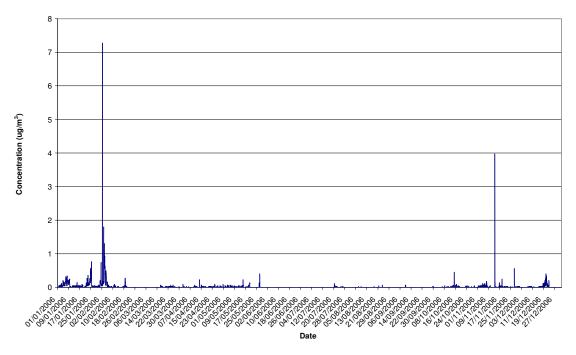


Figure 6. Time series plots for the ratified 1,3-butadiene data from the Harwell site of The UK Hydrocarbon Network, for the period; 1 January 2006 to 31 December 2006

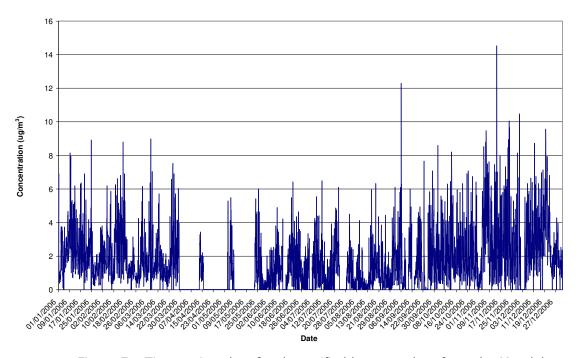


Figure 7. Time series plots for the ratified benzene data from the Marylebone Road site affiliated to the UK Hydrocarbon Network, for the period; 1 January 2006 to 31 December 2006

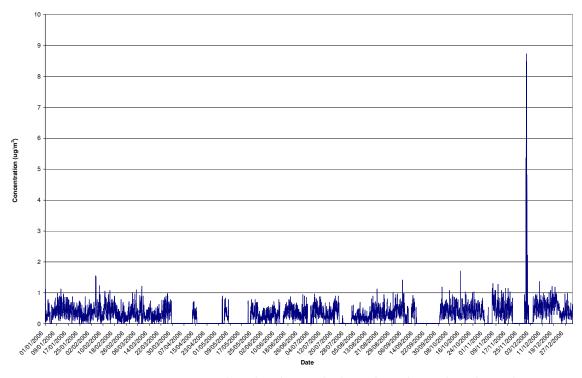


Figure 8. Time series plots for the ratified 1,3-butadiene data from the Marylebone Road site affiliated to the UK Hydrocarbon Network, for the period; 1 January 2006 to 31 December 2006

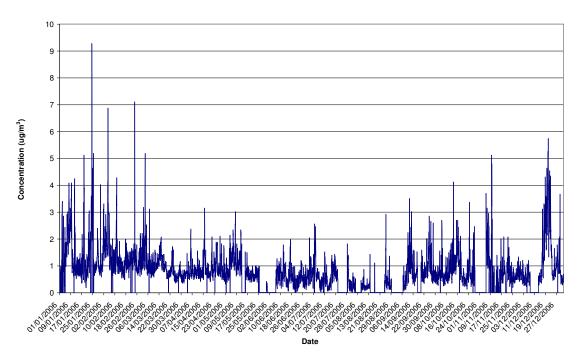


Figure 9. Time series plots for the ratified benzene data from the Eltham site of the UK Hydrocarbon Network, for the period; 1 January 2006 to 31 December 2006

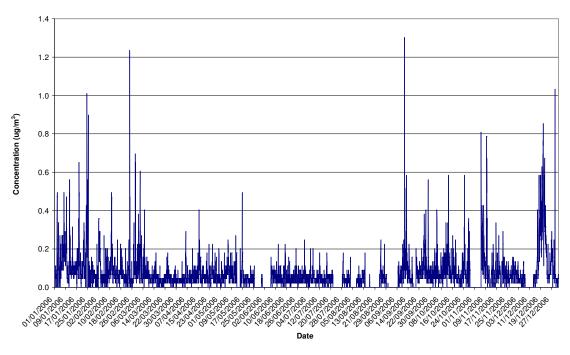


Figure 10. Time series plots for the ratified 1,3-butadiene data from the Eltham site of the UK Hydrocarbon Network, for the period; 1 January 2006 to 31 December 2006

