

## **Annual summary of data produced by the UK Ambient Automatic Hydrocarbon Air Quality Network, 2007**

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 2007 to 31 December 2007. 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.

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 Summary of network changes and related activity**

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

### **2.1 CARDIFF CENTRE**

During the year a strategic review of all monitoring undertaken by Defra and the Devolved Administrations was undertaken in order to prioritise on monitoring requirements for the upcoming revised European Air Quality Directive.

As a result of this review, the monitoring of hydrocarbon species at the Cardiff Centre site was deemed not to be necessary and as a result the site was closed on 5<sup>th</sup> September 2007.

### **2.2 HARWELL**

During the year reported here, a new analyser was procured and installed at the Harwell monitoring site. This analyser is a Perkin Elmer ozone pre-cursor analyser of the type installed at Eltham, Auchencorth Moss and Marylebone Road. This enabled a wider range of VOCs to be reported than were previously reported using the VOC71M BTEX analyser.

The new instrument will be used to provide data for EMEP (European Monitoring and Evaluation Programme) a scientifically based and policy driven programme under the Convention on Long-range Transboundary Air Pollution for international co-operation to solve transboundary air pollution problems. The Auchencorth Moss site is the UK's other EMEP monitoring site.

Following installation and commissioning it was noted that some compounds were showing evidence of interference. Following extensive investigations the interference was traced to another instrument in the monitoring station. This other instrument (the SMPS) uses butanol in it's operation and this was found to co-elute with benzene and to a lesser degree with 1,3 butadiene. For this reason, for the period of this report data for these two compounds continue to be reported from the VOC71M analyser.

### **2.3 EUROPEAN INTERCOMPARISON**

During the reporting year the EU Joint Research Centre (JRC) based at Ispra organised an intercomparison of the measurement of VOC species. This consisted of a 'round-robin' exercise whereby cylinders of gas mixtures were sent around the participants for analysis and subsequent reporting of results to the organisers.

The results of this intercomparison exercise have been reported by JRC in EUR-23529-EN.



### 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  $0.5 \mu\text{g}/\text{m}^3$  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.

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 2007 to 31 December 2007. 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
Cardiff	Benzene	66.0	A
	1,3-Butadiene	66.9	B
Glasgow	Benzene	90.5	A
	1,3-Butadiene	90.5	B
Harwell	Benzene	84.3	A
	1,3-Butadiene	84.3	B
Marylebone Road	Benzene	67.3	A
	1,3-Butadiene	77.8	A
Auchencorth Moss	Benzene	-	-
	1,3-Butadiene	62.0	A
Eltham	Benzene	84.3	A
	1,3-Butadiene	82.6	A

#### **4.2.1 Cardiff**

For the Cardiff site data capture for benzene was 66.0% and for 1,3-butadiene was 66.9%. Data quality code B is applied to 1,3-butadiene and quality code A for all other compounds.

Following a strategic review of Defra's monitoring networks as a whole, monitoring at the Cardiff centre site ceased on 5 September 2007.

#### **4.2.2 Glasgow**

For the Glasgow site the data capture for benzene was 90.5% and for 1,3-butadiene was 90.5%. Data quality code A is applied to all compounds.

From 7 March to 2 April a total of 600 hours of data were lost, due to the failure of the analyser power supply.

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.

#### **4.2.3 Harwell**

For the Harwell site the data capture for benzene was 84.3% and for 1,3-butadiene was 84.3%. Data quality code B is applied to 1,3-butadiene and quality code A for all other compounds.

During March and April a series of faults on the VOC71M analyser (fuse failure, column deterioration and comms. failure) resulted in a total of 807 hours of data lost. Following repair of the analyser there not further periods of significant data loss.

The Perkin Elmer ozone pre-cursor analyser started 9 May.

#### **4.2.4 Marylebone Road**

For the Marylebone Road site the data capture for benzene was 67.3% and for 1,3-butadiene was 77.8%. Data quality code A is applied to all compounds.

Between January and April a number of failures of the analyser and communications with the site resulted in significant data losses. This period accounts for the majority of the missing data throughout the year and hence the low data capture. Additional data were lost during October due to a noisy analyser baseline.

#### **4.2.5 Eltham**

For the Eltham site the data capture for benzene was 84.3% and for 1,3-butadiene was 82.6%. Data quality code A is applied to all compounds.

Significant data gaps at the Eltham site were the result of: - a sample pump failure (26 February to 8 March); power cuts after which the analyser failed to start correctly (12 to 17 April and 26 April to 10 May) for which Perkin Elmer had to attend to the analyser; the analyser not running continuously (1 to 4 June; and a loss of carrier gas due to a regulator failure (20 July to 1 August).

#### **4.2.6 Auchencorth Moss**

For the Auchencorth Moss site the data capture for 1,3-butadiene was 62.0%. Data quality code A is applied to all reported compounds. Benzene data were not reported for 2007 due to ongoing problems related to the column used for the measurement of the heavier (C<sub>6</sub> 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.

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 µg/m<sup>3</sup> on a number of occasions see Figures 2, 4 and 6, Appendix 2. Where concentrations fell below 0.02 µg/m<sup>3</sup> the ratified concentrations have been reported as 0.00 µg/m<sup>3</sup>.

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 2007 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  $16.25 \mu\text{g}/\text{m}^3$  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 quarterly means for benzene and 1,3-butadiene for 2007 together with the annual means since 2000 are given in tables 1, 2, 4 and 5, Appendix 5. The maximum running annual means for 2007 are given in Tables 3 and 6, Appendix 5.

For benzene the annual means for 2000 to 2007 were well below the relevant Air Quality Objective of  $16.25 \mu\text{g}/\text{m}^3$  to be met by the end of 2003. The annual means and maximum running annual means for 2005 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 2007 for all sites were well below the Air Quality Objective of  $2.25 \mu\text{g}/\text{m}^3$  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 2007 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 2007 are plotted in figures 1 to 5, Appendix 4. There is a decreasing trend for 1,3-butadiene at all sites with the exception of Eltham. The Eltham site shows an increasing trend for benzene and 1,3-butadiene during 2007. The running annual mean of both benzene and 1,3-butadiene at Cardiff also shows step changes during 2007, this is the effect of higher concentrations

during episodes in 2006. The running annual mean of benzene shows a decreasing trend at Glasgow and Marylebone Road, and an increasing trend at Harwell and Eltham. There is insufficient information to provide an explanation of the observed increase in the running annual means although seasonal and meteorological variations may well be the cause.

## **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 four sites that comprised the UK Automatic Hydrocarbon Network at the beginning of 2007.

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 the concentrations have generally reached a stable state over the years 2006 to 2007 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. 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 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-butadiene 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  $\mu\text{g}/\text{m}^3$ , not significant relative to the 2.25  $\mu\text{g}/\text{m}^3$  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 its removal by photochemical 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.

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# Appendix 1

## Summary Statistical Information

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Table 1. Percentage data capture maximum, mean and minimum values of ratified data from the Cardiff site of the UK Hydrocarbon Network, for the period 1 January 2007 to 31 December 2007

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	66.9	2.04	0.04	0.00
Benzene	66.0	7.88	0.49	0.00
Toluene	67.2	36.53	1.66	0.11
Ethylbenzene	63.8	10.00	0.26	0.00
(m+p)-Xylene *	67.1	30.19	0.96	0.00
o-Xylene	62.5	11.41	0.58	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 2007 to 31 December 2007

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	90.5	7.66	0.15	0.00
Benzene	90.5	7.10	0.96	0.00
Toluene	90.5	68.81	2.80	0.04
Ethylbenzene	84.1	53.19	0.58	0.00
(m+p)-Xylene *	90.5	127.23	2.14	0.04
o-Xylene	88.2	61.48	1.15	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 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 2007 to 31 December 2007

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	84.3	1.89	0.01	0.00
Benzene	84.3	6.42	0.33	0.00

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	52.1	14.01	1.73	0.35
Ethene	45.9	6.82	0.51	0.00
Propane	50.9	6.65	0.73	0.07
Propene	42.0	2.25	0.22	0.00
Ethyne	22.7	2.89	0.35	0.01
2-Methylpropane	40.8	2.91	0.29	0.00
n-Butane	47.1	4.30	0.38	0.00
trans-2-Butene	52.3	0.66	0.18	0.00
1-Butene	52.6	0.68	0.14	0.01
cis-2-Butene	52.8	0.86	0.07	0.00
2-Methylbutane	52.5	2.44	0.23	0.00
n-Pentane	51.6	1.38	0.11	0.01
1,3-Butadiene				
trans-2-Pentene	3.2	3.2	0.12	0.02
1-Pentene	3.4	3.4	0.10	0.03
2-Methylpentane	32.6	32.6	0.64	0.06
n-Hexane	36.4	36.4	0.56	0.05
Isoprene	14.0	14.0	0.39	0.03
Benzene				
2,2,4-trimethylpentane	44.3	1.85	0.05	0.00
n-Heptane	33.8	1.46	0.05	0.00
n-Octane	37.2	2.38	0.04	0.00
Toluene	80.3	5.77	0.24	0.00
Ethylbenzene	68.7	3.09	0.05	0.00
(m+p)-Xylene *	67.2	1.24	0.11	0.00
o-Xylene	60.1	2.11	0.05	0.00
1,3,5-Trimethylbenzene	23.3	0.81	0.03	0.00
1,2,4-Trimethylbenzene	55.3	3.29	0.10	0.00
1,2,3-Trimethylbenzene	38.4	1.06	0.06	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 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 2007 to 31 December 2007

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	79.3	114.30	10.53	1.55
Ethene	78.1	23.73	3.91	0.02
Propane	77.9	431.55	6.38	0.02
Propene	76.7	11.07	1.72	0.03
Ethyne	75.2	148.64	2.49	0.10
2-Methylpropane	78.0	43.36	4.21	0.05
n-Butane	78.0	70.97	7.72	0.39
trans-2-Butene	76.0	21.21	0.50	0.02
1-Butene	77.2	11.01	0.42	0.02
cis-2-Butene	77.6	1.65	0.31	0.02
2-Methylbutane	77.1	73.07	7.67	0.33
n-Pentane	77.5	16.97	2.27	0.18
1,3-Butadiene	77.8	8.17	0.31	0.04
trans-2-Pentene	77.3	11.38	0.46	0.03
1-Pentene	74.8	11.61	0.21	0.03
2-Methylpentane	77.8	15.23	2.07	0.04
n-Hexane	71.5	10.43	0.29	0.03
Isoprene	77.1	21.20	0.77	0.04
Benzene	67.3	13.49	1.41	0.00
2,2,4-trimethylpentane	72.4	8.20	1.23	0.00
n-Heptane	70.3	7.86	0.49	0.00
n-Octane	61.0	7.16	0.20	0.00
Toluene	72.7	44.26	6.11	0.00
Ethylbenzene	73.8	16.79	0.89	0.00
(m+p)-Xylene *	72.6	149.98	6.41	0.00
o-Xylene	73.7	11.94	1.30	0.00
1,3,5-Trimethylbenzene	66.5	7.38	0.45	0.00
1,2,4-Trimethylbenzene	74.7	15.12	1.75	0.05
1,2,3-Trimethylbenzene	71.3	5.79	0.65	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.

