UK Hydrocarbon Network

Annual Report for 2013

Report for Defra and the Devolved Administrations

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Executive summary

This network comprises automatic and non-automatic systems to measure benzene in compliance with the European Directive 2008/50/EC[1] (AQD) for which a limit value of 5µg.m^{-3} is required to be met as well as compliance with UK Objectives in the UK Air Quality Strategy[2].

The Directive also requires the measurement of ozone precursor volatile organic compounds (VOCs) and this network measures 29 of the 31 substances (including 1,3-butadiene) using automatic analysers

The Directive sets data capture requirements and the mean data capture for benzene measured at the non-automatic hydrocarbon sites in 2013 was 91.0%. The annual mean concentration across all non-automatic measurement sites in the UK was 0.95 µg.m^{-3}.

The mean data capture for benzene measured by the automatic hydrocarbon network in 2013 was 89.0%.The annual mean across all automatic measurement sites in the UK was 0.6 µg.m^{-3}.

In 2013 none of the automatic and non-automatic monitoring sites in the UK exceeded the 5µg m^{-3} annual mean Limit Value or the Upper Assessment Threshold of 3.5 µg.m^{-3} for benzene set out in the AQD. Scunthorpe Town was the only site to exceed the Lower Assessment Threshold of 2 µg.m^{-3}.

The results confirm no exceedances of EU or UK limit values and objectives at any of the Urban, Traffic and Background locations during 2013.

[1] http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2008:152:0001:0044:EN:PDF
[2] https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/69336/pb12654-air-quality-strategy-vol1-070712.pdf

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1 Introduction

This report provides a summary of the site management and data produced in 2013 by the UK Hydrocarbon monitoring network.

This network comprises automatic and non-automatic systems to measure benzene in compliance with the Air Quality Directive 2008/50/EC. The UK's interpretation of the directive is that benzene must be measured at 34 sites and a suggested suite of ozone precursors, should be measured at at least one suburban site in the UK. Up to 29 ozone precursor substances (including 1,3-butadiene) are measured using the automatic system, whereas a more cost effective non-automatic sampling system is used for more widespread benzene measurements.

All hydrocarbon network instruments are co-located at AURN (Automatic Urban and Rural Network) sites with the exception of Bury Roadside. This site was de-affiliated from the AURN on 6th September 2012, the non-automatic sampler remained until 2nd September 2013 and is currently due to be relocated during 2014.

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. A monitoring regime assessment of the number and location of monitoring sites in each Member State is required to be undertaken every 5 years to ensure the network changes in line with the changing UK pollution climate such that it's fit for purpose. The UK carried out this reassessment for the hydrocarbons network and this was published in 2013 [3].

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 correct the data. Latest data can always be accessed at http://uk-air.defra.gov.uk/.

Since August 2012, formaldehyde and acetaldehyde have been measured at five sites as part of a two year pilot study. These five sites have since been moved to new locations following a review of the site selection criteria and assessment of the initial results

1.1 Pollutant Sources and Impacts

Benzene has a variety of sources[4], 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.

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[3] http://uk-air.defra.gov.uk/assets/documents/reports/cat09/1312171445_UK_Air_Quality_Assessment_Regime_Review_for_AQD.pdf

[4] 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

1.2 Regulatory background

1.2.1 UK Air Quality Objectives

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

Table 1 UK Air Quality Objectives.

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

1.2.2 European Limit Value

Hydrocarbons are also governed by Directive 2008/50/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 Member States as well as lower and upper assessment thresholds

Table 2 European Limit Value and Assessment Thresholds

Threshold	Concentration	Measured as
Limit Value	5 µg.m^{-3}	Annual mean
Upper assessment threshold	3.5 µg.m^{-3}	Annual mean
Lower assessment threshold	2 µg.m^{-3}	Annual mean

The limit value for the protection of human health for benzene is 5 µg.m^{-3} as a calendar year mean, to be achieved by 1st January 2010. The upper and lower assessment thresholds, 3.5 µg.m^{3} (70% of limit value) and 2 µg.m^{-3} (40% of limit value), are used to determine how many fixed sampling points are required. The UK uses a combination of monitoring and modelling to assess air quality and report for compliance. Levels relative to the assessment thresholds dictate requirements for fixed monitoring. Where levels are assessed to be below the lower assessment threshold then modelling, objective estimation and indicative measurements are suitable for assessment and fixed monitoring is not required. Therefore, monitoring in the UK is primarily at locations where levels of benzene are modelled or measured to be above the LAT such as for assessment of emissions from industrial sources or from road transport.

The Data Quality Objective for the measurement uncertainty is ±25% with a minimum data capture of 90%, although up to 5% planned equipment maintenance and calibration time may be deducted from the data capture objective for automatic measurements during the ratification process. For the Hydrocarbon network it is estimated that this is <1% based on a typical calibration regime. There is no planned downtime for the non-automatic measurements. 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 instruments and are listed in Table 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%.

1.3 Network background and methods

The UK Hydrocarbon Network is one of several air quality monitoring networks operated by Defra to fulfil statutory reporting requirements and policy needs. These include the Automatic Urban and Rural Network, which measures particulate matter, NO_2, CO, SO_2 and O_3, Heavy Metals Network and Polycyclic Aromatic Hydrocarbon Network, which meet the requirements of the AQD and Fourth Daughter Directive[5]. Other monitoring programmes including the Particles Concentrations and Numbers Network, Black Carbon Network and UK Eutrophying and Acidifying Pollutants Network exist to meet other requirements including those set out in the Air Quality Strategy.

1.3.1 Non-Automatic Monitoring Methodology

The Non-Automatic Hydrocarbon network started operation in 2001, measuring benzene and 1,3-butadiene. Benzene measurements are made using a dual sample tube controlled flow pump unit described in EN 14662-1:2005, 'Ambient air quality – Standard method for measurement of benzene concentrations' by Martin et al , and validated by Quincey et al. In addition, passive diffusion tubes had been used to measure 1,3-butadiene. It currently produces measurements as nominal fortnightly averages at 33 sites (When a replacement for the former Bury Roadside site is installed this number will increase to 34).

The benzene monitoring method involves drawing ambient air at a controlled rate (nominally 10 ml/min) alternately through two tubes (A and B) containing a carbon-based sorbent (Carbopack X). Each tube samples alternately at 10 ml/min for 8 minute periods for a nominal two week period. A designated local site operator manually changes the tubes and returns these to Ricardo-AEA, on completion of the sampling period. The tubes are then sent to the laboratory for subsequent analysis for benzene by gas chromatography-mass spectrometry. The sampling period and sample flow rate are 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

Until 2007, 1,3-butadiene was also monitored in order to assess compliance with the UK Air Quality Strategy Objective (2.25 µgm-3 expressed as a running annual mean). However, the network was reviewed in 2007, and in view of the fact that:

1. 1,3-butadiene levels at all the sites were well below the Objective and
2. levels at half of the sites were at or below the detection limit for the method used

Defra took the decision to discontinue monitoring 1,3-butadiene.

