



UK Hydrocarbon Network

Annual Report for 2011

Report to Defra and the Devolved Administrations

Unrestricted
ED 47833/ED46645
AEA/ENV/R/3307
Issue 1
November 2012


Title	UK Hydrocarbon Network: Annual Report for 2011
Customer	Defra and the Devolved Administrations
Customer reference	RMP 5504/5505
Confidentiality, copyright and reproduction	This report is the Copyright of Defra and Devolved Administrations and has been prepared by AEA Technology plc under contract to Defra. The contents of this report may not be reproduced in the whole or in part, nor passed to any organisation or person without the specific prior written permission of Defra and Devolved Administrations. AEA Technology plc accepts no liability whatsoever to any third party for any loss or damage arising from any interpretation or use of the information contained in this report, or reliance on any views expressed therein.
File reference	
Reference number	ED47833/ED46645- Issue 1 AEA/ENV/R/3307

AEA group
6 New Street Square
London
EC4A 3BF

t: 0870 190 3622

AEA is a business name of AEA Technology plc

AEA is certificated to ISO9001 and ISO14001

Author	Name	Rachel Yardley, James Dernie, Peter Dumitrean
Approved by	Name	Steve Telling
	Signature	
	Date	10/12/12

Executive summary

This report provides a summary of the site management and data produced in 2011 by the UK Hydrocarbon monitoring network.

The network measures benzene, 1,3-butadiene and ozone precursor substances at sites across the UK.

The report includes an introduction to the network, the history of monitoring and the reasons for monitoring these pollutants. Section 2 provides detailed information on the sites currently operating and recent changes to the sites. In section 3 and Appendix 1, summary data is presented and analysed, including a review of the long-term trends and a description of issues that have affected data capture or data quality. The report also includes a summary of the quality assurance and quality control procedures in sections 2 and 4 and an update on future changes in section 5.

The mean data capture for benzene measured by the non-automatic hydrocarbon sites in 2011 was 91%. The annual mean across all measurement sites in the UK was $0.76 \mu\text{g m}^{-3}$ and the highest annual mean for a single site was $1.5 \mu\text{g m}^{-3}$ at Bath Roadside. The mean data capture for benzene measured by the automatic hydrocarbon network in 2011 was 63% and the highest annual mean for a single site was $1.3 \mu\text{g m}^{-3}$ at Marylebone Road. The annual mean across all measurement sites in the UK was $0.57 \mu\text{g m}^{-3}$.

In 2011 none of the monitoring sites in the UK exceeded the Limit Value for benzene set out in Directive 2008/50/EC. All sites measured an annual mean that was less than the Lower Assessment Threshold.

Table of contents

1	Introduction	1
1.1	Pollutant Sources and Impacts	1
1.2	Network background and methods	1
1.3	Regulatory background	4
2	Site Management	5
2.1	Network sites during 2011	5
2.2	Changes to the Network in 2011	9
2.3	Equipment Maintenance and Audits	10
3	Data and data capture for 2011	11
3.1	Comparison with Limit Values and Objectives	11
3.2	Concentration Trends	15
4	Data Quality	19
4.1	Intercomparisons	19
4.2	Estimation of Uncertainty	20
4.3	Standard Methods	21
4.4	Limit of Detection	22
5	Developments and Recommendations	23
5.1	EN14662-3:2005	23
5.2	Acetaldehyde and Formaldehyde	23
5.3	Network Review	26

Appendices

Appendix 1	2011 Audit Schedule
Appendix 2	Copy of 2011 Audit certificate - Accredited low flow measurements
Appendix 3	Data capture, maximum and annual mean values from the Automatic Hydrocarbon Network
Appendix 4	Time Series Graphs for Benzene and 1,3-Butadiene

1 Introduction

This report provides a summary of the site management and data produced in 2011 by the UK Hydrocarbon monitoring network.

The network has been managed and quality controlled by AEA throughout 2011.

All hydrocarbon network instruments are collocated at AURN (Automatic Urban and Rural Network) sites. These have all been assessed with respect to the macroscale and microscale siting criteria in the Directive. The initial assessment indicates that all of the hydrocarbon network sites comply with the Directive, with the exception of Bury Roadside, Bristol Old Market and Leicester Centre. Bury Roadside and Bristol Old Market are believed to be too close to major road junctions to be representative of the local area, and additionally, the Bury Roadside site is too far from the carriageway to be a 'traffic' site. Leicester centre is surrounded by tall buildings and in close proximity to the inlet.

The number and location of sites in the network are based upon a preliminary assessment against the sampling requirements in Annex V of the Air Quality Directive, undertaken in 2006. An assessment of the number and location of monitoring sites in each Member State is required to be undertaken every 5 years, and the UK carried out this reassessment in 2011. Changes resulting from this assessment will be implemented in 2012.

The information and data presented in this report are correct at the time of publication, however, it is possible that data may be rescaled or deleted from the dataset if future audits and calibrations identify a need to change the data. Latest data can always be accessed at <http://uk-air.defra.gov.uk/>.

1.1 Pollutant Sources and Impacts

Benzene has a variety of sources¹, but primarily arises from domestic and industrial combustion and road transport. It is a recognised human carcinogen that attacks the genetic material and, as such, no absolutely safe level can be specified in ambient air. Studies in workers exposed to high levels have shown an excessive risk of leukaemia.

1,3-butadiene is emitted from combustion of petrol. Motor vehicles and other machinery are the dominant sources, but it is also emitted from some processes, such as production of synthetic rubber for tyres. 1,3-butadiene is also a recognised genotoxic human carcinogen, as such, no absolutely safe level can be specified in ambient air. The health effect of most concern is the induction of cancer of the lymphoid system and blood-forming tissues, lymphoma and leukaemia.

1.2 Network background and methods

The UK Hydrocarbon Network exists within the framework of Defra's Atmosphere and Local Environment Programme. This aims to determine the magnitude of sources and effects of air

¹ The Air Quality Strategy for England, Scotland, Wales and Northern Ireland (Volume 1), Department for Environment, Food and Rural Affairs in partnership with the Scottish Executive, Welsh Assembly Government and Department of the Environment Northern Ireland, July 2007

pollutants on human health and the environment, and to comply with national and EU legislation.

1.2.1 Non-Automatic Hydrocarbon Sites

The Non-Automatic Hydrocarbon Sites started operation in 2001, measuring benzene and 1,3-butadiene. It currently produces measurements as fortnightly averages at 36 sites. The network was reviewed in 2007 and 1,3-butadiene monitoring was discontinued due to the measurement of very low concentrations.

The benzene monitoring method involves pumping ambient air at a rate nominally 10 ml/min alternately through two tubes containing a sorbent (Carbopack X). The tubes are then sent to the laboratory for subsequent analysis of their benzene content. The exposure period and flow rate is important such that enough benzene is captured onto the sorbent to enable fully quantifiable analysis, but not too much that there is breakthrough of the sample. This dual sample tube controlled flow pump unit uses a method described in EN 14662:2005, 'Ambient air quality – Standard method for measurement of benzene concentrations' by Martin et al, and validated by Quincey et al.

1.2.2 Automatic Hydrocarbon Sites

Automatic gas chromatography is used to measure hourly hydrocarbon concentrations. During 2011, hydrocarbons at all sites were measured using automatic Perkin Elmer Ozone Precursor Analysers. A known volume of air is dried and drawn through the cold trap, which contains adsorbent material. The cold trap is held at about -30°C to ensure that all the ozone precursor target analytes are retained. Following a 40 minute period of sampling, components are desorbed from the cold trap and are transferred to the capillary column where they are separated using gas-chromatography. The analyser is calibrated using an on-site multi-component gas mixture.

Automatic hourly measurements of speciated hydrocarbons, made using advanced automatic gas chromatography, started in the UK in 1991. By 1995, monitoring had expanded considerably with the formation of a 13-site dedicated network measuring 26 species continuously at urban, industrial and rural locations. Over the following years, the number of sites was reduced. In 2011 there were four sites, measuring the following species by automatic gas chromatographs:

Table 1 Species measured by the Automatic chromatographs.

Pollutant	Pollutant	Pollutant
1,2,3-trimethylbenzene	ethane	n-heptane
1,2,4-trimethylbenzene	ethene	n-hexane
1,3,5-trimethylbenzene	ethylbenzene	n-octane
1,3-Butadiene	ethyne (acetylene)	n-pentane
1-butene	iso-butane (I-butane)	o-xylene
1-pentene	iso-octane	propane
2-methylpentane	iso-pentane	propene
3-methylpentane	isoprene	toluene
benzene	m+p-xylene	trans-2-butene
cis-2-butene	methylpentane	trans-2-pentene
cis-2-pentene	n-butane	

1.3 Regulatory background

1.3.1 UK Air Quality Objectives

The Air Quality Strategy for England, Scotland, Wales and Northern Ireland, (July 2007) sets out the UK Air Quality Objectives for benzene and 1,3-butadiene:

Table 2 UK Air Quality Objectives.

Pollutant	Applicable to	Concentration	Measured As	To be achieved by
Benzene	All authorities	16.25 $\mu\text{g m}^{-3}$	Running annual mean	31 December 2003
	England and Wales Only	5.00 $\mu\text{g m}^{-3}$	Annual mean	31 December 2010
	Scotland and N. Ireland	3.25 $\mu\text{g m}^{-3}$	Running annual mean	31 December 2010
1,3-Butadiene	All authorities	2.25 $\mu\text{g m}^{-3}$	Running annual mean	31 December 2003

1.3.2 European Limit Value

Hydrocarbons are also governed by Directive 2008/E50/EC of the European Parliament and of the Council of 21 May 2008, on ambient air quality and cleaner air for Europe (the Directive). The Directive sets a limit value for annual mean benzene concentrations across the UK.

Table 3 European Limit Value and Assessment Thresholds

Threshold	Concentration	Measured as
Limit Value	5 $\mu\text{g m}^{-3}$	Annual mean
Upper assessment threshold	3.5 $\mu\text{g m}^{-3}$	Annual mean
Lower assessment threshold	2 $\mu\text{g m}^{-3}$	Annual mean

The limit value for the protection of human health for benzene is 5 $\mu\text{g/m}^3$ as a calendar year mean, to be achieved by 1st January 2010. The determination of requirements for assessment of concentrations of benzene in ambient air is between 3.5 $\mu\text{g/m}^3$ (70% of limit value) and 2 $\mu\text{g/m}^3$ (40% of limit value) as upper and lower assessment threshold respectively.

The Data Quality Objective for the measurement uncertainty is $\pm 25\%$ with a minimum data capture of 90%. The minimum time coverage is 35% (distributed over the year) for urban background and traffic sites and 90% for industrial sites.

Annex X of the Directive lists 31 other Volatile Organic Compounds (VOCs) which are ozone precursors and which are recommended to be measured in urban or suburban areas to support the understanding of ozone formation. With the exception of formaldehyde and total non-methane hydrocarbons, these VOCs are all measured by the automatic hydrocarbon network and are listed in section 1. Neither data quality objectives nor limit values are given for measurement of these species, however, Defra have specified that all other VOC compounds have a minimum data capture target of 50%.

2 Site Management

2.1 Network sites during 2011

2.1.1 Non-Automatic Hydrocarbon Network

The sites in the Non-Automatic Hydrocarbon Network are shown in Figure 1. Table 4 lists the sites and the Local Site Operators.

Figure 1 Map of Non-Automatic Hydrocarbon Network sites in 2011



Table 4 Non-Automatic Hydrocarbon Network sites in 2011.

Site	Classification	Zone	Grid Ref Easting / Northing	Local Site Operator
Barnsley Gawber	Urban Background	Yorkshire & Humberside	432529, 407472	Barnsley Council
Bath Roadside	Urban Traffic	South West	375882, 166096	Bath & North Somerset Council
Belfast Centre	Urban Background	Belfast Urban Area	333900, 374400	Belfast City Council
Birmingham Tyburn	Urban Background	West Midlands Urban Area	411561, 290431	Birmingham City Council
Birmingham Tyburn Roadside	Urban Traffic	West Midlands Urban Area	411556, 290456	AECOM
Bristol Old Market	Urban Traffic	Bristol Urban Area	359570, 173173	Bristol City Council
Bury Roadside	Urban Traffic	Greater Manchester Urban Area	380922, 404772	Bury Metropolitan Council
Cambridge Roadside	Urban Traffic	Eastern	545248, 258155	Cambridge Council
Camden Kerbside	Urban Traffic	Greater London Urban Area	526640, 184433	AEA
Carlisle Caldewgate	Urban Traffic	North West & Merseyside	339442, 555956	Carlisle Council
Chatham Centre Roadside	Urban Traffic	South East	577435, 166993	Medway Council
Chesterfield	Urban Background	East Midlands	436351, 370682	Chesterfield Council
Coventry Memorial Park	Urban Background	Coventry/Bedworth	432801, 277340	Coventry City Council
Glasgow Kerbside	Urban Traffic	Glasgow Urban Area	258708, 665200	AEA
Grangemouth	Urban Industrial	Central Scotland	293837, 681035	Falkirk Council
Haringey Roadside	Urban Traffic	Greater London Urban Area	533885, 190669	KCL
Leamington Spa	Urban Background	West Midlands	431932, 265743	Warwick District Council
Leeds Centre	Urban Background	West Yorkshire Urban Area	429976, 434268	Leeds City Council
Leicester Centre	Urban Background	Leicester Urban Area	458767, 304083	Leicester City Council
Liverpool Speke	Urban Background	Liverpool Urban Area	343860, 383598	Fabermaunsell/AECOM
London Bloomsbury	Urban Background	Greater London Urban Area	530107, 182041	Bureau Veritas / AEA
Manchester Picadilly	Urban Background	Greater Manchester Urban Area	384310, 398325	Manchester City Council
Middlesbrough	Urban Background	Teesside Urban Area	450480, 519632	Middlesbrough BC
Newcastle Centre	Urban Background	Tyneside	425016, 564940	Newcastle City Council
Northampton	Urban Background	East Midlands	476111, 264524	Northampton BC
Norwich Lakenfields	Urban Background	Eastern	623637, 306940	Mark Leach
Nottingham Centre	Urban Background	Nottingham Urban Area	457420, 340050	Nottingham City Council
Oxford Centre	Urban Traffic	South East	451366, 206152	Oxford City Council
Oxford St Ebbes	Urban Background	South East	451225, 206009	Oxford City Council
Plymouth Centre	Urban Background	South West	247742, 54610	Plymouth City Council
Sheffield Centre	Urban Background	Sheffield Urban Area	435134, 386885	Sheffield City Council
Southampton Centre	Urban Background	Southampton Urban Area	442565, 112255	Southampton City Council
Stockton-on-Tees - Eaglescliffe	Urban Traffic	North East	441620, 513673	Stockton on Tees BC
Stoke-on-Trent Centre	Urban Background	The Potteries	388348, 347894	City of Stoke on Trent Council
Wigan Centre	Urban Background	North West & Merseyside	357825, 406025	Wigan Metropolitan BC
York Fishergate	Urban Traffic	Yorkshire & Humberside	460744, 451033	City of York Council

As part of an ongoing investigation, there are also pumped samplers operating at Marylebone Road since 2007, and at London Eltham since 2011. The pumped samplers are not part of the Non-Automatic Network.

Further details on the sites can be found on the UK Automatic Urban and Rural Network Site Information Archive at <http://uk-air.defra.gov.uk/>

2.1.2 Automatic Hydrocarbon Network

The sites in the Automatic Hydrocarbon Network are shown in Figure 2.

Figure 2 Map of Automatic Network sites in 2011



Table 5 Automatic Hydrocarbon Network sites in 2011.

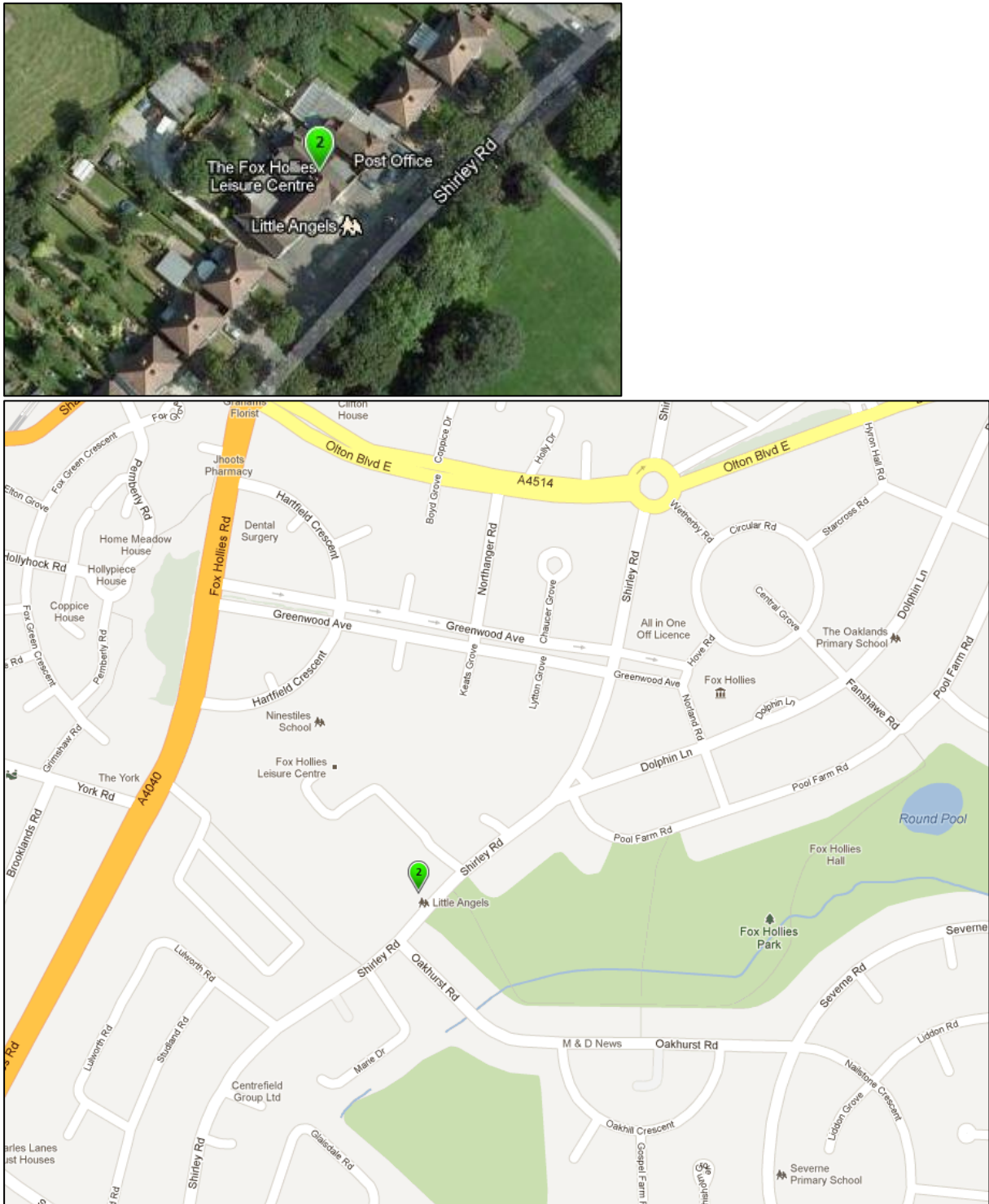
Site	Classification	Zone	Grid Ref Easting / Northing	Local Site Operator
Harwell	Rural Background	South West	446772, 186020	AEA
Marylebone Road	Urban Traffic	Greater London Urban Area	528120, 182000	KCL
Auchencorth Moss	Rural Background	Scotland	322050, 656250	CEH
London Eltham	Suburban Background	Greater London Urban Area	543978, 174668	Greenwich Borough Council

2.2 Changes to the Network in 2011

2.2.1 Birmingham Roadside

In order to ensure the security and continuity of the network sites, in May 2011 the Non Automatic Hydrocarbon Network benzene sampler was moved from Birmingham Tyburn to Birmingham Acocks Green, which is an Automatic Urban and Rural Network (AURN) site.

Figure 3 Photograph and Location of Birmingham Acocks Green, map images courtesy of Google.



2.2.2 London Eltham

A non-automatic benzene pump box was installed at London Eltham in December 2010. This will operate alongside the automatic analyser throughout 2011 and the intercomparison results for 2011 are available in Section 4, Figure 9.