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 2007 to 31 December 2007

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	83.0	1.22	6.61	86.78
Ethene	78.8	0.01	1.17	19.17
Propane	83.6	0.26	3.53	174.36
Propene	80.2	0.00	0.53	7.82
Ethyne	81.1	0.01	0.58	7.51
2-Methylpropane	83.5	0.10	2.14	54.04
n-Butane	82.8	0.00	3.57	54.38
trans-2-Butene	84.1	0.02	0.14	2.03
1-Butene	81.0	0.00	0.13	2.51
cis-2-Butene	83.3	0.00	0.08	1.05
2-Methylbutane	79.8	0.00	1.54	33.02
n-Pentane	82.2	0.03	0.59	8.92
1,3-Butadiene	82.6	0.00	0.10	2.72
trans-2-Pentene	79.2	0.00	0.09	1.80
1-Pentene	79.5	0.00	0.08	1.69
2-Methylpentane	84.4	0.00	0.58	9.30
n-Hexane	79.9	0.00	0.36	22.24
Isoprene	84.3	0.00	0.22	2.83
Benzene	84.3	0.06	0.91	14.37
2,2,4-trimethylpentane	59.3	0.05	0.57	21.47
n-Heptane	84.3	0.04	0.39	18.67
n-Octane	73.2	0.00	0.13	21.23
Toluene	84.3	0.11	2.21	35.50
Ethylbenzene	84.2	0.04	0.39	20.54
(m+p)-Xylene *	84.3	0.04	1.15	57.47
o-Xylene	84.2	0.04	0.40	20.01
1,3,5-Trimethylbenzene	78.1	0.00	0.20	22.35
1,2,4-Trimethylbenzene	79.1	0.00	0.56	23.50
1,2,3-Trimethylbenzene	82.7	0.05	0.37	20.95

\* (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 2007 to 31 December 2007

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	65.5	3.18	0.40	0.00
Ethene	50.2	1.21	0.06	0.00
Propane	62.5	19.45	0.29	0.00
Propene	53.0	1.24	0.03	0.00
Ethyne	39.3	0.36	0.05	0.00
2-Methylpropane	61.2	7.19	0.10	0.00
n-Butane	61.4	17.02	0.17	0.00
trans-2-Butene	60.0	0.30	0.02	0.00
1-Butene	58.8	0.16	0.01	0.00
cis-2-Butene	55.5	0.16	0.01	0.00
2-Methylbutane	64.8	5.84	0.08	0.00
n-Pentane	65.0	6.05	0.06	0.00
1,3-Butadiene	62.0	0.29	0.01	0.00
trans-2-Pentene				
1-Pentene				
2-Methylpentane				
n-Hexane	23.7	0.99	0.05	0.00
Isoprene	65.5	3.18	0.40	0.00
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				

\* (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 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 2007 to 31 December 2007
- 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 2007 to 31 December 2007

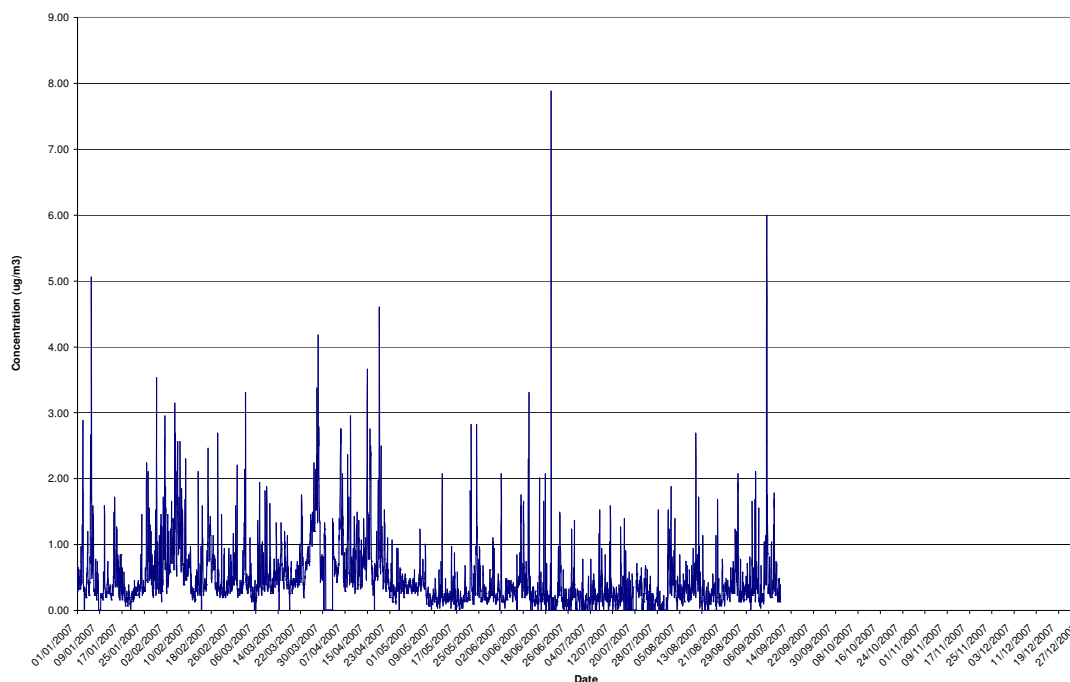


Figure 1. Time series plots for the ratified benzene data from the Cardiff site of the UK Hydrocarbon Network, for the period; 1 January 2007 to 31 December 2007

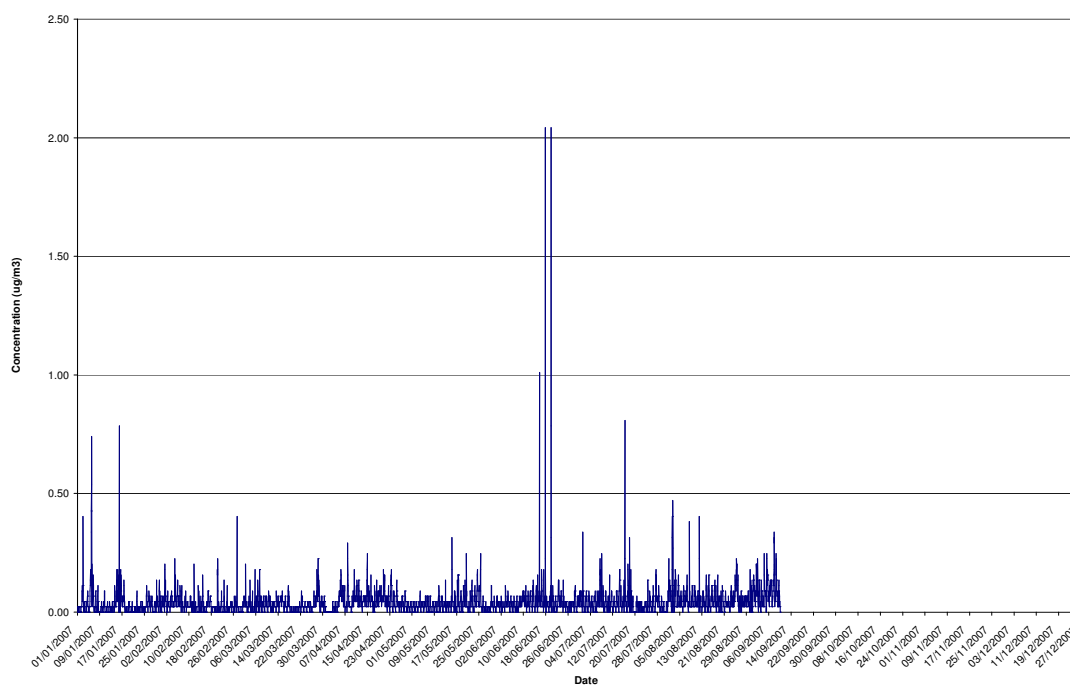


Figure 2. Time series plots for the ratified 1,3-butadiene data from the Cardiff site of the UK Hydrocarbon Network, for the period; 1 January 2007 to 31 December 2007

