## **REPORT**

# Annual summary of data produced by the UK Ambient Automatic Hydrocarbon Air Quality Network, 2008

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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Title

Annual summary of data produced by the UK Ambient Automatic Hydrocarbon Air Quality Network, 1 January 2008 to 31 December 2008

Customer

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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 2008 to 31 December 2008. 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 and other significant events during the reported year.

#### 2.1 Marylebone Road

During the year reported here, a new analyser was procured and installed at the Marylebone Road monitoring site. This analyser is a Perkin Elmer ozone pre-cursor analyser of the type installed at Eltham, Auchencorth Moss and Harwell. This instrument replaced the existing Perkin Elmer analyser which had been operational since the monitoring site was established in 1996.

#### 2.2 European Intercomparison

During the reporting year the EU Joint Research Centre (JRC) based at Ispra organised an intercomparison of the measurement of BTEX species.

The results of this intercomparison exercise have been reported by JRC in JRC50545.

### 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 EU Ambient Air Quality Directive 2008/50/EC 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 directive relating to limit values for benzene 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 2008 to 31 December 2008. 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
Classow	Benzene	96.3	А
Glasgow	1,3-Butadiene	96.3	В
Harwell	Benzene	89.2	Α
пагмен	1,3-Butadiene	89.8	В
Marylebone	Benzene	76.5	Α
Road	1,3-Butadiene	79.9	Α
Auchencorth	Benzene	27.0	А
Moss	1,3-Butadiene	28.6	Α
Eltham	Benzene	85.6	Α
Citiaiii	1,3-Butadiene	82.4	Α

#### 4.2.1 Glasgow

For the Glasgow site the data capture for benzene was 96.3% and for 1,3-butadiene was 96.3%. Data quality code A is applied to all compounds with the exception of 1,3 butadiene which has been assigned data quality code B as described in section 4.3.

Periods of significant (> 50 hours) data loss are as follows:-

From 12 to 16 December a total of 121 hours of data were lost, due to a problem with the internal pressure regulator of the analyser.

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.

#### 4.2.2 Harwell

For the Harwell site the data capture for benzene was 89.2% and for 1,3-butadiene was 89.8%. Data quality code B is applied to 1,3-butadiene and quality code A for all other compounds.

Periods of significant (> 50 hours) data loss are as follows:-

- 13 to 23 June analyser removed for intercomparison
- 12 to 24 December 290 hours data lost as data were rejected due to poor chromatography

Following installation and commissioning of the PerkinElmer ozone pre-cursor analyser in 2007 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.

#### 4.2.3 Marylebone Road

For the Marylebone Road site the data capture for benzene was 76.5% and for 1,3-butadiene was 79.9%. Data quality code A is applied to all compounds.

Periods of significant (> 50 hours) data loss are as follows:-

22 April to 28 May 860 hours data lost, old analyser failed, new analyser installed 19 to 28 October 230 hours data lost, broken transfer line and compressor failure

21 to 29 November 196 hours data lost, analyser stopped as carrier gas cylinder was empty

19 to 31 December 298 hours data lost, oven off warning

#### 4.2.4 Eltham

For the Eltham site the data capture for benzene was 85.6% and for 1,3-butadiene was 82.4%. Data quality code A is applied to all compounds.

Periods of significant (> 50 hours) data loss are as follows:-

16 to 19 May 86 hours data lost as analyser did not re-start following power cut

15 to 21 July 150 hours data lost due to sample pump failure

18 November to 10 December 547 hours lost due to compressor failure

16 to 18 December 52 hours analyser stopped

20 to 22 December 60 hours lost due to system not maintaining temperature set points

23 to 31 December 215 hours lost due to continuation of above fault and there being no access as the Curriculum Centre had closed for the holiday period

#### 4.2.5 Auchencorth Moss

For the Auchencorth Moss site the data capture for benzene was 27.0% and for 1,3-butadiene was 28.6%. Data quality code A is applied to all reported compounds. Concentrations have been very low for the entire period, often below the limit of detection for the analyser system. Both Perkin Elmer and AEA have investigated the issues surrounding this at great length. The analyser measured and reported calibration data, therefore there does not appear to be any faults with the instrument. Other more abundant compounds give a better indication of data capture for this site/instrument.

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 affected 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 Glasgow 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 10, 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, 6, 8 and 10, 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 Auchencorth Moss, 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 each of the sites in the network operating PE-OPA analysers has been made for 2008. From this plot the relationship between a roadside site (Marylebone Road) and an urban background site (Eltham) measuring the same air mass can be made. 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. Harwell and Auchencorth Moss are also included to illustrate how much lower the concentrations observed at these sites are.

#### 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 and Northern Ireland the objective has been set for benzene of  $3.25~\mu g/m^3$  specified as a running annual mean 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 2008 together with the annual means since 2003 are given in tables 1, 2, 4 and 5, Appendix 5. The maximum running annual means for 2008 are given in Tables 3 and 6, Appendix 5.

For benzene the annual means for 2003 to 2008 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 2008 were also below the relevant Air Quality Objectives to be met by 2010 for the respective region.

For 1,3-butadiene the maximum running annual means for 2008 for all sites were well below the Air Quality Objective of 2.25  $\mu$ g/m³ to be met by the end of 2003.