There were no other changes to either the automatic or non automatic sampling sites during 2011.

2.3 Equipment Maintenance and Audits

All non-automatic monitoring sites are visited by field engineers on a 6 monthly basis to calibrate the sampling flows and carry out routine maintenance of the equipment. The purpose of the audit and maintenance visits are to:

- Carry out a flow calibration using a low flow BIOS instrument (UKAS accredited)
- Ensure no blockages or leaks in the system
- Clean or replace dirty filters and inspect/replace the inlet
- Replace o-rings and leak test all connections
- Carry out electrical Portable Appliance Testing (annually)
- Review the site infrastructure and surroundings
- Review health and safety risks at the site
- Replace or refurbish non automatic sampler pumps

Non-Automatic Hydrocarbon benzene samplers were audited in April 2011 and October 2011. The schedule and results of these visits can be seen in Appendix 1. The calibration data from these audits have been used to rescale the benzene concentrations during the ratification process. A copy of the certificate of accredited measurements is available in Appendix 2.

Automatic Hydrocarbon Network analysers are audited once each year, and in 2011 the audits took place between March and May:

- Harwell 14th March 2011
- Marylebone 15th March 2011
- Eltham 16th March 2011
- Auchencourth Moss 18th May 2011

Following the audits the automatic monitoring sites are serviced by the Equipment Support Unit (Perkin Elmer) where the following routine tasks are undertaken:-

- Change automatic GC cold trap and clean the gas generators and detectors
- Carry out a gas calibration for the automatic analysers

3 Data and data capture for 2011

3.1 Comparison with Limit Values and Objectives

The annual average concentration of benzene and butadiene over the calendar year 2011 is given in Table 6 and Table 7, alongside the data capture statistics. Data capture for sites where measurements started or finished during the year are calculated for the period that the equipment was operational.

Annual average concentrations at all sites were below the Limit Value of $5 \mu\text{g}/\text{m}^3$ for benzene set by the European Ambient Air Quality Directive.

3.1.1 Non-Automatic Hydrocarbon Sites

Table 6 Benzene Statistics

Site	Annual Mean Benzene ($\mu\text{g}/\text{m}^3$)	Maximum Fortnightly Mean Benzene ($\mu\text{g}/\text{m}^3$)	Data capture (%)
Barnsley Gawber	0.51	1.5	100.0%
Bath Roadside ^{NB}	1.5	3.2	67.9%
Belfast Centre	0.54	1.5	100.0%
Birmingham Acock's Green ^{NB}	0.50	1.0	52.9%
Birmingham Tyburn ^{NB}	0.81	1.5	33.9%
Birmingham Tyburn Roadside	0.79	1.6	96.1%
Bristol Old Market	0.92	1.6	100.0%
Bury Roadside	0.78	1.9	100.0%
Cambridge Roadside	0.72	1.8	98.4%
Camden Kerbside ^{NB}	0.94	2.1	68.1%
Carlisle Roadside	0.77	2.1	100.0%
Chatham Roadside	0.83	1.4	100.0%
Chesterfield Roadside	1.3	3.8	100.0%
Coventry Memorial Park	0.48	1.9	93.0%
Glasgow Kerbside	0.85	2.6	100.0%
Grangemouth	1.3	3.5	100.0%
Haringey Roadside	1.1	2.0	75.8%
Leamington Spa	0.58	1.4	88.5%
Leeds Centre	0.67	1.5	100.0%
Leicester Centre	0.59	1.3	100.0%
Liverpool Speke	0.94	2.5	84.8%
London Bloomsbury	0.70	1.7	90.7%
Manchester Piccadilly ^{NB}	0.69	1.3	60.4%
Middlesbrough	0.89	2.2	96.2%
Newcastle Centre	0.48	1.2	96.1%
Northampton	0.53	1.1	100.0%
Norwich – Lakenfields	0.57	1.4	96.1%
Nottingham Centre	0.57	1.2	79.8%
Oxford Centre	0.68	1.7	100.0%
Oxford St Ebbes	0.48	1.3	100.0%
Plymouth Centre	0.56	1.3	100.0%

Site	Annual Mean Benzene ($\mu\text{g}/\text{m}^3$)	Maximum Fortnightly Mean Benzene ($\mu\text{g}/\text{m}^3$)	Data capture (%)
Sheffield Centre	0.67	1.5	100.0%
Southampton Centre	0.67	1.3	99.9%
Stockton on Tees Eaglescliffe	0.81	1.5	99.0%
Stoke Centre	0.78	1.8	100.0%
Wigan Centre	0.73	1.7	95.9%
York Fishergate	0.76	1.5	93.6%

^{NB} Data capture <75% of the year

During 2011, the following site faults and failures were recorded:

Bath Roadside

A circuit board failure resulted in erroneous measurements between 11th October and 8th December 2011. The sampler was removed from the site on 8th December 2011 and fixed by AEA at Harwell before re-installation on 12th December 2011.

Camden Kerbside

The sampler at Camden worked only when 'the tubes rested on the top of the tubing, but not when pushed down fully' according to the LSO data recording sheet. The inlet was blocked and the tubes were therefore sampling from inside the sampling enclosure for the period. The data for this period has not been reported. After several investigations including a sampler replacement the fault was rectified on 4th April 2012.

Haringey Roadside

There was a fire at a building in close proximity to the site during the London Riots on 14th August 2011, the damage caused to the site resulted in a temporary site closure from 15th August until 31st October 2011. The sampler was switched off for this period.

Leamington Spa

Analytical results showed erroneous data between 7th April and 19th May 2011. The sampler was replaced with a spare on 14th June 2011. It was not clear what caused the sampling fault.

Liverpool Speke

The data between 18th May and 13th July 2011 appeared erratic; the data looks good following a pump replacement on 13th July 2011. There has been intermittent erroneous data from samples running between 24th August to 7th September and 21st September to 5th October 2011, the cause of this is not known, however the sampler later failed in April 2012 resulting in the sampler only sampling through one tube.

Manchester Piccadilly

A circuit board failure resulted in unusually low measurements between 24th March and 30th June 2011. The results between both tubes were consistently low. The circuit board was replaced on 14th June 2011. Another circuit board failure preventing the sampler from switching the sample flow from one tube to another occurred. The data from 20th October and 13th December 2011 was calculated using data from Tube B only.

Nottingham Centre

The Mass Flow Controller failed at Nottingham Centre causing erroneous data from 15th November to 21st December 2011. The sampler was removed on 21st December, fixed by AEA at Harwell and re-installed on 11th January 2012. There is no benzene data from 15th November 2011 to 11th January inclusive.

3.1.2 Automatic Hydrocarbon Network

Table 7 Benzene and 1,3-butadiene Statistics

Site	Pollutant	Annual Mean ($\mu\text{g}/\text{m}^3$)	Maximum ($\mu\text{g}/\text{m}^3$)	Data capture
Harwell	Benzene	0.33	2.2	93.3%
	1,3-Butadiene	0.10	0.43	93.9%
Marylebone Road	Benzene	1.4	6.5	46.8%
	1,3-Butadiene	0.24	1.7	44.2%
Auchencorth Moss	Benzene	0.21	3.4	53.9%
	1,3-Butadiene	0.02	0.74	38.4%
London Eltham	Benzene	0.37	2.4	58.0%
	1,3-Butadiene	0.06	0.38	63.8%

Annual Mean concentrations for all measured hydrocarbons at all sites are given in Appendix 3.

Data capture is currently calculated based on the number of valid data points in the year. The calculation does not take into account any instrument downtime for planned services and maintenance or calibrations. It also does not take into account periods when no data are recorded because the ambient concentrations are less than the limit of detection. This is particularly significant at Auchencorth Moss, where concentrations of many pollutants are very low. In future years data which are reported to the European Commission will be required to include flags to identify data less than the detection limit, and these data will be included in the data capture calculation, so the reported data capture is likely to improve.

Harwell

Data capture for benzene and 1,3-butadiene was over 90 % for 2011. Data capture for some of the other hydrocarbons was lower due to co-eluting peaks and low ambient levels.

Marylebone Road

There were a number of faults which affected the data at Marylebone Road during 2011. The hydrogen generator failed twice and the zero air generator failed for a significant period with no suitable replacement available. Also significant data were deleted during ratification due to poor chromatography following these breakdowns. These issues have been rectified.

Auchencorth Moss

At Auchencorth Moss there are ongoing issues with data loss due to the very low ambient levels of hydrocarbons, which are often below the limit of detection. During 2011, measurements which were below the limit of detection for any species were not reported and this has had an impact on the data capture. Furthermore, the analyser suffered a hydrogen generator fault in October.

London Eltham

There was a fault with the zero air generator in January. Significant data were deleted during ratification due to poor chromatography following this breakdown. This issue was rectified in April.

Three new generators have been purchased by the Network in early 2012 and these are being used as 'hot spares' by the equipment support unit. It is expected that this additional equipment will reduce the amount of instrument downtime due to breakdowns.

3.2 Concentration Trends

3.2.1 Trends in 2011

Time series graphs for benzene and 1,3 butadiene are available in Appendix 4. The majority of Traffic Urban and Background Urban sites show a distinct trend with benzene concentrations highest in the winter months, and lowest around July to September. At Urban and Rural sites there tends to be a pattern of seasonal variation with higher levels during the winter when emissions are higher, dispersion is generally poorer and photochemical removal is at a minimum. This trend is less evident at Industrial sites including Middlesbrough and Grangemouth, where the emissions from the industry are significant.

3.2.2 Long Term Trends

Figures 4 to 5 show annual mean benzene concentrations at long running sites from the Non-Automatic Hydrocarbon Network. Concentrations have dropped significantly since the start of this network in 2002, but appear to be levelling out over the past couple of years. The exceptions are Bath Roadside and Chesterfield Roadside, both which continue to rise over the past four years.

Figure 4 Long term Non-Automatic benzene trends – higher concentration sites

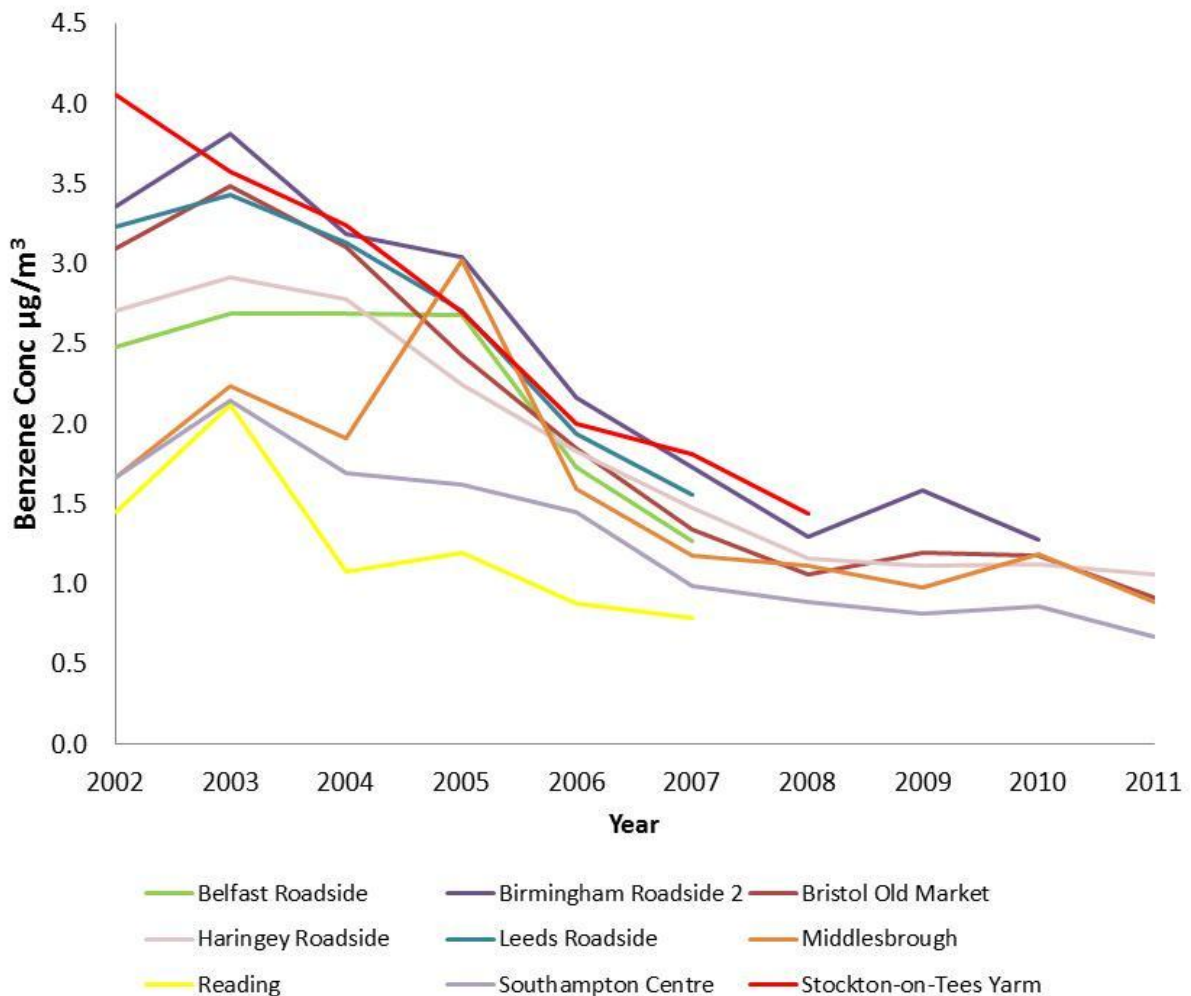
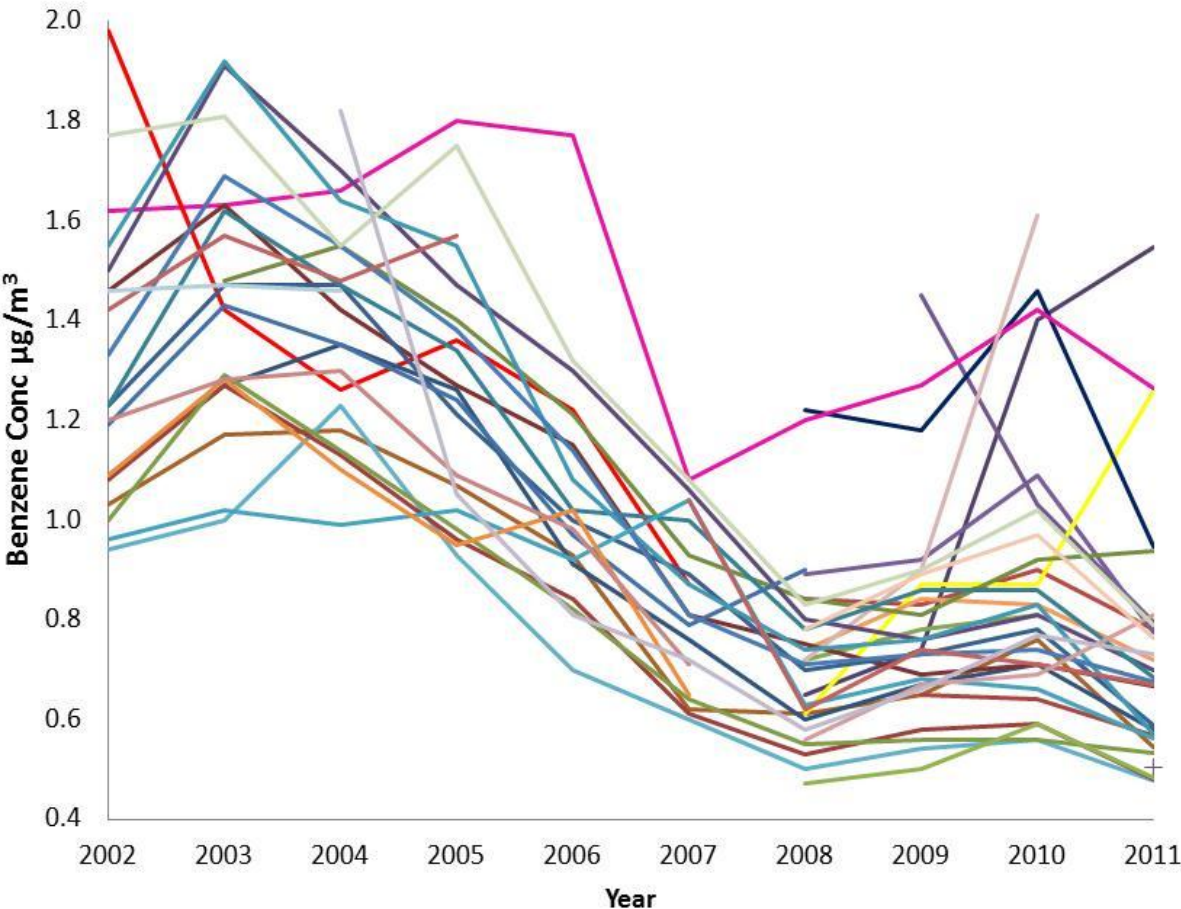


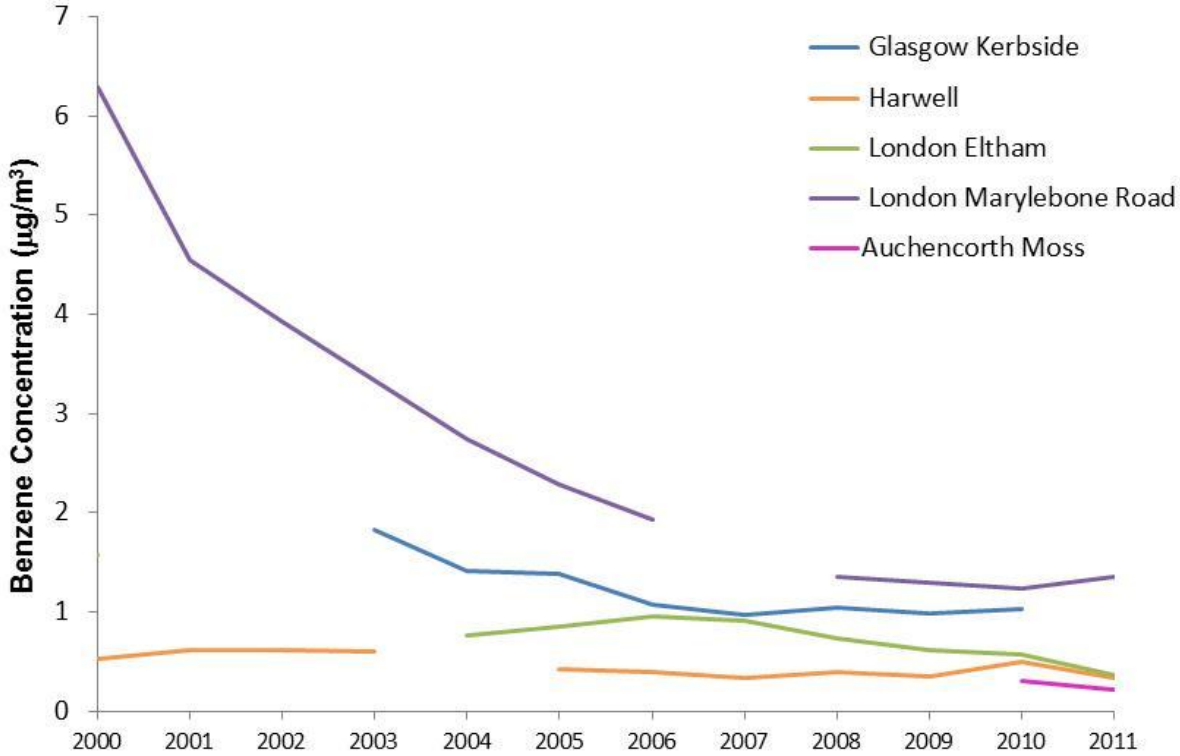
Figure 5 Long term Non-Automatic benzene trends – lower concentration sites



