Ratification of data produced by the UK Ambient Hydrocarbon Automatic Air Quality Network, 1 October 2003 to 31 December 2003

A report produced for the Department for Environment, Food and Rural Affairs, the Scottish Executive, the Welsh Assembly Government and the Department of the Environment in Northern Ireland

AEAT/ENV/R/1717 Issue 1
June 2004
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| File reference | ED45010 |
| Report number | AEAT/ENV/R/1717 |
| Report status | Issue 1 |

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| Approved by | Ken Stevenson |      |
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1 Introduction

This report contains information on the quality and statistical parameters associated with ratified data from the UK Ambient Hydrocarbon Automatic Air Quality Network (The UK Hydrocarbon Network). The presented information and data cover the period 1 October 2003 to 31 December 2003, with annual statistics for 2003 and comparison with air quality objectives. The ratified data have been made available on the World Wide Web at http://www.airquality.co.uk/archive/data_and_statistics_home.php

This report contains:

- The definition of a Data Quality Code for each reported hydrocarbon.
- The Data Quality Codes assigned to the data presented on the web.
- A list of periods of data loss, reasons for data loss and descriptions of the most significant causes of data loss.
- Statistical information for each measured hydrocarbon for each individual month.
- Information on air quality objectives for benzene and 1,3-butadiene for 2003.

During this quarter an additional monitoring site was established at London Eltham. Data from this site will be presented in future reports.

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$^3$).
2 Hydrocarbon Data Quality

All hydrocarbon data are assigned a quality value. In general ratified hourly data have an uncertainty (at 95% confidence) of ±10% for values above 0.5 µg/m³ and ±0.05 µg/m³ for values below 0.5 µg/m³. These data are termed 'good quality'.

In some cases, because of instrument problems, data cannot be described as 'good' quality, but the data may still be of use to modellers and is therefore included in the archive. This is termed 'acceptable' quality data, and has an uncertainty (at 95% confidence) of ± 25% above 0.5 µg/m³ and ± 0.1 µg/m³ below 0.5 µg/m³.

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

Each month’s data are assigned a Data Quality Code for each species as follows:

A. all 'good' quality data
B. most (> 75%) data points 'good', remainder 'acceptable' quality
C. roughly equal numbers of 'good' and 'acceptable' quality data
D. some (< 25%) data points 'good' quality; remainder 'acceptable' quality
E. all points 'acceptable' quality
3 Monthly Data Reports

The following sections give details of issues affecting data on a month by month basis. Data quality codes have been assigned for each monthly set of data.

### 3.1 CARDIFF

#### 3.1.1 October

**3.1.1.1 Data Quality Codes**

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

**3.1.1.2 Missing Data – All hydrocarbons**

- PC/GC communication problem 03/10/03 hours 01 to 02.
- Calibration 20/10/03 hours 12 to 14.
- Calibration 31/10/03 hours 12 to 15.

**3.1.1.3 Missing Data – Specific hydrocarbons**

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

#### 3.1.2 November

**3.1.2.1 Data Quality Codes**

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

**3.1.2.2 Missing Data - All hydrocarbons**

- Calibration 13/11/03 hours 15 to 17.
- PC/GC communication problem 21/11/03 hours 18 to 19.
- Calibration 28/11/03 hours 15 to 17.

**3.1.2.3 Missing Data - Specific hydrocarbons**

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

#### 3.1.3 December

**3.1.3.1 Data Quality Codes**

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

**3.1.3.2 Missing Data - All hydrocarbons**

- Calibration 16/12/03 hours 13 to 14.
- Calibration 22/12/03 hours 10 to 12.

**3.1.3.3 Missing Data - Specific hydrocarbons**

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

3.2.1 October

3.2.1.1 Data Quality Codes

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

3.2.1.2 Missing Data - All hydrocarbons

- Calibration 01/10/03 hours 11 to 14.
- Calibration 07/10/03 hours 11 to 14.
- Calibration 21/10/03 hours 11 to 15.

3.2.1.3 Missing Data - Specific hydrocarbons

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

3.2.2 November

3.2.2.1 Data Quality Codes

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

3.2.2.2 Missing Data - All hydrocarbons

- Calibration 04/11/03 hours 12 to 16.
- PC/GC communication problem 08/11/03 hours 14 to 16.
- Calibration 18/11/03 hours 12 to 16.

3.2.2.3 Missing Data - Specific hydrocarbons

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

3.2.3 December

3.2.3.1 Data Quality Codes

Data quality code A for all data for all of the month except:
Data quality code E for 1,3-butadiene, toluene, ethylbenzene, (m+p)-xylene and o-xylene for all of the month.