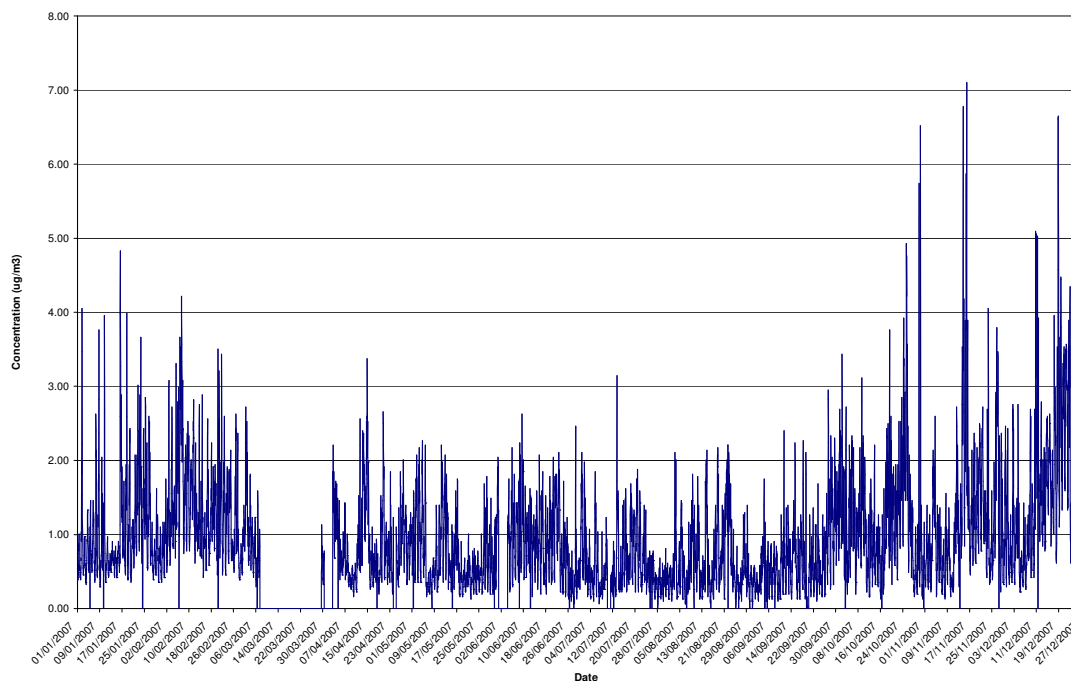


Figure 3. Time series plots for the ratified benzene data from the Glasgow site of the UK Hydrocarbon Network, for the period; 1 January 2007 to 31 December 2007

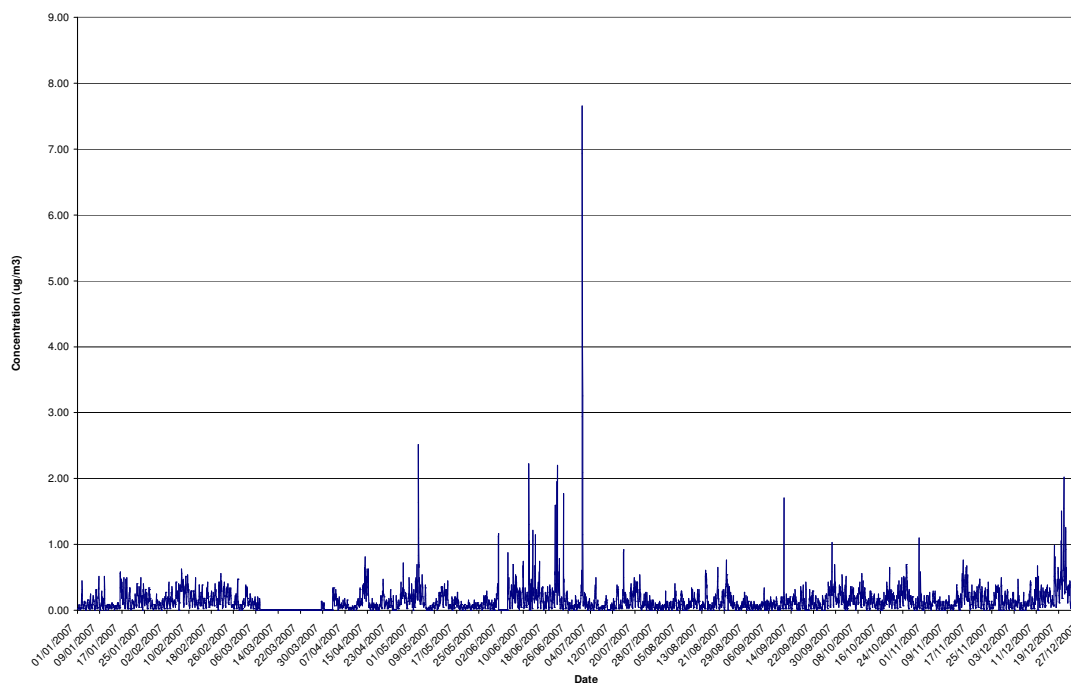


Figure 4. Time series plots for the ratified 1,3-butadiene data from the Glasgow site of the UK Hydrocarbon Network, for the period; 1 January 2007 to 31 December 2007

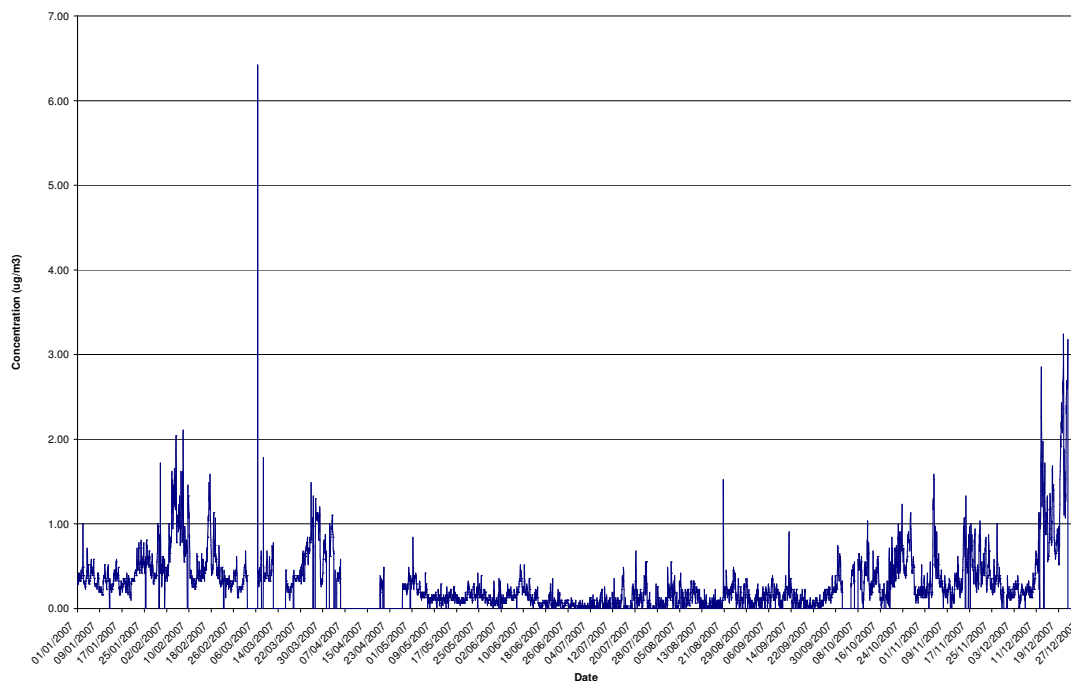


Figure 5. Time series plots for the ratified benzene data from the Harwell site of the UK Hydrocarbon Network, for the period; 1 January 2007 to 31 December 2007

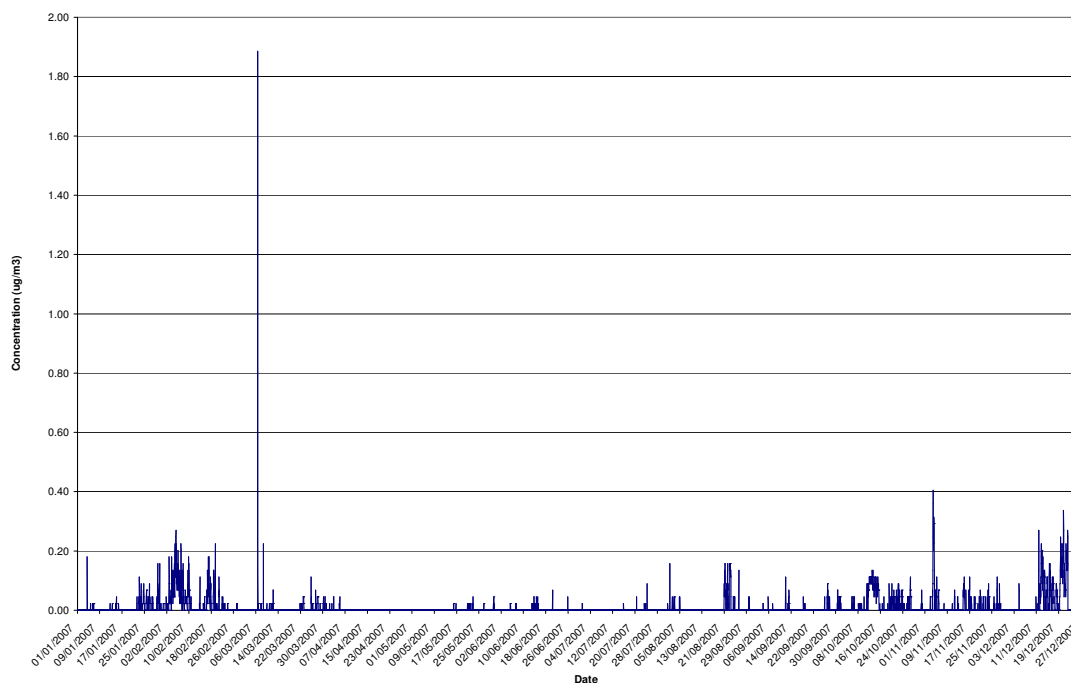


Figure 6. Time series plots for the ratified 1,3-butadiene data from the Harwell site of The UK Hydrocarbon Network, for the period; 1 January 2007 to 31 December 2007