- Bath Roadside
- Birmingham Tyburn
- Carlisle Roadside
- Cambridge Roadside
- Grangemouth
- Leamington Spa
- Liverpool Speke
- Newcastle Centre
- Norwich Lakenfields
- Oxford St Ebbes
- Sheffield Centre
- Stoke-on-Trent Centre
- York Fishergate
- Belfast Centre
- Birmingham Tyburn Roadside
- Chesterfield Roadside
- Camden Kerbside
- Hull Freetown
- Leeds Centre
- London Bloomsbury
- Northampton
- Nottingham Centre
- Plymouth Centre
- Southend-on-Sea
- Wigan Centre
- Birmingham Acocks Green
- Bury Roadside
- Coventry Memorial Park
- Glasgow kerbside
- Killingholme
- Leicester Centre
- Manchester Piccadilly
- Norwich Centre
- Oxford Centre Roadside
- Portsmouth
- Stockton-on-Tees Eaglescliffe
- Wigan Leigh

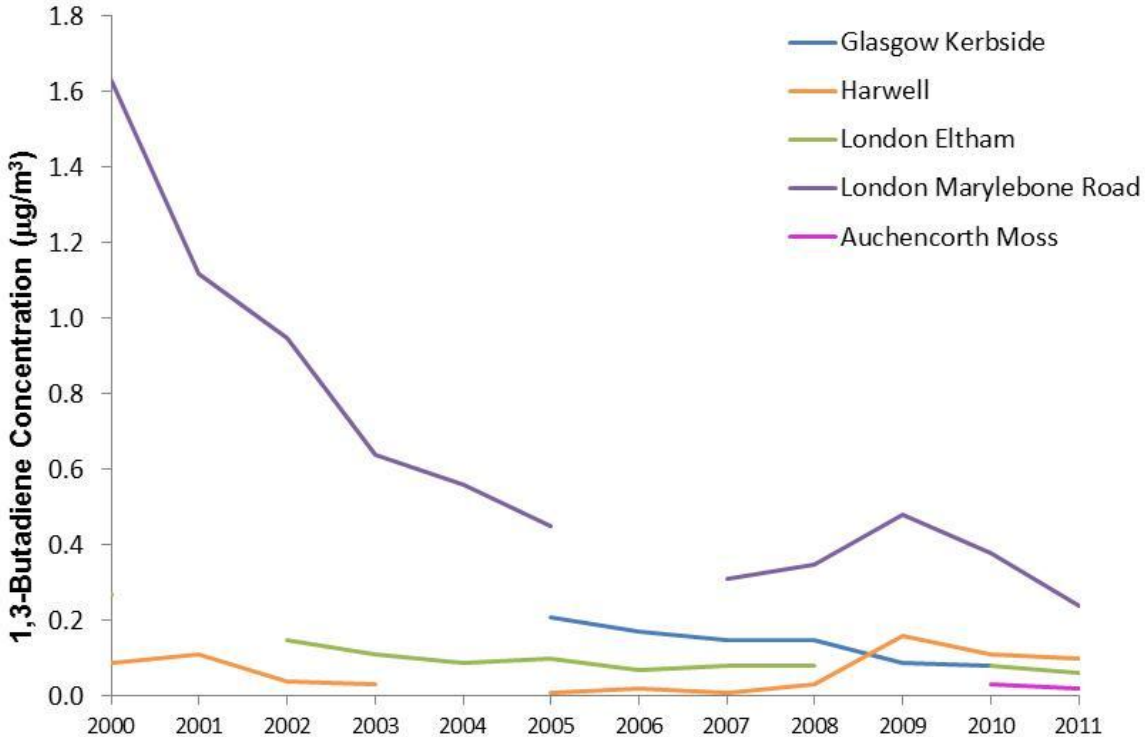
Figure 6 and Figure 7 show the long-term trends of the annual mean concentrations of benzene and 1,3-butadiene at the four sites with long running datasets within the Automatic Hydrocarbon Network, and Auchencorth Moss. Note that in 2010 and 2011 annual mean benzene concentrations have been included for sites where data capture was less than 75%. In other years no data are included where the data capture in the year was less than 75%.

Figure 6 Long term Automatic benzene trends



Note that in 2010 and 2011 annual mean 1,3 butadiene concentrations have been included for sites where data capture was less than 75%. In other years no data are included where the data capture in the year was less than 75%.

Figure 7 Long term Automatic 1,3-butadiene trends



4 Data Quality

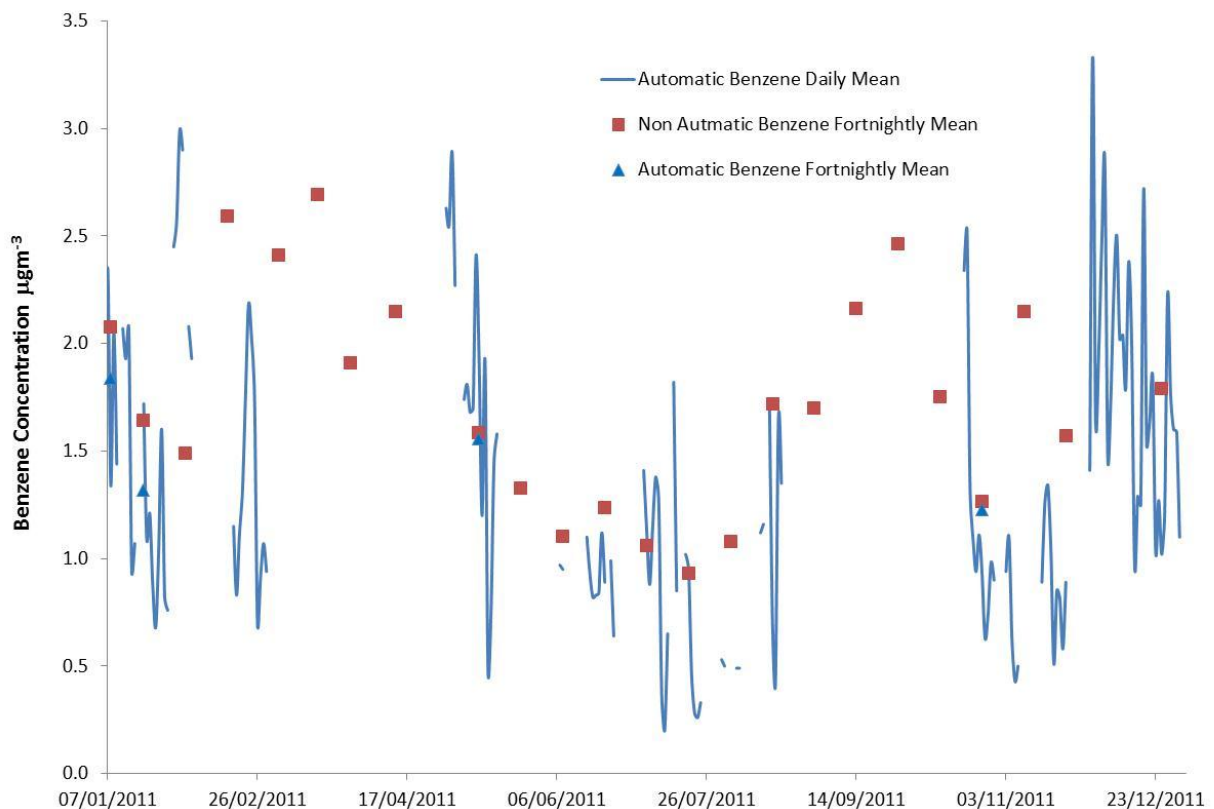
4.1 Intercomparisons

In 2011 there were two sites at which Non-Automatic samplers and Automatic analysers were collocated. These sites were Marylebone Road and London Eltham. Comparing data from collocated samplers is a good way to validate the data. Comparisons from these two sites are shown below.

4.1.1 Marylebone Road

Data is available from the two collocated samplers at Marylebone Road in 2011. Figure 8 shows the daily mean concentrations from the automatic analyser and a fortnightly mean which has been calculated from the daily means (only where data capture >75%). These automatic fortnightly means correspond to the dates of sampling with the non-automatic benzene samplers, so the data may be directly compared.

Figure 8 Comparison of collocated samplers at Marylebone Road

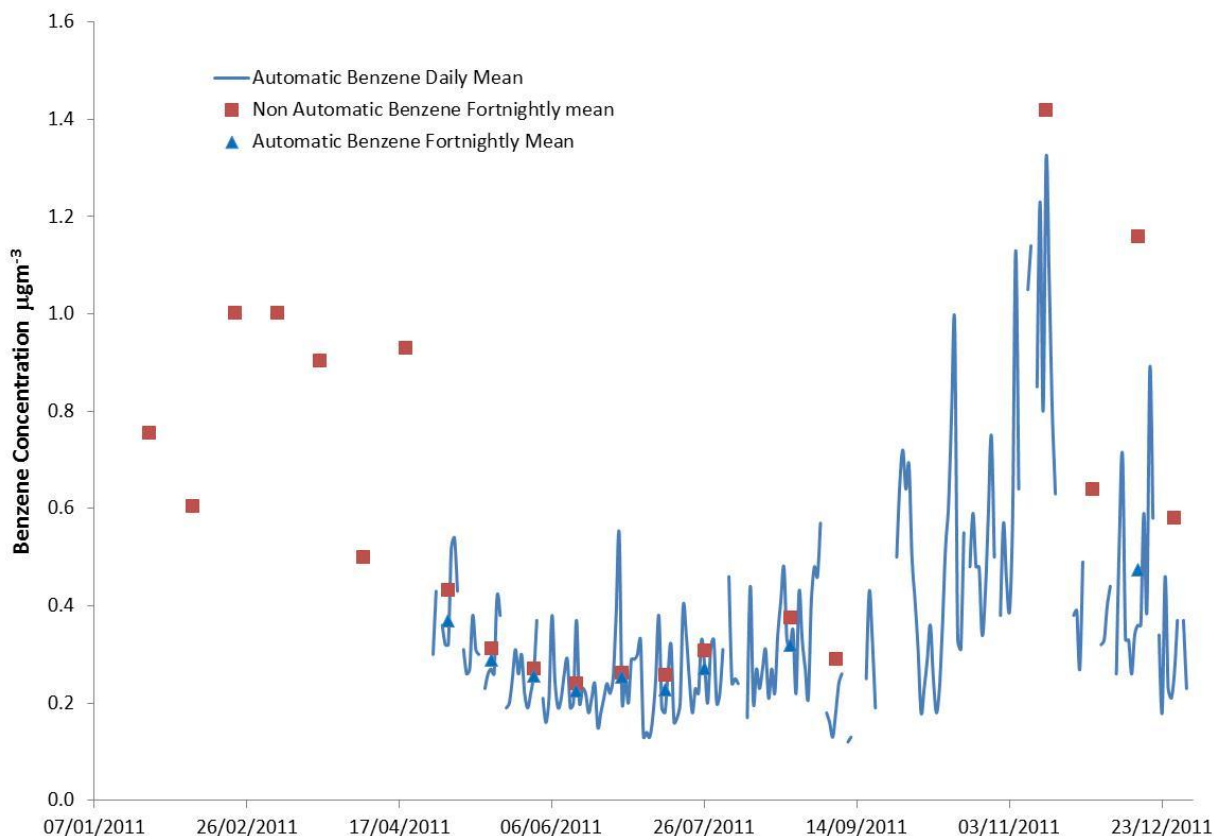


Unfortunately, data capture from the automatic instrument at Marylebone Road was low during 2011 due to repeated generator faults and this has prevented a valid comparison with many of the non-automatic measured data.

4.1.2 London Eltham

Data from the collocated samplers at London Eltham have been compared in a similar way and are presented in Figure 9

Figure 9 Comparison of collocated samplers at London Eltham



Within the uncertainty of the measurements it can be seen that the two measurement methods agree well with each other for the majority of the summer period, but an absence of automatic data in the first few months of the year prevents a comparison until April. There is an unexplained, significant difference in the two measurements in mid-December. The comparison will continue until the end of 2012.

4.2 Estimation of Uncertainty

Calculated uncertainty for the Non-Automatic Hydrocarbon sites in 2011 for benzene is 15%, expressed at a 95% level of confidence. This includes contributions from AEA's flow measurements, desorption efficiency and analysis uncertainty.

Calculated uncertainty for the Automatic Hydrocarbon Network in 2011 for benzene is 24%, expressed at a level of confidence of 95%. This includes contributions from:

- Repeatability and lack of fit
- Variation in sample gas pressures, surrounding temperature and electrical voltage
- Interference of ozone
- Memory effects

- Differences between the sample and calibration port
- Uncertainty in calibration gas
- Reproducibility under field conditions
- Long term drift

All data from the network therefore meets the 2008/50/EC Directive Data Quality Objective for the measurement uncertainty of $\pm 25\%$.

4.3 Standard Methods

European Standard EN14662-3:2005 is the Ambient Air Quality Standard method for the measurements of benzene concentrations – Part 3: Automated pumped sampling with in-situ gas chromatography. This Standard is for the determination of benzene in ambient air for the purpose of comparing measurement results with annual mean limit values. It describes guidelines for measurements with automated gas chromatographs, between 0 and 50 $\mu\text{g}/\text{m}^3$. Measurements undertaken by the Automatic Hydrocarbon Network are carried out in accordance with this Standard.

European Standard EN14662-1:2005 is the Ambient Air Quality Standard method for measurement of benzene concentrations – Part 1: Pumped sampling followed by thermal desorption and gas chromatography. This Standard gives general guidance for the sampling and analysis of benzene in air by pumped sampling, thermal desorption and capillary gas chromatography. The pumped sampler was developed by NPL in compliance with this standard. AEA contract Environmental Scientifics Groups (ESG) to analyse the samples, the analysis is also carried out in accordance with this standard.

4.4 Limit of Detection

The Limit of Detection for the mass of benzene on a desorption tube from the Non-Automatic Hydrocarbon Network is approximately 2ng. This is equivalent to about 0.02 $\mu\text{g}/\text{m}^3$

The Limit of Detection for each species measured by the Perkin Elmer Ozone Precursor Analysers used by the Automatic Hydrocarbon Network is shown in Table 8.

Table 8 Automatic Analyser Limits of Detections

Compound	Limit of Detection ($\mu\text{g}/\text{m}^3$)
Ethane	0.10
Ethene	0.01
Propane	0.02
Propene	0.02
Ethyne	0.01
i-Butane	0.02
n-Butane	0.02
trans-2-Butene	0.02
1-Butene	0.02
cis-2-Butene	0.02
i-Pentane	0.03
n-Pentane	0.03
1,3-Butadiene	0.02
trans-2-Pentene	0.03
1-Pentene	0.03
2-Methylpentane	0.04
Isoprene	0.03
n-Hexane	0.04
Benzene	0.03
i-Octane	0.05
n-Heptane	0.04
n-Octane	0.05
Toluene	0.04
Ethylbenzene	0.04
(m+p)-Xylene	0.04
o-Xylene	0.04
1,3,5-Trimethylbenzene	0.05
1,2,4-Trimethylbenzene	0.05
1,2,3-Trimethylbenzene	0.05

5 Developments and Recommendations

5.1 EN14662-3:2005

European Standard EN14662-3:2005 is currently under review by Working Group 12, to bring it in line with the other gaseous pollutants' standards. AEA are involved in the review through a representative on the Working Group, and are providing appropriate contributions and feedback to Defra and the Devolved Administrations regarding the potential implications for the Automatic Hydrocarbon Network.

5.2 Acetaldehyde and Formaldehyde

In 2011 the UK Air Quality Expert Group (AQEG) published an advice note on road transport biofuels and their impact on UK air quality for Defra and the Devolved Administrations. The AQEG note can be found at

http://uk-air.defra.gov.uk/documents/110322_AQEG_Biofuels_advice_note.pdf.

The note accepts that results from research studies on the effects of biofuels on vehicle emission are inconclusive and show a high degree of variability, but concludes that any increased use of bioethanol and biodiesel are likely to significantly increase acetaldehyde and formaldehyde emissions. The note goes on to say that 'the likely continued growth in biofuel consumption in the UK means that evidence for any atmospheric change in pollutant concentrations should be monitored in parallel with direct measurements of biofuel emissions from road vehicles'.

Starting in 2012, AEA will undertake a pilot study of monitoring for acetaldehyde and formaldehyde at a small number of roadside and background sites. This will help the UK to prepare for potential legislative change in the future and will start a dataset useful for long term trend analysis.

Use of biofuels in the UK

Biodiesel is a generic term for a product which has variable chemical composition, whereas bioethanol is a specific chemical. Over the past 2-3 years bioethanol and biodiesel consumption has grown, driven by domestic targets and EU Directives. The UK still uses relatively small amounts of low strength bioethanol and biodiesel, but consumption is expected to continue to increase over the next decade as a result of the EU Directive 2009/28/EC which raised the target set for the share of biofuels as a % of energy content by 2020 to 10%.

Most bioethanol in the UK is likely to be consumed as weak (<5%) blends in fossil fuel petrol sold at regular filling stations. Research by AEA, undertaken for the Department for Transport in 2011, indicated that in 2008 176 ktonnes of bioethanol were used in road transport. In 2009 361 ktonnes were used (compared to over 900 ktonnes of biodiesel used each year). Data from HM Revenue and Customs, used for the National Atmospheric Emissions Inventory (NAEI), indicate that bioethanol consumption in the UK was about 3% of total petrol consumption in 2010.

Currently 100% of the UK fleet of passenger cars and light commercial vehicles (both new and older models) can use low ethanol blends, up to 5%. Only 84% of the current fleet can run on 10% bioethanol and less than 1% of the fleet can operate with a high 85% bioethanol/petrol blend. The uptake of high concentration blends of bioethanol (E85) may

increase in future if the fuel supply infrastructure develops and the population of vehicles capable of running on this fuel increases.

Bioethanol is mainly added to petrol at refineries and main fuel distribution centres so there is unlikely to be any regional consumption hot spot, rather it is used by all petrol vehicles without motorists being aware. High strength bioethanol (E85) is a niche fuel which can only be used by petrol vehicles that have undergone a conversion, engine re-tuning or flexi-fuelled vehicles able to run on regular unleaded or E85. There may be some dedicated fleets using this fuel in some areas, but these are not believed to be common in the UK.

Effect of bioethanol on acetaldehyde and formaldehyde

The Air Quality Expert Group's report on Road Transport Biofuels (2011) suggests that overall, low strength blends of bioethanol reduce or have little effect on emissions of air quality pollutants. But, even at low strength blends of bioethanol, literature studies show that consumption of bioethanol leads to the significant increase in acetaldehyde and formaldehyde emissions from vehicles compared to petrol consumption. Other VOCs may be increased if a high proportion of bioethanol is used due to its effect on increasing fuel volatility.

Geography of bioethanol consumption

In the UK, consumption is likely to be well dispersed across the country, with no particular hot spots. This is likely to continue, although there may be localised use of some biofuels by captive fleets in areas close to where they are produced, but it is unlikely that consumption would be high enough to observe any changes in ambient concentrations.

The UK NAEI uses HM Revenue and Customs (HMRC) national statistics on the consumption of biofuels in the UK. The HMRC produces monthly national statistics on the volume of bioethanol and biodiesel released for consumption. However, this information does not split the bioethanol consumption by region. For the report, *'Improving the Greenhouse Gas Inventories for Road Transport in Scotland, Wales and Northern Ireland'* (Murrells et al. 2011), Devolved Administration contacts and biofuel experts within AEA were consulted regarding data on regional biofuel consumption; however, this information does not seem to be available. Information on the location of the major biofuel producers in the UK is available, however, this does not necessarily represent where the biofuels are consumed. Any variation will also only be a matter of whether the fuel sold is a 0% blend (no bioethanol in petrol) or 5% bioethanol blend and any differences between filling stations in this respect are likely to be random, not with any regional bias. Most large scale biofuel production is used to produce 5% biofuel blends which are expected to be sold uniformly around the UK.

Selection of monitoring sites

The likely continued growth in biofuel consumption in the UK means that evidence for any atmospheric changes in pollutant concentrations should be monitored in parallel with estimates of biofuel emissions from road vehicles. The pilot monitoring project delivers this and monitors the roadside effect of bioethanol use within the UK fleet.

Given that the pattern of consumption of bioethanol relative to petrol consumption is likely to be quite uniform, the strongest signature for ambient concentrations of acetaldehyde and formaldehyde derived from bioethanol consumption will be where petrol vehicle emissions are highest. The places where these emissions will be relatively high will be at roads where:

- The traffic flow is high
- There is a high proportion of petrol car activity – this would favour an urban roadside site rather than a rural or motorway site where there is generally more diesel activity

- The petrol car fleet is relatively old, hence there will be a higher proportion of older Euro standards with higher VOC emissions
- The traffic flow is slow and congested. This enhances vehicle emissions of VOCs.