3.2.3.2 Missing Data - All hydrocarbons

- Calibration 02/12/03 hours 10 to 16.
- CMCU service visit and calibration 09/11/03 hour 20 to 10/11/03 hour 02.
- Calibration 16/12/03 hours 10 to 15.
- Calibration 30/12/03 hours 12 to 15.

3.2.3.3 Missing Data - Specific hydrocarbons

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

3.3.1 October

3.3.1.1 Data Quality Codes
Data quality code A for all data for all of the month except:
Data quality code E for 1,3-butadiene for all of the month.

3.3.1.2 Missing Data - All hydrocarbons
- Calibration 09/10/03 hours 08 to 09.
- Calibration 16/10/03 hours 15 to 18.
- Calibration 23/10/03 hours 09 to 10.

3.3.1.3 Missing Data - Specific hydrocarbons
None, except where the integration was unreliable due to very low concentrations.

3.3.2 November

3.3.2.1 Data Quality Codes
Data quality code A for all data for all of the month except:
Data quality code E for 1,3-butadiene for all of the month.

3.3.2.2 Missing Data - All hydrocarbons
- Calibration 07/11/03 hours 09 to 11.
- Calibration 20/11/03 hours 13 to 17.

3.3.2.3 Missing Data - Specific hydrocarbons
None, except where the integration was unreliable due to very low concentrations.

3.3.3 December

3.3.3.1 Data Quality Codes
Data quality code A for all data for all of the month except:
Data quality code E for 1,3-butadiene for all of the month.

3.3.3.2 Missing Data - All hydrocarbons
- Calibration 04/12/03 hours 09 to 11.
- PC/GC communication problem 05/12/03 hours 10 to 12.
- Calibration 19/12/03 hours 10 to 11.

3.3.3.3 Missing Data - Specific hydrocarbons
None, except where the integration was unreliable due to very low concentrations.
3.4 MARYLEBONE ROAD

3.4.1 October

3.4.1.1 Data Quality Codes
Data quality code A for all data for all of the month.

3.4.1.2 Missing Data - All hydrocarbons
- Calibration 01/10/03 hours 13 to 16.
- Calibration 15/10/03 hours 13 to 16.
- Calibration 30/10/03 hours 04 to 07.

3.4.1.3 Missing Data - Specific hydrocarbons
None.

3.4.2 November

3.4.2.1 Data Quality Codes
Data quality code A for all data for all of the month.

3.4.2.2 Missing Data - All hydrocarbons
- Calibration 05/11/03 hours 14 to 17.
- Calibration 20/11/03 hours 05 to 08.
- PC/GC communication problem 21/11/03 hours 09 to 11.
- Calibration 26/11/03 hours 13 to 16.

3.4.2.3 Missing Data - Specific hydrocarbons
None.

3.4.3 December

3.4.3.1 Data Quality Codes
Data quality code A for all data for all of the month.

3.4.3.2 Missing Data - All hydrocarbons
- Calibration 10/12/03 hours 16 to 19.
- Calibration 25/12/03 hours 07 to 10.
- Calibration 31/12/03 hours 16 to 19.

3.4.3.3 Missing Data - Specific hydrocarbons
None.
4 Discussion

4.1 THE RATIFIED DATA

Tables 1 to 4, Appendix 1 contain statistical information relating to the ratified data, for each measured hydrocarbon, over the period 1 October 2003 to 31 December 2003. The tables list the percentage data capture, maximum concentration, mean concentration and minimum concentration of each hydrocarbon. The data capture is the number of ratified hourly data values expressed as a percentage of the number of hours in the specified period.

4.1.1 Cardiff

For the Cardiff site the data capture for benzene was 99% and for 1,3-butadiene was 99%.

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

4.1.2 Glasgow

For the Glasgow site the data capture for benzene was 97% and for 1,3-butadiene was 97%.

During December it was observed in some chromatograms that the peak width of toluene, ethylbenzene, (m+p)-xylene and o-xylene had increased. At very wide peak widths the integration of the reported peak areas becomes unreliable and these data have been removed. Approximately 2% of toluene, 13% of ethylbenzene, 13% of (m+p)-xylene and 15% of o-xylene have been removed for quarter 4, 2003.