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

The annual means for benzene and 1,3-butadiene for 2000 to 2008 are plotted in figures 1 to 3, Appendix 3. The plots show the significant decrease of the concentration of these hydrocarbons over the last 8 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 2008 are plotted in figures 1 to 4, Appendix 4. Data are not presented for Auchencorth Moss due to the low data capture during the reporting period.

The plot for both compounds for the Glasgow site show no significant change in RAM concentration across the period.

The data for the Harwell site shows a rises in the RAM concentration for both compounds, with a more significant increase for 1,3 butadiene.

The Marylebone Road site shows no significant change in RAM concentration for 1,3 butadiene, whereas the benzene RAM decreases through the early months of the year and then increases to a final value which is similar to that observed at the start of the year. The Eltham site shows a decreasing trend for both benzene and 1,3-butadiene during 2008.

There is insufficient information to provide an explanation of the observed changes 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 with long running data sets within the UK Automatic Hydrocarbon Network at the beginning of 2008. Data for Auchencorth Moss are not presented due to the low data capture experienced at this remote site.

Figures 1 and 4, the plots for the Glasgow and Eltham sites, cover a shorter time period due to the fact the sites were established during 2002 and 2004 respectively.

Figure 1, the plot for the Glasgow site, shows that the concentrations have generally reached a stable state over the years 2006 to 2008 with some evidence of seasonal variations. Figure 2, the plot for the Harwell site, shows an overall decrease of the benzene, 1,3-butadiene concentrations over the period of the plot.

Figure 3, the plot for the Marylebone Road site shows a significant decrease of the concentration of all three hydrocarbons.

Figure 4, the plot for the Eltham site shows significant decreases in 1,3 butadiene and toluene concentrations, but less so for benzene.

#### 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-butadiene ratio occurs when the concentrations of 1,3-butadiene are low. Further investigation 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.

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# Appendix 1 Summary Statistical Information

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- Table 2. 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 2008 to 31 December 2008
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- Table 4. 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 2008 to 31 December 2008
- Table 5. 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 2008 to 31 December 2008

Table 1. 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 2008 to 31 December 2008

Compound	% Data capture	Maximum hourly	Mean concentration	Minimum hourly
		concentration (μg/m³)	(μg/m³)	concentration (μg/m³)
1,3-Butadiene	96.3	3.93	0.15	0.00
Benzene	96.3	14.17	1.04	0.00
Toluene	96.3	53.13	2.75	0.08
Ethylbenzene	87.7	10.00	0.52	0.04
(m+p)-Xylene *	96.2	65.71	2.10	0.04
o-Xylene	90.7	14.01	0.77	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 Harwell site of the UK Hydrocarbon Network, for the period; 1 January 2008 to 31 December 2008

Compound (Reported from VOC71M)	% Data capture	Maximum hourly concentration (μg/m³)	Mean concentration (μg/m³)	Minimum hourly concentration (µg/m³)
1,3-Butadiene	89.8	0.92	0.03	0.00
Benzene	89.2	4.54	0.39	0.00

Compound	% Data	Maximum	Mean	Minimum
(Reported from PE-OPA)	capture	hourly	concentration	hourly
,		concentration	$(\mu g/m^3)$	concentration
		$(\mu g/m^3)$		$(\mu g/m^3)$
Ethane	82.0	12.69	2.24	0.02
Ethene	71.7	15.15	0.47	0.00
Propane	75.2	10.54	1.45	0.02
Propene	62.9	3.39	0.28	0.00
Ethyne	58.0	1.81	0.29	0.01
2-Methylpropane	67.7	6.34	0.56	0.00
n-Butane	70.5	9.26	0.86	0.00
trans-2-Butene	75.0	1.12	0.20	0.02
1-Butene	76.0	0.77	0.16	0.00
cis-2-Butene	68.6	0.63	0.09	0.00
2-Methylbutane	78.0	6.29	0.56	0.00
n-Pentane	75.6	3.11	0.31	0.00
1,3-Butadiene				
trans-2-Pentene	0.1	0.09	0.04	0.03
1-Pentene	0.1	0.03	0.02	0.00
2-Methylpentane	60.4	1.79	0.17	0.00
n-Hexane	55.7	1.93	0.15	0.00
Isoprene	8.2	0.48	0.09	0.00
Benzene				
2,2,4-trimethylpentane	30.6	4.41	0.21	0.00
n-Heptane	34.0	2.12	0.16	0.00
n-Octane	13.9	1.23	0.13	0.00
Toluene	78.5	13.39	0.61	0.04
Ethylbenzene	44.3	4.98	0.19	0.00
(m+p)-Xylene *	55.6	3.31	0.34	0.00
o-Xylene	49.7	3.26	0.17	0.00
1,3,5-Trimethylbenzene	16.7	2.15	0.17	0.00
1,2,4-Trimethylbenzene	68.2	5.19	0.30	0.00
1,2,3-Trimethylbenzene	41.3	2.74	0.15	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 3. 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 2008 to 31 December 2008