The following indicators have therefore been used to select the monitoring sites to be used for the study:

- The type of road the monitoring station is located by
- Traffic flow per day
- Proportion of diesel and petrol vehicles which drive by the monitoring site (since the focus of this study is only bioethanol).

To ensure that the results of the monitoring showed the difference in bioethanol consumption specifically, it is also important that the roadside monitoring sites are located at similar heights and are similar distances away from the road.

AEA's recent work using Automatic Number Plate Recognition (ANPR) data for the NAEI confirmed the mix of petrol cars is highest on urban roads. Previous work analysing ANPR and licensing data suggested the age of the car fleet on the same type of road was fairly uniform in the UK, but there were certain areas of the country which had a consistently older car fleet registered. One of these was the south-west of England.

Acetaldehyde and formaldehyde are types of VOCs that are formed in the atmosphere from the photochemical degradation of other VOCs. In fact, the majority of these aldehydes detected at a given location will be from this secondary background source rather than direct emissions. It will therefore be important to do paired measurements at a reasonably close background site to determine the photochemically produced background. This background concentration will vary by region around the UK and be strongest during photochemically active periods in the spring and summer, but there should be little difference between an urban roadside and urban background site in the same region (e.g. county). The difference (delta) between the two measurements will be a measure of the direct traffic emissions. The delta will vary with time of day and time of year and should be strongest when there is least photochemical activity (e.g. during the winter). The delta should increase over the campaign if the national bioethanol consumption increases by increasing the strength of bioethanol/petrol mix.

Two paired sites are proposed:

- Chesterfield urban roadside and Chesterfield urban background.
- Exeter roadside and the new Honiton urban background

The Honiton and Exeter sites should be sufficiently close to have the same photochemical background contribution. The Exeter roadside site is also in an area where the petrol car fleet is known to be slightly older than the national average.

A fifth location is recommended at the rural Yarnar Wood (Devon) site. This will provide further evidence on the photochemical background and its seasonal variation and would be a useful indicator of this contribution in its own right for regional scale photochemical air pollution modelling.

Table 9 Specifications of the five monitoring sites selected for the study

Monitoring site	Type of road nearby	Distance away from the road	Environment type	% of diesel and petrol vehicles
Chesterfield Roadside	A619	3m	Urban Traffic	35% diesel 65% petrol
Chesterfield	B-road to the west, minor roads on other sides	100m	Urban Background	35% diesel 65% petrol
Exeter Roadside	Single carriageway urban street	3m	Urban Traffic	35% diesel 65% petrol
Yarner Wood	Access road	60m to access road, 1km to nearest B-road	Rural	38% diesel 62% petrol
Honiton*	Quiet residential road	10m	Urban Background	35% diesel 65% petrol

5.3 Network Review

Under Article V to Article VII of Directive 2008/50/EC all Member States must carry out a periodic review of monitoring networks. In the UK, this assessment was undertaken in 2011. It is likely that some changes to the UK Hydrocarbon Network will be required, and these can be implemented when the review is published and agreed by Defra.

Appendices

- Appendix 1: 2011 Audit Schedule and Results
- Appendix 2: Copy of 2011 audit certificate - Accredited low flow measurements
- Appendix 3: Data capture, maximum and annual mean values from the Automatic Hydrocarbon Network
- Appendix 4: 2011 Benzene and 1,3-Butadiene Concentration data

Appendix 1

2011 Audit Schedule of the Non-Automatic Hydrocarbon Network

Table 10 Audit Schedule of the Non-Automatic Hydrocarbon Network

Site	Date	Measured flow, ml/min	Adjusted flow, ml/min	Date	Measured flow, ml/min	Adjusted flow, ml/min	Date	Measured flow, ml/min	Adjusted flow, ml/min
Barnsley Gawber	12/04/11	9.80	10.07	18/10/11	10.05	10.00	18/04/12	9.88	10.00
Bath Roadside	15/04/11	9.57	9.80	14/11/11	9.53	9.96	28/03/12	10.12	10.00
Belfast Centre	18/04/11	10.18	10.07	18/11/11	9.64	10.00	27/04/12	9.29	10.03
Birmingham Acocks Green	-	-	-	03/11/11	10.86	9.96	23/04/12	9.39	9.99
Birmingham Tyburn	04/05/11	10.20	-	-	-	-	-	-	-
Birmingham Tyburn Roadside	04/05/11	9.98	10.00	03/11/11	10.38	10.01	04/04/12	10.15	10.05
Bloomsbury	16/05/11	9.97	10.00	19/10/11	9.45	9.93	19/04/12	9.87	9.98
Bristol Old Market	05/05/11	9.82	9.95	21/10/11	9.66	9.99	23/04/12	10.77	10.04
Bury Roadside	04/05/11	10.23	10.10	20/10/11	9.43	10.02	19/04/12	9.88	10.01
Cambridge Roadside	12/05/11	10.16	10.06	03/11/11	9.97	9.99	16/04/12	9.69	10.00
Camden Kerbside	07/08/11	10.95	10.08	18/10/11	9.79	9.89	24/04/12	9.88	9.91
Carlisle Caldewgate	06/05/11	10.31	10.01	10/10/11	9.98	10.03	03/04/12	9.63	9.95
Chatham Roadside	05/04/11	9.63	9.61	03/10/11	10.17	10.03	13/03/12	9.36	10.01
Chesterfield	13/04/11	10.19	9.94	19/10/11	9.54	10.00	17/04/12	9.54	10.01
Coventry Memorial Park	07/04/11	9.80	10.00	24/10/11	10.06	10.06	23/04/12	10.39	10.01
Eaglescliffe – Yarm	05/04/11	10.20	10.10	11/10/11	9.80	10.03	11/04/12	9.83	10.04
Glasgow Kerbside	14/04/11	9.77	10.00	05/10/11	10.09	10.09	02/05/12	8.70	10.00

Site	Date	Measured flow, ml/min	Adjusted flow, ml/min	Date	Measured flow, ml/min	Adjusted flow, ml/min	Date	Measured flow, ml/min	Adjusted flow, ml/min
Grangemouth	11/04/11	9.5	10.00	25/10/11	10.51	10.01	04/04/12	8.55	10.06
Haringey Roadside	16/05/11	9.78	9.96	22/12/11	9.63	9.99	26/04/12	9.88	9.96
Leamington Spa	07/04/11	9.90	10.00	24/10/11	10.04	9.96	19/03/12	10.13	10.02
Leeds Centre	12/04/11	9.80	9.91	08/11/11	9.92	9.99	13/03/12	9.53	9.78
Leicester Centre	04/04/11	10.00	10.10	25/10/11	10.34	10.03	17/04/12	10.09	10.01
Liverpool Speke	05/04/11	10.30	10.00	04/10/11	9.68	9.87	25/04/12	10.33	10.06
London Eltham (non-network site)	-	-	-	05/09/11	10.40	10.03	22/03/12	9.34	10.04
Manchester Piccadilly	04/05/11	10.12	10.03	20/10/11	9.39	9.99	19/04/12	10.51	10.01
Marylebone Rd (non-network site)	16/05/11	9.9	10.11	19/10/11	10.07	10.18	24/04/12	9.65	9.87
Middlesbrough	05/04/11	10.50	10.10	11/10/11	10.01	10.00	11/04/12	9.55	10.02
Newcastle	04/04/11	10.10	10.00	11/10/11	10.36	10.05	03/04/12	9.05	9.97
Northampton	06/04/11	9.9	10.00	26/10/11	9.92	9.95	19/03/12	9.55	10.10
Norwich - Lakenfields	13/04/11	7.77*	10.00	03/11/11	10.02	10.02	01/05/12	9.71	9.95
Nottingham Centre	13/04/11	10.16	9.94	26/10/11	10.12	9.98	03/04/12	10.43	10.14
Oxford Centre	06/05/11	10.20	10.10	17/10/11	9.93	9.97	02/02/12	10.02	10.00
Oxford St Ebbes	06/05/11	9.83	9.89	17/10/11	10.19	10.04	05/04/12	9.20	10.03
Plymouth	18/04/11	9.79	9.93	14/11/11	9.91	10.05	03/05/12	9.76	9.90
Sheffield	12/04/11	10.15	10.00	18/10/11	9.85	10.06	17/04/12	9.96	10.01
Southampton	05/04/11	10.10	10.00	25/10/11	10.66	10.10	03/04/12	9.75	9.92
Stoke Centre	06/04/11	9.80	10.00	05/10/11	10.27	10.08	22/03/12	9.24	9.65
Wigan Centre	05/04/11	10.40	9.90	03/10/11	10.42	10.12	23/04/12	9.68	9.98
York Fishergate Roadside	11/04/11	9.39	9.94	17/10/11	9.99	10.02	16/04/12	9.64	10.01

*Sampler and pump replaced, pump fault

2011 Audit Schedule of the Automatic Hydrocarbon Network

Table 11 **Audit and Service Schedule of the Automatic Hydrocarbon Network**

Site	Service Date	Audit Date	Audit Date	Audit Date
Auchencorth Moss	27/10/11	04/11/09	18/05/11	28/03/12
Harwell	27/06/11	26/10/09	14/03/11	12/04/12
Eltham	22/11/11	27/10/09	16/03/11	22/03/12
Marylebone Road	15/03/11	28/10/09	15/03/11	20/03/12

Appendix 2

Copy of 2011 Audit certificate - Accredited low flow measurements



Certificate of Calibration

AEA, 551.11 Harwell IBC, Didcot, Oxfordshire OX11 0QJ 01235 436465



0401

Certificate Number: 2454

Page 1 of 2

Approved Signatories:

S Eaton
B Stacey

J Green
S Stratton

D Hector

Signed:

This copy is representative of the official certificate

Date of issue:

31 May 2011

Customer Name and Address:

Dr Emily Connolly
Science and Evidence Team
Atmosphere and Local Environment (ALE) Programme
Department for Environment, Food and Rural Affairs
Area 5E Ergon House, 17 Smith Square, London, SW1P 3JR

Description:

Measured flow rates for samplers in the Non-Automatic
Hydrocarbon Monitoring Network

Measured flowrates

Site	Date of measurement	Flow A (mlmin ⁻¹)	Flow B (mlmin ⁻¹)	Difference (mlmin ⁻¹)	Uncertainty (mlmin ⁻¹)
Barnsley Gawber	12/04/2011	10.07	10.20	0.13	0.004
Bath Roadside	15/04/2011	9.80	9.80	0.00	0.002
Belfast Centre	18/04/2011	10.07	10.14	0.07	0.003
Birmingham Acocks Green*	04/05/2011	10.10	10.10	0.00	0.002
Birmingham Tyburn Roadside	04/05/2011	10.00	10.02	0.02	0.002
London Bloomsbury	16/05/2011	10.00	9.99	0.01	0.002
Bristol Old Market	05/05/2011	9.95	9.94	0.01	0.002
Bury Roadside	04/05/2011	10.10	10.15	0.05	0.003
Cambridge Roadside	12/05/2011	10.06	10.07	0.01	0.002
Camden Kerbside	07/08/2011	10.08	10.13	0.05	0.003
Carlisle Roadside	06/05/2011	10.01	10.09	0.08	0.003
Chatham Centre Roadside	05/04/2011	9.61	9.60	0.01	0.002
Chesterfield Roadside	13/04/2011	9.94	10.03	0.09	0.004
Coventry Memorial Park	07/04/2011	10.00	10.00	0.00	0.002
Glasgow Kerbside	14/04/2011	10.03	10.08	0.05	0.003
Grangemouth	12/04/2011	10.00	10.08	0.08	0.003
Haringey Roadside	16/05/2011	9.96	9.99	0.03	0.003
Leamington Spa	07/04/2011	9.96	9.97	0.01	0.002
Leeds Centre	12/04/2011	9.91	9.95	0.04	0.003

The reported expanded uncertainty is based on a standard uncertainty multiplied by a coverage factor k=2 providing a level of confidence of approximately 95%. The uncertainty evaluation has been carried out in accordance with UKAS requirements.

This certificate is issued in accordance with the laboratory accreditation requirements of the United Kingdom Accreditation Service. It provides traceability of measurement to recognised national standards, and to units of measurement realised at the National Physical Laboratory or other recognised national standards laboratories. This certificate may not be reproduced other than in full, except with the prior written approval of the issuing laboratory.

A business name of AEA Technology plc.
Registered office 6 New Street Square, London, EC4A 3BF
Registered in England and Wales no 3095862

Site	Date of measurement	Flow A (mlmin ⁻¹)	Flow B (mlmin ⁻¹)	Difference (mlmin ⁻¹)	Uncertainty (mlmin ⁻¹)
Leicester Centre	04/04/2011	10.12	10.12	0.00	0.002
Liverpool Speke	05/04/2011	9.97	9.97	0.00	0.002
Manchester Piccadilly	04/05/2011	10.03	10.11	0.08	0.003
Marylebone Road	19/04/2011	10.11	10.04	0.07	0.003
Middlesbrough Centre	05/04/2011	10.10	10.10	0.00	0.002
Newcastle Centre	04/04/2011	10.01	10.09	0.08	0.003
Northampton	06/04/2011	10.00	10.00	0.00	0.002
Norwich Lakenfields	12/05/2011	10.04	10.04	0.00	0.002
Nottingham Centre	13/04/2011	9.94	10.01	0.07	0.003
Oxford Centre	06/05/2011	10.22	10.21	0.01	0.002
Oxford St Ebbes	06/05/2011	9.89	9.89	0.00	0.002
Plymouth Centre	18/04/2011	9.93	9.93	0.00	0.002
Sheffield Centre	12/04/2011	10.00	10.06	0.06	0.003
Southampton	05/04/2011	10.03	10.02	0.01	0.002
Stockton-on-Tees Eaglescliffe	05/04/2011	10.10	10.10	0.00	0.002
Stoke-on-Trent Centre	06/04/2011	9.96	9.97	0.01	0.002
Wigan Centre	05/04/2011	10.00	9.90	0.10	0.004
York Fishergate	11/04/2011	9.94	9.95	0.01	0.002

*The sampler at Birmingham Tyburn was removed and installed at Birmingham Acocks Green on the same day.

The measured flow rate (where this is applicable) is the flow rate through the two sample tubes on the day of audit using documented methods. Flows are corrected to 20°C and 1 atm. . Note that the test results are valid on the day of test only, as flowrate drift over time cannot be quantified.

The reported uncertainty is based on a standard uncertainty multiplied by a coverage factor $k = 2$, providing a level of confidence of approximately 95%. The uncertainty evaluation has been carried out in accordance with UKAS requirements.

Appendix 3

Data capture, maximum and annual mean values from the Automatic Hydrocarbon Network

Percentage data capture, maximum and annual mean values of ratified data from the Auchencorth Moss site of the Automatic Hydrocarbon Network. Note that the annual mean concentrations have been calculated even where the data capture at the site is less than 75%. These annual means therefore may not be representative of an average year and the data should be used with caution.

Table 12 Auchencorth Moss

Compound	% Data capture	Maximum hourly concentration ($\mu\text{g}/\text{m}^3$)	Annual Mean concentration ($\mu\text{g}/\text{m}^3$)
1,2,3-trimethylbenzene	<LoD	<LoD	<LoD
1,2,4-trimethylbenzene	<LoD	<LoD	<LoD
1,3,5-trimethylbenzene	<LoD	<LoD	<LoD
1,3-butadiene	38	0.74	0.017
1-butene	<LoD	<LoD	<LoD
1-pentene	<LoD	<LoD	<LoD
2-methylpentane	54	7.0	0.058
benzene	54	3.4	0.21
ethane	66	18.3	1.9
ethylbenzene	24	2.5	0.083
ethene	32	4.1	0.25
ethyne	61	2.6	0.16
isoprene	21	0.88	0.069
propane	68	145	1.3
propene	49	2.6	0.088
toluene	49	10	0.23
cis-2-butene	<LoD	<LoD	<LoD
iso-butane	61	23	0.34
iso-octane	15	1.5	0.076
iso-pentane	55	19	0.26
m+p-xylene	26	8.3	0.15
n-butane	58	53	0.49
n-heptane	27	4.9	0.072
n-hexane	53	18	0.084
n-octane	21	1.2	0.038
n-pentane	56	12	0.15
o-xylene	26	2.9	0.070
trans-2-butene	<LoD	<LoD	<LoD
trans-2-pentene	<LoD	<LoD	<LoD

Percentage data capture, maximum and annual mean values of ratified data from the Harwell site of the Automatic Hydrocarbon Network. Note that the annual mean concentrations have been calculated even where the data capture at the site is less than 75%. These annual means therefore may not be representative of an average year and the data should be used with caution.

Table 13 Harwell

Compound	% Data capture	Maximum hourly concentration ($\mu\text{g}/\text{m}^3$)	Annual Mean concentration ($\mu\text{g}/\text{m}^3$)
1,2,3-trimethylbenzene	56	0.75	0.092
1,2,4-trimethylbenzene	73	5.0	0.14
1,3,5-trimethylbenzene	19	0.55	0.11
1,3-butadiene	94	0.43	0.10
1-butene	54	0.63	0.11
1-pentene	<LoD	<LoD	<LoD
2-methylpentane	93	3.4	0.13
benzene	93	2.2	0.33
ethane	94	15	2.6
ethylbenzene	57	1.0	0.12
ethene	90	4.9	0.42
ethyne	91	2.0	0.27
isoprene	42	0.76	0.036
propane	93	39	1.5
propene	87	8.7	0.25
toluene	95	14	0.51
cis-2-butene	76	0.16	0.055
iso-butane	93	5.6	0.48
iso-octane	31	1.3	0.15
iso-pentane	94	5.9	0.43
m+p-xylene	68	3.0	0.25
n-butane	93	8.5	0.82
n-heptane	46	0.79	0.11
n-hexane	93	1.0	0.11
n-octane	29	0.38	0.071
n-pentane	94	6.9	0.25
o-xylene	60	1.7	0.14
trans-2-butene	90	0.26	0.066
trans-2-pentene	<LoD	<LoD	<LoD

Percentage data capture, maximum and annual mean values of ratified data from the London Eltham site of the Automatic Hydrocarbon Network. Note that the annual mean concentrations have been calculated even where the data capture at the site is less than 75%. These annual means therefore may not be representative of an average year and the data should be used with caution.

Table 14 London Eltham

Compound	% Data capture	Maximum hourly concentration ($\mu\text{g}/\text{m}^3$)	Annual Mean concentration ($\mu\text{g}/\text{m}^3$)
1,2,3-trimethylbenzene	65	3.1	0.24
1,2,4-trimethylbenzene	69	3.1	0.37
1,3,5-trimethylbenzene	61	1.2	0.12
1,3-butadiene	64	0.38	0.056
1-butene	84	1.1	0.11
1-pentene	83	1.4	0.047
2-methylpentane	85	6.2	0.32
benzene	58	2.6	0.37
ethane	46	81	7.4
ethylbenzene	83	3.5	0.24
ethene	21	17	1.7
ethyne	68	2.8	0.39
isoprene	75	2.7	0.16
propane	77	242	2.4
propene	76	2.9	0.30
toluene	79	23	1.4
cis-2-butene	84	1.2	0.061
iso-butane	82	58	1.4
iso-octane	74	3.7	0.20
iso-pentane	83	25	1.5
m+p-xylene	80	6.6	0.69
n-butane	81	65	2.6
n-heptane	79	1.1	0.14
n-hexane	84	15	0.19
n-octane	78	1.9	0.079
n-pentane	83	14	0.67
o-xylene	82	2.2	0.26
trans-2-butene	75	1.8	0.063
trans-2-pentene	85	2.4	0.062

Percentage data capture, maximum and annual mean values of ratified data from the Marylebone Road site of the Automatic Hydrocarbon Network. Note that the annual mean concentrations have been calculated even where the data capture at the site is less than 75%. These annual means therefore may not be representative of an average year and the data should be used with caution.