It was also observed that the calibration samples for these compounds were affected by increased peak width. The response factor for these compounds has been derived from the relative response to benzene using an approach similar to that used for 1,3-butadiene, described in section 4.2. Because of the increased uncertainty of this method all data for toluene, ethylbenzene, (m+p)-xylene and o-xylene have been assigned data quality code E for December. This problem was caused by a breakdown of the sorbent packing in the focussing tube, which was replaced in quarter 1, 2004. Benzene and 1,3-butadiene were not affected by this problem.

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

It should be noted that the hydrocarbon instrumentation at the Glasgow site samples air through a separate inlet from that used for the inorganic measurements. The inlet for the inorganic measurements is within one metre from the kerb and hence these are classed as kerbside measurements. The sample inlet for the hydrocarbon measurements is more than one metre from the kerb (but less than five metres) and hence these are classed as roadside measurements.

4.1.3 Harwell

For the Harwell site the data capture for benzene was 97% and for 1,3-butadiene was 97%.

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

4.1.4 Marylebone Road

For the Marylebone Road site the data capture for benzene was 95% and for 1,3-butadiene was 98%.

There have been no significant problems for the period covered by this report.
4.2 1,3-BUTADIENE DATA FOR THE VOC71M

During the process of calculating response factors for the data covered in this report it was observed that the 1,3-butadiene peak had merged with a neighbouring peak, trans-2-butene, in the chromatograms of the calibration samples. The reported peak areas for 1,3-butadiene in the standards were therefore, overestimated. As a result an accurate response factor for 1,3-butadiene could not be generated as the degree of overestimation could not be accurately quantified.

An alternative approach was used to generate the response factor for 1,3-butadiene. The response factor for cis-2-butene, a well-resolved peak, was used to derive a response factor for 1,3-butadiene. The relative response factors for 1,3-butadiene and cis-2-butene are fairly constant over time when both peaks are well resolved. The cis-2-butene response factor and relative response factor were used to derive a response factor for 1,3-butadiene.

It is likely that this approach generates a relatively accurate response factor for 1,3-butadiene. However due to the increased uncertainty associated with this method, all the 1,3-butadiene data at Cardiff, Glasgow and Harwell has been assigned data quality code E.

4.3 CONCENTRATION TRENDS

The periods when data for benzene and 1,3-butadiene were available, for all the sites, are plotted graphically in Figures 1 to 8, Appendix 2. The measured concentrations of 1,3-butadiene fell below 0.02 µg/m³ on a number of occasions see Figure 6, Appendix 2. Where concentrations fell below 0.02 µg/m³ the ratified concentrations have been reported as 0.00 µg/m³.

At Cardiff and Harwell the measured concentrations of hydrocarbons were low for most of the period covered by this report. At these urban background and rural sites there tends to be a pattern of seasonal variation with higher levels during the winter when dispersion is generally poorer and photochemical removal is at a minimum.

The Glasgow and Marylebone Road data tend to exhibit higher levels with less seasonal variation than is apparent in data from the other two sites. The measured concentrations and trends are typical of sites close to busy roads where the source of the measured hydrocarbons is close to the monitoring location. The emitted hydrocarbons will have had little time to mix and react in the atmosphere. The measured concentrations at Glasgow and Marylebone Road for October to December 2003 exhibited no significant episodes of elevated concentrations. There is insufficient information to provide an explanation of the observed difference in the trends from site to site, although spatial variations in meteorological conditions may well be the cause. The variation in trends from site to site is probably due to variations in atmospheric dispersion.

4.4 ROLLING ANNUAL MEANS

The rolling annual means (RAMs) for benzene and 1,3-butadiene for 2003 are plotted in figures 1 to 4, Appendix 3. For the Cardiff and Glasgow sites there is only data for part of the year because these sites were established in 2002. There appears to be no significant trend at the Cardiff, Glasgow and Harwell sites although the plots for Glasgow and for Harwell show a decrease during December 2003. This is the effect of higher concentrations during an episode in December 2002 no longer being included in the running annual mean. The concentrations have decreased to some extent at the Marylebone Road site where concentrations are higher.
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 µg/m³ 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 µg/m³ 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 µg/m³ 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 µg/m³ to be met by the end of 2003.

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

The means for both benzene and 1,3-butadiene for quarter 1, 2003 were slightly higher than the annual means for 2002. The means for both benzene and 1,3-butadiene for quarters 2 and 3, 2003 were lower than the annual means for 2002 and the means for quarter 1, 2003. The means for quarter 4, 2003 were approximately the same as the means for quarter 1, 2003. The observed trends in concentrations are probably due to seasonal variation.