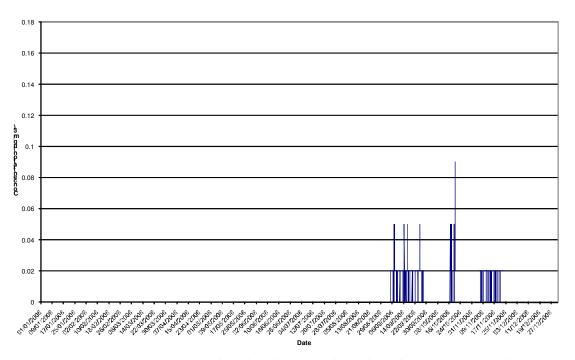


Figure 11. Time series plots for the ratified 1,3-butadiene data from the Auchencorth Moss site of the UK Hydrocarbon Network, for the period; 1 January 2006 to 31 December 2006

# **Appendix 3 Annual Mean Plots**

Figure 1.	Mean Benzene concentrations for the UK Automatic Hydrocarbon Network, 1993-2006
Figure 2.	Mean Benzene concentrations for the UK Automatic Hydrocarbon Network, 1993-2006 (magnified y-axis),
Figure 3.	Mean 1,3-Butadiene concentrations for the UK Automatic Hydrocarbon Network, 1993-2006
Figure 4.	Mean concentrations for all compounds measured at Marylebone road and Eltham for the UK Automatic Hydrocarbon Network, for 2006

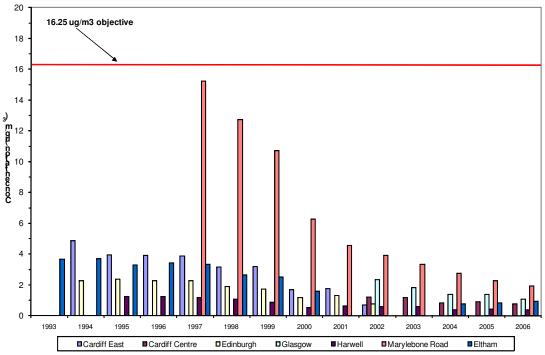


Figure 1. Mean benzene concentrations for the UK Automatic Hydrocarbon Network, 1993-2006

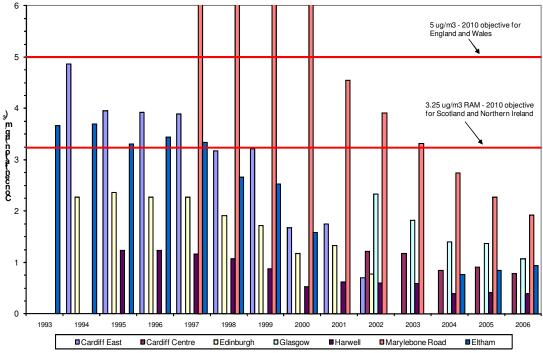


Figure 2. Mean Benzene concentrations for the UK Automatic Hydrocarbon Network, 1993-2006 (magnified y-axis)

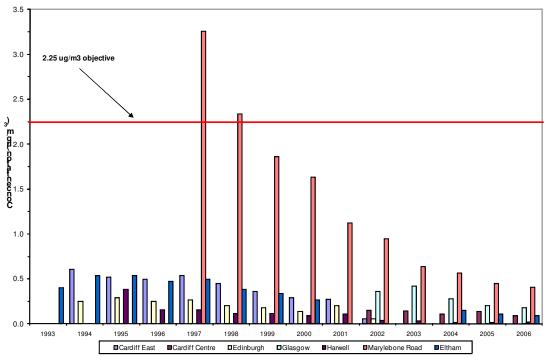


Figure 3. Mean 1,3-Butadiene concentrations for the UK Automatic Hydrocarbon Network, 1993-2006