Compound	% Data	Maximum	Mean	Minimum
	capture	hourly	concentration	hourly
		concentration	(μg/m³)	concentration
		(μg/m³)		(μg/m³)
Ethane	79.9	103.99	10.43	1.33
Ethene	79.9	29.91	3.45	0.24
Propane	79.9	100.27	5.75	0.80
Propene	79.8	7.44	1.54	0.10
Ethyne	79.5	19.78	2.19	0.11
2-Methylpropane	79.9	45.24	3.82	0.39
n-Butane	79.9	109.36	6.21	0.53
trans-2-Butene	79.8	4.89	0.47	0.02
1-Butene	79.9	3.56	0.47	0.05
cis-2-Butene	79.7	3.19	0.27	0.02
2-Methylbutane	79.8	74.48	6.54	0.39
n-Pentane	79.9	15.36	1.99	0.24
1,3-Butadiene	79.9	2.42	0.35	0.04
trans-2-Pentene	79.3	2.74	0.38	0.03
1-Pentene	78.7	1.31	0.21	0.03
2-Methylpentane	79.9	17.20	2.46	0.11
n-Hexane	77.1	2.40	0.26	0.00
Isoprene	79.8	7.72	0.69	0.04
Benzene	76.5	8.53	1.36	0.03
2,2,4-trimethylpentane	79.1	13.08	1.27	0.00
n-Heptane	79.2	7.28	0.47	0.00
n-Octane	76.4	4.74	0.21	0.00
Toluene	75.2	33.58	5.42	0.00
Ethylbenzene	77.3	28.96	0.91	0.00
(m+p)-Xylene *	76.2	273.73	6.00	0.00
o-Xylene	79.1	28.60	1.24	0.00
1,3,5-Trimethylbenzene	79.5	22.45	0.53	0.00
1,2,4-Trimethylbenzene	80.0	91.65	1.55	0.00
1,2,3-Trimethylbenzene	72.8	19.06	0.54	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 4. 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 2008 to 31 December 2008

Compound	% Data	Maximum	Mean	Minimum
·	capture	hourly	concentration	hourly
		concentration	(μg/m³)	concentration
		(μg/m³)		(μg/m³)
Ethane	85.1	78.19	5.47	0.85
Ethene	79.7	13.35	0.83	0.01
Propane	85.0	51.79	3.05	0.24
Propene	79.6	6.16	0.39	0.00
Ethyne	84.3	6.86	0.46	0.00
2-Methylpropane	84.7	38.00	1.83	0.07
n-Butane	84.2	56.26	2.82	0.12
trans-2-Butene	83.9	1.84	0.09	0.00
1-Butene	78.6	1.70	0.09	0.00
cis-2-Butene	73.7	1.30	0.06	0.00
2-Methylbutane	82.7	41.22	1.21	0.06
n-Pentane	83.7	13.32	0.50	0.03
1,3-Butadiene	82.4	1.26	0.07	0.00
trans-2-Pentene	78.2	1.22	0.07	0.00
1-Pentene	79.2	1.46	0.07	0.00
2-Methylpentane	85.5	7.08	0.51	0.00
n-Hexane	76.0	5.03	0.19	0.00
Isoprene	83.8	11.69	0.34	0.00
Benzene	85.6	7.85	0.73	0.06
2,2,4-trimethylpentane	78.4	4.46	0.43	0.05
n-Heptane	85.6	2.49	0.27	0.04
n-Octane	69.6	1.42	0.11	0.00
Toluene	85.7	26.13	1.71	0.11
Ethylbenzene	85.4	10.84	0.29	0.00
(m+p)-Xylene *	85.7	42.40	0.87	0.04
o-Xylene	85.5	14.32	0.32	0.04
1,3,5-Trimethylbenzene	77.5	11.62	0.16	0.00
1,2,4-Trimethylbenzene	78.0	13.32	0.63	0.15
1,2,3-Trimethylbenzene	78.0	6.94	0.32	0.05

<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 Auchencorth Moss site of the UK Hydrocarbon Network for the period; 1 January 2008 to 31 December 2008

Compound	% Data capture	Maximum hourly concentration	Mean concentration (µg/m³)	Minimum hourly concentration
		$(\mu g/m^3)$		$(\mu g/m^3)$
Ethane	53.3	13.81	1.85	0.47
Ethene	45.9	3.99	0.23	0.00
Propane	52.8	74.42	1.42	0.11
Propene	33.8	1.97	0.12	0.00
Ethyne	42.3	2.22	0.21	0.01
2-Methylpropane	51.3	30.22	0.46	0.02
n-Butane	51.4	77.46	0.82	0.02
trans-2-Butene	0.4	16.65	0.48	0.00
1-Butene	1.4	0.40	0.05	0.00
cis-2-Butene	0.4	1.05	0.06	0.00
2-Methylbutane	50.6	26.19	0.35	0.00
n-Pentane	50.8	27.96	0.26	0.00
1,3-Butadiene	28.6	3.35	0.04	0.00
trans-2-Pentene				
1-Pentene	0.9	0.49	0.08	0.00
2-Methylpentane	27.5	5.11	0.10	0.00
n-Hexane	30.0	6.97	0.12	0.00
Isoprene	5.7	2.29	0.11	0.00
Benzene	27.0	1.33	0.21	0.00
2,2,4-trimethylpentane	3.4	19.15	0.19	0.00
n-Heptane	5.3	22.99	0.26	0.00
n-Octane	0.6	0.14	0.05	0.00
Toluene	19.9	17.17	0.30	0.00
Ethylbenzene	5.5	20.05	0.29	0.00
(m+p)-Xylene *	6.5	38.83	0.46	0.00
o-Xylene	4.3	19.26	0.30	0.00
1,3,5-Trimethylbenzene	0.0	0.05	0.05	0.05
1,2,4-Trimethylbenzene	0.0	0.50	0.25	0.15
1,2,3-Trimethylbenzene	0.1	0.35	0.17	0.05

<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.