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1.3.2 Automatic Hydrocarbon Monitoring Methodology

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

[5] http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32004L0107&from=EN

number of sites was reduced. In 2013 there were four sites, measuring the following 29 species by automatic gas chromatographs:

There is no standard reference method for measuring ozone precursor substances in ambient air.

Automated thermal desorption with in situ gas chromatography and flame ionisation detection (FID) is used to measure hourly hydrocarbon concentrations. There is no reference method for ozone precursor measurements, however benzene measurements by automated pumped sampling with in situ gas chromatography is covered by BS EN 14662-3:2005. During 2013, hydrocarbons at all sites were measured using automatic Perkin Elmer Ozone Precursor Analysers. A known volume of air is dried and drawn through a cold trap, which contains adsorbent material. The cold trap is held at about -30ºC 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 and subsequently detected by a flame ionising detector. The analyser is calibrated using an on-site multi-component gas mixture.

Table 3 Species measured by the Automatic chromatographs

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

1.3.3 Two-Year Aldehyde Pilot Study

In order to reduce the burden on fossil fuels and to help mitigate climate change, the European Union introduced the Renewable Energy Directive (FQD, 98/70/EC)[6]. Obligations under articles 7a to 7e require Member States to implement a strategy to increase renewable fuel use for transport. In response to this the UK introduced the Renewables Transport Fuel Obligation (RTFO)[7] identifying Bioethanol as a renewable fuel that can be added to conventional petrol for use in modern conventional engines.

In 2011, the UK Air Quality Expert Group (AQEG) provided advice to Defra and the Devolved Administrations suggesting the potential for increases in aldehyde emissions following the introduction of bioethanol to conventional petroleum used in road transport[8]. The advice suggests that low blends ≤5% could significantly increase emission of acetaldehyde from

[6] EC(1998). Directive 1998/70/EC Of The European Parliament and of the Council of 13 October 1998 relating to the quality of petrol and diesel fuels and amending Council Directive 93/12/EEC
[7] Renewable Transport Fuels Obligations Order 2007, SI 2007 No.3072
[8] AQEG, 2011. Road Transport Biofuels: Impact on UK Air Quality. Advice note prepared for Department for Environment, Food and Rural Affairs; Scottish Government; Welsh Assembly Government; and Department of the Environment in Northern Ireland

motor vehicle exhaust. For higher strength blends >5%, an increase of formaldehyde may also be seen.

In response to this advice, Defra requested a two year pilot study to monitor ambient aldehyde concentrations to assess levels at representative roadside and urban background locations in the UK. This study would enable assessment of whether a roadside increment could be evaluated as well as providing a comparative baseline for future assessment.

1.3.4 Aldehyde methodology

An aldehyde monitoring method was developed under guidance from EMEP[9] that involves drawing ambient air through a packed bed silica tube containing dinitriphenylhydrazine (DNPH).

DNPH Tubes are known as an indicative means to quantify airborne concentrations. In order to validate the method, Ricardo-AEA used flow rates (700ml/min), sample time (24 hours for ideal sample volume) as recommended by the sorbent tube manufacturer, Waters Inc[10]. Further testing was then carried out to ensure:

1. The measurements are within the upper and lower limit of detection
2. No sample breakthrough is possible
3. Analysis precision is acceptable

Ricardo-AEA performed five tests using all the samplers with two inline DNPH tubes; no sample breakthrough to the second tube was found for any of the measurements. All five samplers were used at the same time to check precision. An additional 10 tubes were spiked with a known amount of aldehydes, 5 of which were analysed immediately, another 5 were analysed after 14 days at ambient temperature, to gauge potential losses in transit. On average there was a 9% loss of formaldehyde and a 2% increase in acetaldehyde found.

Sampling is for a 24 hour period, twice a week on Tuesdays and Thursdays (midnight to midnight). Local site operators were contracted to change the samples during the day on Mondays and Wednesdays, removing the Thursday tube again on a Friday. The samples were run on a timer.

The exposed tubes are sent to the laboratory for acetaldehyde and formaldehyde analysis by high performance liquid chromatography (HPLC). The exposure period and flow rate are selected to optimise capture onto the sorbent and minimise breakthrough. As there is not yet a reference method for measuring aldehydes, the bespoke samplers have been built by Ricardo-AEA specifically for the commercially available DNPH tubes.

[9] Nilu, 2001. EMEP Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe EMEP manual for sampling and chemical analysis
[10] http://www.waters.com/webassets/cms/support/docs/wat047204.pdf

2 Site Management

2.1 Network sites during 2013

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 2013

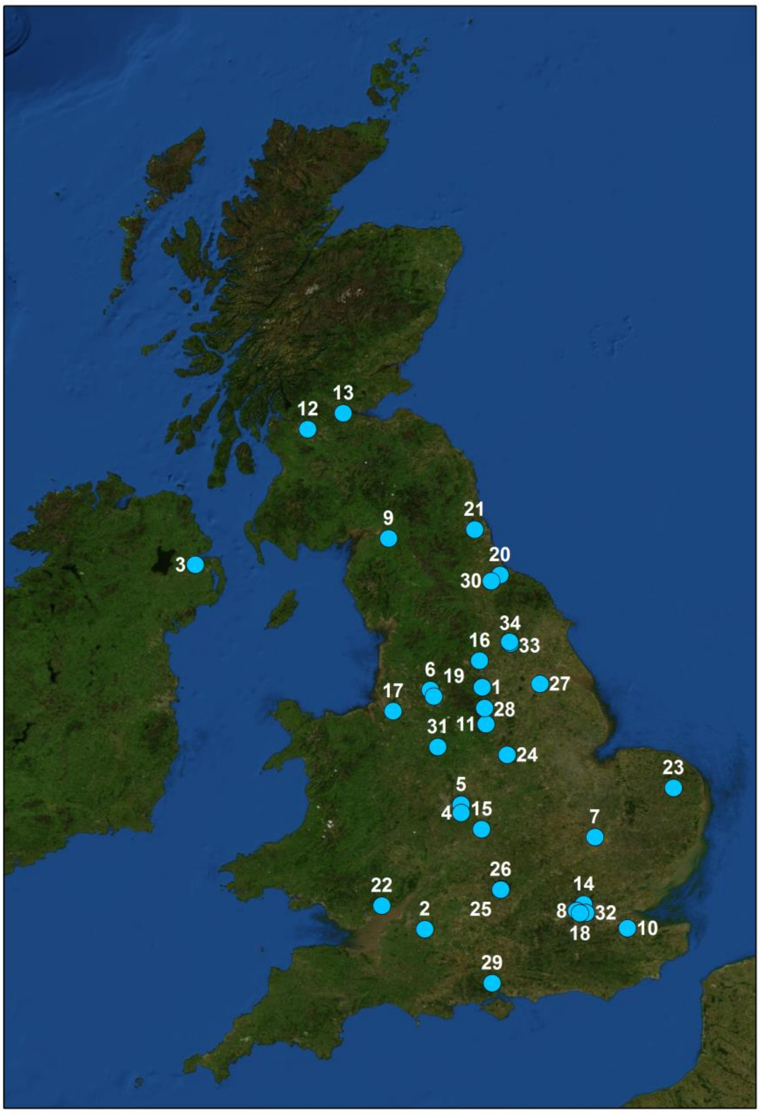


Table 4 Non-Automatic Hydrocarbon Network sites in 2013.