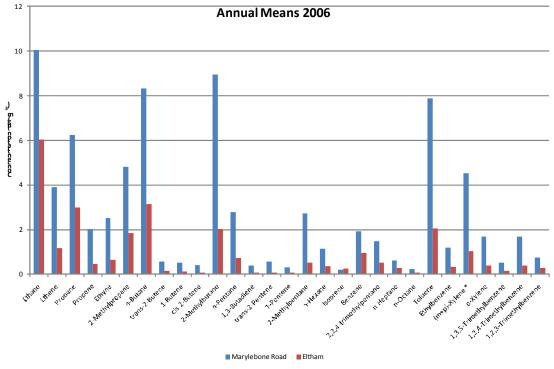


Figure 4. Mean concentrations for all compounds measured at Marylebone Road and Eltham for the UK Automatic Hydrocarbon Network, for 2006

# **Appendix 4 Running Annual Mean Plots**

- Figure 1. Time series plot of the running annual mean for benzene and 1,3-butadiene data from the Cardiff site of the UK Hydrocarbon Network, for the period; January 2006 to December 2006
- Figure 2. Time series plot of the running annual mean for benzene and 1,3-butadiene data from the Glasgow site of the UK Hydrocarbon Network, for the period; January 2006 to December 2006
- Figure 3. Time series plot of the running annual mean for benzene and 1,3-butadiene data from the Harwell site of the UK Hydrocarbon Network, for the period; January 2006 to December 2006
- Figure 4. Time series plot of the running annual mean for benzene and 1,3-butadiene data from the Marylebone Road site affiliated to the UK Hydrocarbon Network, for the period; January 2006 to December 2006
- Figure 5. Time series plot of the running annual mean for benzene and 1,3-butadiene data from the Eltham site of the UK Hydrocarbon Network, for the period; January 2006 to December 2006

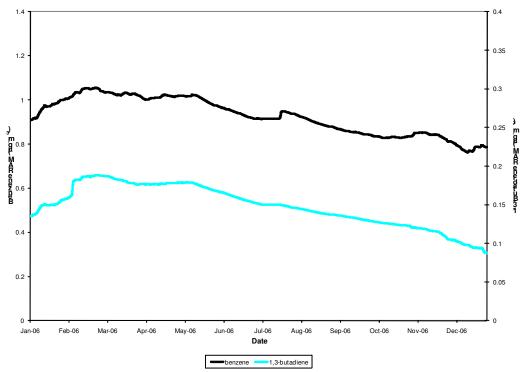


Figure 1. Time series plot of the running annual mean for benzene and 1,3-butadiene data from the Cardiff site of the UK Hydrocarbon Network, for the period; January 2006 to December 2006

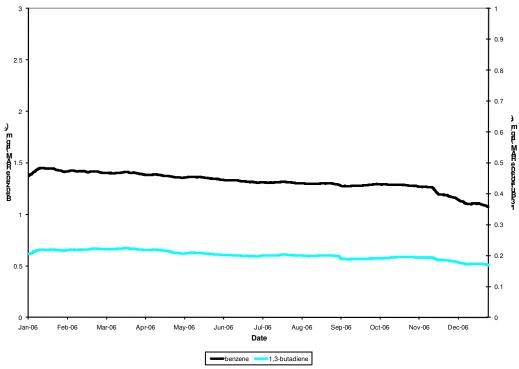


Figure 2. Time series plot of the running annual mean for benzene and 1,3-butadiene data from the Glasgow site of the UK Hydrocarbon Network, for the period; January 2006 to December 2006

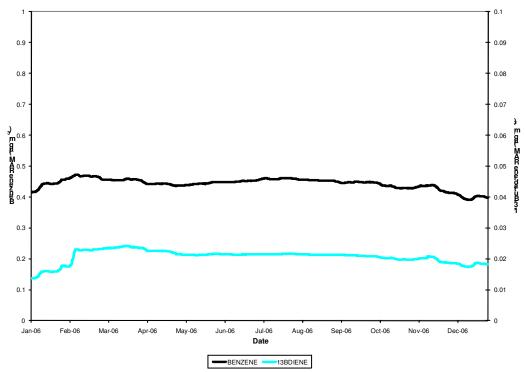


Figure 3. Time series plot of the running annual mean for benzene and 1,3-butadiene data from the Harwell site of the UK Hydrocarbon Network, for the period; January 2006 to December 2006