# Appendix 2 Time Series Plots of Hydrocarbon Concentrations

- Figure 1. Time series plot of the ratified benzene data from the Glasgow site of the UK Hydrocarbon Network, for the period; 1 January 2008 to 31 December 2008
- Figure 2. Time series plot of the ratified 1,3-butadiene data from the Glasgow site of the UK Hydrocarbon Network, for the period; 1 January 2008 to 31 December 2008
- Figure 3. Time series plot of the ratified benzene data from the Harwell site of the UK Hydrocarbon Network, for the period; 1 January 2008 to 31 December 2008
- Figure 4. Time series plot of the ratified 1,3-butadiene data from the Harwell site of the UK Hydrocarbon Network, for the period; 1 January 2008 to 31 December 2008
- Figure 5. Time series plot of the ratified benzene data from the Marylebone Road site affiliated to the UK Hydrocarbon Network, for the period; 1 January 2008 to 31 December 2008
- Figure 6. 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 2008 to 31 December 2008
- Figure 7. Time series plot of the ratified benzene data from the Eltham site of the UK Hydrocarbon Network, for the period; 1 January 2008 to 31 December 2008
- Figure 8. Time series plot of the ratified 1,3-butadiene data from the Eltham site of the UK Hydrocarbon Network, for the period; 1 January 2008 to 31 December 2008
- Figure 9. Time series plot of the ratified benzene data from the Auchencorth Moss site of the UK Hydrocarbon Network, for the period; 1 January 2008 to 31 December 2008

Figure 10. 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 2008 to 31 December 2008

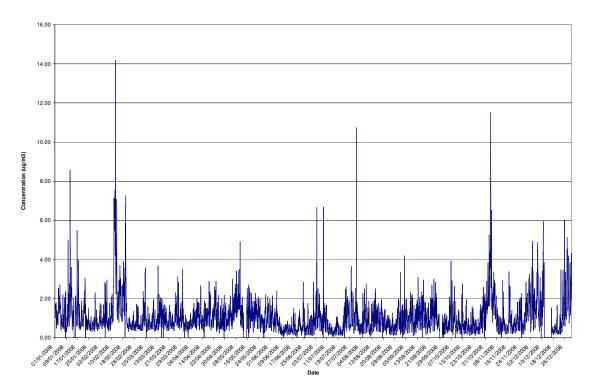


Figure 1. Time series plots for the ratified benzene data from the Glasgow site of the UK Hydrocarbon Network, for the period; 1 January 2008 to 31 December 2008

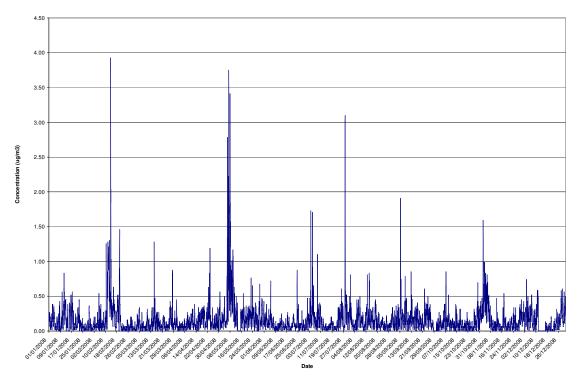


Figure 2. Time series plots for the ratified 1,3-butadiene data from the Glasgow site of the UK Hydrocarbon Network, for the period; 1 January 2008 to 31 December 2008

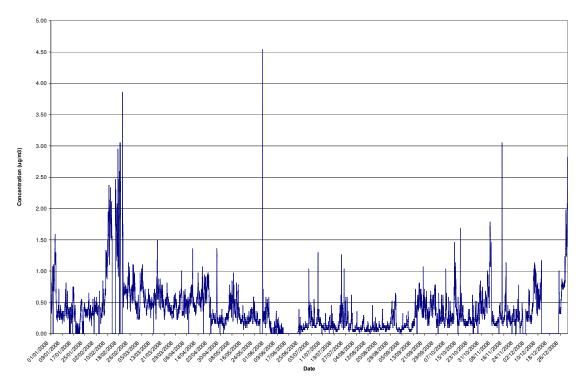


Figure 3. Time series plots for the ratified benzene data from the Harwell site of the UK Hydrocarbon Network, for the period; 1 January 2008 to 31 December 2008

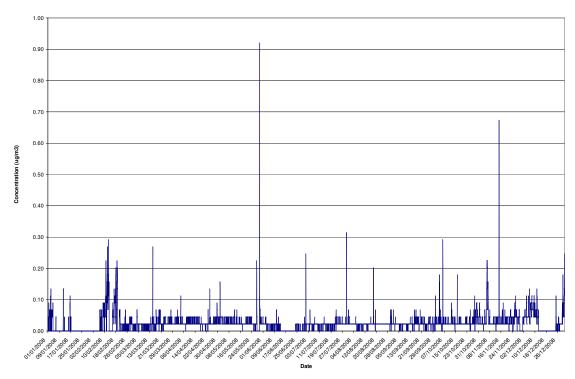


Figure 4. Time series plots for the ratified 1,3-butadiene data from the Harwell site of The UK Hydrocarbon Network, for the period; 1 January 2008 to 31 December 2008