	Site	Classification	Zone	Grid Ref Easting / Northing	Local Site Operator
1	Barnsley Gawber	Urban Background	Yorkshire & Humberside	432529, 407472	Barnsley Council
2	Bath Roadside	Urban Traffic	South West	375882, 166096	Bath & North Somerset Council
3	Belfast Centre	Urban Background	Belfast Urban Area	333900, 374400	Belfast City Council
4	Birmingham Acocks Green	Urban Background	West Midlands Urban Area	411654, 282146	AECOM
5	Birmingham Tyburn Roadside	Urban Traffic	West Midlands Urban Area	411556, 290456	AECOM
6	Bury Roadside	Urban Traffic	Greater Manchester Urban Area	380922, 404772	Bury Metropolitan Council
7	Cambridge Roadside	Urban Traffic	Eastern	545248, 258155	Cambridge Council
8	Camden Kerbside	Urban Traffic	Greater London Urban Area	526640, 184433	Ricardo-AEA
9	Carlisle Roadside	Urban Traffic	North West & Merseyside	339442, 555956	Carlisle Council
10	Chatham Roadside	Urban Traffic	South East	577435, 166993	Medway Council
11	Chesterfield Roadside	Urban Background	East Midlands	436351, 370682	Chesterfield Council
12	Glasgow Kerbside	Urban Traffic	Glasgow Urban Area	258708, 665200	Ricardo-AEA
13	Grangemouth	Urban Industrial	Central Scotland	293837, 681035	Falkirk Council
14	Haringey Roadside	Urban Traffic	Greater London Urban Area	533885, 190669	Ricardo-AEA
15	Leamington Spa	Urban Background	West Midlands	431932, 265743	Warwick District Council
16	Leeds Centre	Urban Background	West Yorkshire Urban Area	429976, 434268	Leeds City Council
17	Liverpool Speke	Urban Background	Liverpool Urban Area	343860, 383598	Fabermaunsell/AECOM
18	London Bloomsbury	Urban Background	Greater London Urban Area	530107, 182041	Bureau Veritas
19	Manchester Piccadilly	Urban Background	Greater Manchester Urban Area	384310, 398325	Manchester City Council
20	Middlesbrough	Urban Background	Teesside Urban Area	450480, 519632	Middlesbrough BC
21	Newcastle Centre	Urban Background	Tyneside	425016, 564940	Newcastle City Council
22	Newport	Urban Background	South Wales	33410, 189604	Newport City Council
23	Norwich Lakenfields	Urban Background	Eastern	623637, 306940	Mark Leach
24	Nottingham Centre	Urban Background	Nottingham Urban Area	457420, 340050	Nottingham City Council
25	Oxford Centre Roadside	Urban Traffic	South East	451366, 206152	Oxford City Council
26	Oxford St Ebbes	Urban Background	South East	451225, 206009	Oxford City Council
27	Scunthorpe Town	Urban Industrial	Yorkshire & Humberside	490338, 410836	North Lincs CBC

	Site	Classification	Zone	Grid Ref Easting / Northing	Local Site Operator
28	Sheffield Centre	Urban Background	Sheffield Urban Area	435134, 386885	Sheffield City Council
29	Southampton Centre	Urban Background	Southampton Urban Area	442565, 112255	Southampton City Council
30	Stockton-on-Tees - Eaglescliffe	Urban Traffic	North East	441620, 513673	Stockton on Tees BC
31	Stoke-on-Trent Centre	Urban Background	The Potteries	388348, 347894	City of Stoke on Trent Council
32	Tower Hamlets Roadside	Urban Traffic	Greater London	535927, 182218	Kings College, London
33	York Bootham	Urban Backgorund	Yorkshire & Humberside	460024, 452768	City of York Council
34	York Fishergate	Urban Traffic	Yorkshire & Humberside	460744, 451033	City of York Council

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/

2.1.1 Automatic Hydrocarbon Network

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

Figure 2 Map of Automatic Network sites in 2013

Table 5 Automatic Hydrocarbon Network sites in 2013.

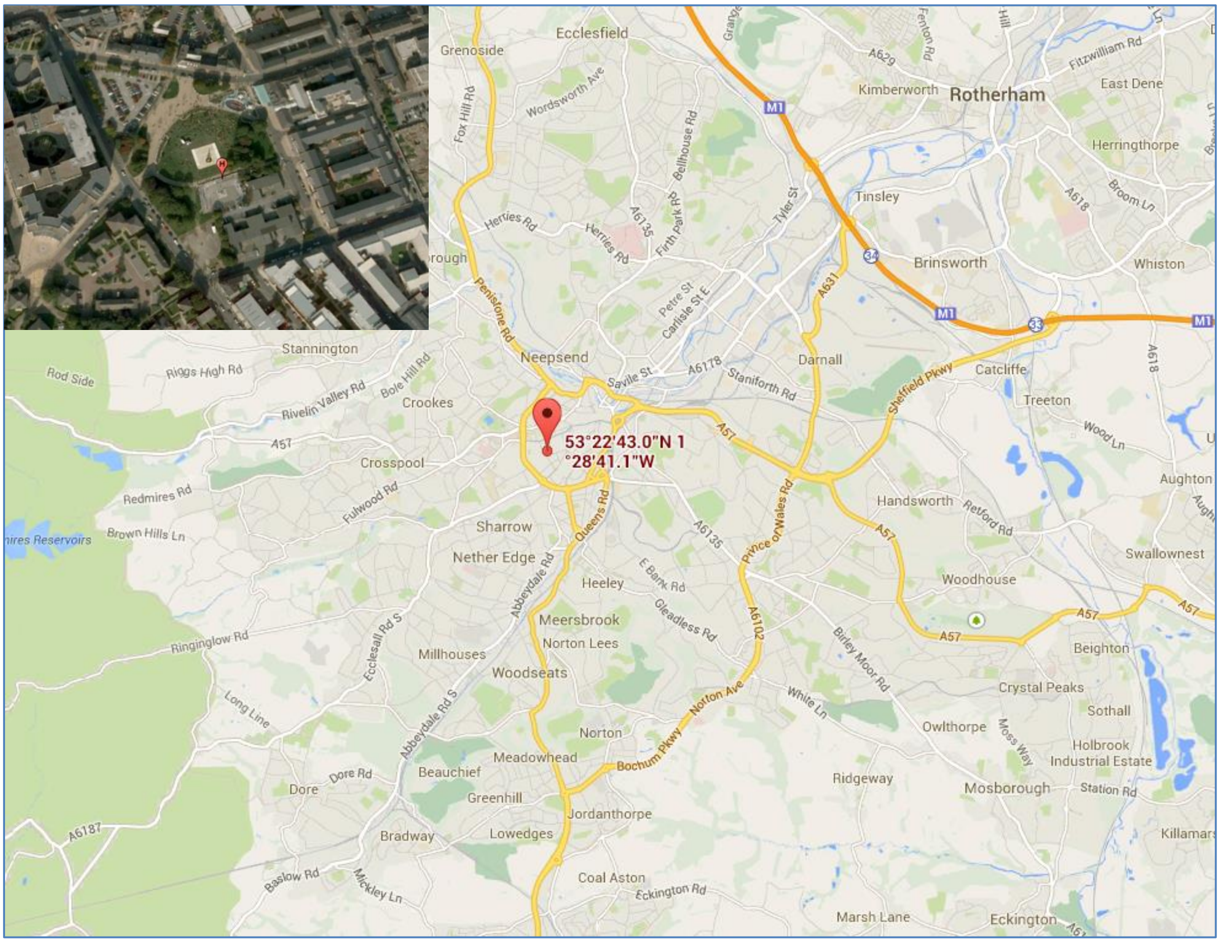
	Site	Classification	Zone	Grid Ref Easting / Northing	Local Site Operator
1	Harwell	Rural Background	South West	446772, 186020	Ricardo-AEA
2	Marylebone Road	Urban Traffic	Greater London Urban Area	528120, 182000	KCL
3	Auchencorth Moss	Rural Background	Scotland	322050, 656250	CEH
4	London Eltham	Suburban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