Table 15 Marylebone Road

Compound	% Data capture	Maximum hourly concentration ($\mu\text{g}/\text{m}^3$)	Annual Mean concentration ($\mu\text{g}/\text{m}^3$)
1,2,3-trimethylbenzene	49	5.0	0.51
1,2,4-trimethylbenzene	47	10	1.3
1,3,5-trimethylbenzene	41	8.0	0.55
1,3-butadiene	44	1.7	0.24
1-butene	42	1.8	0.31
1-pentene	41	1.4	0.15
2-methylpentane	39	14	1.6
benzene	47	9.2	1.3
ethane	58	72	7.9
ethylbenzene	65	15	0.96
ethene	51	58	2.2
ethyne	48	8.6	1.1
isoprene	19	2.1	0.22
propane	57	192	4.3
propene	41	21	1.3
toluene	65	36	4.9
cis-2-butene	28	3.1	0.23
iso-butane	57	38	2.9
iso-octane	63	10	0.77
iso-pentane	54	57	5.3
m+p-xylene	63	47	3.1
n-butane	57	70	5.4
n-heptane	64	11	0.49
n-hexane	42	6.9	0.53
n-octane	62	2.5	0.19
n-pentane	55	16	1.8
o-xylene	64	14	1.2
trans-2-butene	34	1.8	0.19
trans-2-pentene	58	2.6	0.24

Appendix 4

Automatic Hourly Mean Graphs for Benzene and 1,3-Butadiene

Figure 10 Auchencorth Moss Automatic Benzene

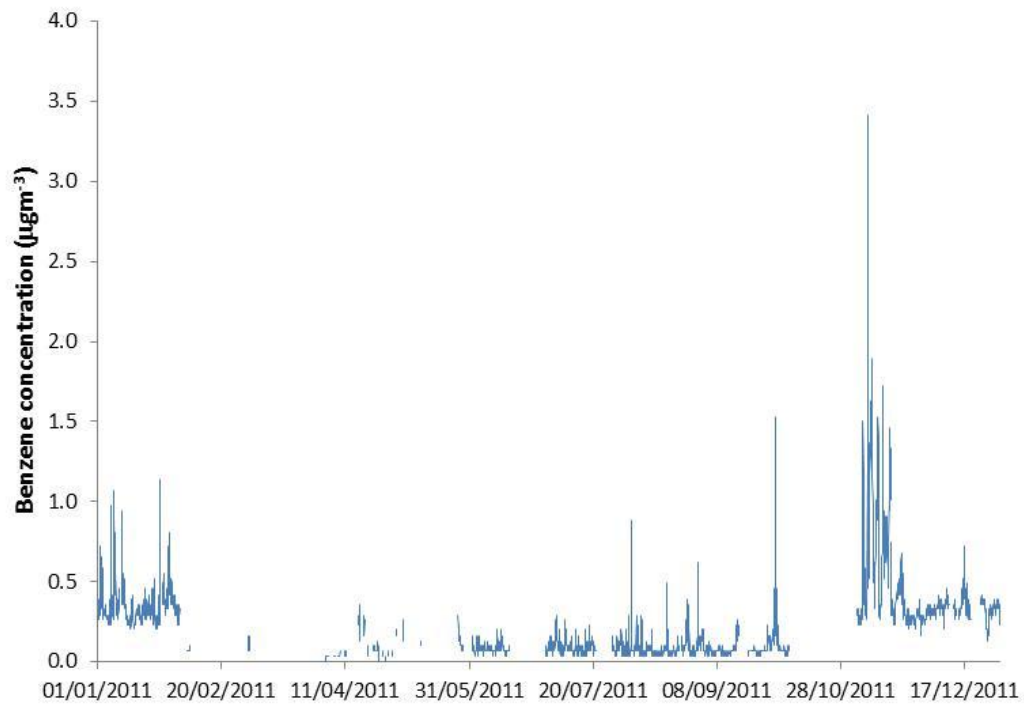


Figure 11 Auchencorth Moss Automatic 1,3-Butadiene

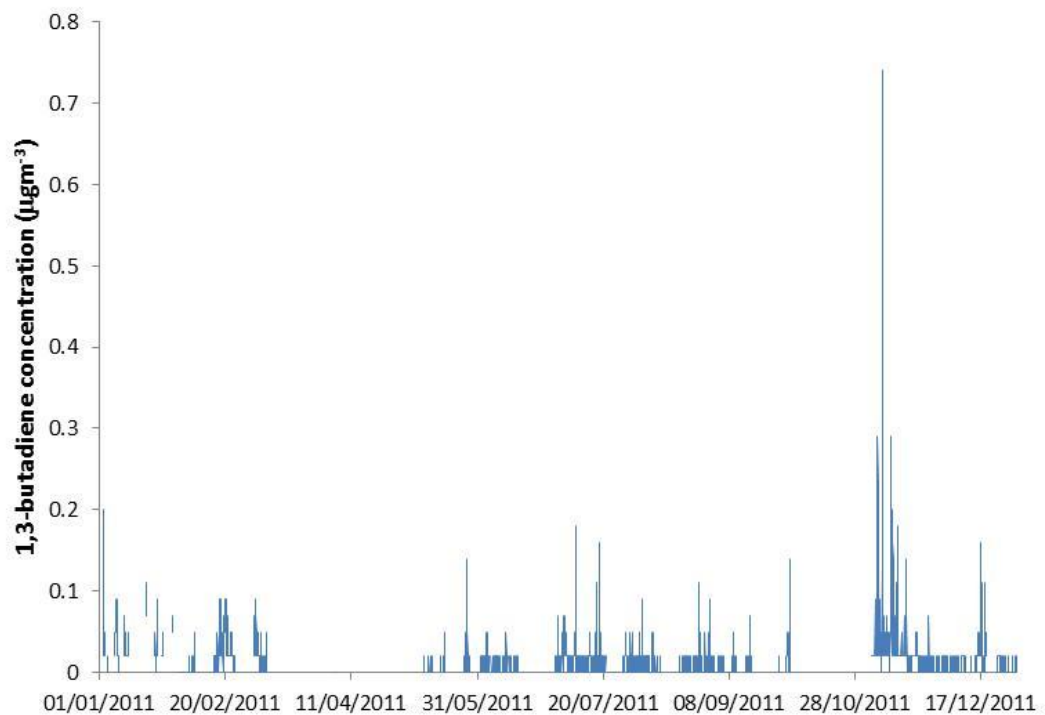


Figure 12 Harwell Automatic Benzene

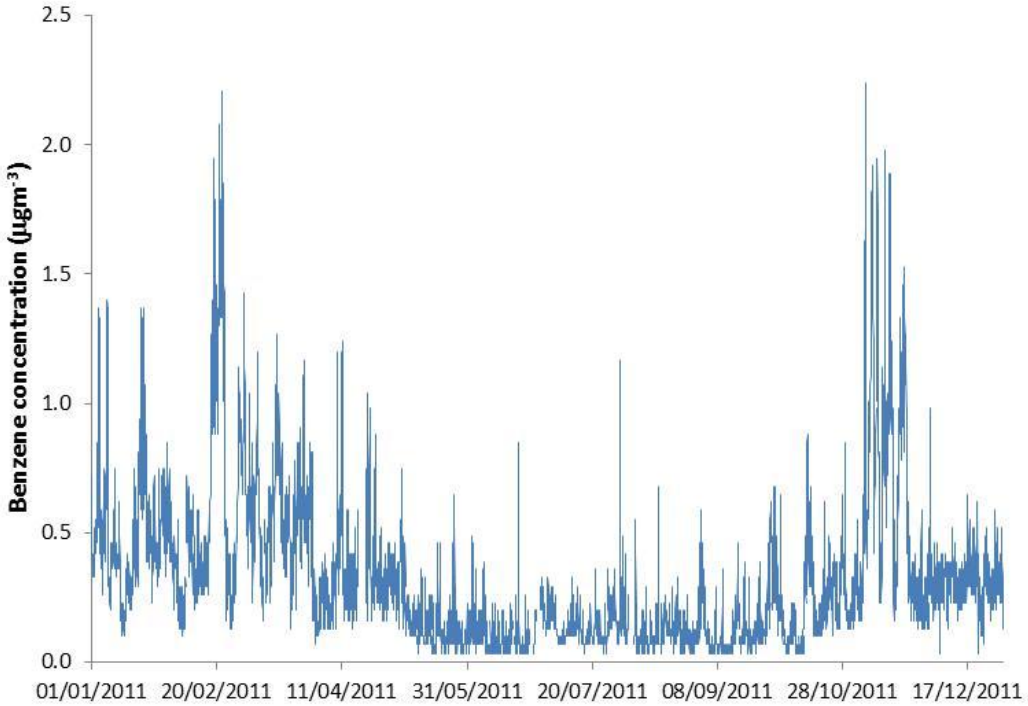


Figure 13 Harwell Automatic 1,3-Butadiene

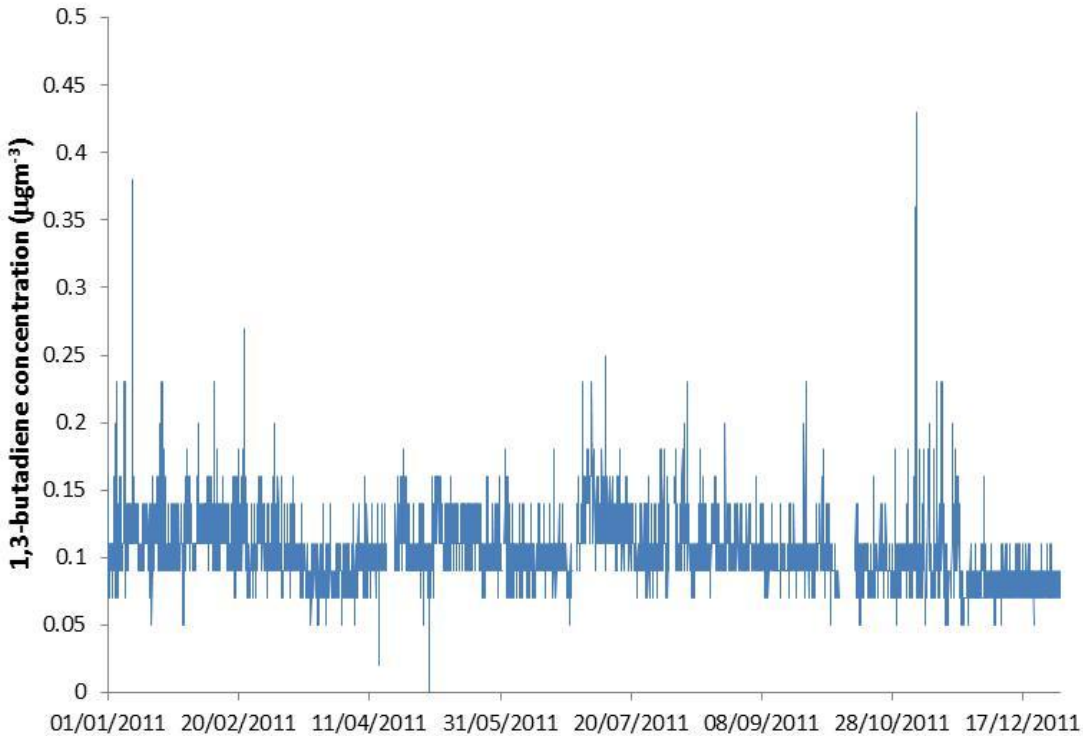


Figure 14 London Eltham Automatic Benzene

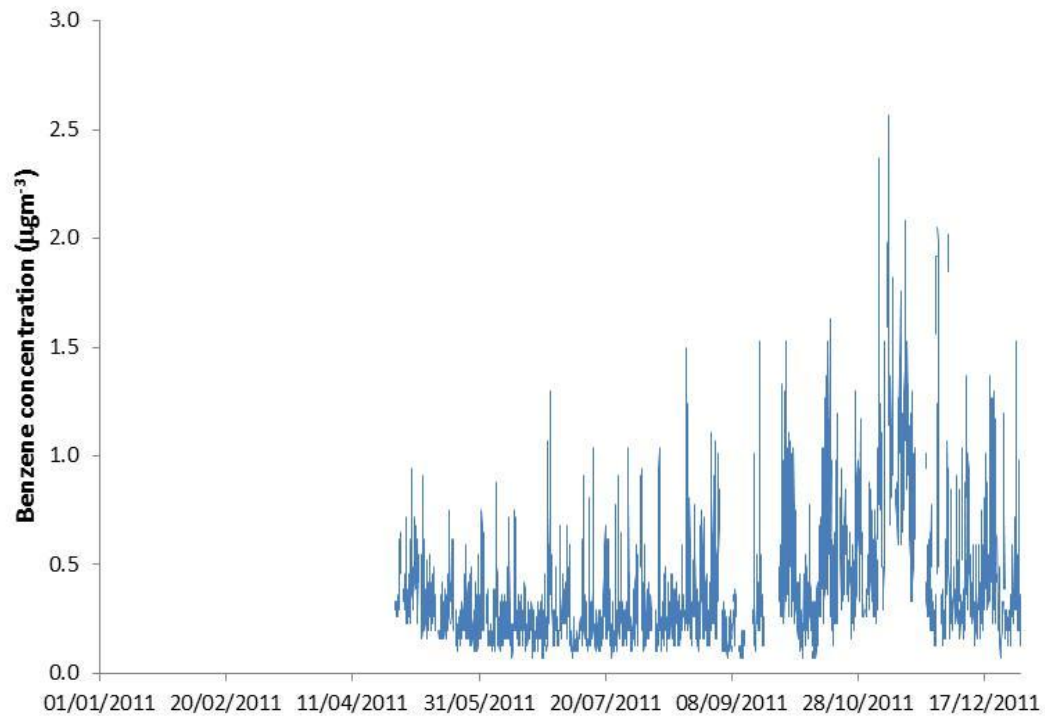


Figure 15 London Eltham Automatic 1,3-Butadiene

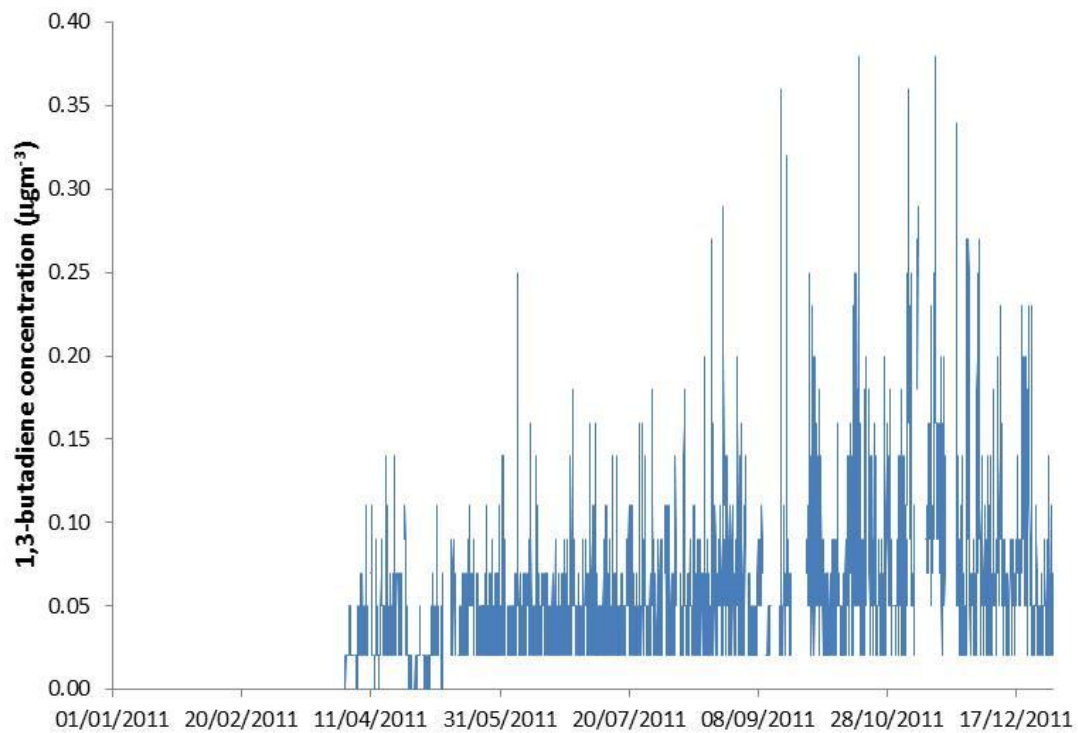


Figure 16 Marylebone Road Automatic Benzene

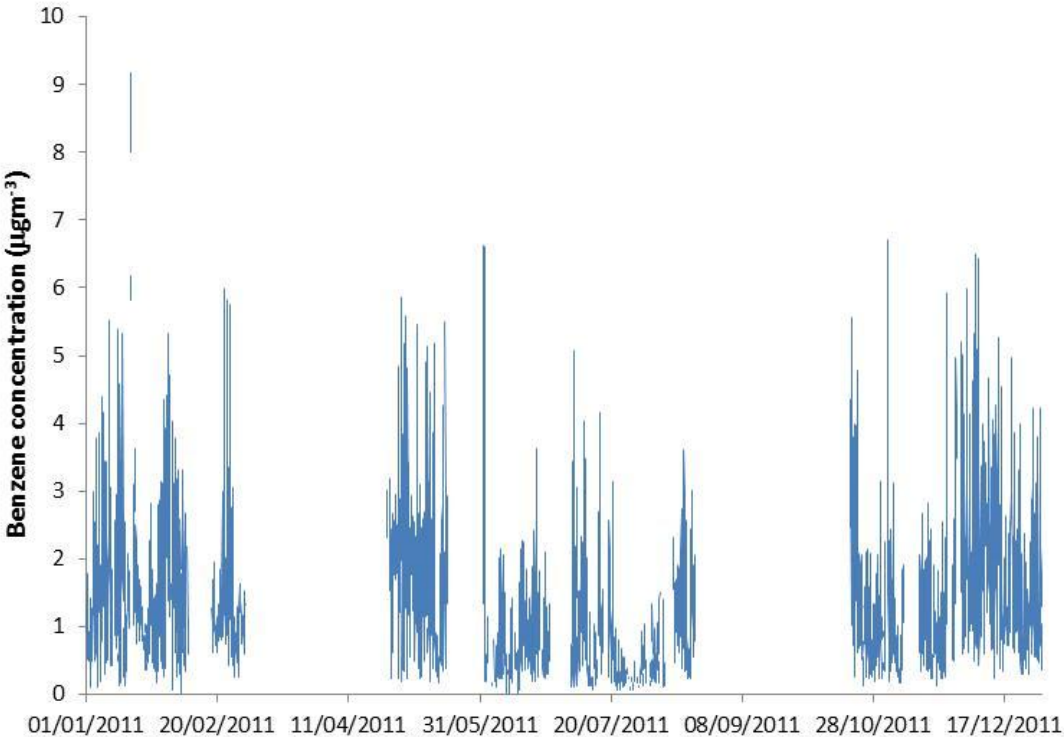
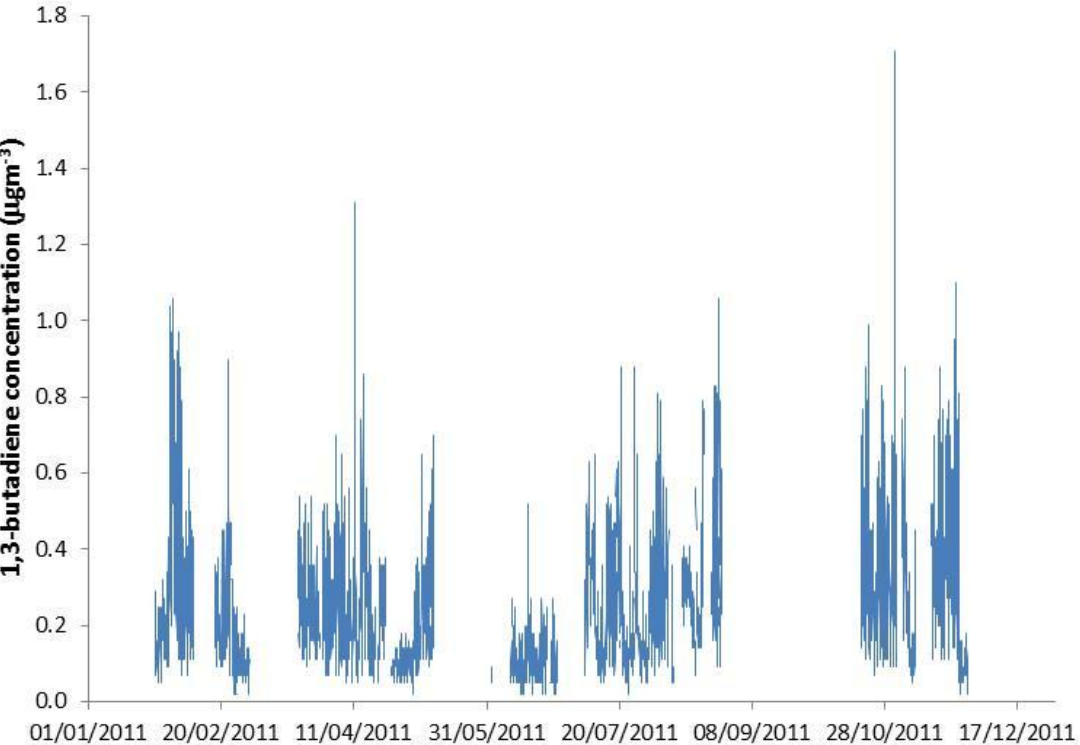