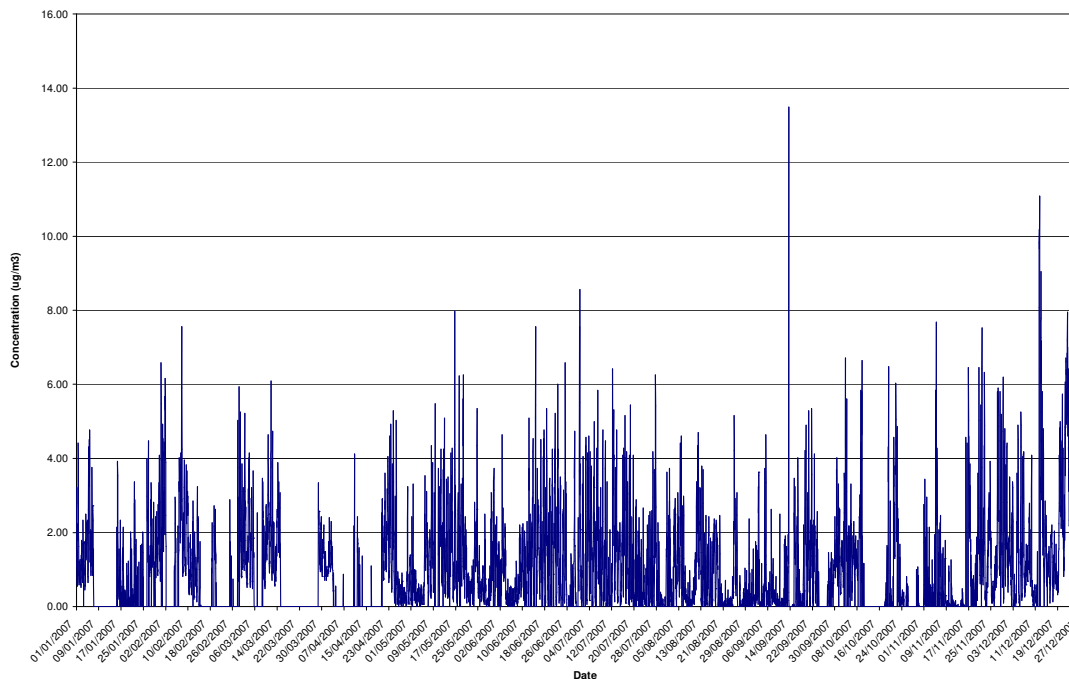


Figure 7. Time series plots for the ratified benzene data from the Marylebone Road site affiliated to the UK Hydrocarbon Network, for the period; 1 January 2007 to 31 December 2007

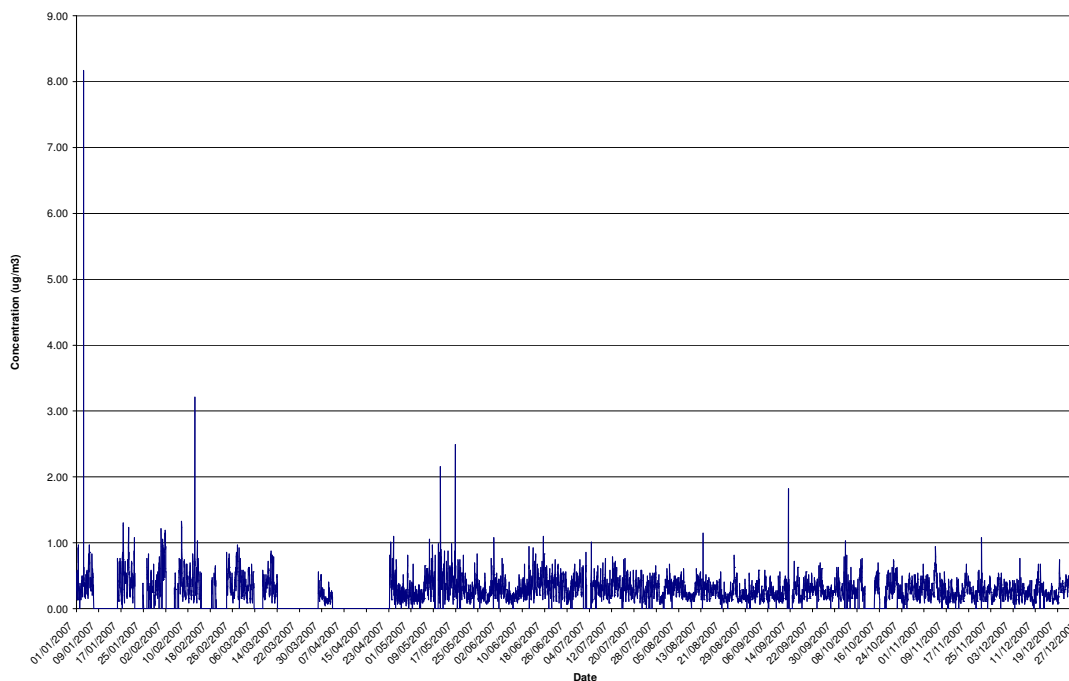


Figure 8. Time series plots for the ratified 1,3-butadiene data from the Marylebone Road site affiliated to the UK Hydrocarbon Network, for the period; 1 January 2007 to 31 December 2007

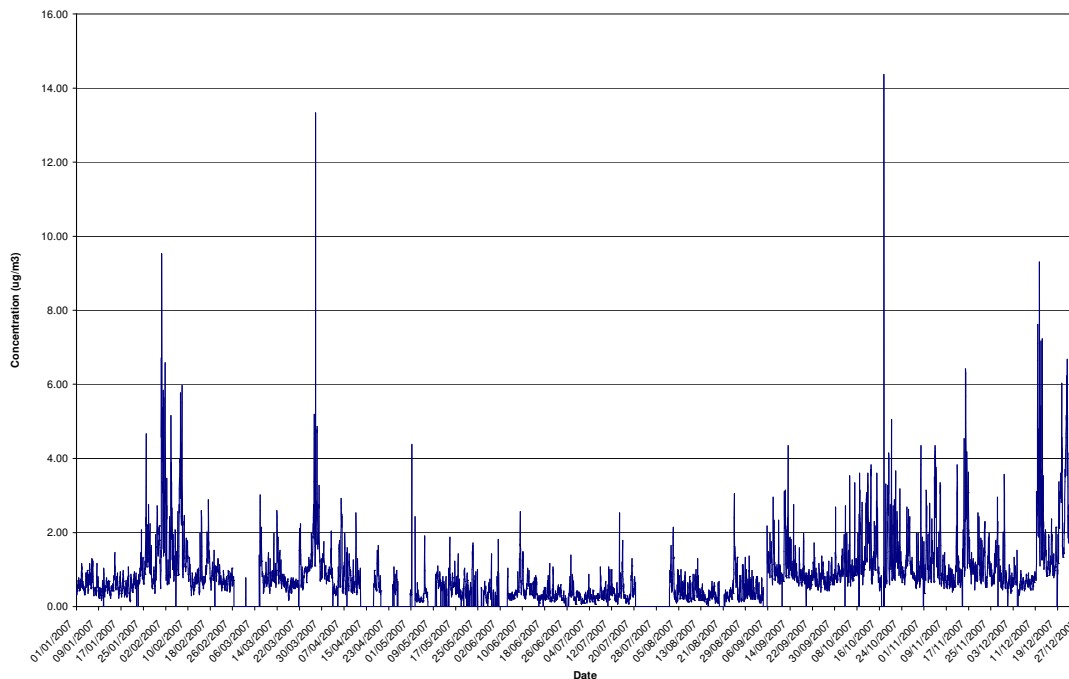


Figure 9. Time series plots for the ratified benzene data from the Eltham site of the UK Hydrocarbon Network, for the period; 1 January 2007 to 31 December 2007

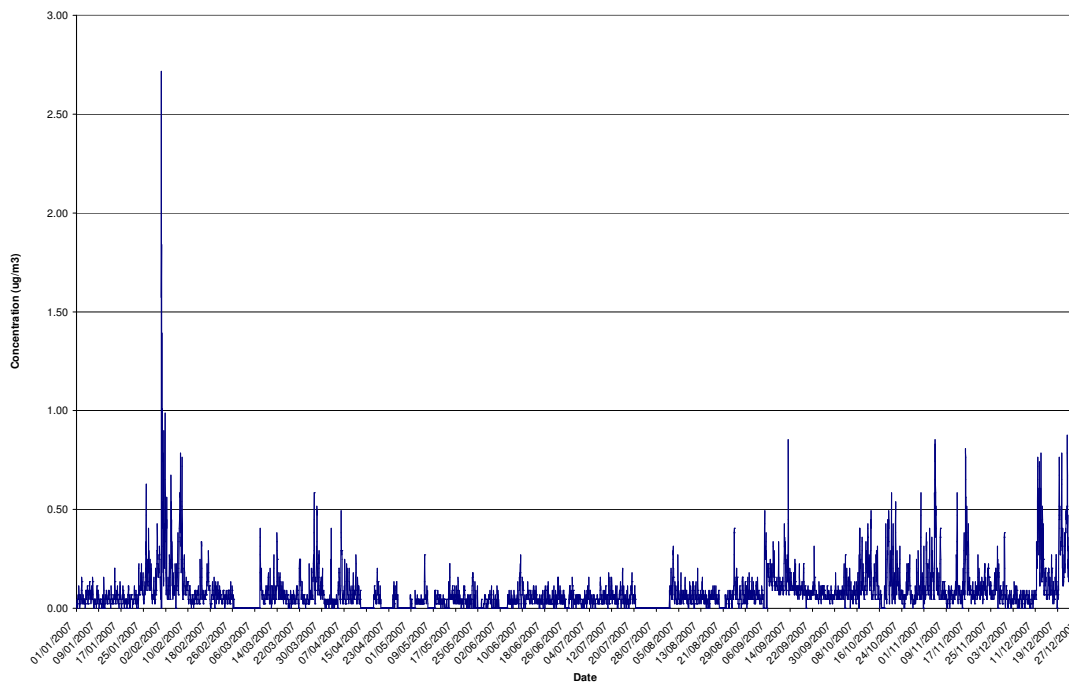


Figure 10. Time series plots for the ratified 1,3-butadiene data from the Eltham site of the UK Hydrocarbon Network, for the period; 1 January 2007 to 31 December 2007