2.2 Additional Sites in 2013

2.2.1 Sheffield Devonshire Green

Following the monitoring regime assessment, the Sheffield Centre AURN site was deemed non-compliant with the AQD (covering all pollutants). An alternative site was designated at Sheffield Devonshire Green. The final benzene sample at the Sheffield Centre site finished on 29th August 2013 when the enclosure was removed. A replacement site was commissioned at Sheffield Devonshire Green (Figure 3 Location of the Sheffield Devonshire Green Site), the first benzene sample started on 7th November 2013 when the enclosure had been re-commissioned.

Figure 3 Location of the Sheffield Devonshire Green Site



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 measurement and 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 sample 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 October 2012, April 2013, October 2013 and April 2014. All of these measurements have been used to calculate sample volumes for the 2013 data set by means of interpolation. 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 3.

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

- Annual preventative maintenance visits
- Change automatic GC cold trap and clean the gas generators and detectors
- Carry out a reference gas calibration

Data validity from automatic systems such as these can be affected for a period of time following ad-hoc repairs are required or power cuts occur, the stability of the chromatography can be affected for a period. This means that an analyser that was only off for an hour might produce poor chromatography for a few days that isn't representative of the monitoring location, the ratification team will remove the erroneous data until the instrument stabilises.

Ancillary equipment failure is the cause of most prolonged downtime. A spare hydrogen generator, TOC zero air generator and air compressor is kept by the ESU such that equipment can be swapped quickly if necessary.

3 Data and Data capture for 2013

3.1 Comparison with Limit Values and Objectives

The annual mean concentration of benzene and 1,3 butadiene over the calendar year 2013 are provided in Table 6 and Table 8, alongside the data capture statistics. Table 7 details reasons behind data loss or data removal. Data capture for sites where measurements started or finished during the year are calculated for the period that the equipment was operational.

Annual time weighted average concentrations at all sites were below the Limit Value of 5 µg.m^{-3} for benzene set by the European Ambient Air Quality Directive as well as the UK Air Quality Objectives as defined in the Air Quality Strategy 2007.

3.1.1 Non-Automatic Hydrocarbon Network Statistics

Table 6 Non-Automatic Benzene statistics 2013

Site	Annual Mean Benzene (µg.m^{-3})	Maximum Fortnightly Mean Benzene (µg.m^{-3})	Data capture
Barnsley Gawber	0.68	1.3	96.1%*
Bath Roadside	1.70	3.9	96.1%*
Belfast Centre	0.61	1.3	88.7%†
Birmingham Acocks Green	0.65	1.3	92.3%†
Birmingham Tyburn Roadside	0.95	2.0	92.3%†
Bury Roadside	0.84	1.5	63.4%†
Cambridge Roadside	0.85	1.5	97.7%†
Camden Kerbside	1.20	2.2	100%
Carlisle Roadside	0.88	1.8	96.1%*
Chatham Roadside	1.00	2.1	80.0%†
Chesterfield Roadside	1.40	5.8	91.6%†
Glasgow Kerbside	0.89	1.8	81.4%†
Grangemouth	1.10	2.0	100%
Haringey Roadside	1.20	2.1	65.4%†
Leamington Spa	0.69	1.6	100%
Leeds Centre	0.65	1.5	100%
Liverpool Speke	0.95	1.8	92.4%*
London Bloomsbury	0.85	1.6	82.2%†
Manchester Piccadilly	0.85	1.8	100%
Middlesbrough	1.50	4.5	100%
Newcastle Centre	0.65	1.6	100%
Newport	0.77	1.4	92.5%*
Norwich Lakenfields	0.66	1.4	100%
Nottingham Centre	0.85	1.5	96.1%*

Site	Annual Mean Benzene (µg.m^{-3})	Maximum Fortnightly Mean Benzene (µg.m^{-3})	Data capture
Oxford Centre	0.78	1.5	95.6%*
Oxford st Ebbes	0.68	1.5	91.9%†
Scunthorpe Town	2.20	5.4	65.8%†
Sheffield Centre	0.76	1.8	65.3%
Sheffield Devonshire Green	0.76	1.5	15.0%
Southampton Centre	0.88	1.7	92.2%†
Stockton-on-Tees Eaglescliffe	0.86	1.5	96.1%*
Stoke-on-Trent Centre	0.91	1.4	95.9%*
Tower Hamlets Roadside	1.40	2.2	81.0%
York Bootham	0.64	1.2	81.1%
York Fishergate	0.84	1.7	100%

*Loss in data capture as a result of analytical failure
†Partial loss in data capture as a result of analytical failure, additional losses as described in Table 7