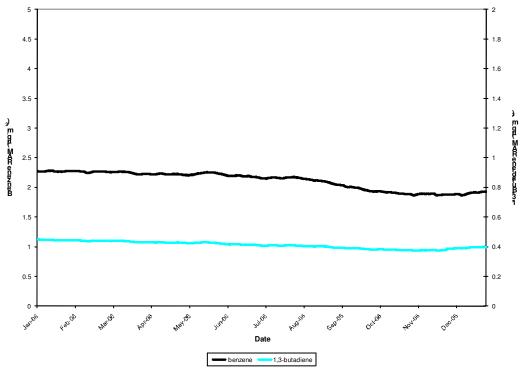


Figure 4. Time series plot of the running annual mean for benzene and 1,3-butadiene data from the Marylebone Road site affiliated to the UK Hydrocarbon Network, for the period; January 2006 to December 2006

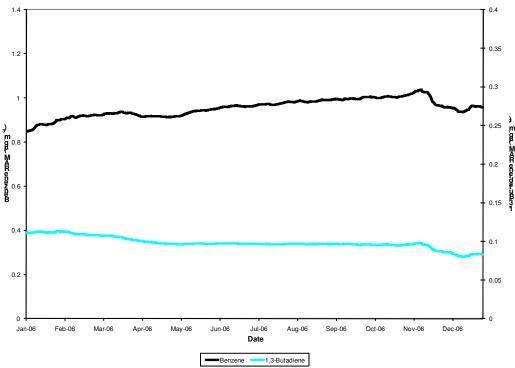


Figure 5. Time series plot of the running annual mean for benzene and 1,3-butadiene data from the Eltham site of the UK Hydrocarbon Network, for the period; January 2006 to December 2006

# Appendix 5 Quarterly, annual and maximum running means

- Table 1. Quarterly means of measured benzene concentrations  $(\mu g/m^3)$  at each of the UK Automatic Hydrocarbon Sites.
- Table 2. Annual means of measured benzene concentrations ( $\mu$ g/m<sup>3</sup>) at each of the UK Automatic Hydrocarbon Sites.
- Table 3. Maximum running means of measured benzene concentrations ( $\mu g/m^3$ ) at each of the UK Automatic Hydrocarbon Sites.
- Table 4. Quarterly means of measured 1,3-butadiene concentrations  $(\mu g/m^3)$  at each of the UK Automatic Hydrocarbon Sites.
- Table 5. Annual Means of measured 1,3-butadiene concentrations  $(\mu g/m^3)$  at each of the UK Automatic Hydrocarbon Sites.
- Table 6. Maximum running means of measured 1,3-butadiene concentrations ( $\mu g/m^3$ ) at each of the UK Automatic Hydrocarbon Sites.

Table 1. Quarterly means of measured benzene concentrations (μg/m³) at each of the UK Automatic Hydrocarbon Sites, 2006.

Monitoring Site	Quarter 1	Quarter 2	Quarter 3	Quarter 4
	2006	2006	2006	2006
	Mean	Mean	Mean	Mean
Cardiff Centre	1.06	0.60	0.59	0.88
Glasgow	1.57	0.74	0.78	1.18
Harwell	0.78	0.30	0.21	0.39
Marylebone Road	1.97	1.38	1.42	2.53
Eltham	1.26	0.79	0.65	1.01

<sup>\$</sup> No benzene measured for the quarter.

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

Monitoring Site	2002	2003	2004	2005	2006	2006
	Annual	Annual	Annual	Annual	Annual	Data
	Mean	Mean	Mean	Mean	Mean	Capture
						%
Cardiff Centre	1.22\$	1.17	0.84	0.91	0.78	89.3
Glasgow	2.33 \$	1.82	1.40	1.36	1.07	92.3
Harwell	0.60	0.59	0.40	0.42	0.39	87.1
Marylebone Road	3.91	3.32	2.75	2.27	1.92	77.1
Eltham	\$\$\$\$	\$\$\$\$	0.76	0.84	0.94	80.5

<sup>\$</sup> Annual means calculated from significantly less than 12 months data

Table 3. Maximum running annual means of measured benzene concentrations (μg/m³) at each of the UK Automatic Hydrocarbon Sites.