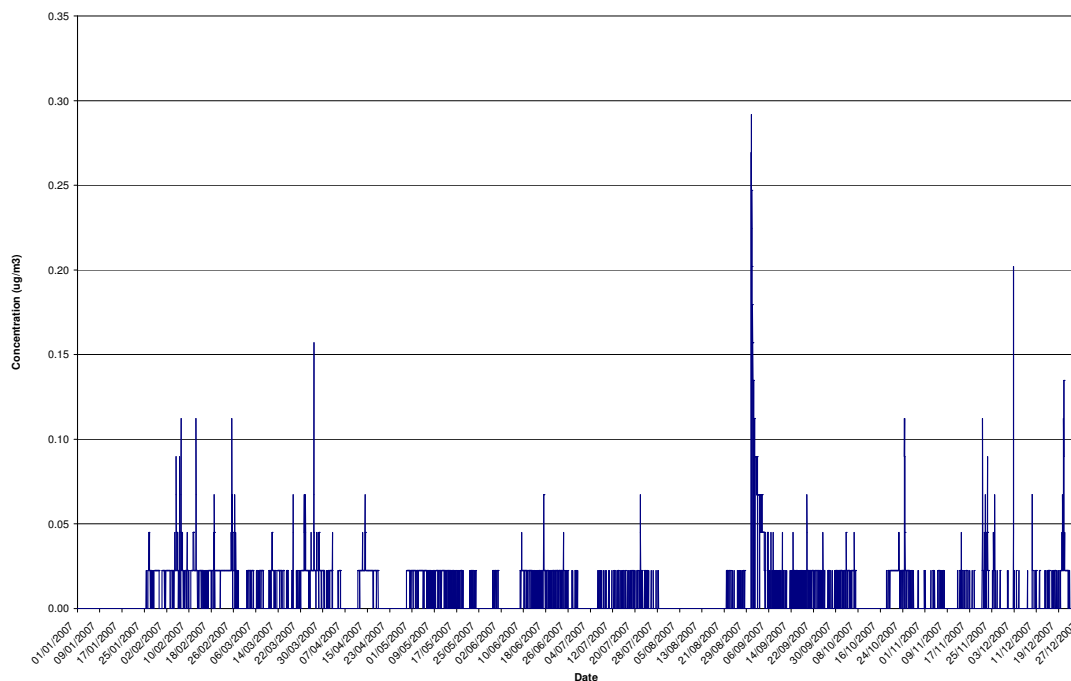


Figure 11. Time series plots for the ratified 1,3-butadiene data from the Auchencorth Moss site of the UK Hydrocarbon Network, for the period; 1 January 2007 to 31 December 2007

# Appendix 3

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- Figure 4. Mean concentrations for all compounds measured at Marylebone road and Eltham for the UK Automatic Hydrocarbon Network, for 2007
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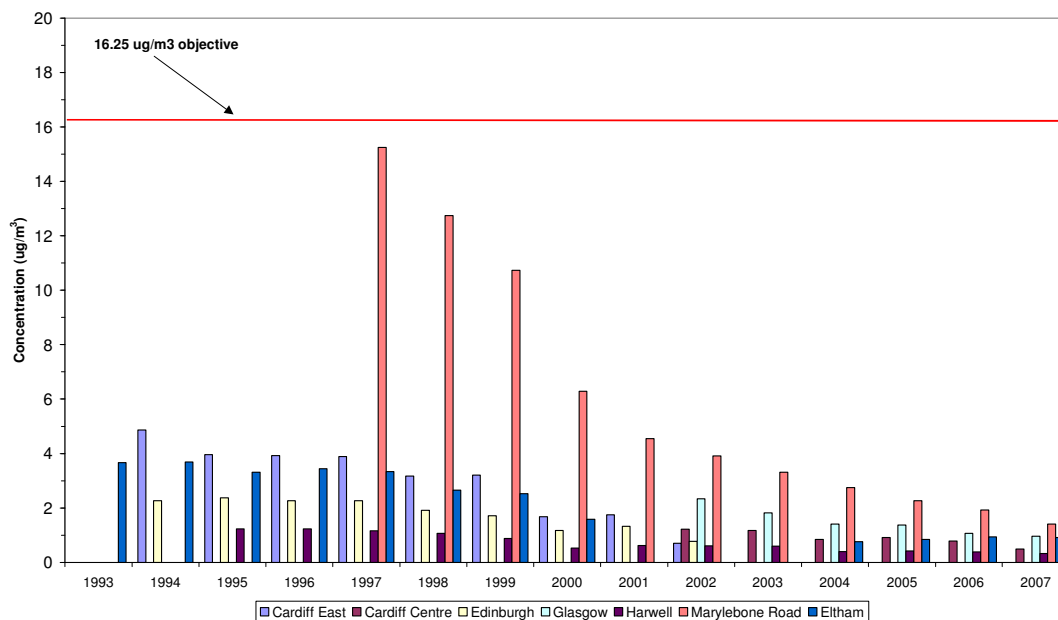


Figure 1. Mean benzene concentrations for the UK Automatic Hydrocarbon Network, 1993-2007

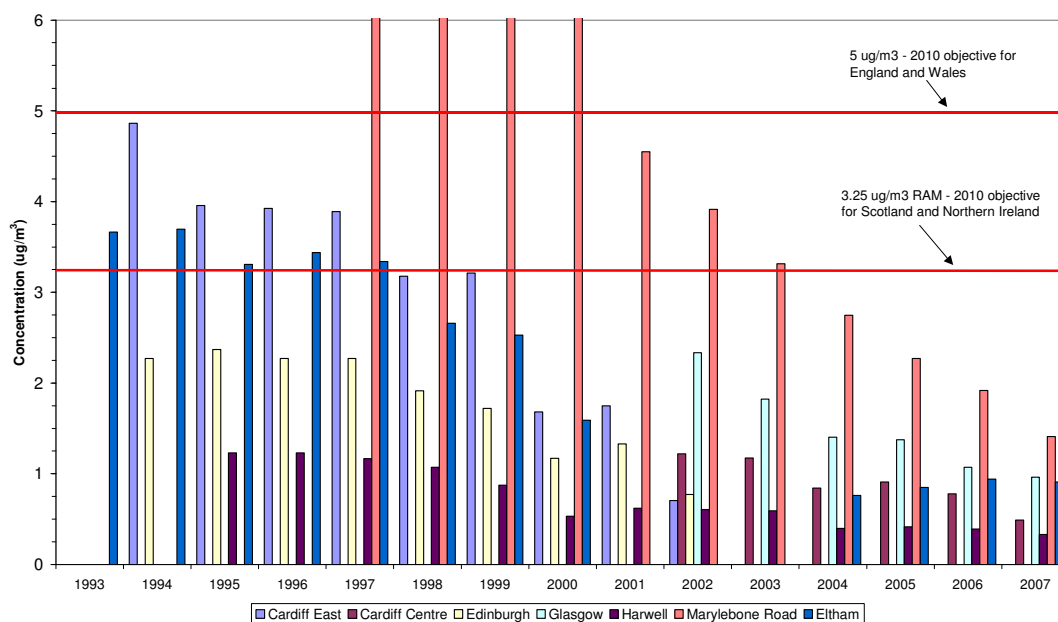


Figure 2. Mean Benzene concentrations for the UK Automatic Hydrocarbon Network, 1993-2007 (magnified y-axis)

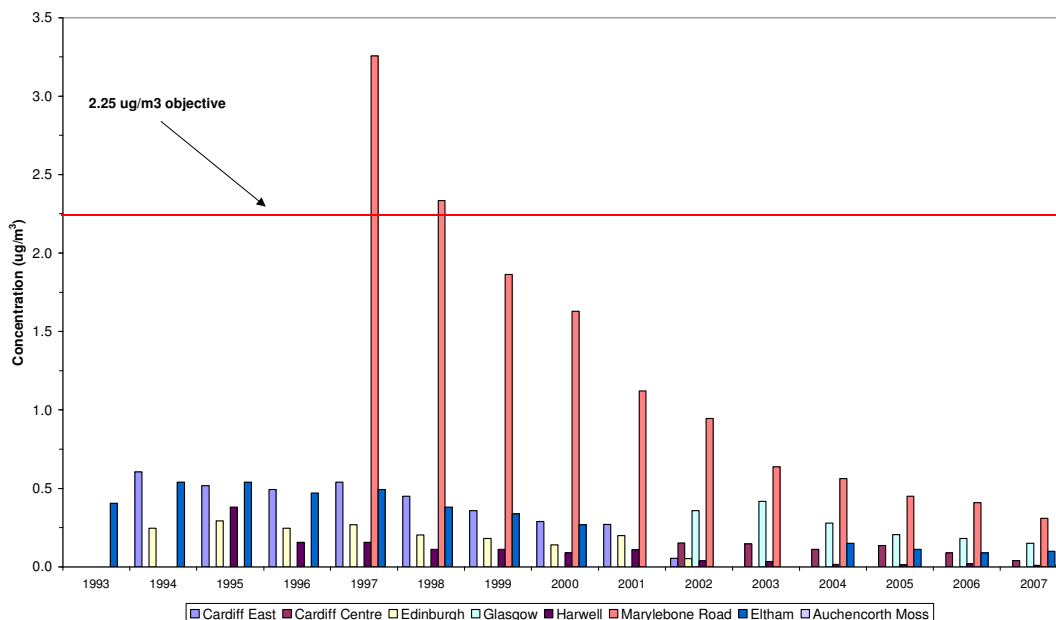


Figure 3. Mean 1,3-Butadiene concentrations for the UK Automatic Hydrocarbon Network, 1993-2007

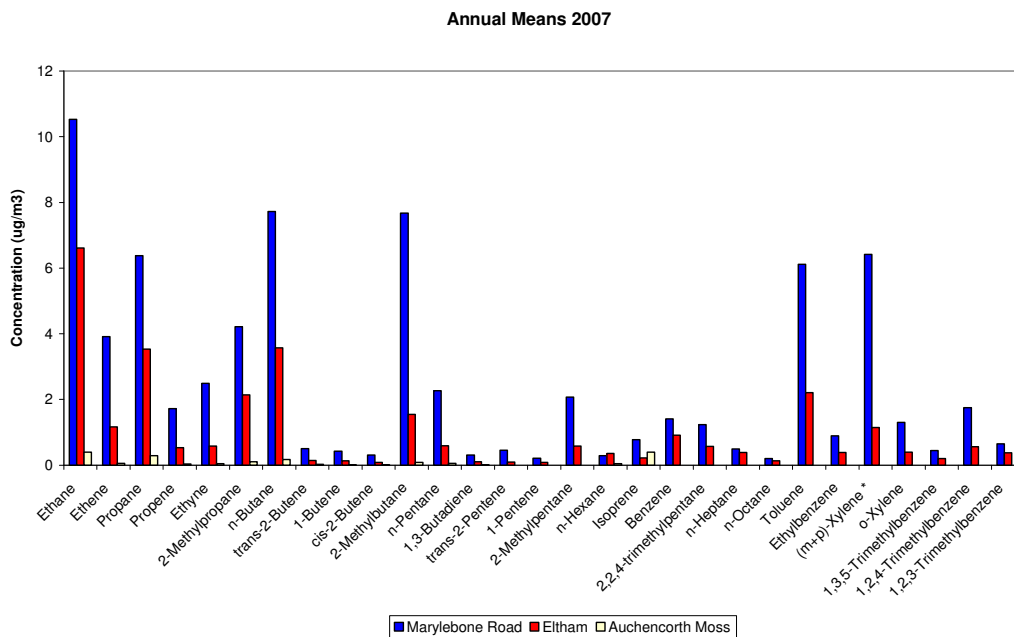


Figure 4. Mean concentrations for all compounds measured at Marylebone Road and Eltham for the UK Automatic Hydrocarbon Network, for 2007