Table 7 Non-Automatic Sampler Faults and failures in 2013

Site	Start	End	Days lost in 2013	Comment
Belfast Centre	01/02/2013	13/02/2013	12	Site re-roofing, sampling suspended to avoid sampling HCs from roofing material
Birmingham Acocks Green	12/02/2013	26/02/2013	14	Removed erroneous data at Quality circle
Birmingham Tyburn Roadside	12/02/2013	26/02/2013	14	Removed erroneous data at Quality circle
Chatham Roadside	09/07/2013	04/09/2013	57	Sampler blockage
Chesterfield Roadside	09/05/2013	23/05/2013	14	Removed erroneous data at Quality circle
Glasgow Kerbside	01/03/2013	24/04/2013	54	Inlet failure caused water ingress
Haringey Roadside	06/12/12	19/04/2013	109*	New sampler fitted, followed by new pump. Erroneous data covering the relevant period removed at the quality circle
London Bloomsbury	31/07/2013	12/09/2013	43	Inlet failure caused water ingress
Oxford St Ebbes	18/12/2013	02/01/2014	13*	Removed erroneous data at Quality circle
Scunthorpe Town	19/06/2013	08/10/2013	111	Operator error, sampler partially internal sampling. Operators re-trained
Southampton Centre	03/09/2013	17/09/2013	14	Removed erroneous data at Quality circle
Tower Hamlets Roadside	05/11/2013	13/03/2014	69	Sampling air inside the enclosure
York Bootham	16/10/2013	24/12/2013	69	Sampling fault, erroneous data removed at quality circle

*The value indicated shows losses for 2013 only

3.1.1 Automatic Hydrocarbon Network Statistics

Table 8 Benzene and 1,3-butadiene Statistics

Site	Pollutant	Annual Mean ($\mu g.m^{-3}$)	Maximum ($\mu g.m^{-3}$)	Data capture (%)
Harwell	Benzene	0.4	3.08	88.1
	1,3-Butadiene	0.06	0.31	88.0
Marylebone Road	Benzene	1.15	8.37	96.5
	1,3-Butadiene	0.21	1.66	96.4
Auchencorth Moss	Benzene	0.25	4.99	90.2
	1,3-Butadiene	0.03	0.56	92.6
London Eltham	Benzene	0.59	6.29	80.4
	1,3-Butadiene	0.09	1.53	80.4

Table 9 Automatic Analyser Faults and failures in 2013

Site	Start	Finish	Days lost	Reason
Harwell	04/02/2013	14/02/2013	10	Baseline cycling, instrument checked by Engineers
	08/03/2013	14/03/2013	6	Sample pump failed, replaced on 14/03/2013
	21/05/2013	30/05/2013	9	Transfer line broken, replacement ordered and re-fitted on 30/05/2013
	16/09/2013	18/09/2013	2	Sample Pump failed, repaired on 18/09/2013
	07/10/2013	14/10/2013	7	Compressor leak, compressor fixed on 14/10/2013
Eltham	01/01/2013	04/01/2013	3	Power cut
	25/01/2013	03/02/2013	9	Turbomatrix failed, new part order delayed, fitted on 03/02/2013
	20/05/2013	25/05/2013	5	Data removed, poor data
	09/10/2013	26/11/2013	48	Poor data. Investigation finally diagnosed as a Valco valve failure
London Marylebone Road	19/02/2013	21/02/2013	2	Hydrogen generator failure
	30/12/2013	31/12/2013	1	Compressor failure
Auchencorth Moss	16/01/2013	17/01/2013	1	Unstable data. Data deleted for some species, data capture varies depending on decision during ratification
	14/03/2013	15/03/2013	1	Power cut

Annual Mean concentrations for all measured hydrocarbons at all sites are given in Appendix 2.

The 2011 Implementing Provisions Regulations[11] (Commission Implementing Decision 2011/850/EU) will affect how the UK reports statutory air quality data to Europe. For VOCs, IPR requires measurements below the instrument's limit of detection to be reported as half the limit of detection. Data capture from 2013 onwards is calculated based on the number of valid data points in the year, including data below the limit of detection, recorded as half that of the limit. Previous flags recorded <LoD as 'not measured'.

The new data capture calculation also includes an allowance of 5% for planned maintenance and calibration. These two changes have increased data capture but introduced a small step change in long term trends that is not representative of atmospheric conditions in the UK. The change from 2012 to 2013 is negligible in terms of absolute concentrations but significant in 2012/2013 ratio for components that were previously not measured as a result of measurements being below the detection limit. For example, using the new IPR flags, Trimethylbenzene measurements at Auchencorth Moss change from no data capture to 90.24% data capture and a concentration of 0.12 $\mu g.m^{-3}$.

The data flags used in the Implementing Provisions Regulations (IPR) are applied using a program, written by Ricardo-AEA.

The automatic system comprises several components listed below:

- Turbomatrix Thermal Desorber (TD)
- Sample vacuum pump
- Clarus 500 Gas Chromatograph (GC)
- Zero Air generator
- Air Compressor
- Hydrogen Generator
- High Volume Flow Inlet
- Site PC including Totalchrom software

These components are checked by local site operators on a fortnightly basis. The system manufacturer (Perkin Elmer) carry out annual preventative maintenance. The data from the system is checked Monday to Friday by Ricardo-AEAs daily data checking team. If there is an instrument failure Perkin Elmer are called out to the site to repair the problem. There are no hot spare Thermal Desorbers or gas Chromatographs, so some considerable downtime is possible if the instrument fault cannot be diagnosed and/or repaired quickly.

Further data loss is likely due to instrument detector stability following power cuts, preventative maintenance visits and instrument faults. It can take several days for the instrument to stabilise. This problem is unavoidable with chromatography, we ensure all faults are diagnosed within 48 hours (excluding weekends and public holidays), and all faults are repaired following diagnosis unless this is not possible, for example where a component has failed that needs to be ordered.

3.1.2 Long Term Trends

The following figures show the benzene concentration ($\mu g.m^{-3}$) timeseries since the start of monitoring for each Non-automatic site (Figures 4 – 9) and each automatic site (Figure 12 - 13).

[11] http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2011:335:0086:0106:EN:PDF

These plots have been grouped on the basis of their original concentrations highest (Figure 4) to lowest (Figure 8).

Figure 4 Long term Non-Automatic benzene annual mean timeseries.