Monitoring Site	2006	2006
	Maximum running	MRAM Data
	annual mean	Capture %
Cardiff Centre	1.05	49.9
Glasgow	1.45	93.3
Harwell	0.47	96.3
Marylebone Road	2.28	86.1
Eltham	1.04	82.0

<sup>\$\$</sup> 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 \$\$\$\$ The Eltham site was installed on 17<sup>th</sup> October 2003

Table 4. Quarterly means of measured 1,3-butadiene concentrations (µg/m³) at each of the UK Automatic Hydrocarbon Sites.

Monitoring Site	Quarter 1	Quarter 2	Quarter 3	Quarter 4
	2006	2006	2006	2006
	Mean	Mean	Mean	Mean
Cardiff Centre	0.17	0.06	0.05	0.07
Glasgow	0.26	0.10	0.13	0.19
Harwell	0.07	0.00	0.00	0.01
Marylebone Road	0.37	0.34	0.35	0.50
Eltham	0.10	0.06	0.06	0.11

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

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

Monitoring Site	2002	2003	2004	2005	2006	2006
	Annual	Annual	Annual	Annual	Annual	Data
	Mean	Mean	Mean	Mean	Mean	Capture %
Cardiff Centre	0.15\$	0.15	0.11	0.13	0.09	89.4
Glasgow	0.36\$	0.42	0.28	0.20	0.18	92.4
Harwell	0.04	0.03	0.02	0.02	0.02	87.1
Marylebone Road	0.95	0.64	0.56	0.45	0.41	70.7
Eltham	\$\$\$\$	\$\$\$\$	0.15	0.11	0.09	79.7

<sup>\$</sup> Annual means calculated from significantly less than 12 months data \$\$ The Cardiff Centre site was installed on  $5^{th}$  September 2002 \$\$\$ The Glasgow site was installed on  $1^{st}$  August 2002 \$\$\$\$ The Eltham site was installed on  $17^{th}$  October 2003

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

Monitoring Site	2006	2006	
	Maximum running	MRAM Data	
	annual mean	Capture %	
Cardiff Centre	0.19	49.9	
Glasgow	0.22	93.9	
Harwell	0.02	89.5	
Marylebone Road	0.45	89.2	
Eltham	0.11	93.6	

## **Appendix 6 Trend Analysis Plots**

- Figure 1. Plot of the monthly mean concentrations of benzene, toluene and 1,3-butadiene at the Cardiff Centre site of the UK Hydrocarbon Network
- Figure 2. Plot of the monthly mean concentrations of benzene, toluene and 1,3-butadiene at the Glasgow site of the UK Hydrocarbon Network
- Figure 3. Plot of the monthly mean concentrations of benzene, toluene and 1,3-butadiene at the Harwell site of the UK Hydrocarbon Network
- Figure 4. Plot of the monthly mean concentrations of benzene, toluene and 1,3-butadiene at the Marylebone Road 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 Eltham site of the UK Hydrocarbon Network
- Figure 6. Plot of the monthly mean benzene: 1,3-butadiene ratio for all sites of the UK Hydrocarbon Network

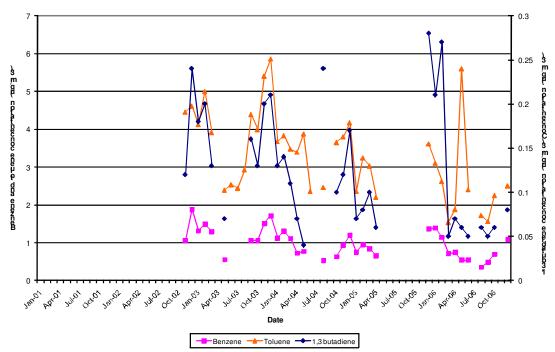


Figure 1. Plot of the monthly mean concentrations of benzene, toluene and 1,3-butadiene at the Cardiff Centre site of the UK Hydrocarbon Network