# Appendix 4

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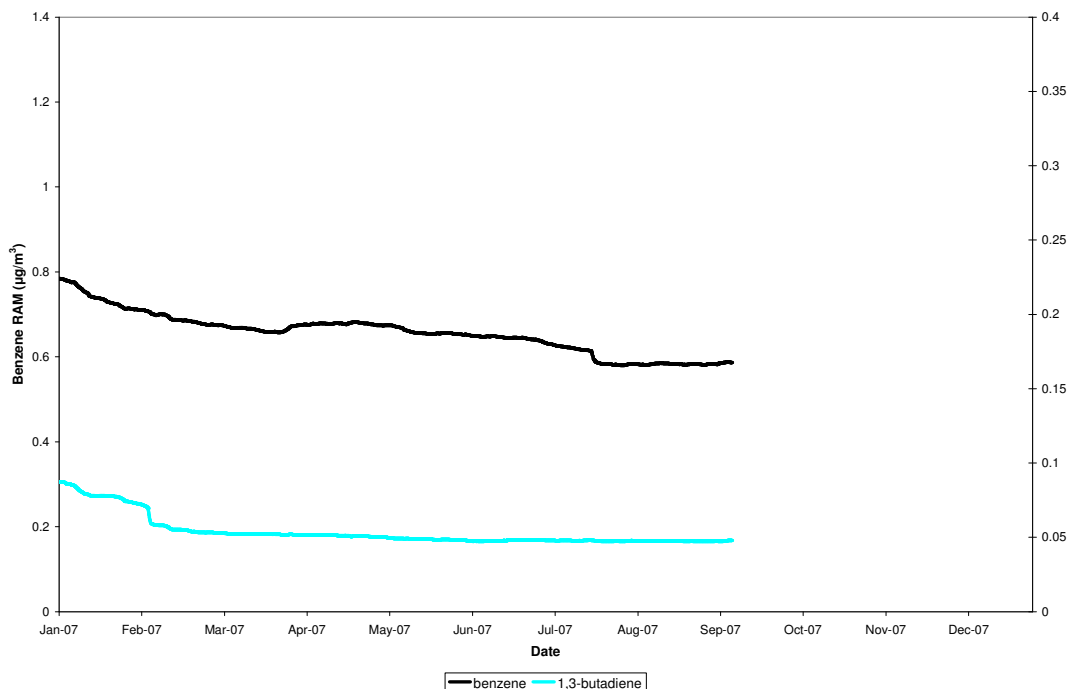


Figure 1. Time series plot of the running annual mean for benzene and 1,3-butadiene data from the Cardiff site of the UK Hydrocarbon Network, for the period; January 2007 to December 2007.

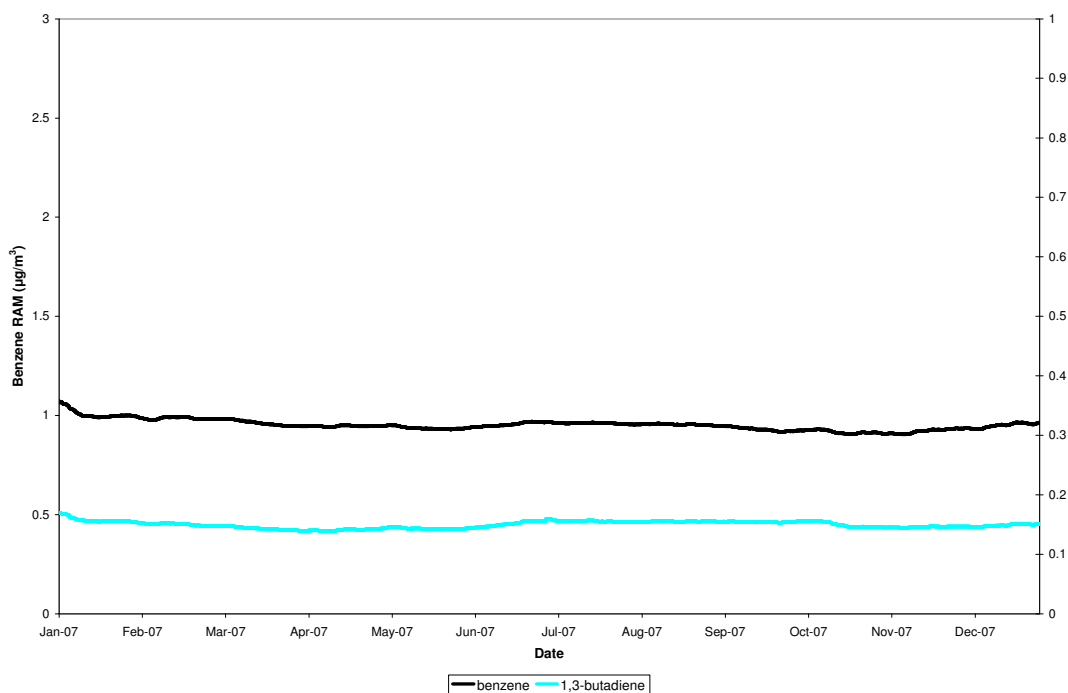


Figure 2. Time series plot of the running annual mean for benzene and 1,3-butadiene data from the Glasgow site of the UK Hydrocarbon Network, for the period; January 2005 to December 2005.

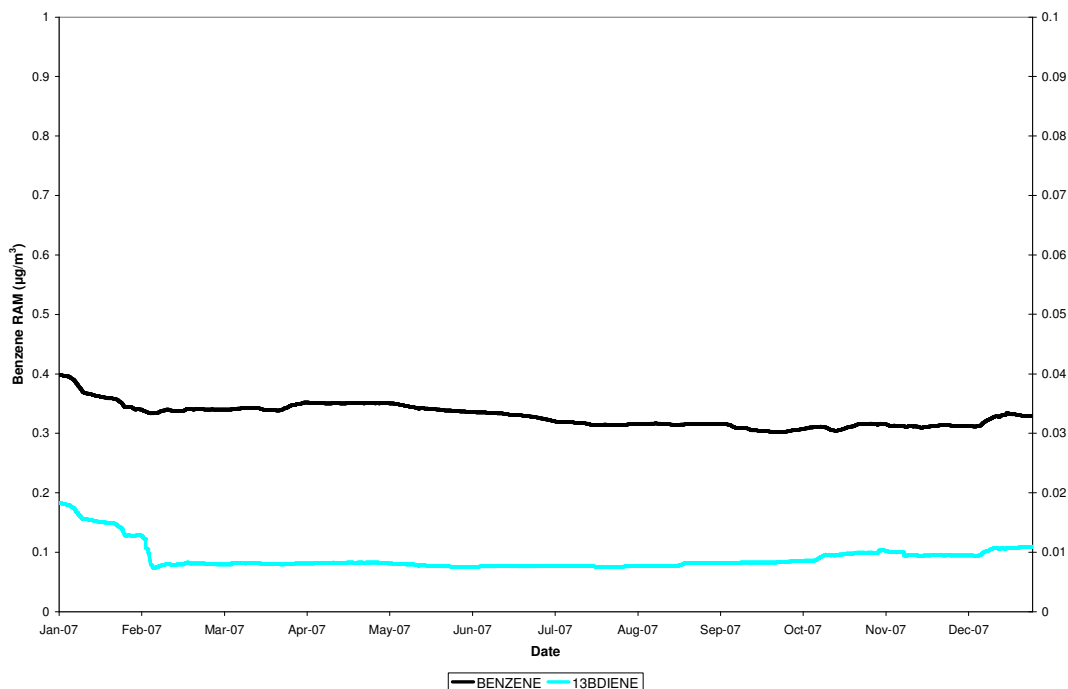


Figure 3. Time series plot of the running annual mean for benzene and 1,3-butadiene data from the Harwell site of the UK Hydrocarbon Network, for the period; January 2007 to December 2007.

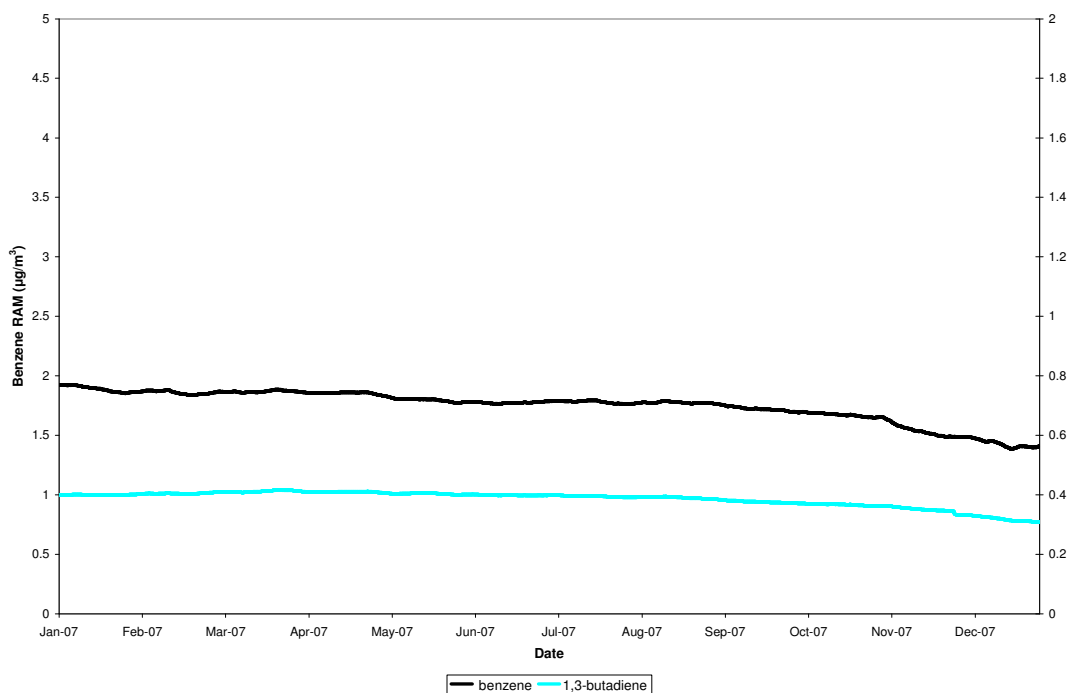


Figure 4. Time series plot of the running annual mean for benzene and 1,3-butadiene data from the Marylebone Road site affiliated to the UK Hydrocarbon Network, for the period; January 2007 to December 2007.