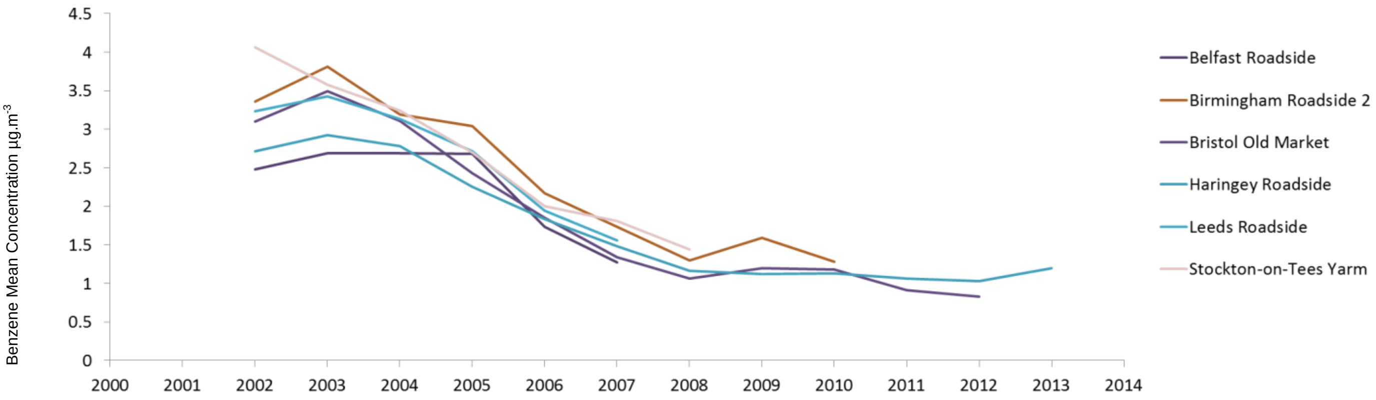


Figure 5 Long term Non-Automatic benzene annual mean timeseries

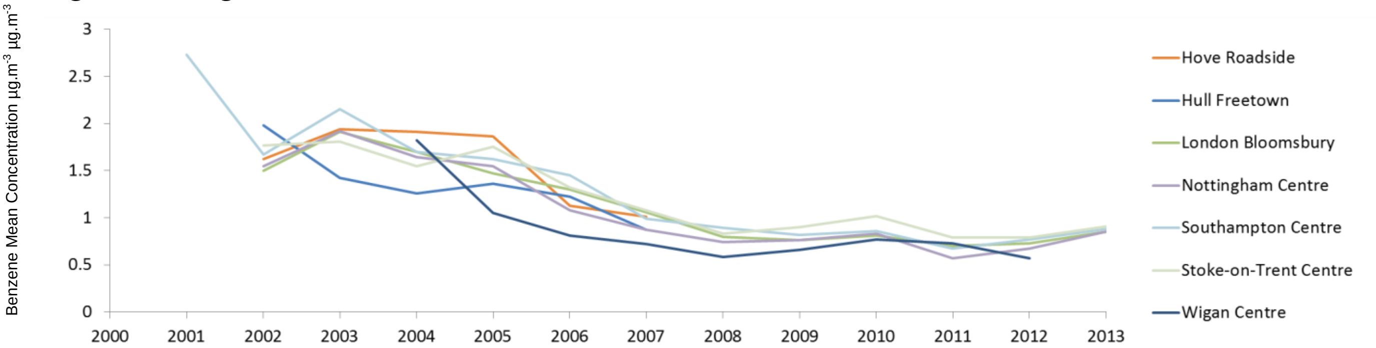


Figure 6 Long term Non-Automatic benzene annual mean timeseries

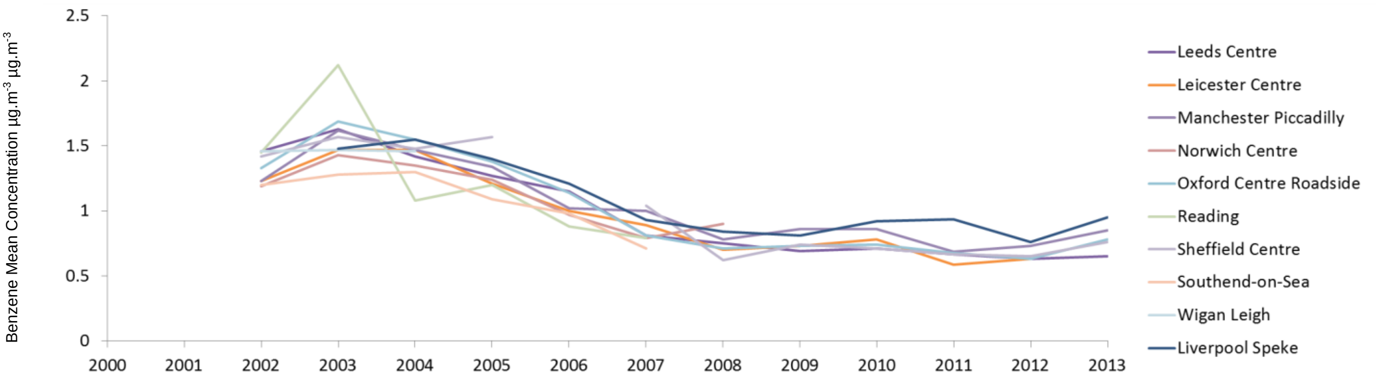


Figure 7 Long term Non-Automatic benzene annual mean timeseries

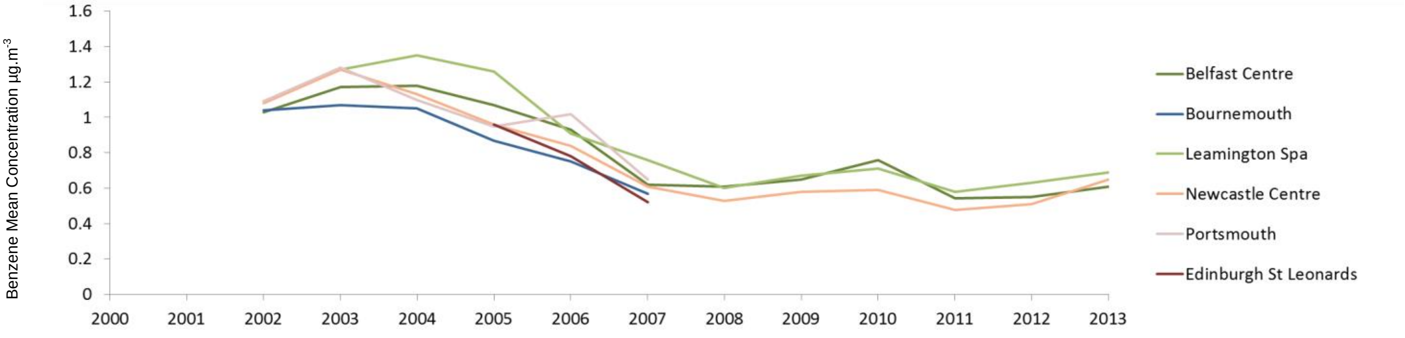
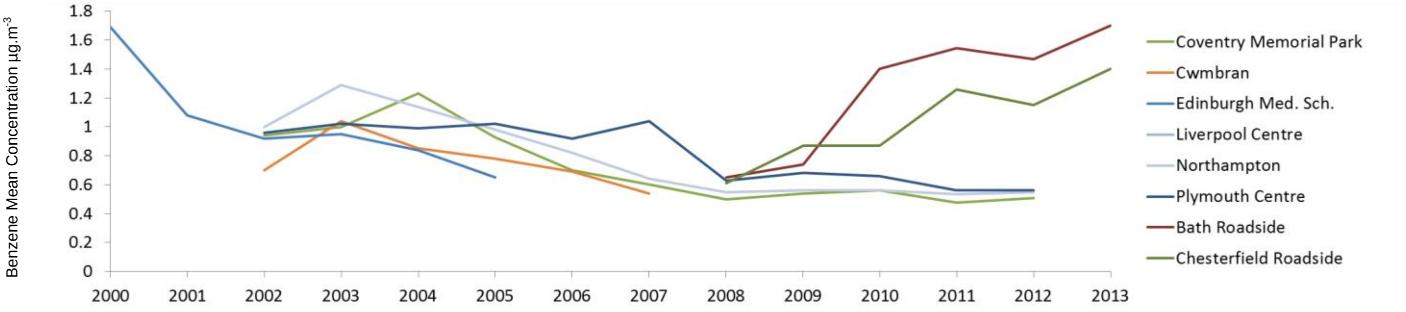
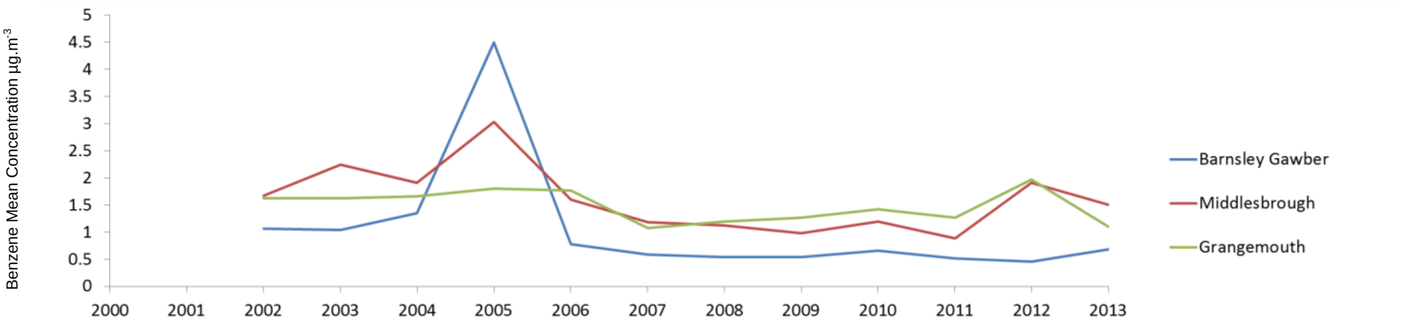