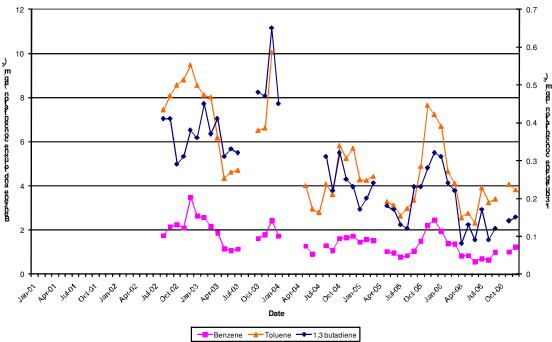


Figure 2. Plot of the monthly mean concentrations of benzene, toluene and 1,3-butadiene at the Glasgow site of the UK Hydrocarbon Network

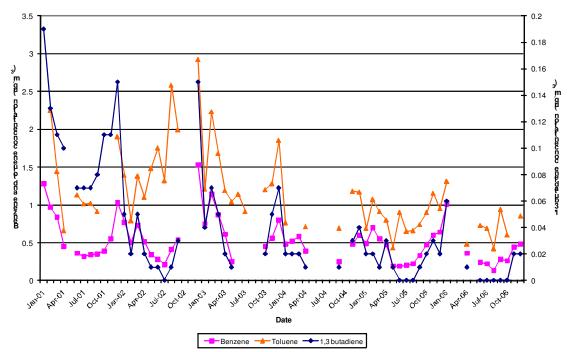


Figure 3. Plot of the monthly mean concentrations of benzene, toluene and 1,3-butadiene at the Harwell site of the UK Hydrocarbon Network

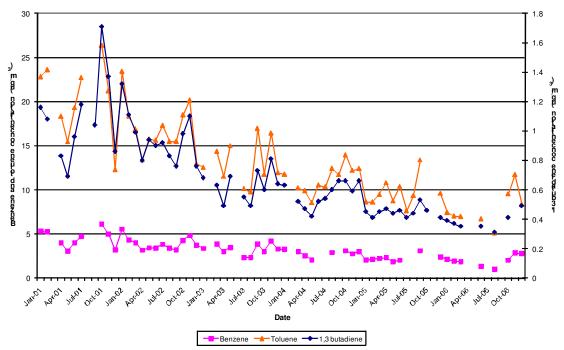


Figure 4. Plot of the monthly mean concentrations of benzene, toluene and 1,3-butadiene at the Marylebone Road site of the UK Hydrocarbon Network

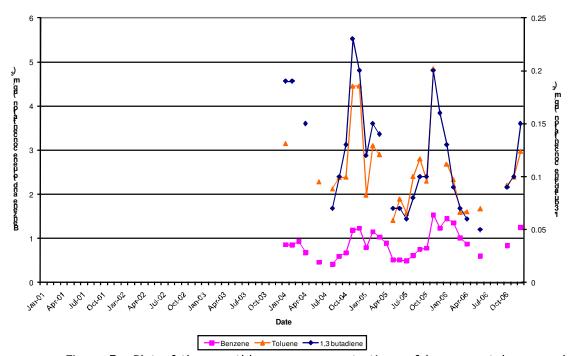


Figure 5. Plot of the monthly mean concentrations of benzene, toluene and 1,3-butadiene at the Eltham site of the UK Hydrocarbon Network

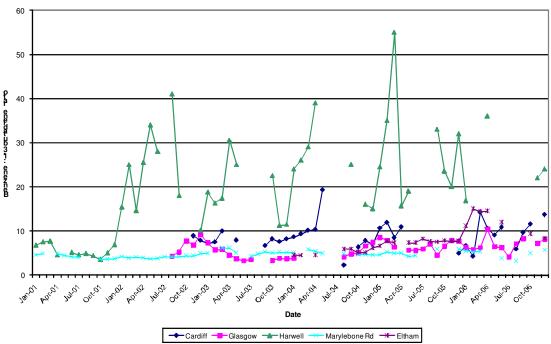


Figure 6. Plot of the monthly mean benzene: 1,3-butadiene ratio for all sites of the UK Hydrocarbon Network 2006

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