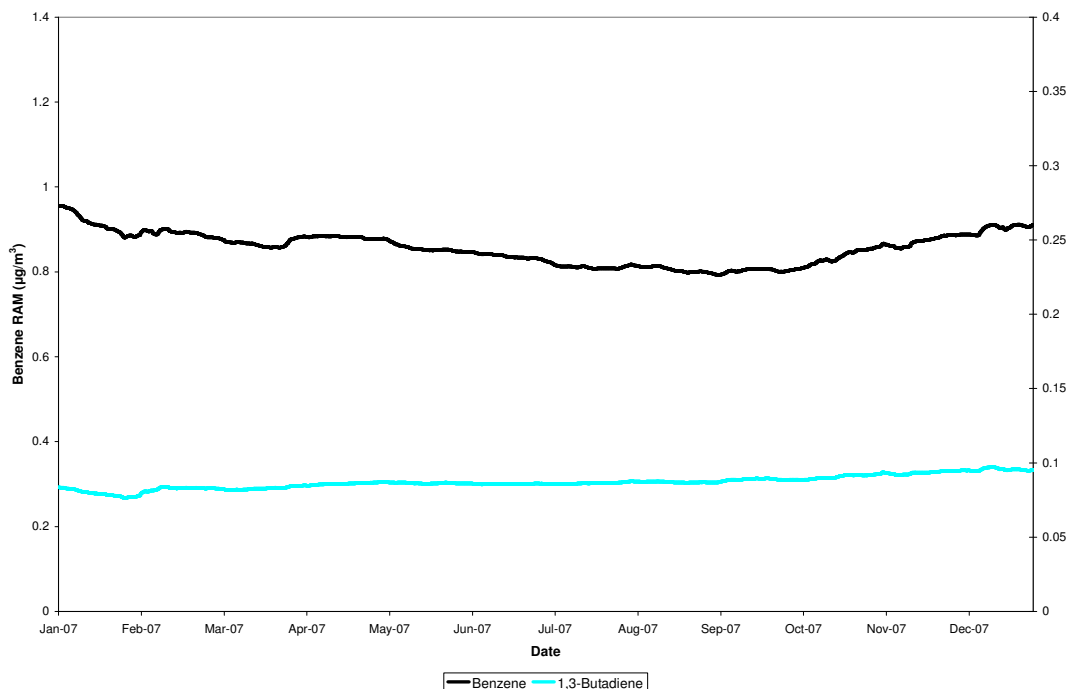


Figure 5. Time series plot of the running annual mean for benzene and 1,3-butadiene data from the Eltham site of the UK Hydrocarbon Network, for the period; January 2007 to December 2007.

# Appendix 5

## Quarterly, annual and maximum running means

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-

Table 1. Quarterly means of measured benzene concentrations ( $\mu\text{g}/\text{m}^3$ ) at each of the UK Automatic Hydrocarbon Sites, 2007.

Monitoring Site	Quarter 1 2007 Mean	Quarter 2 2007 Mean	Quarter 3 2007 Mean	Quarter 4 2007 Mean
Cardiff Centre	0.65	0.45	0.36	
Glasgow	1.14	0.81	0.62	1.30
Harwell	0.52	0.16	0.13	0.52
Marylebone Road	1.69	1.26	1.10	1.72
Eltham	1.04	0.58	0.58	1.33

§ No benzene measured for the quarter.

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

Monitoring Site	2002 Annual Mean	2003 Annual Mean	2004 Annual Mean	2005 Annual Mean	2006 Annual Mean	2007 Annual Mean	2007 Data Capture %
Cardiff Centre	1.22§	1.17	0.84	0.91	0.78	0.49	66.0
Glasgow	2.33 §	1.82	1.40	1.36	1.07	0.96	90.5
Harwell	0.60	0.59	0.40	0.42	0.39	0.33	84.3
Marylebone Road	3.91	3.32	2.75	2.27	1.92	1.41	77.8
Eltham	§§§§	§§§§	0.76	0.84	0.94	0.91	82.6

§ 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

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

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

Monitoring Site	2007 Maximum running annual mean	2007 MRAM Data Capture %
Cardiff Centre	0.79	89.3
Glasgow	1.07	92.3
Harwell	0.40	87.1
Marylebone Road	1.93	77.1
Eltham	0.96	80.5



Table 4. Quarterly means of measured 1,3-butadiene concentrations ( $\mu\text{g}/\text{m}^3$ ) at each of the UK Automatic Hydrocarbon Sites.

Monitoring Site	Quarter 1 2007 Mean	Quarter 2 2007 Mean	Quarter 3 2007 Mean	Quarter 4 2007 Mean
Cardiff Centre	0.02	0.04	0.04	
Glasgow	0.13	0.16	0.13	0.18
Harwell	0.02	0.00	0.00	0.02
Marylebone Road	0.40	0.31	0.29	0.27
Eltham	0.11	0.07	0.09	0.13

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

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

Monitoring Site	2002 Annual Mean	2003 Annual Mean	2004 Annual Mean	2005 Annual Mean	2006 Annual Mean	2007 Annual Mean	2007 Data Capture %
Cardiff Centre	0.15§	0.15	0.11	0.13	0.09	0.04	66.9
Glasgow	0.36§	0.42	0.28	0.20	0.18	0.15	90.5
Harwell	0.04	0.03	0.02	0.02	0.02	0.01	84.3
Marylebone Road	0.95	0.64	0.56	0.45	0.41	0.31	77.8
Eltham	§§§§	§§§§	0.15	0.11	0.09	0.10	82.6

§ 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

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

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

Monitoring Site	2007 Maximum running annual mean	2007 MRAM Data Capture %
Cardiff Centre	0.09	89.4
Glasgow	0.17	92.4
Harwell	0.02	87.1
Marylebone Road	0.42	60.8
Eltham	0.10	82.6

# Appendix 6

## Trend Analysis Plots

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

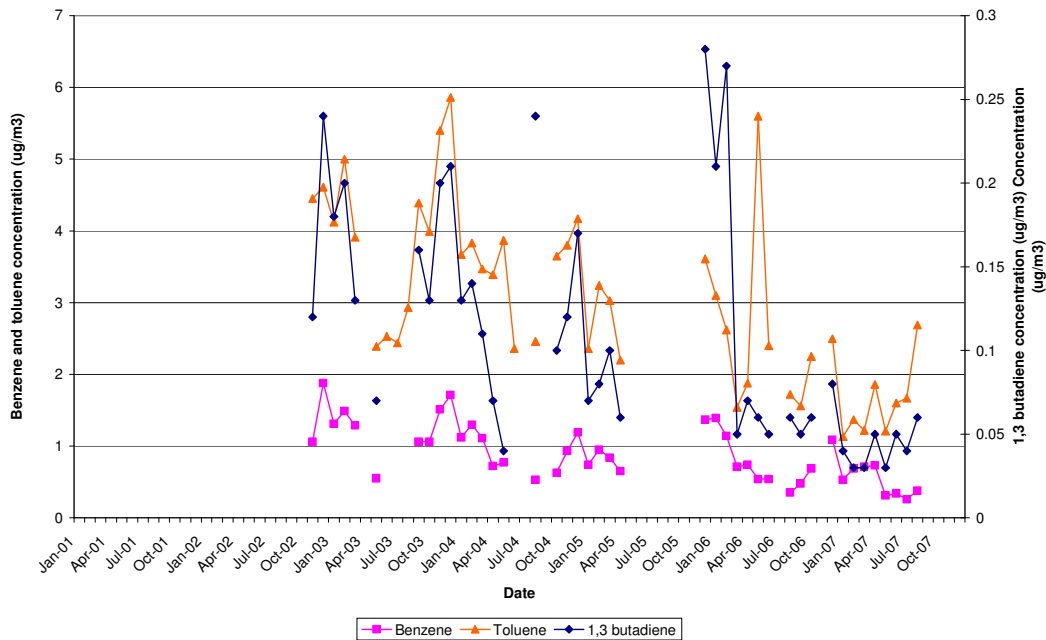


Figure 1. Plot of the monthly mean concentrations of benzene, toluene and 1,3-butadiene at the Cardiff Centre site of the UK Hydrocarbon Network

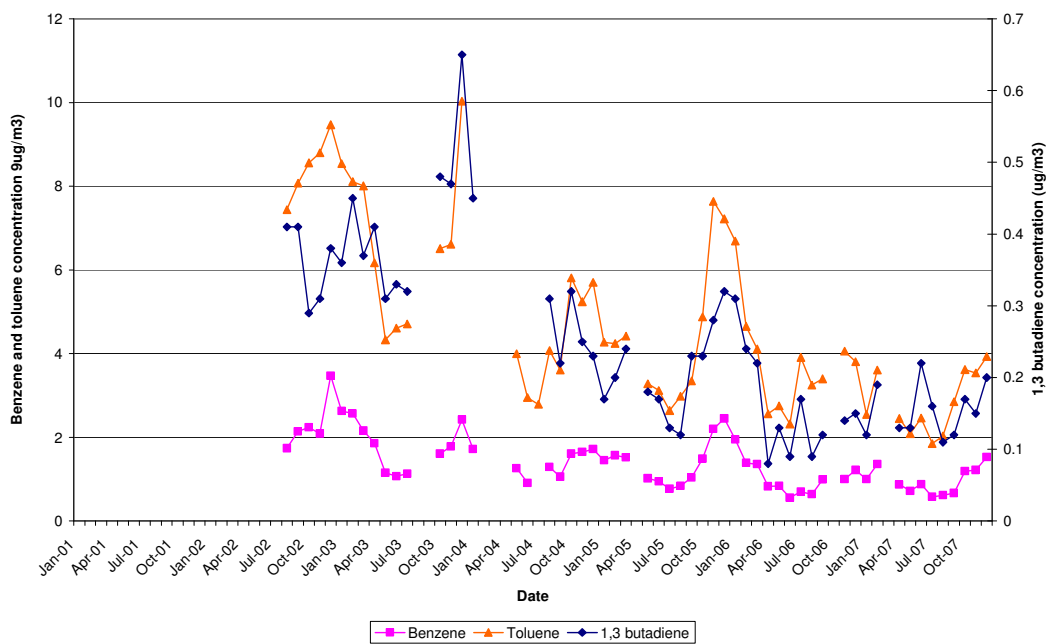


Figure 2. Plot of the monthly mean concentrations of benzene, toluene and 1,3-butadiene at the Glasgow site of the UK Hydrocarbon Network