Figure 17 Marylebone Road Automatic 1,3-Butadiene



Non Automatic Fortnightly Mean Graphs for Benzene

Figure 20 Barnsley Gawber Non Automatic Benzene

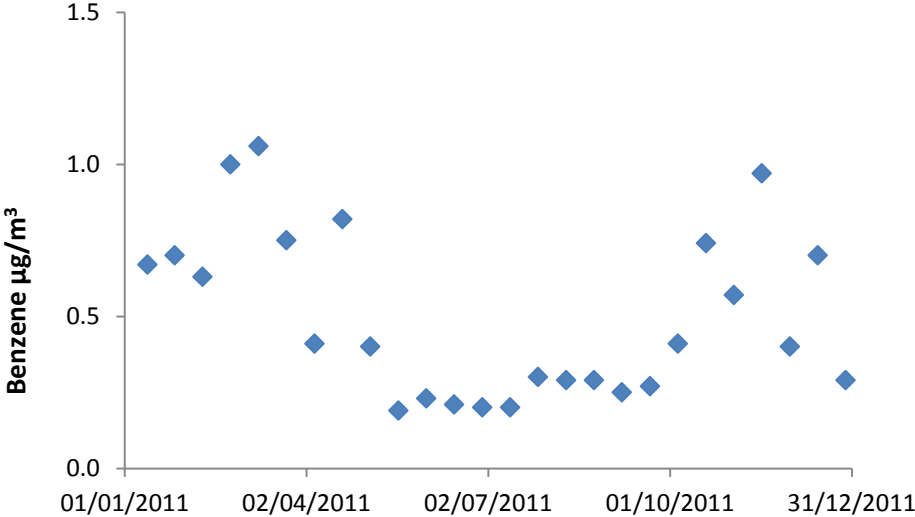


Figure 21 Bath Roadside Non Automatic Benzene

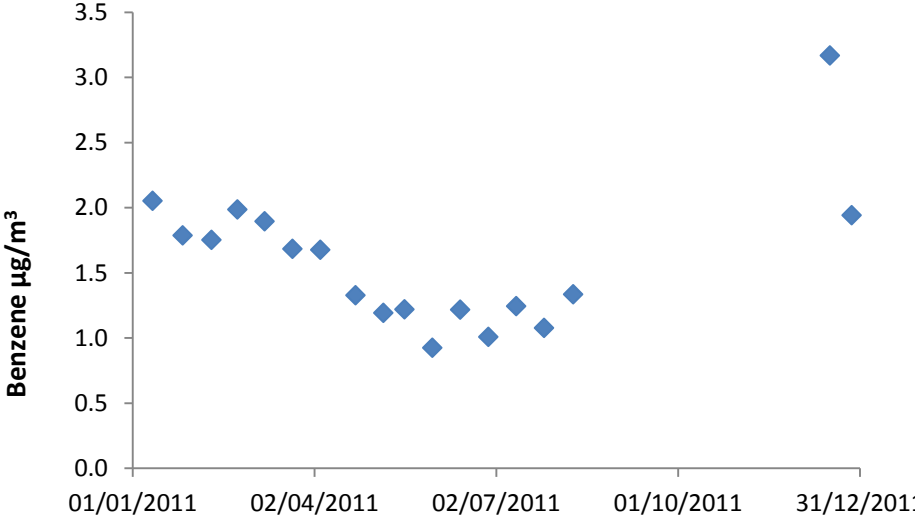


Figure 22 **Belfast Centre Non Automatic Benzene**

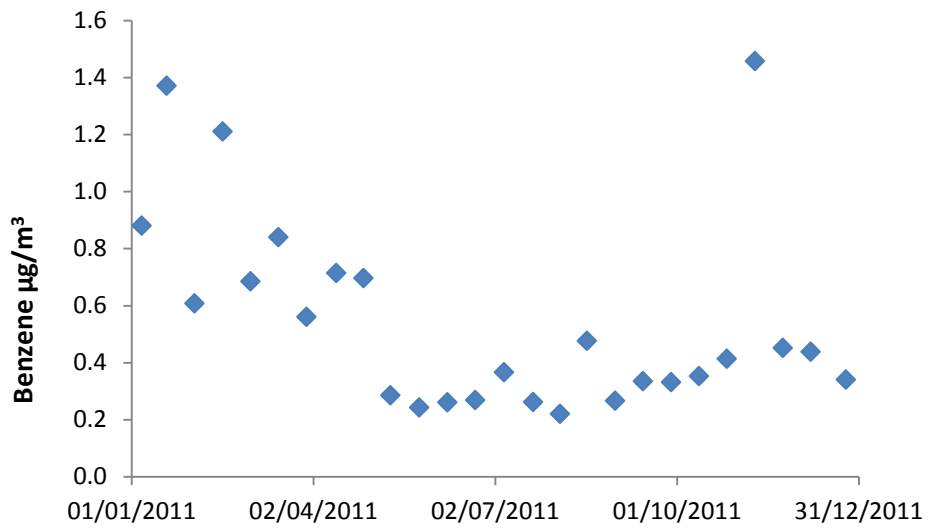


Figure 23 **Birmingham Acocks Green Non Automatic Benzene**

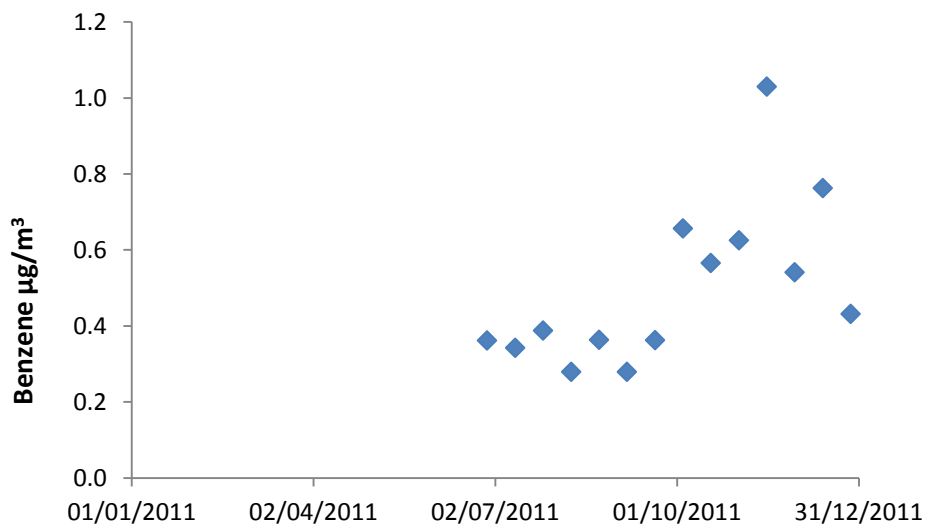


Figure 24 Birmingham Tyburn Non automatic Benzene

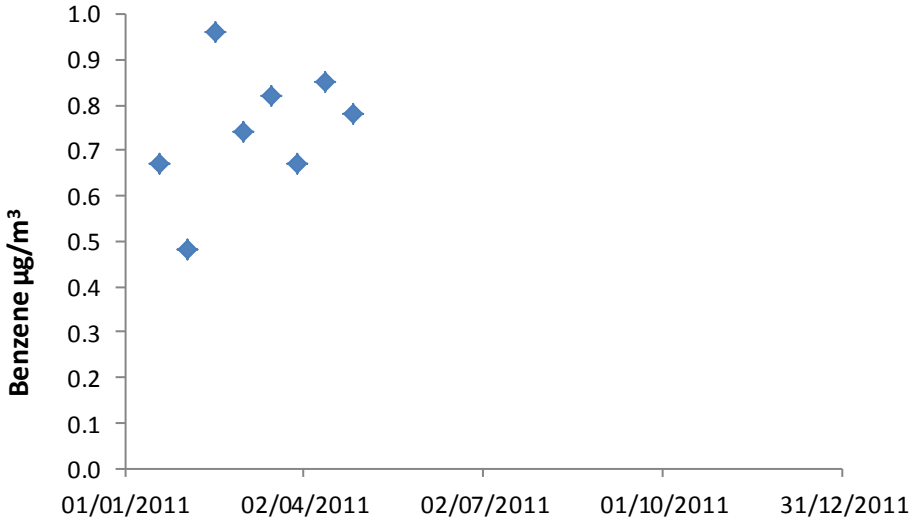


Figure 25 Birmingham Tyburn Roadside Non Automatic Benzene

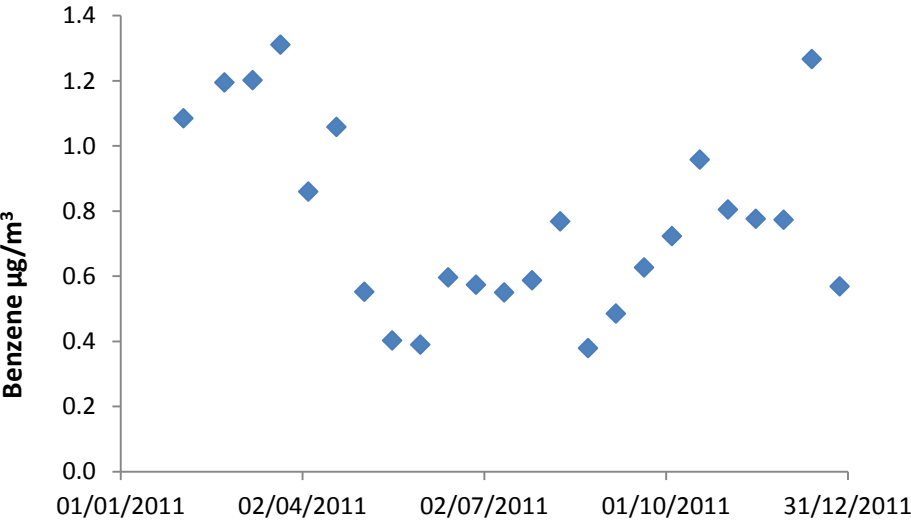


Figure 26 Bristol Old Market Non Automatic Benzene

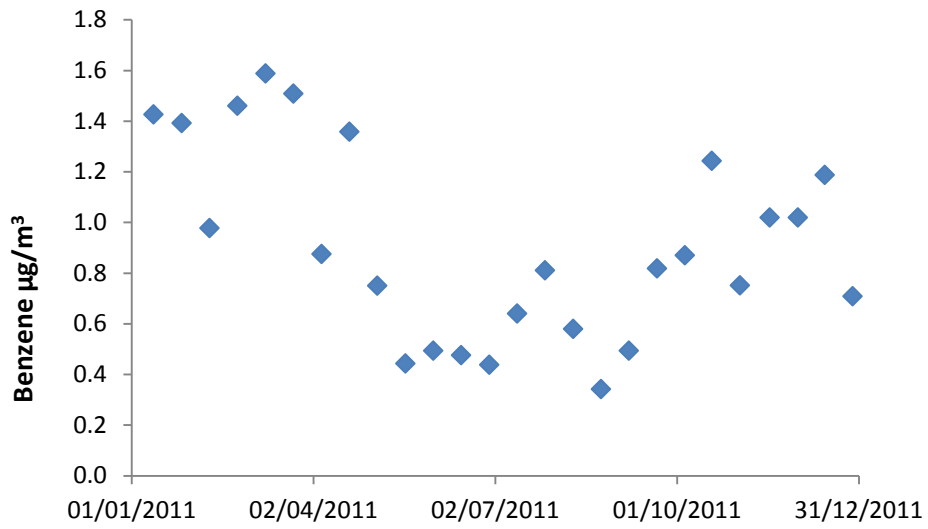


Figure 27 Bury Roadside Non Automatic Benzene

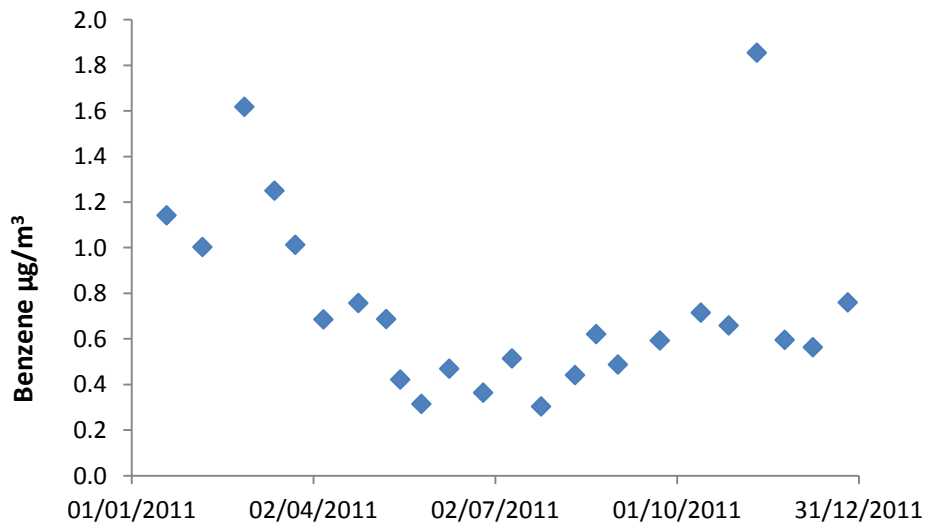


Figure 28 Cambridge Roadside Non Automatic Benzene

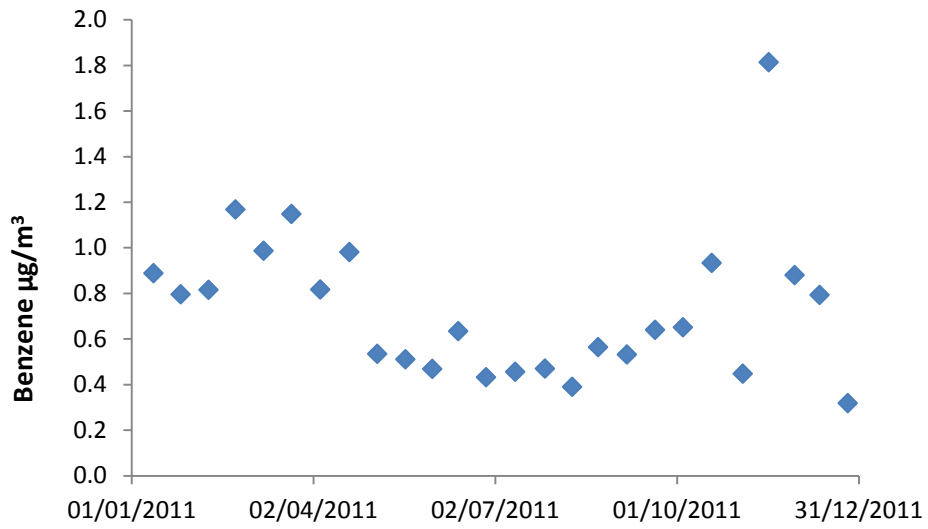


Figure 29 Camden Kerbside Non Automatic Benzene

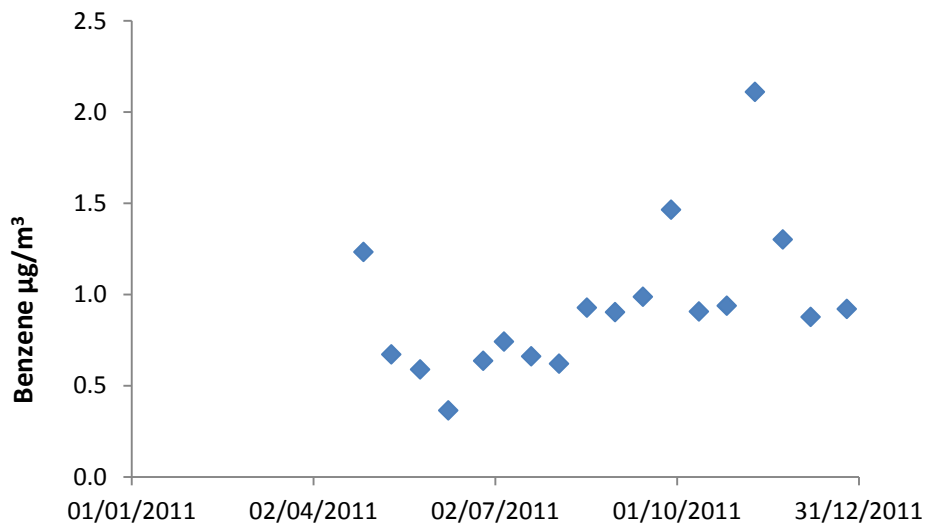


Figure 30 Carlisle Roadside Non Automatic Benzene

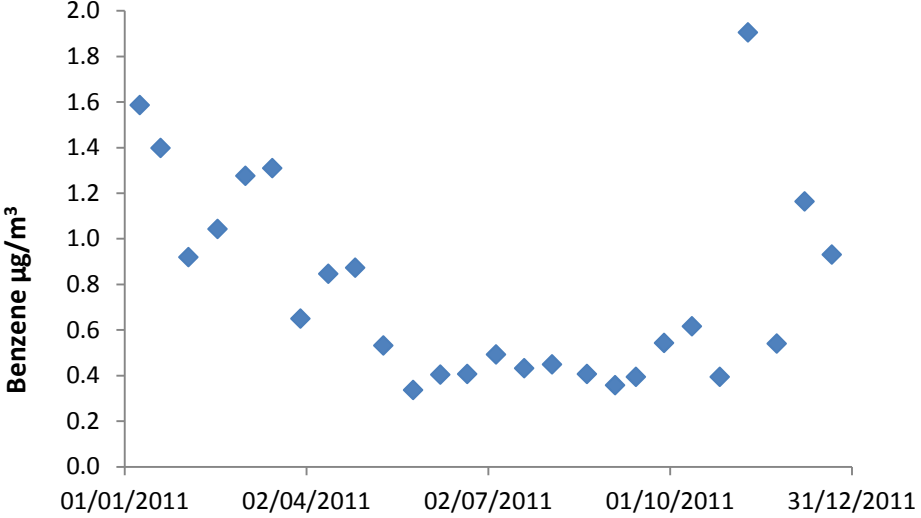


Figure 31 Chatham Roadside Non Automatic Benzene