Figure 8 Long term Non-Automatic benzene annual mean timeseries



Trends in Figure 4 to 8 show a steady decline of benzene concentrations. The introduction of reduced benzene in vehicle fuels in 1997 resulted in a steady reduction of observed benzene concentrations. The concentrations increase negligibly for most sites from 2012 to 2013. It's not clear what the cause of this is, although it could be associated with an increase in vehicle numbers.

Figure 9 Long term Non-Automatic benzene annual mean timeseries



In Figure 8 ***Long term Non-Automatic benzene annual mean t***(Bath Roadside and Chesterfield Roadside) the plots show some clear inconsistencies with the rest of the network, including comparable roadside locations. To investigate this, the fortnightly benzene measurements are plotted in the figures 10 and 11 below, alongside NOx (as NO_2) measurements from the UK Automatic Urban and Rural Network (the predominant source of both pollutants is road traffic).These unusual trends are also shown in the NOx automatic analyser measurements indicating the measurements are likely to be representative of the local environment. Ricardo-AEA are not sure why the trend is not consistent with other sites, the two species are considered to share the same traffic source and as such, a similarity in trend shows the data represents the monitoring location therefore the data has not been removed.

Unusual trends in ***Figure*** 9 ***Long term Non-Automatic benzene annual mean t*** (Grangemouth and Middlesbrough) in 2012 have been discussed in the network report for

2012[12]. Raised levels of benzene at Barnsley Gawber in 2005 (Figure 9) were due to coal tar deposits uncovered by housing development that contained significant amounts of benzene (NPL, 2006). Elevated levels at Middlesbrough during 2005 (Figure 9) are considered a result of industrial activity in the area. These two incidents are not linked.