For benzene the annual means for 2000, 2001, 2002 and 2003 were well below the respective Air Quality Objective of 16.25 µg/m³ to be met by the end of 2003. The annual means and maximum rolling annual means for 2003 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 2003 for all sites were well below the Air Quality Objective of 2.25 µg/m³ 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 Hydrocarbon Automatic Air Quality Network.

The annual means for benzene and 1,3-butadiene for 1994 to 2003 are plotted in figures 1 to 3, Appendix 5. The plots show the significant decrease of the concentration of these hydrocarbons over the last 10 years. In figure 2 the y axis scale has been expanded to show this trend at the sites with lower concentrations.

4.6 ANALYSIS OF TRENDS OF MEASURED HYDROCARBONS

4.6.1 Long term Trends

Figures 1 to 4, Appendix 6 are plots of the long term trends of the monthly mean concentrations of benzene, toluene and 1,3-butadiene at the four sites that comprised the UK Automatic Hydrocarbon Network at the end of December 2003.

Figure 1, the plot for the Marylebone Road site shows a significant decrease of the concentration of all three hydrocarbons. Figure 2, the plot for the Harwell site, shows a decrease of the benzene and 1,3-butadiene concentrations but apparently less so for the toluene.

Figures 3 and 4, the plots for the Cardiff Centre and Glasgow Hope Street sites, cover a much shorter time period due to the fact the sites were established during autumn 2002.
4.6.2 Ratios of the concentrations of the measured hydrocarbons

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

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

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

Initial inspection would suggest that the two instruments give significantly different results. An intercomparison of the two instruments at the Harwell site demonstrated that the results were quite comparable with very similar time series plots. Investigation of the data reveals that the elevated values for the benzene:1,3-butadien ratio occurs when the concentrations of 1,3-butadiene are low. Further investigation has revealed that the VOCAIR had a small but not significant 1,3-butadiene 'blank'. The level of the blank was such that the chromatographic peak was below the integration threshold so did not appear as a 'blank' value. Analysis of the ambient air samples collected by the VOCAIR included additional 1,3-butadiene sufficient to increase the peak areas above the integration threshold. The reported concentrations therefore, included the ‘blank’ due to the VOCAIR system. The level of the ‘blank’ was quite low, equivalent to about 0.07 to 0.11 µg/m³, not significant relative to the 2.25 µg/m³ Air Quality Standard. The level of the blank is therefore, only significant at very low ambient concentrations.

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

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

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

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Table 2. Percentage data capture, maximum, mean and minimum values of ratified data from the Glasgow site of the UK Hydrocarbon Network, for the period; 1 October 2003 to 31 December 2003

Table 3. Percentage data capture, maximum, mean and minimum values of ratified data from the Harwell site of the UK Hydrocarbon Network, for the period; 1 October 2003 to 31 December 2003

Table 4. Percentage data capture, maximum, mean and minimum values of ratified data from the Marylebone Road site affiliated to the UK Hydrocarbon Network, for the period; 1 October 2003 to 31 December 2003
Table 1. Percentage data capture, maximum, mean and minimum values of the ratified data from the Cardiff site of the UK Hydrocarbon Network, for the period 1 October 2003 to 31 December 2003

<table>
<thead>
<tr>
<th>Compound</th>
<th>%Data capture</th>
<th>Maximum hourly concentration (µg/m³)</th>
<th>Mean concentration (µg/m³)</th>
<th>Minimum hourly concentration (µg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3-Butadiene</td>
<td>99.00</td>
<td>2.18</td>
<td>0.18</td>
<td>0.00</td>
</tr>
<tr>
<td>Benzene</td>
<td>99.00</td>
<td>13.43</td>
<td>1.43</td>
<td>0.10</td>
</tr>
<tr>
<td>Toluene</td>
<td>99.00</td>
<td>48.43</td>
<td>5.09</td>
<td>0.46</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>98.51</td>
<td>20.32</td>
<td>1.01</td>
<td>0.04</td>
</tr>
<tr>
<td>(m+p)-Xylene *</td>
<td>98.96</td>
<td>55.44</td>
<td>3.22</td>
<td>0.09</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>98.01</td>
<td>20.23</td>
<td>1.54</td>
<td>0.04</td>
</tr>
</tbody>
</table>

* (m+p)-Xylene data are reported as the sum of the 2 individual components due to the fact that they are not sufficiently well resolved in the chromatogram.
Table 2. Percentage data capture maximum, mean and minimum values of ratified data from the Glasgow site of the UK Hydrocarbon Network, for the period 1 October 2003 to 31 December 2003