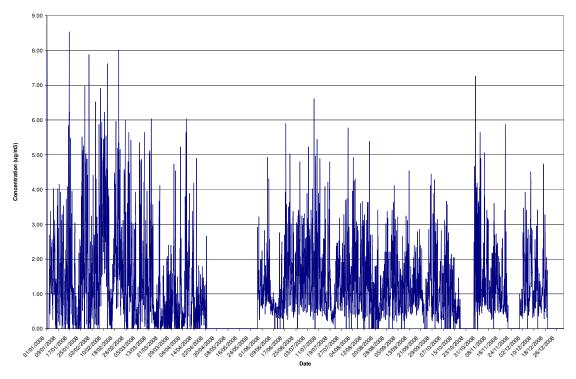


Figure 5. Time series plots for the ratified benzene data from the Marylebone Road site affiliated to the UK Hydrocarbon Network, for the period; 1 January 2008 to 31 December 2008

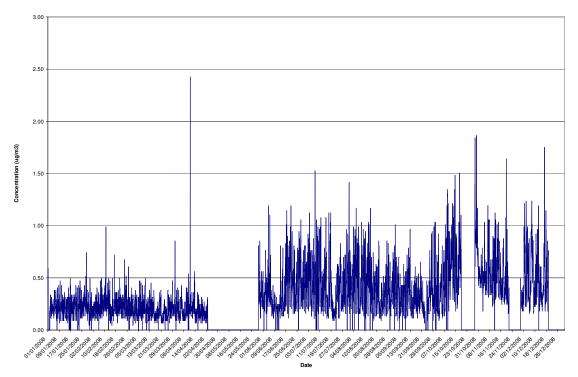


Figure 6. Time series plots for the ratified 1,3-butadiene data from the Marylebone Road site affiliated to the UK Hydrocarbon Network, for the period; 1 January 2008 to 31 December 2008

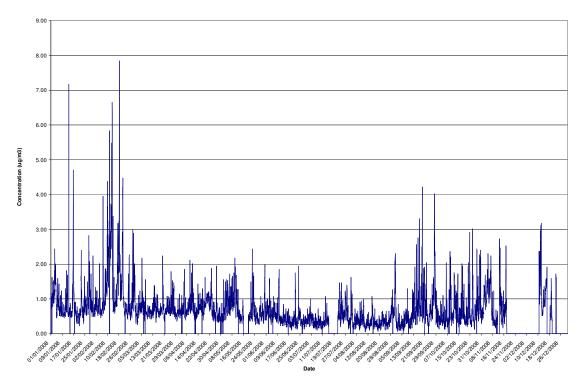


Figure 7. Time series plots for the ratified benzene data from the Eltham site of the UK Hydrocarbon Network, for the period; 1 January 2008 to 31 December 2008

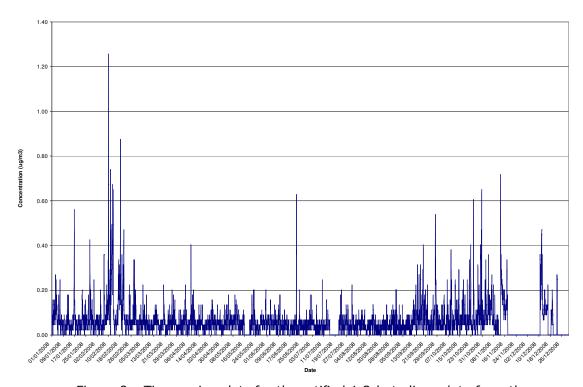


Figure 8. Time series plots for the ratified 1,3-butadiene data from the Eltham site of the UK Hydrocarbon Network, for the period; 1 January 2008 to  $31\ \text{December}\ 2008$ 

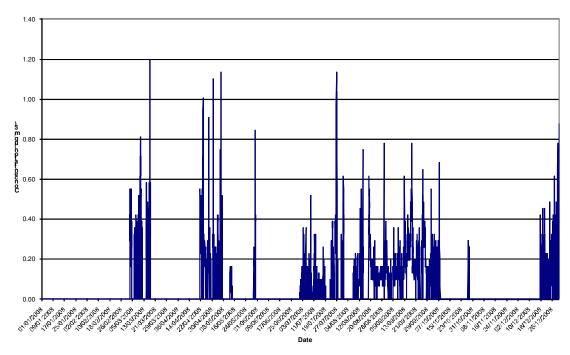


Figure 9. Time series plots for the ratified benzene data from the Auchencorth Moss site of the UK Hydrocarbon Network, for the period; 1 January 2008 to 31 December 2008

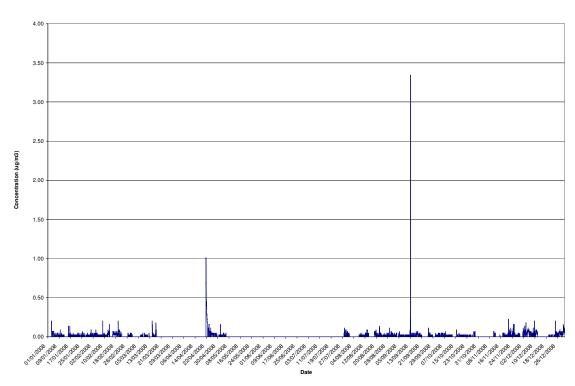


Figure 10. Time series plots for the ratified 1,3-butadiene data from the Auchencorth Moss site of the UK Hydrocarbon Network, for the period; 1 January 2008 to 31 December 2008