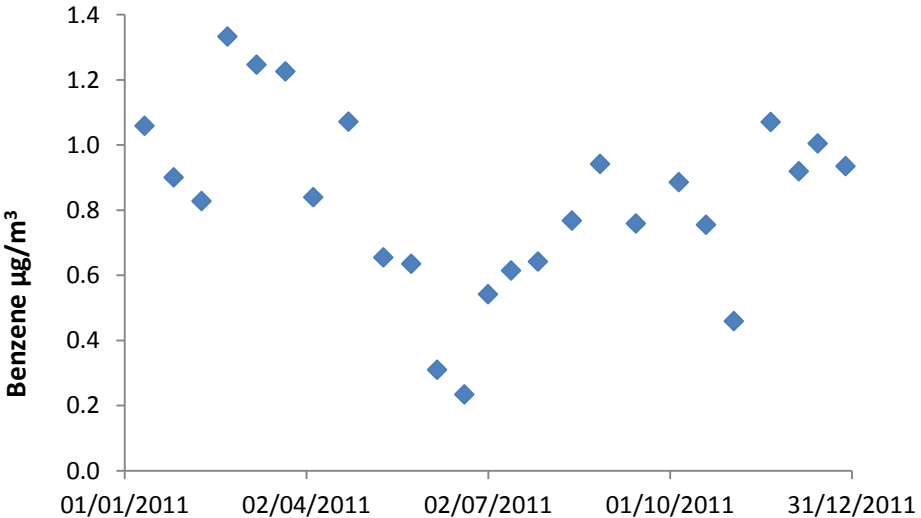


Figure 32 Chesterfield Roadside Non Automatic Benzene

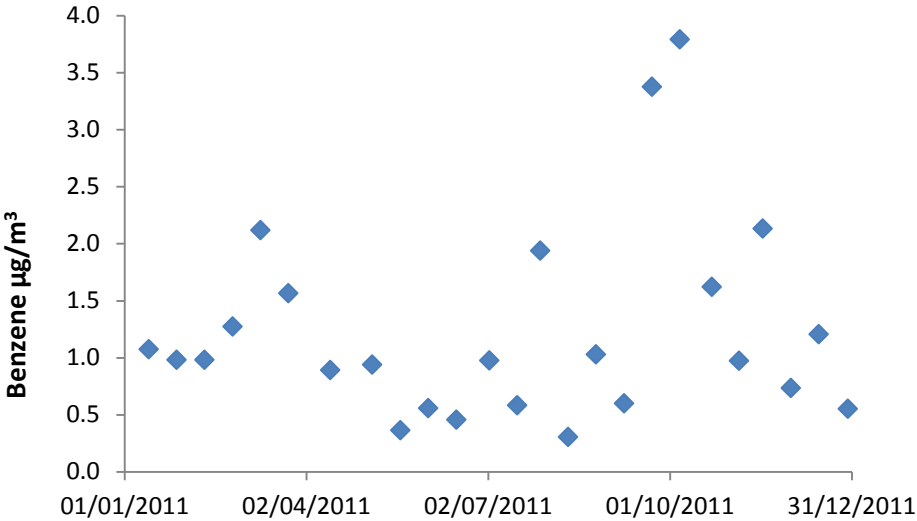


Figure 33 Coventry Memorial Park Non Automatic Benzene

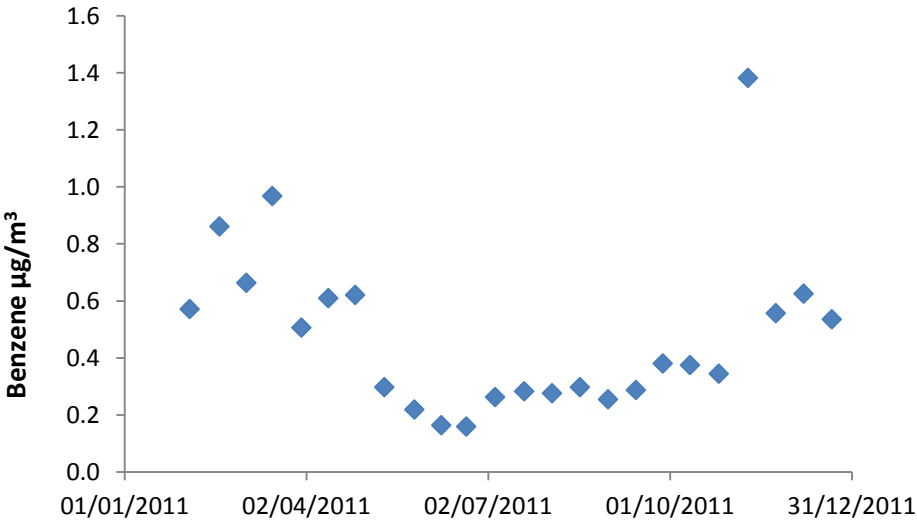


Figure 34 Glasgow Kerbside Non Automatic Benzene

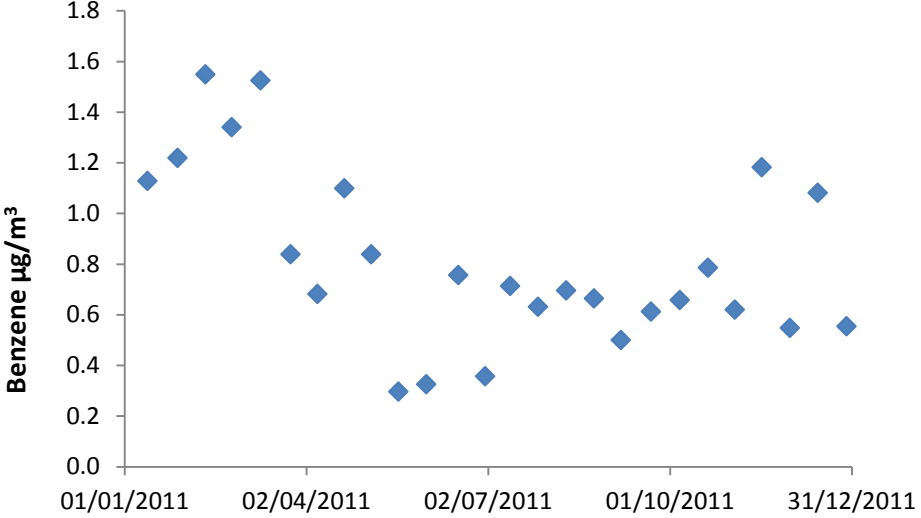


Figure 35 Grangemouth Non Automatic Benzene

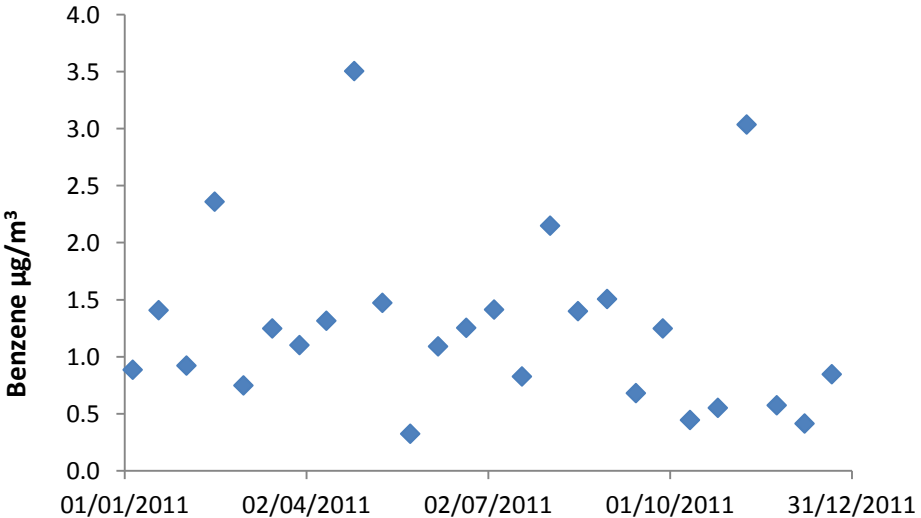


Figure 36 Haringey Roadside Non Automatic Benzene

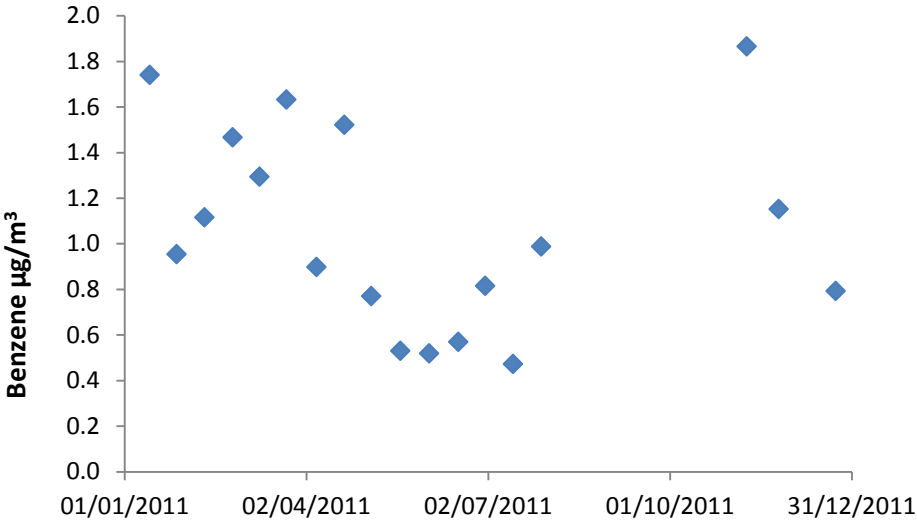


Figure 37 Leamington Spa Non Automatic Benzene

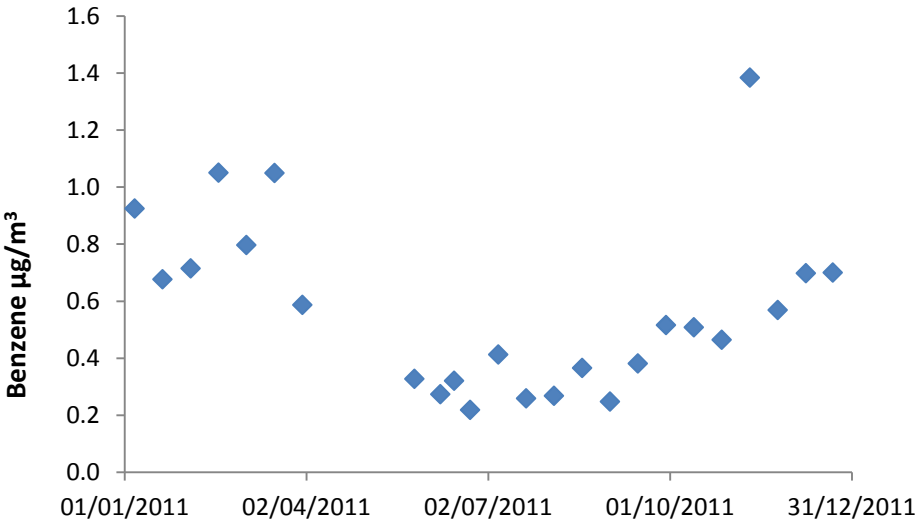


Figure 38 Leeds Centre Non Automatic Benzene

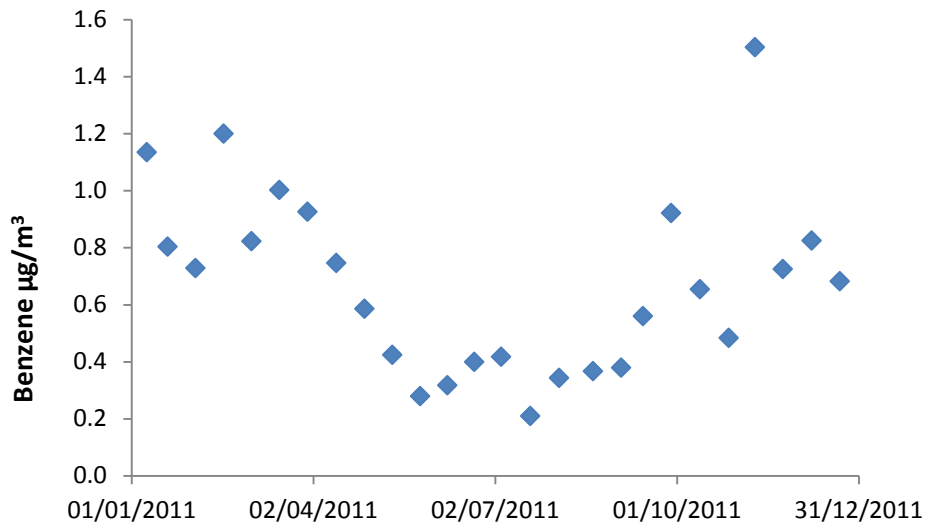


Figure 39 Leicester Centre Non Automatic Benzene

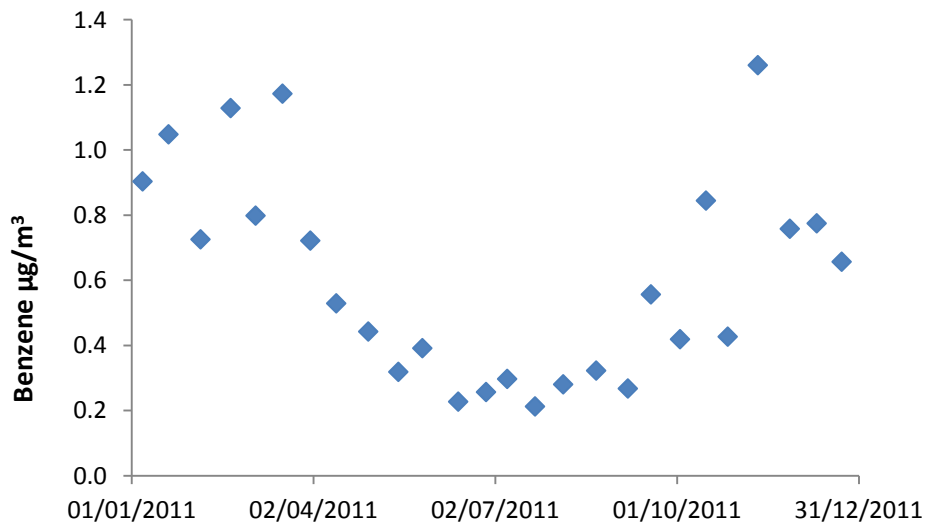


Figure 40 Liverpool Speke Non Automatic Benzene

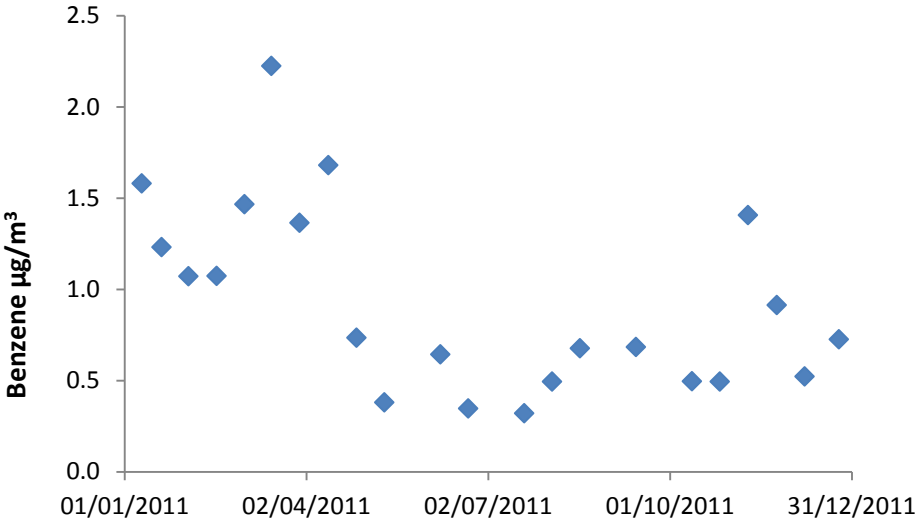


Figure 41 London Bloomsbury Non Automatic Benzene

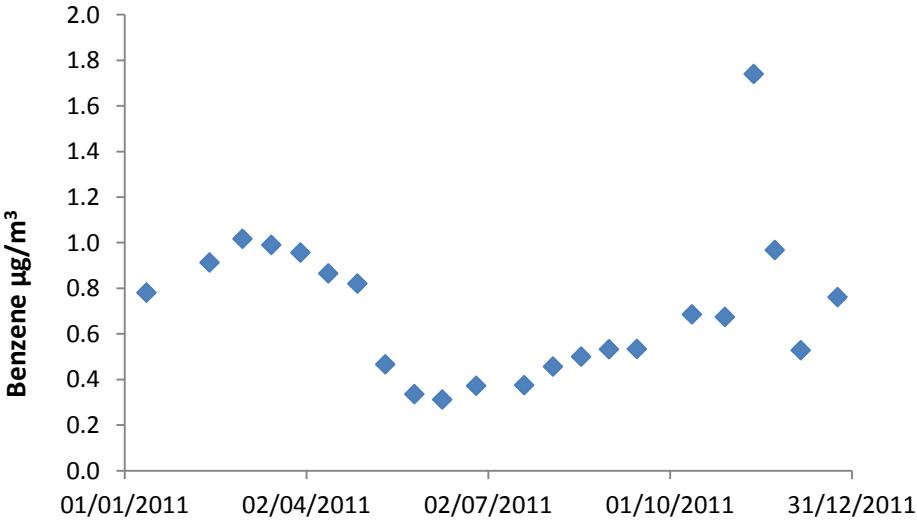


Figure 42 Manchester Piccadilly Non Automatic Benzene

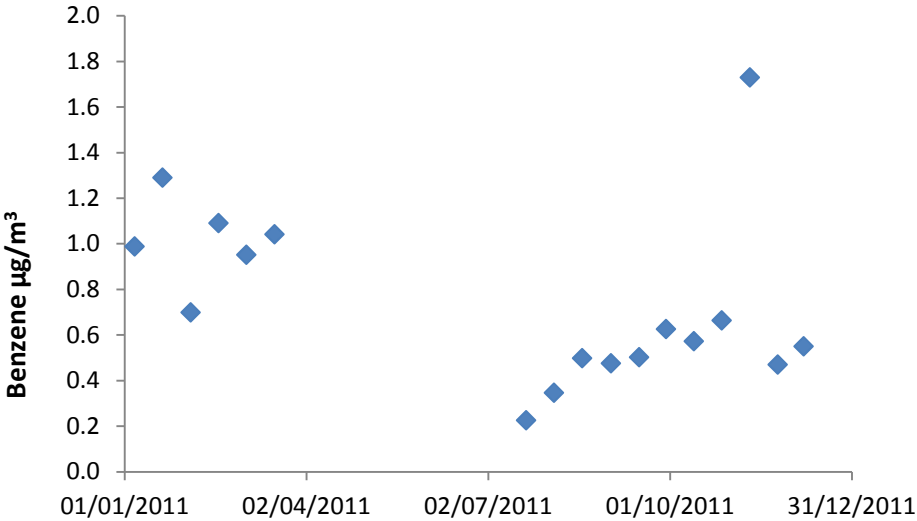


Figure 43 Middlesbrough Centre Non Automatic Benzene

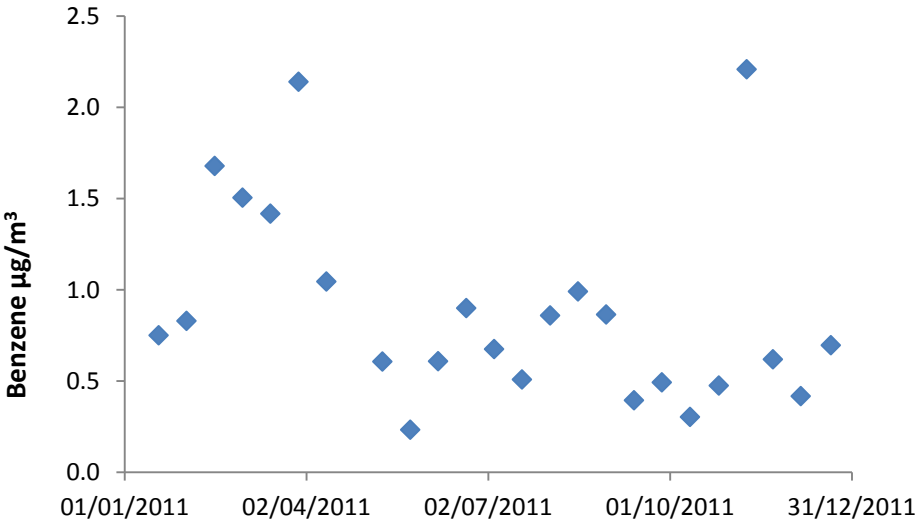


Figure 44 Newcastle Centre Non Automatic Benzene