<table>
<thead>
<tr>
<th>Compound</th>
<th>%data capture</th>
<th>Maximum hourly concentration (µg/m³)</th>
<th>Mean concentration (µg/m³)</th>
<th>Minimum hourly concentration (µg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3-Butadiene</td>
<td>97.74</td>
<td>6.26</td>
<td>0.54</td>
<td>0.00</td>
</tr>
<tr>
<td>Benzene</td>
<td>97.74</td>
<td>14.79</td>
<td>1.95</td>
<td>0.13</td>
</tr>
<tr>
<td>Toluene</td>
<td>95.20</td>
<td>87.29</td>
<td>7.65</td>
<td>0.42</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>84.38</td>
<td>12.12</td>
<td>1.28</td>
<td>0.04</td>
</tr>
<tr>
<td>(m+p)-Xylene *</td>
<td>84.47</td>
<td>65.62</td>
<td>4.98</td>
<td>0.04</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>82.65</td>
<td>26.27</td>
<td>1.81</td>
<td>0.04</td>
</tr>
</tbody>
</table>

* (m+p)-Xylene data are reported as the sum of the 2 individual components due to the fact that they are not sufficiently well resolved in the chromatogram.
Table 3. Percentage data capture, maximum, mean and minimum values of ratified data from the Harwell site of the UK Hydrocarbon Network, for the period; 1 October 2003 to 31 December 2003

<table>
<thead>
<tr>
<th>Compound</th>
<th>%data capture</th>
<th>Maximum hourly concentration (µg/m³)</th>
<th>Mean concentration (µg/m³)</th>
<th>Minimum hourly concentration (µg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3-Butadiene</td>
<td>97.87</td>
<td>0.47</td>
<td>0.04</td>
<td>0.00</td>
</tr>
<tr>
<td>Benzene</td>
<td>97.87</td>
<td>3.96</td>
<td>0.62</td>
<td>0.00</td>
</tr>
<tr>
<td>Toluene</td>
<td>94.52</td>
<td>24.94</td>
<td>1.45</td>
<td>0.04</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>51.63</td>
<td>2.64</td>
<td>0.31</td>
<td>0.00</td>
</tr>
<tr>
<td>(m+p)-Xylene *</td>
<td>67.53</td>
<td>8.73</td>
<td>0.71</td>
<td>0.00</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>51.95</td>
<td>3.53</td>
<td>0.31</td>
<td>0.00</td>
</tr>
</tbody>
</table>

* (m+p)-Xylene data are reported as the sum of the 2 individual components due to the fact that they are not sufficiently well resolved in the chromatogram.
Table 4. Percentage data capture, maximum, mean and minimum values of ratified data from the Marylebone Road site affiliated to the UK Hydrocarbon Network for the period; 1 October 2003 to 31 December 2003