# **Appendix 3 Annual Mean Plots**

Figure 1.	Mean Benzene concentrations for the UK Automatic Hydrocarbon Network, 1993-2008
Figure 2.	Mean Benzene concentrations for the UK Automatic Hydrocarbon Network, 1993-2008 (magnified y-axis),
Figure 3.	Mean 1,3-Butadiene concentrations for the UK Automatic Hydrocarbon Network, 1993-2008
Figure 4.	Mean concentrations for all compounds measured at Marylebone Road, Harwell, Eltham and Auchencorth Moss for the UK Automatic Hydrocarbon Network, for 2008

#### Mean Benzene Concentrations (ug/m³) for UK Hydrocarbon Network sites from 2000

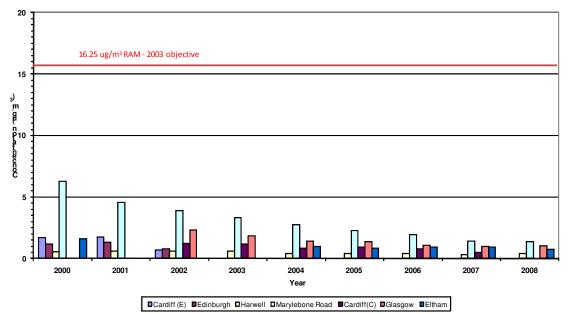


Figure 1. Mean benzene concentrations for the UK Automatic Hydrocarbon Network, 2000-2008

#### Mean Benzene Concentrations (ug/m³) for UK Hydrocarbon Network sites from 2000

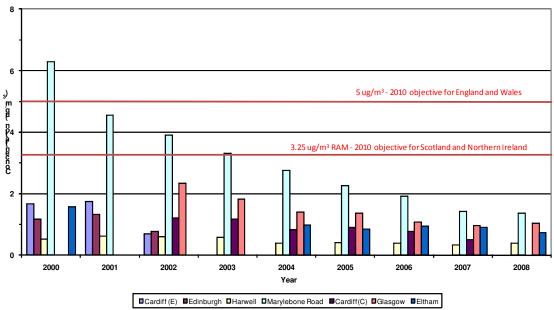


Figure 2. Mean Benzene concentrations for the UK Automatic Hydrocarbon Network, 2000-2008 (magnified y-axis)

#### $\label{eq:mean13-Butadiene Concentrations (ug/m^3) for UK Hydrocarbon Network sites from 2000$

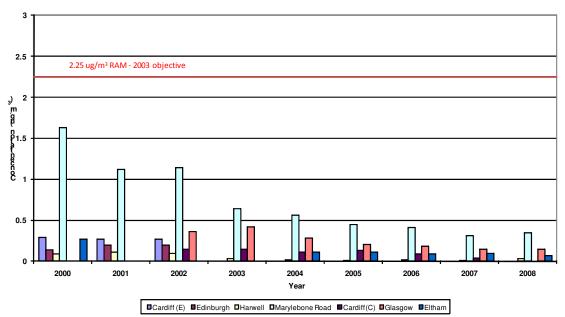


Figure 3. Mean 1,3-Butadiene concentrations for the UK Automatic Hydrocarbon Network, 2000-2008

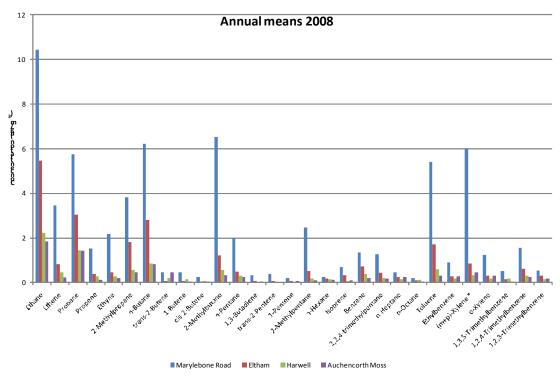


Figure 4. Mean concentrations for all compounds measured at Marylebone Road, Eltham, Harwell and Auchencorth Moss for the UK Automatic Hydrocarbon Network, for 2008

# **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 Glasgow site of the UK Hydrocarbon Network, for the period; January 2008 to December 2008.
- Figure 2. 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 2008 to December 2008.
- Figure 3. 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 2008 to December 2008.
- Figure 4. 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 2008 to December 2008.

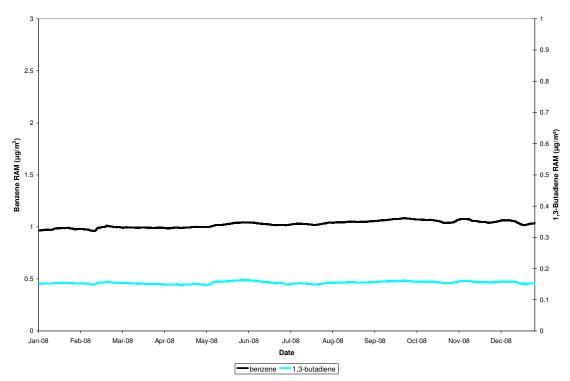


Figure 1. Time series plot of the running annual mean for benzene and 1,3-butadiene data from the Glasgow site of the UK Hydrocarbon Network, for the period; January 2008 to December 2008.