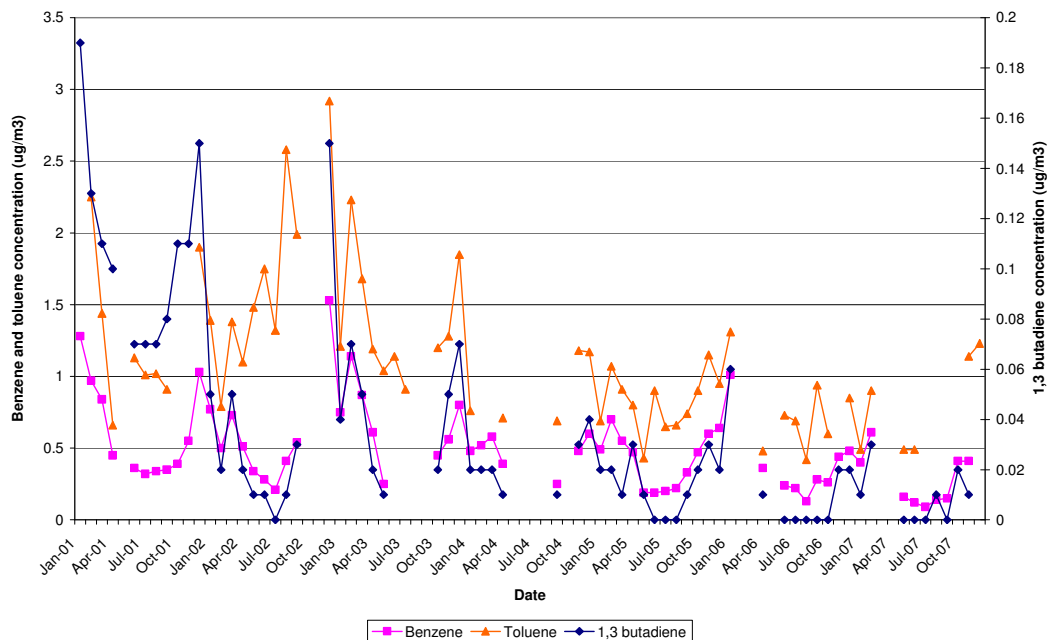


Figure 3. Plot of the monthly mean concentrations of benzene, toluene and 1,3-butadiene at the Harwell site of the UK Hydrocarbon Network

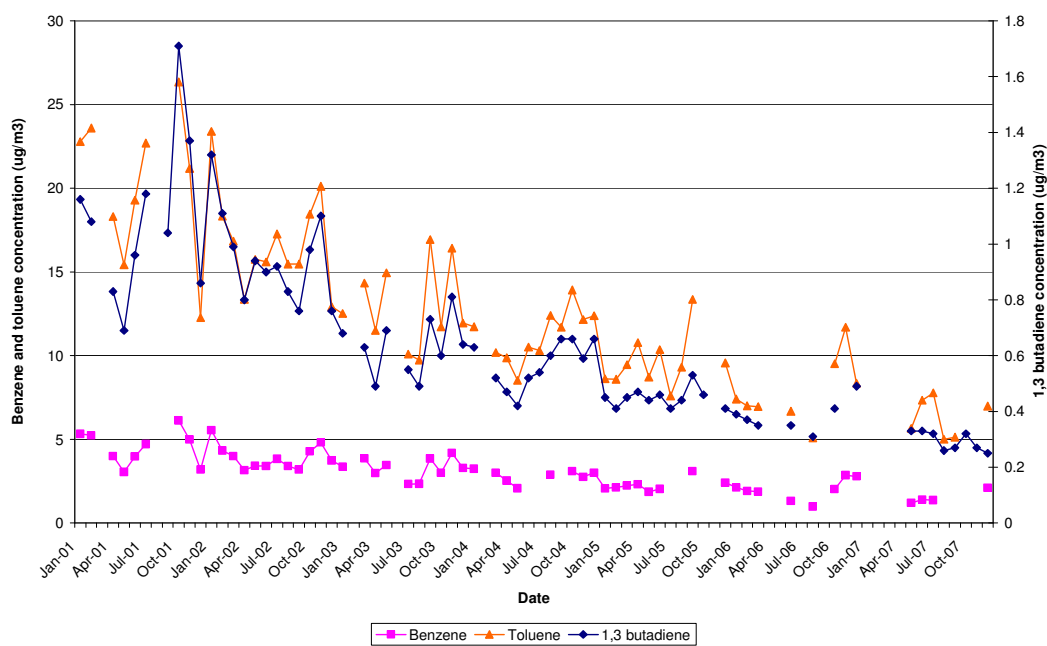


Figure 4. Plot of the monthly mean concentrations of benzene, toluene and 1,3-butadiene at the Marylebone Road site of the UK Hydrocarbon Network

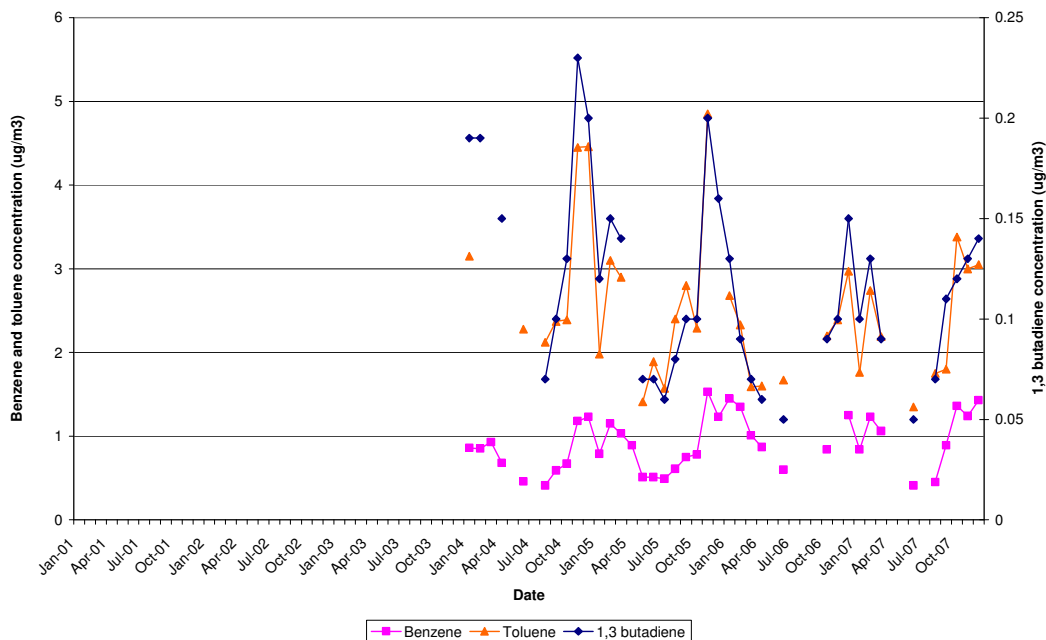


Figure 5. Plot of the monthly mean concentrations of benzene, toluene and 1,3-butadiene at the Eltham site of the UK Hydrocarbon Network

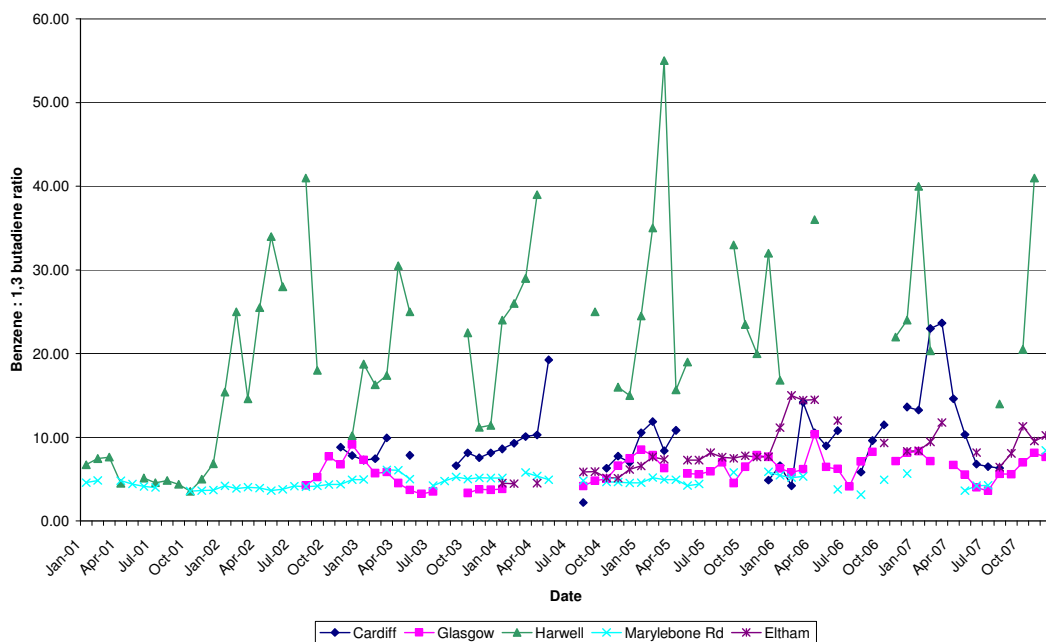


Figure 6. Plot of the monthly mean benzene: 1,3-butadiene ratio for all sites of the UK Hydrocarbon Network 2007