<table>
<thead>
<tr>
<th>Compound</th>
<th>%data capture</th>
<th>Maximum hourly concentration (µg/m³)</th>
<th>Mean concentration (µg/m³)</th>
<th>Minimum hourly concentration (µg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>98.10</td>
<td>70.76</td>
<td>11.84</td>
<td>2.87</td>
</tr>
<tr>
<td>Ethene</td>
<td>98.10</td>
<td>30.58</td>
<td>6.65</td>
<td>0.44</td>
</tr>
<tr>
<td>Propane</td>
<td>98.10</td>
<td>67.12</td>
<td>7.56</td>
<td>1.39</td>
</tr>
<tr>
<td>Propene</td>
<td>98.10</td>
<td>15.28</td>
<td>3.28</td>
<td>0.28</td>
</tr>
<tr>
<td>Ethyne</td>
<td>98.05</td>
<td>27.75</td>
<td>5.19</td>
<td>0.39</td>
</tr>
<tr>
<td>2-Methylpropane</td>
<td>98.10</td>
<td>36.80</td>
<td>7.38</td>
<td>0.60</td>
</tr>
<tr>
<td>n-Butane</td>
<td>98.10</td>
<td>64.77</td>
<td>12.06</td>
<td>1.09</td>
</tr>
<tr>
<td>trans-2-Butene</td>
<td>98.10</td>
<td>5.38</td>
<td>1.05</td>
<td>0.23</td>
</tr>
<tr>
<td>1-Butene</td>
<td>98.01</td>
<td>4.94</td>
<td>0.93</td>
<td>0.07</td>
</tr>
<tr>
<td>cis-2-Butene</td>
<td>98.05</td>
<td>4.07</td>
<td>0.77</td>
<td>0.12</td>
</tr>
<tr>
<td>2-Methylbutane</td>
<td>98.10</td>
<td>66.94</td>
<td>12.03</td>
<td>0.66</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>98.10</td>
<td>15.99</td>
<td>3.11</td>
<td>0.33</td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td>98.05</td>
<td>2.72</td>
<td>0.67</td>
<td>0.07</td>
</tr>
<tr>
<td>trans-2-Pentene</td>
<td>97.78</td>
<td>5.01</td>
<td>0.87</td>
<td>0.03</td>
</tr>
<tr>
<td>cis-2-Pentene</td>
<td>96.15</td>
<td>2.56</td>
<td>0.49</td>
<td>0.03</td>
</tr>
<tr>
<td>2-Methylpentane</td>
<td>98.10</td>
<td>21.13</td>
<td>4.04</td>
<td>0.25</td>
</tr>
<tr>
<td>3-Methylpentane</td>
<td>98.05</td>
<td>12.94</td>
<td>2.47</td>
<td>0.14</td>
</tr>
<tr>
<td>Isoprene</td>
<td>97.10</td>
<td>1.27</td>
<td>0.34</td>
<td>0.06</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>98.05</td>
<td>9.26</td>
<td>1.54</td>
<td>0.07</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>97.55</td>
<td>7.98</td>
<td>0.91</td>
<td>0.04</td>
</tr>
<tr>
<td>Benzene</td>
<td>95.20</td>
<td>18.03</td>
<td>3.50</td>
<td>0.06</td>
</tr>
<tr>
<td>Toluene</td>
<td>98.05</td>
<td>76.35</td>
<td>13.31</td>
<td>0.27</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>98.05</td>
<td>13.84</td>
<td>2.38</td>
<td>0.04</td>
</tr>
<tr>
<td>(m+p)-Xylene *</td>
<td>80.30</td>
<td>53.46</td>
<td>9.92</td>
<td>0.22</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>98.05</td>
<td>17.63</td>
<td>3.00</td>
<td>0.04</td>
</tr>
<tr>
<td>1,3,5-Trimethylbenzene</td>
<td>97.60</td>
<td>6.49</td>
<td>1.10</td>
<td>0.00</td>
</tr>
<tr>
<td>1,2,4-Trimethylbenzene</td>
<td>98.05</td>
<td>19.81</td>
<td>3.44</td>
<td>0.10</td>
</tr>
</tbody>
</table>

* (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 1. Time series plot of the ratified benzene data from the Cardiff site of the UK Hydrocarbon Network, for the period; 1 October 2003 to 31 December 2003

Figure 2. Time series plot of the ratified 1,3-butadiene data from the Cardiff site of the UK Hydrocarbon Network, for the period; 1 October 2003 to 31 December 2003

Figure 3. Time series plot of the ratified benzene data from the Glasgow site of the UK Hydrocarbon Network, for the period; 1 October 2003 to 31 December 2003

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 October 2003 to 31 December 2003

Figure 5. Time series plot of the ratified benzene data from the Harwell site of the UK Hydrocarbon Network, for the period; 1 October 2003 to 31 December 2003

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 October 2003 to 31 December 2003

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 October 2003 to 31 December 2003

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 October 2003 to 31 December 2003
Figure 1. Time series plot of the ratified benzene data from the Cardiff site of the UK Hydrocarbon Network, for the period; 1 October 2003 to 31 December 2003

Figure 2. Time series plot of the ratified 1,3-butadiene data from the Cardiff site of the UK Hydrocarbon Network, for the period; 1 October 2003 to 31 December 2003
Figure 3. Time series plots for the ratified benzene data from the Glasgow site of the UK Hydrocarbon Network, for the period; 1 October 2003 to 31 December 2003.

Figure 4. Time series plots for the ratified 1,3-butadiene data from the Glasgow site of the UK Hydrocarbon Network, for the period; 1 October 2003 to 31 December 2003.
Figure 5. Time series plots for the ratified benzene data from the Harwell site of the UK Hydrocarbon Network, for the period; 1 October 2003 to 31 December 2003

Figure 6. Time series plots for the ratified 1,3-butadiene data from the Harwell site of The UK Hydrocarbon Network, for the period; 1 October 2003 to 31 December 2003
Figure 7. Time series plots for the ratified benzene data from the Marylebone Road site affiliated to the UK Hydrocarbon Network, for the period; 1 October 2003 to 31 December 2003

Figure 8. Time series plots for the ratified 1,3-butadiene data from the Marylebone Road site affiliated to the UK Hydrocarbon Network, for the period; 1 October 2003 to 31 December 2003
Appendix 3
Rolling Annual Mean Plots

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Figure 1. Time series plot of the rolling annual mean for benzene and 1,3-butadiene data from the Cardiff site of the UK Hydrocarbon Network, for the period; January 2003 to December 2003.