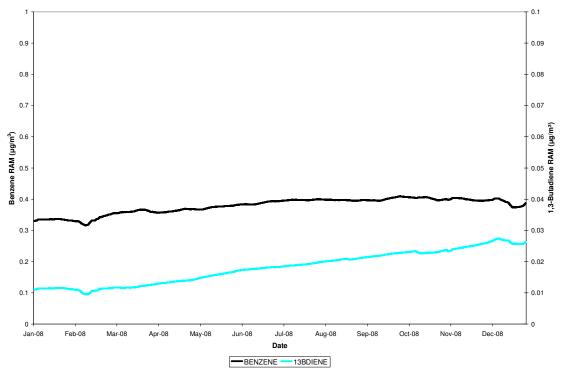


Figure 2. Time series plot of the running annual mean for benzene and 1,3-butadiene data from the Harwell site of the UK Hydrocarbon Network, for the period; January 2008 to December 2008.

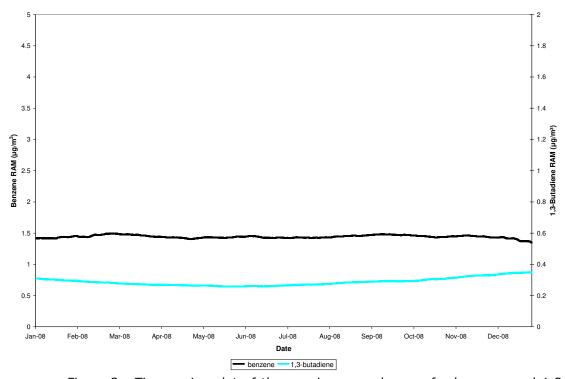


Figure 3. Time series plot of the running annual mean for benzene and 1,3-butadiene data from the Marylebone Road site affiliated to the UK Hydrocarbon Network, for the period; January 2008 to December 2008.

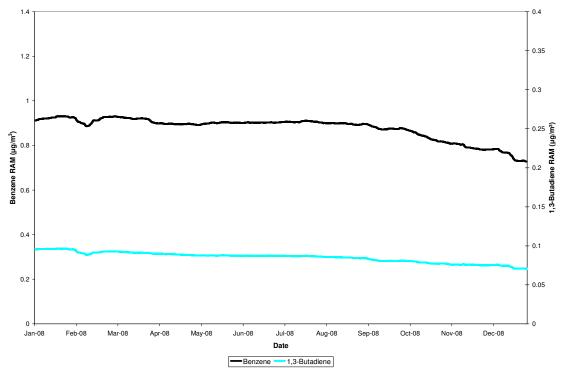


Figure 4. Time series plot of the running annual mean for benzene and 1,3-butadiene data from the Eltham site of the UK Hydrocarbon Network, for the period; January 2008 to December 2008.

# 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 ( $\mu g/m^3$ ) 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 ( $\mu g/m^3$ ) at each of the UK Automatic Hydrocarbon Sites, 2008.

Monitoring Site	Quarter 1	Quarter 2	Quarter 3	Quarter 4
	2008	2008	2008	2008
	Mean	Mean	Mean	Mean
Auchencorth Moss	0.32	0.25	0.17	0.37
Glasgow	1.21	0.92	0.88	1.16
Harwell	0.60	0.34	0.20	0.43
Marylebone Road	1.66	1.15	1.30	1.20
Eltham	0.97	0.65	0.51	0.78

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

Monitoring Site	2003 Annual Mean	2004 Annual Mean	2005 Annual Mean	2006 Annual Mean	2007 Annual Mean	2008 Annual Mean	2008 Data Capture %
Auchencorth Moss						0.21	27.0
Cardiff Centre	1.17	0.84	0.91	0.78	0.49		
Glasgow	1.82	1.40	1.36	1.07	0.96	1.04	96.3
Harwell	0.59	0.40	0.42	0.39	0.33	0.39	89.2
Marylebone Road	3.32	2.75	2.27	1.92	1.41	1.36	76.5
Eltham		0.76	0.84	0.94	0.91	0.73	85.6

Table 3. Maximum running annual means of measured benzene concentrations ( $\mu g/m^3$ ) at each of the UK Automatic Hydrocarbon Sites. Data for Auchencorth Moss are not included due to the low data capture during 2008.

Monitoring Site	2008	2008		
	Maximum running	MRAM Data		
	annual mean	Capture %		
Glasgow	1.08	98.1		
Harwell	0.41	89.4		
Marylebone Road	1.49	73.7		
Eltham	0.93	84.3		

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

Monitoring Site	Quarter 1	Quarter 2	Quarter 3	Quarter 4
	2008	2008	2008	2008
	Mean	Mean	Mean	Mean
Auchencorth Moss	0.03	0.07	0.04	0.04
Glasgow	0.14	0.17	0.15	0.14
Harwell	0.02	0.03	0.02	0.04
Marylebone Road	0.21	0.30	0.39	0.53
Eltham	0.08	0.05	0.05	0.10

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

Monitoring Site	2003	2004	2005	2006	2007	2008	2008
	Annual	Annual	Annual	Annual	Annual	Annual	Data
	Mean	Mean	Mean	Mean	Mean	Mean	Capture %
Auchencorth Moss					0.01	0.04	28.6
Cardiff Centre	0.15	0.11	0.13	0.09	0.04		
Glasgow	0.42	0.28	0.20	0.18	0.15	0.15	96.3
Harwell	0.03	0.02	0.02	0.02	0.01	0.03	89.8
Marylebone Road	0.64	0.56	0.45	0.41	0.31	0.35	79.9
Eltham		0.15	0.11	0.09	0.10	0.07	82.4

Table 6. Maximum running annual means of measured 1,3-butadiene concentrations  $(\mu g/m^3)$  at each of the UK Automatic Hydrocarbon Sites. Data for Auchencorth Moss are not included due to the low data capture during 2008.