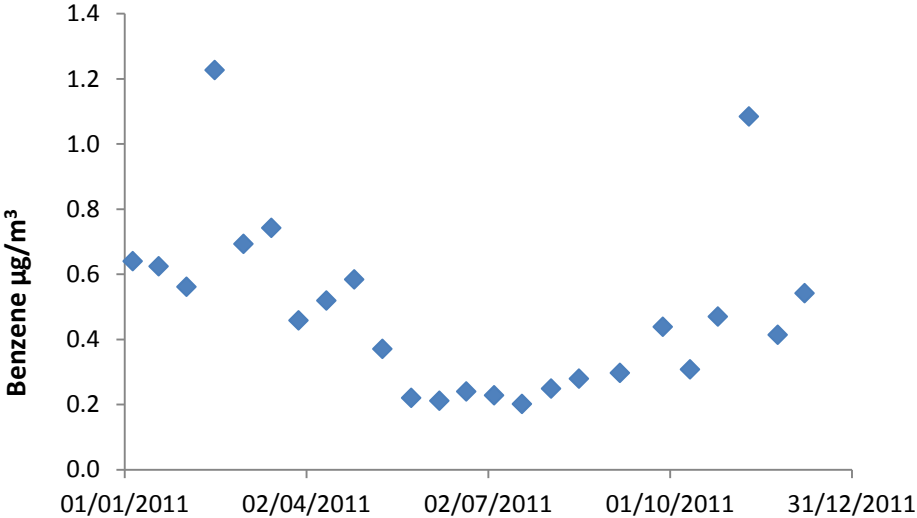


Figure 45 Northampton Non Automatic Benzene

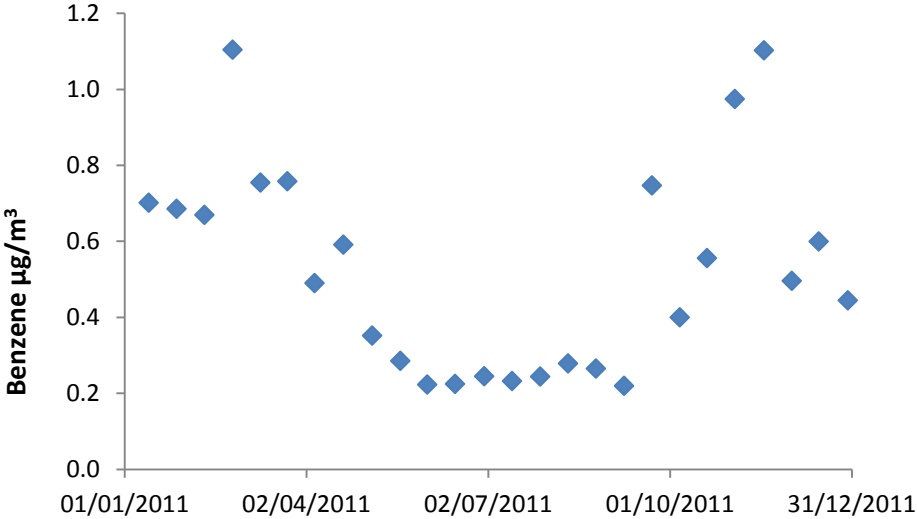


Figure 46 Norwich Lakenfields Non Automatic Benzene

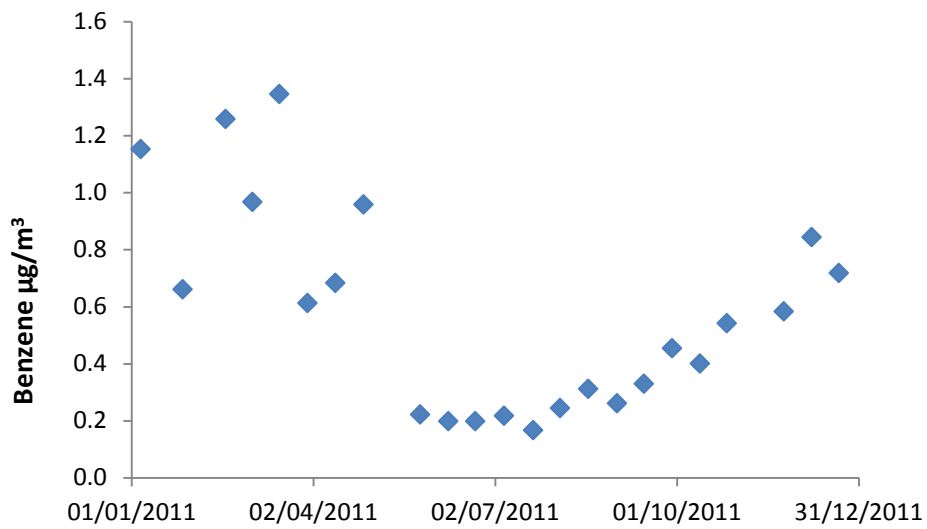


Figure 47 Nottingham Centre Non Automatic Benzene

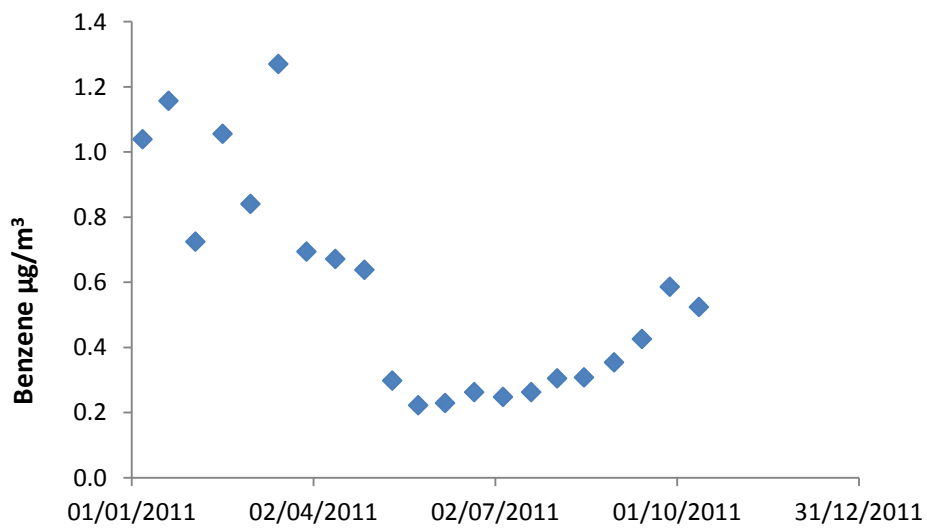


Figure 48 Oxford Centre Non Automatic Benzene

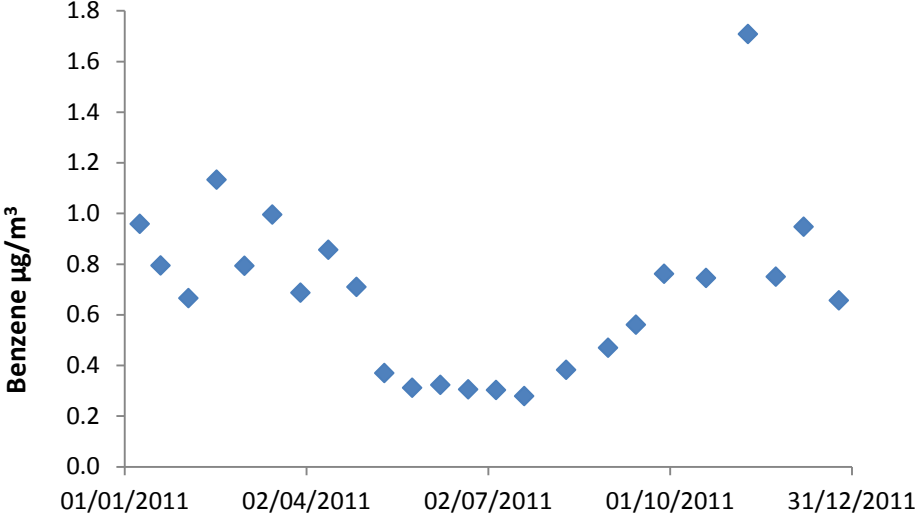


Figure 49 Oxford St Ebbes Non Automatic Benzene

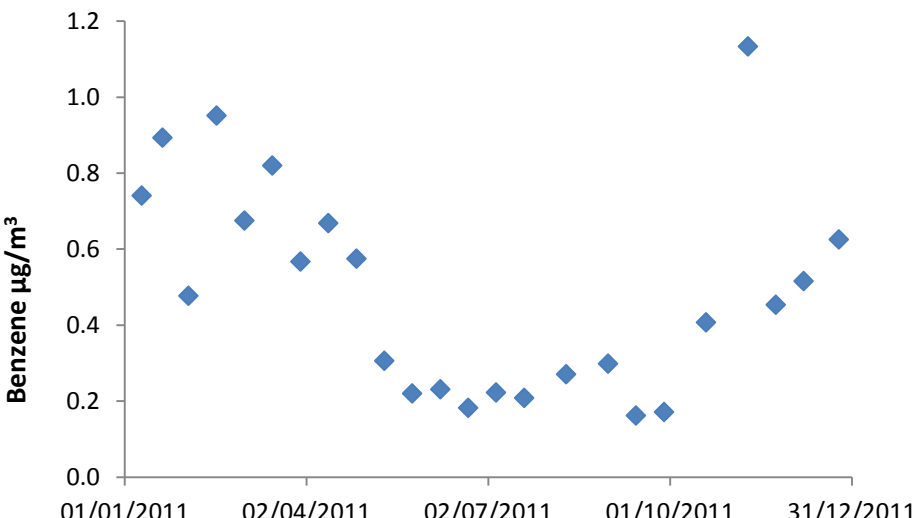


Figure 50 Plymouth Centre Non Automatic Benzene

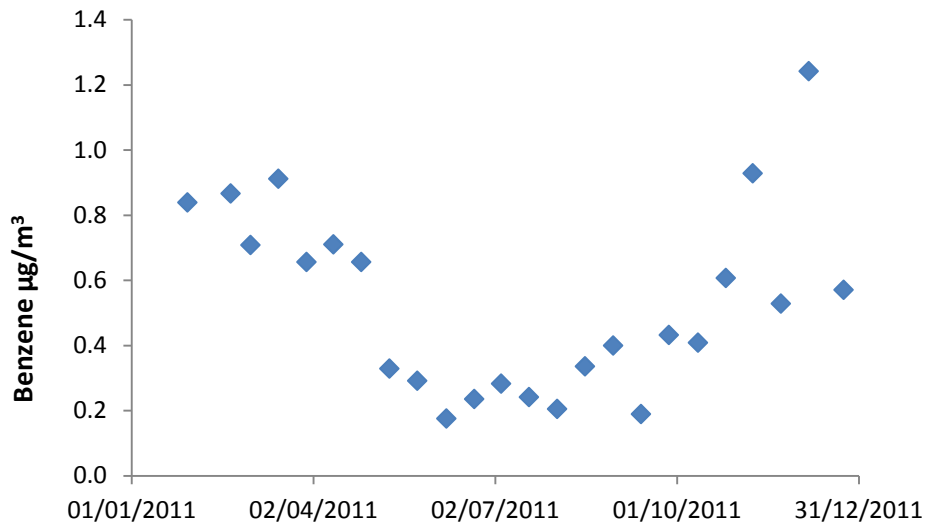


Figure 51 Sheffield Centre Non Automatic Benzene

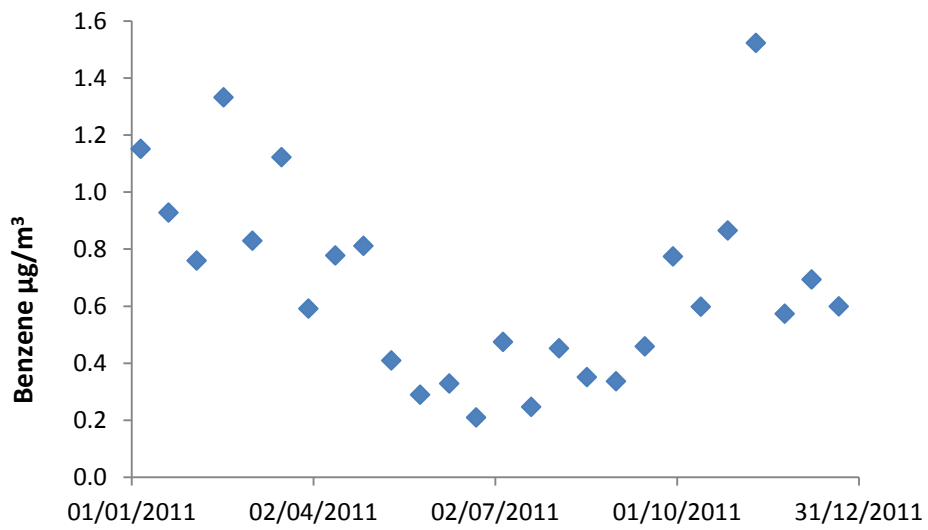


Figure 52 Southampton Centre Non Automatic Benzene

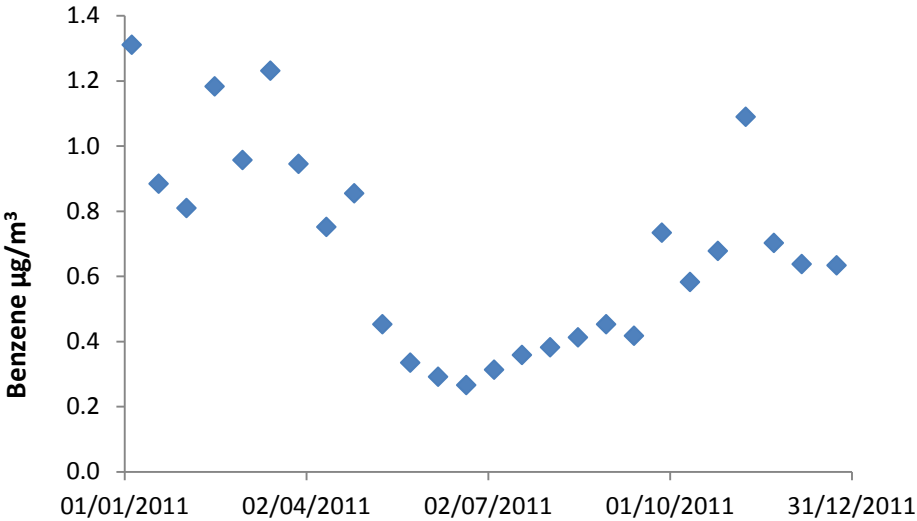


Figure 53 Stockton on Tees Eaglescliffe Non Automatic Benzene

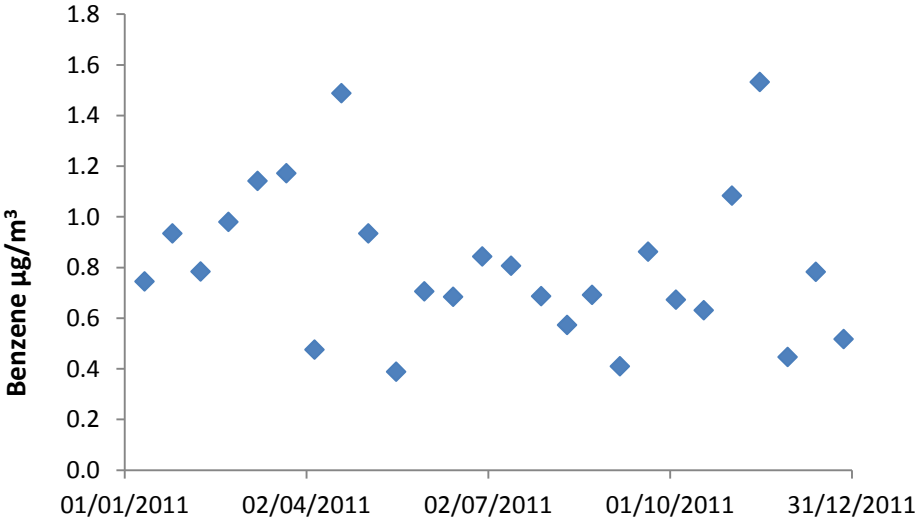


Figure 54 Stoke-on-Trent Centre Non Automatic Benzene

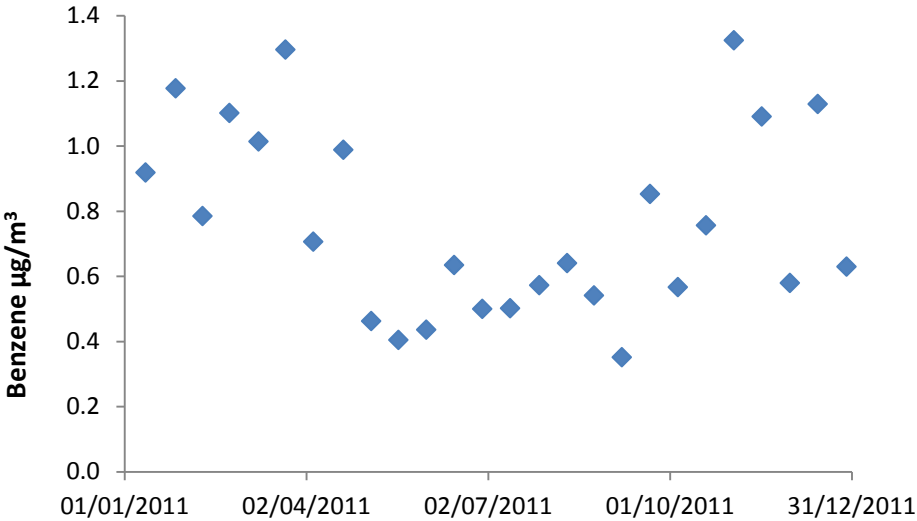


Figure 55 Wigan Centre Non Automatic Benzene

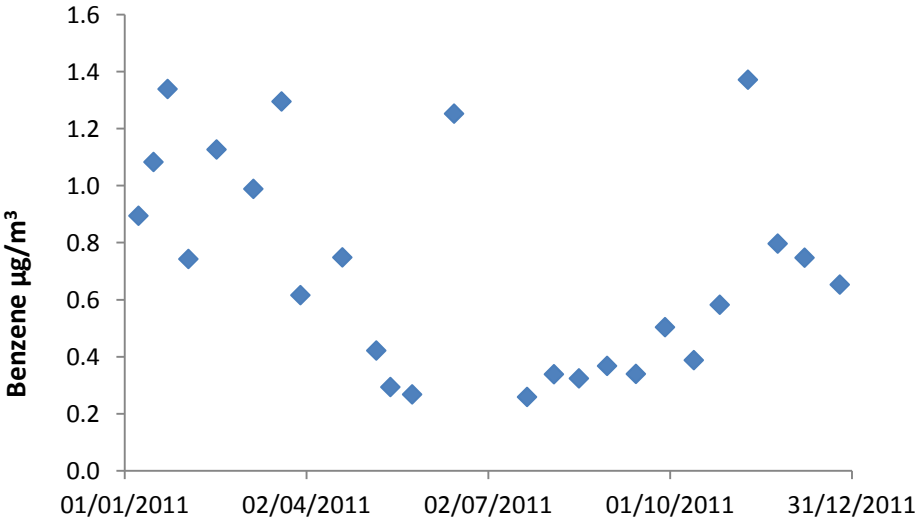
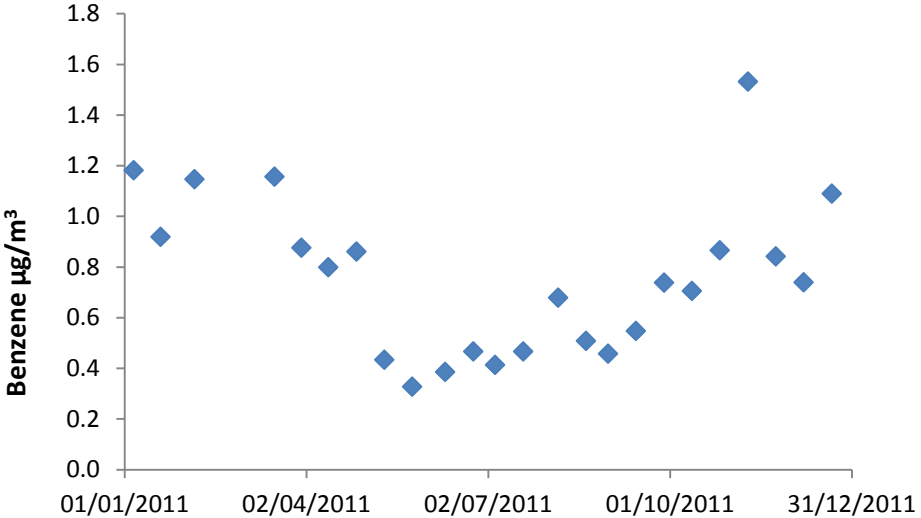


Figure 56 York Fishergate Non Automatic Benzene



AEA group
6 New Street Square
London
EC4A 3BF

Tel: 0870 190 3622