Figure 2. Time series plot of the rolling annual mean for benzene and 1,3-butadiene data from the Glasgow site of the UK Hydrocarbon Network, for the period; January 2003 to December 2003.

Figure 3. Time series plot of the rolling annual mean for benzene and 1,3-butadiene data from the Harwell site of the UK Hydrocarbon Network, for the period; January 2003 to December 2003.

Figure 4. Time series plot of the rolling annual mean for benzene and 1,3-butadiene data from the Marylebone Road site affiliated to the UK Hydrocarbon Network, for the period; January 2003 to December 2003.
Figure 1. Time series plot of the rolling annual mean for benzene and 1,3-butadiene data from the Cardiff site of the UK Hydrocarbon Network, for the period; January 2003 to December 2003.

Figure 2. Time series plot of the rolling annual mean for benzene and 1,3-butadiene data from the Glasgow site of the UK Hydrocarbon Network, for the period; January 2003 to December 2003.
Figure 3. Time series plot of the rolling annual mean for benzene and 1,3-butadiene data from the Harwell site of the UK Hydrocarbon Network, for the period; January 2003 to December 2003.

Figure 4. Time series plot of the rolling annual mean for benzene and 1,3-butadiene data from the Marylebone Road site affiliated to the UK Hydrocarbon Network, for the period; January 2003 to December 2003.
Appendix 4
Quarterly, annual and maximum running means

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

Table 2. Annual means of measured benzene concentrations (µg/m³) at each of the UK Automatic Hydrocarbon Sites.

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

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

Table 5. Annual Means of measured 1,3-butadiene concentrations (µg/m³) at each of the UK Automatic Hydrocarbon Sites.

Table 6. Maximum running means of measured 1,3-butadiene concentrations (µg/m³) 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.

<table>
<thead>
<tr>
<th>Monitoring Site</th>
<th>Quarter 1 2003 Mean</th>
<th>Quarter 2 2003 Mean</th>
<th>Quarter 3 2003 Mean</th>
<th>Quarter 4 2003 Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cardiff Centre</td>
<td>1.36</td>
<td>0.58</td>
<td>0.94</td>
<td>1.43</td>
</tr>
<tr>
<td>Glasgow</td>
<td>2.43</td>
<td>1.36</td>
<td>1.30</td>
<td>1.95</td>
</tr>
<tr>
<td>Harwell</td>
<td>0.91</td>
<td>0.36</td>
<td>0.39</td>
<td>0.62</td>
</tr>
<tr>
<td>Marylebone Road</td>
<td>3.86</td>
<td>3.08</td>
<td>2.85</td>
<td>3.50</td>
</tr>
</tbody>
</table>

Table 2. Annual means of measured benzene concentrations (µg/m³) at each of the UK Automatic Hydrocarbon Sites.

<table>
<thead>
<tr>
<th>Monitoring Site</th>
<th>2000 Annual Mean</th>
<th>2001 Annual Mean</th>
<th>2002 Annual Mean</th>
<th>2003 Annual Mean</th>
<th>2003 Data Capture %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cardiff Centre</td>
<td>$$</td>
<td>$$</td>
<td>1.22$</td>
<td>1.17</td>
<td>75.86</td>
</tr>
<tr>
<td>Glasgow</td>
<td>$$$</td>
<td>$$$</td>
<td>2.33 $</td>
<td>1.82</td>
<td>84.92</td>
</tr>
<tr>
<td>Harwell</td>
<td>0.53</td>
<td>0.62</td>
<td>0.60</td>
<td>0.59</td>
<td>84.73</td>
</tr>
<tr>
<td>Marylebone Road</td>
<td>6.29</td>
<td>4.55</td>
<td>3.91</td>
<td>3.32</td>
<td>90.62</td>
</tr>
</tbody>
</table>

$ Annual means calculated from significantly less than 12 months data
$$ The Cardiff Centre site was installed on 5th September 2002.
$$$ The Glasgow site was installed on 1st August 2002.

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

<table>
<thead>
<tr>
<th>Monitoring Site</th>
<th>2003 Maximum running annual mean</th>
<th>2003 MRAM Data Capture %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cardiff Centre</td>
<td>1.19</td>
<td>75.84</td>
</tr>
<tr>
<td>Glasgow</td>
<td>2.03</td>
<td>89.92</td>
</tr>
<tr>
<td>Harwell</td>
<td>0.71</td>
<td>76.16</td>
</tr>
<tr>
<td>Marylebone Road</td>
<td>3.91</td>
<td>96.16</td>
</tr>
</tbody>
</table>
Table 4. Quarterly means of measured 1,3-butadiene concentrations (µg/m³) at each of the UK Automatic Hydrocarbon Sites.