Monitoring Site	2008	2008	
	Maximum running	MRAM Data	
	annual mean	Capture %	
Glasgow	0.16	96.7	
Harwell	0.03	90.9	
Marylebone Road	0.35	80.1	
Eltham	0.10	82.6	

# **Appendix 6 Trend Analysis Plots**

- Figure 1. Plot of the monthly mean concentrations of benzene, toluene and 1,3-butadiene at the Glasgow 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 Marylebone Road site of the UK Hydrocarbon Network
- Figure 4. Plot of the monthly mean concentrations of benzene, toluene and 1,3-butadiene at the Eltham site of the UK Hydrocarbon Network
- Figure 5. Plot of the monthly mean benzene: 1,3-butadiene ratio for all sites of the UK Hydrocarbon Network

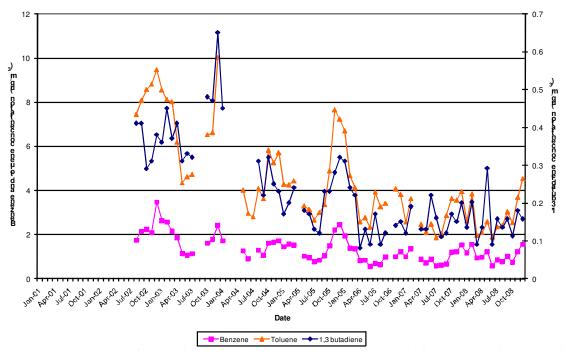


Figure 1. Plot of the monthly mean concentrations of benzene, toluene and 1,3-butadiene at the Glasgow site of the UK Hydrocarbon Network

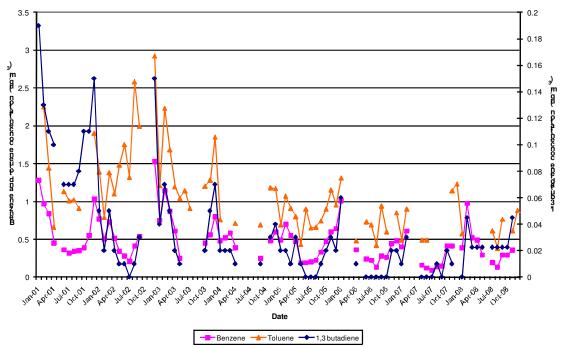


Figure 2. Plot of the monthly mean concentrations of benzene, toluene and 1,3-butadiene at the Harwell site of the UK Hydrocarbon Network

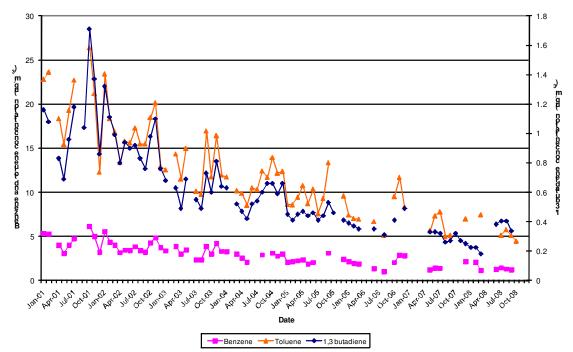


Figure 3. Plot of the monthly mean concentrations of benzene, toluene and 1,3-butadiene at the Marylebone Road site of the UK Hydrocarbon Network

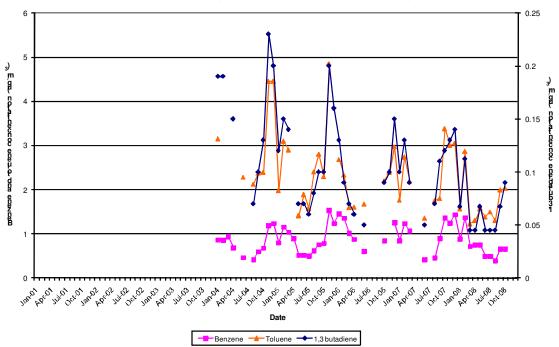


Figure 4. Plot of the monthly mean concentrations of benzene, toluene and 1,3-butadiene at the Eltham site of the UK Hydrocarbon Network

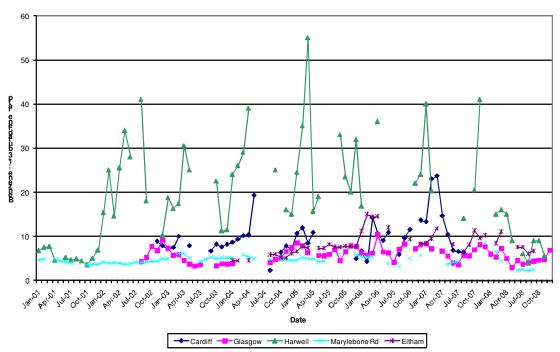


Figure 5. Plot of the monthly mean benzene: 1,3-butadiene ratio for all sites of the UK Hydrocarbon Network 2008

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