<table>
<thead>
<tr>
<th>Monitoring Site</th>
<th>Quarter 1 2003 Mean</th>
<th>Quarter 2 2003 Mean</th>
<th>Quarter 3 2003 Mean</th>
<th>Quarter 4 2003 Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cardiff Centre</td>
<td>0.16</td>
<td>0.07</td>
<td>0.11</td>
<td>0.18</td>
</tr>
<tr>
<td>Glasgow</td>
<td>0.38</td>
<td>0.34</td>
<td>0.38</td>
<td>0.54</td>
</tr>
<tr>
<td>Harwell</td>
<td>0.04</td>
<td>0.02</td>
<td>0.02</td>
<td>0.04</td>
</tr>
<tr>
<td>Marylebone Road</td>
<td>0.70</td>
<td>0.61</td>
<td>0.58</td>
<td>0.67</td>
</tr>
</tbody>
</table>

Table 5. Annual Means of measured 1,3-butadiene concentrations (µg/m³) at each of the UK Automatic Hydrocarbon Sites.

<table>
<thead>
<tr>
<th>Monitoring Site</th>
<th>2000 Annual Mean</th>
<th>2001 Annual Mean</th>
<th>2002 Annual Mean</th>
<th>2003 Annual Mean</th>
<th>2003 Data Capture %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cardiff Centre</td>
<td>$$ $$</td>
<td>0.15$</td>
<td>0.15</td>
<td>76.13</td>
<td></td>
</tr>
<tr>
<td>Glasgow</td>
<td>$$$ $$$</td>
<td>0.36$</td>
<td>0.42</td>
<td>84.62</td>
<td></td>
</tr>
<tr>
<td>Harwell</td>
<td>0.09</td>
<td>0.11</td>
<td>0.04</td>
<td>0.03</td>
<td>84.90</td>
</tr>
<tr>
<td>Marylebone Road</td>
<td>1.63</td>
<td>1.12</td>
<td>0.95</td>
<td>0.64</td>
<td>92.32</td>
</tr>
</tbody>
</table>

$ Annual means calculated from significantly less than 12 months data
$$ The Cardiff Centre site was installed on 5th September 2002.
$$$ The Glasgow site was installed on 1st August 2002.

Table 6. Maximum running means of measured 1,3-butadiene concentrations (µg/m³) at each of the UK Automatic Hydrocarbon Sites.

<table>
<thead>
<tr>
<th>Monitoring Site</th>
<th>2003 Maximum running annual mean</th>
<th>2003 MRAM Data Capture %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cardiff Centre</td>
<td>0.15</td>
<td>76.12</td>
</tr>
<tr>
<td>Glasgow</td>
<td>0.42</td>
<td>84.60</td>
</tr>
<tr>
<td>Harwell</td>
<td>0.05</td>
<td>77.15</td>
</tr>
<tr>
<td>Marylebone Road</td>
<td>0.94</td>
<td>96.40</td>
</tr>
</tbody>
</table>
Appendix 5
Annual Mean Plots

CONTENTS

Figure 1. Mean Benzene concentrations for the UK Automatic Hydrocarbon Network, 1994-2003

Figure 2. Mean Benzene concentrations for the UK Automatic Hydrocarbon Network, 1994-2003 (magnified y-axis)

Figure 3. Mean 1,3-Butadiene concentrations for the UK Automatic Hydrocarbon Network, 1994-2003
Figure 1. Mean benzene concentrations for the UK Automatic Hydrocarbon Network, 1994-2003

Figure 2. Mean benzene concentrations for the UK Automatic Hydrocarbon Network, 1994-2003 (magnified y-axis)
Figure 3. Mean 1,3-Butadiene concentrations for the UK Automatic Hydrocarbon Network, 1994-2003
Appendix 6
Trend Analysis Plots

CONTENTS

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

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

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

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

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

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

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

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

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

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

Figure 6. Plot of the monthly mean concentrations of benzene, 1,3-butadiene and the benzene:1,3-butadiene ratio for the Harwell site of the UK Hydrocarbon Network.
Figure 7. Plot of the monthly mean concentrations of benzene, 1,3-butadiene and the benzene:1,3-butadiene ratio for the Cardiff Centre site of the UK Hydrocarbon Network.

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