Figure 10 Bath Roadside long term fortnightly measurements vs AURN NOx

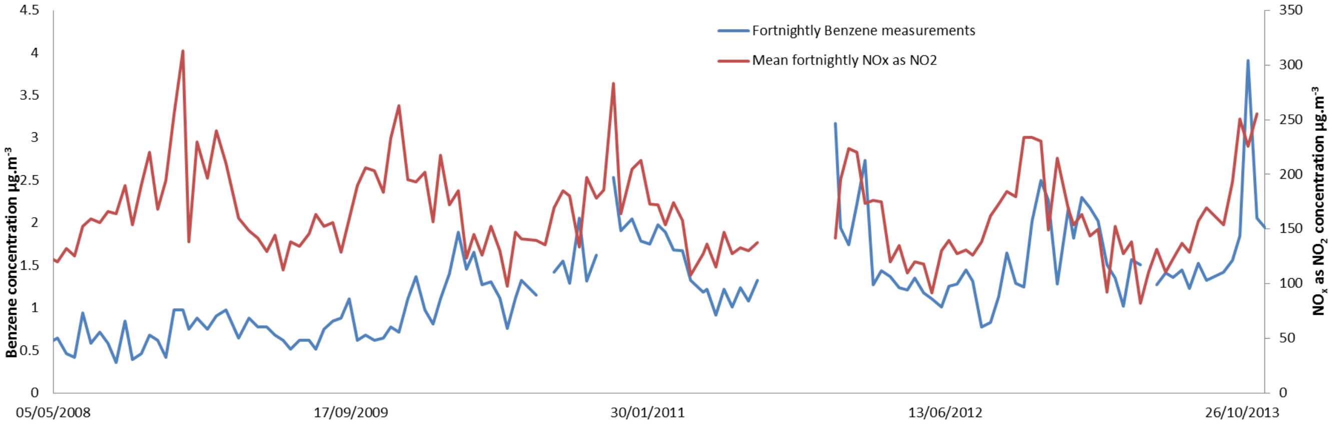


Figure 11 Chesterfield Roadside long term fortnightly measurements vs AURN NOx

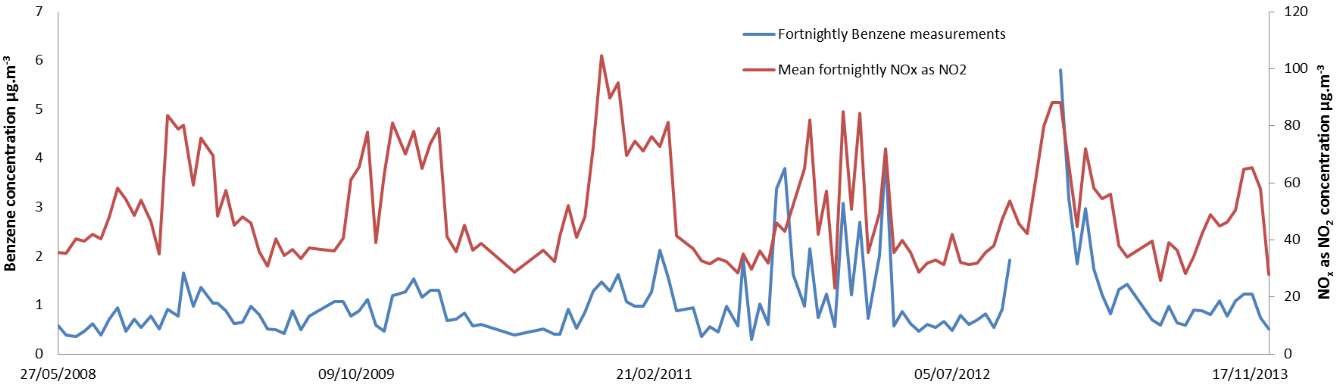


Figure 12 Long term automatic annual mean benzene to Figure 14 show the long-term timeseries of the annual mean concentrations of benzene and 1,3-butadiene at the four sites with long running datasets within the Automatic Hydrocarbon Network. Note that in 2010 and 2011 annual mean benzene concentrations have been included for sites where data capture was less than 75%. In other years data have been excluded where the data capture in the year was less than 75%. The trend shows a similar curve seen from the National Atmospheric Emissions Inventory (NAEI). These declines demonstrate that motor vehicle exhaust catalysts and evaporative canisters have effectively and efficiently controlled vehicular emissions of hydrocarbons in the UK[13]. This implies reduced health effects to individuals living in the UK as a result of long term exposure to these pollutants. Our measurements show the measurements plateau from 2012 to 2013.

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[12] I http://uk-air.defra.gov.uk/?report_id=771

[13] R.G. Derwent et al. Twenty years of continuous high time resolution volatile organic compound monitoring in the United Kingdom from 1993 – 2012 Atmospheric Environment 99 (2014) 239-247

Figure 12   Long term automatic annual mean benzene timeseries and emissions

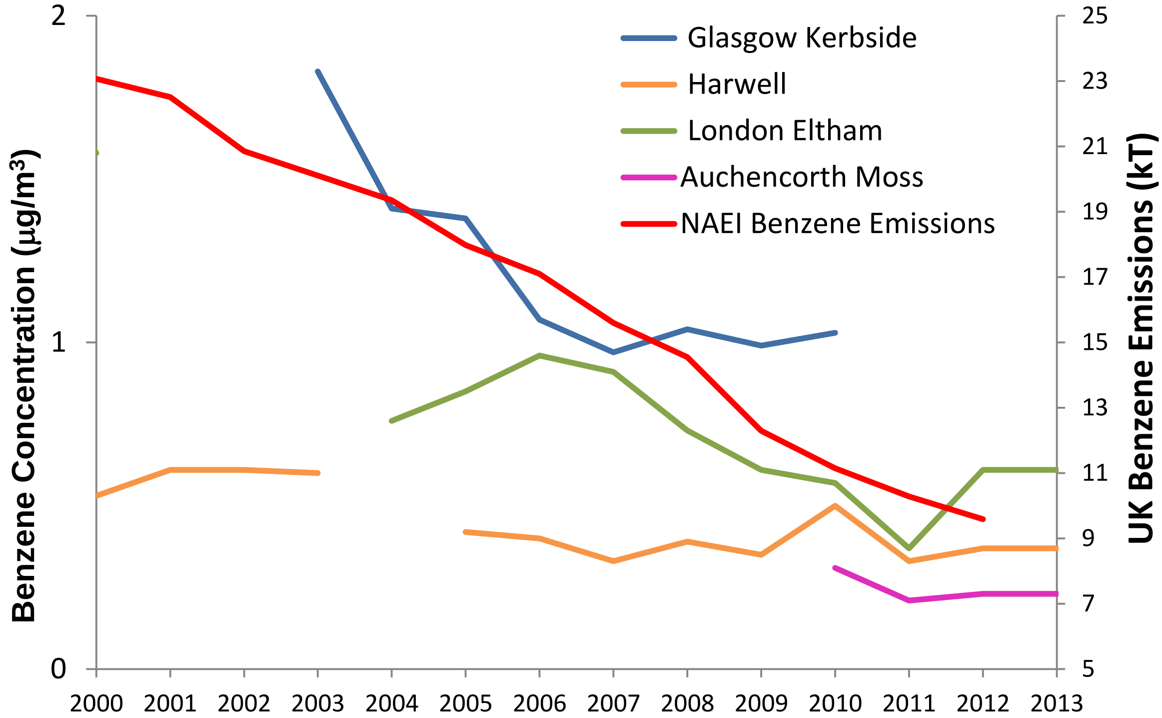


Figure 13   Long term automatic annual mean benzene timeseries and emissions

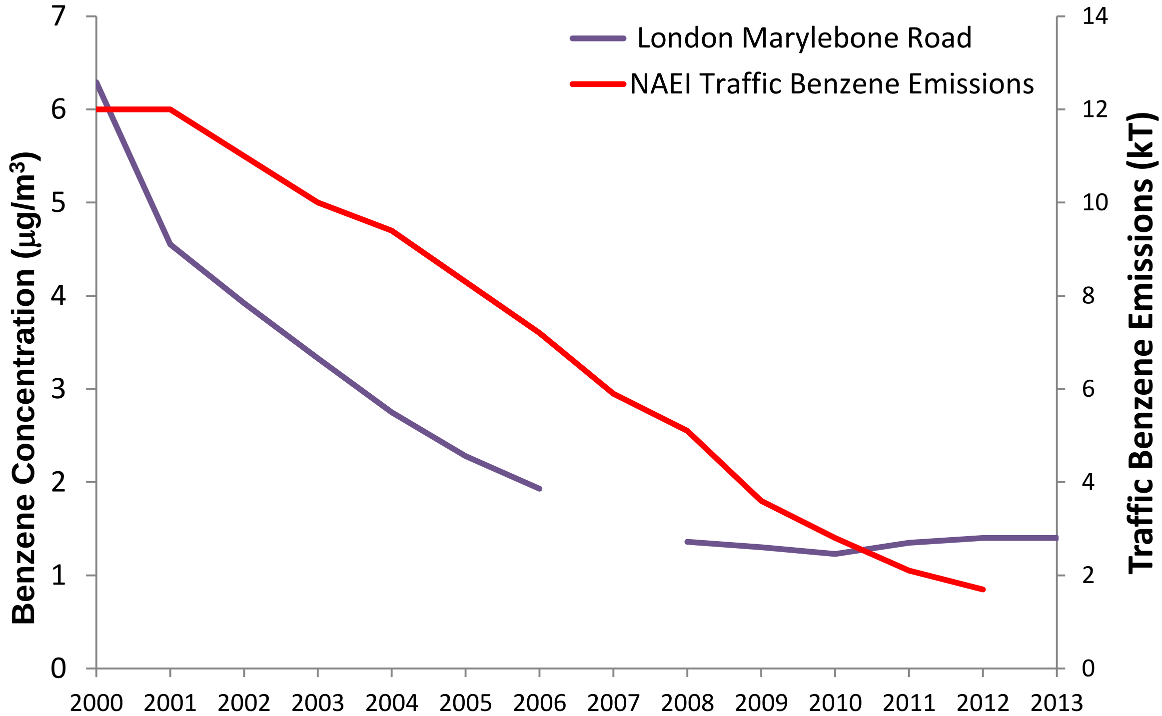
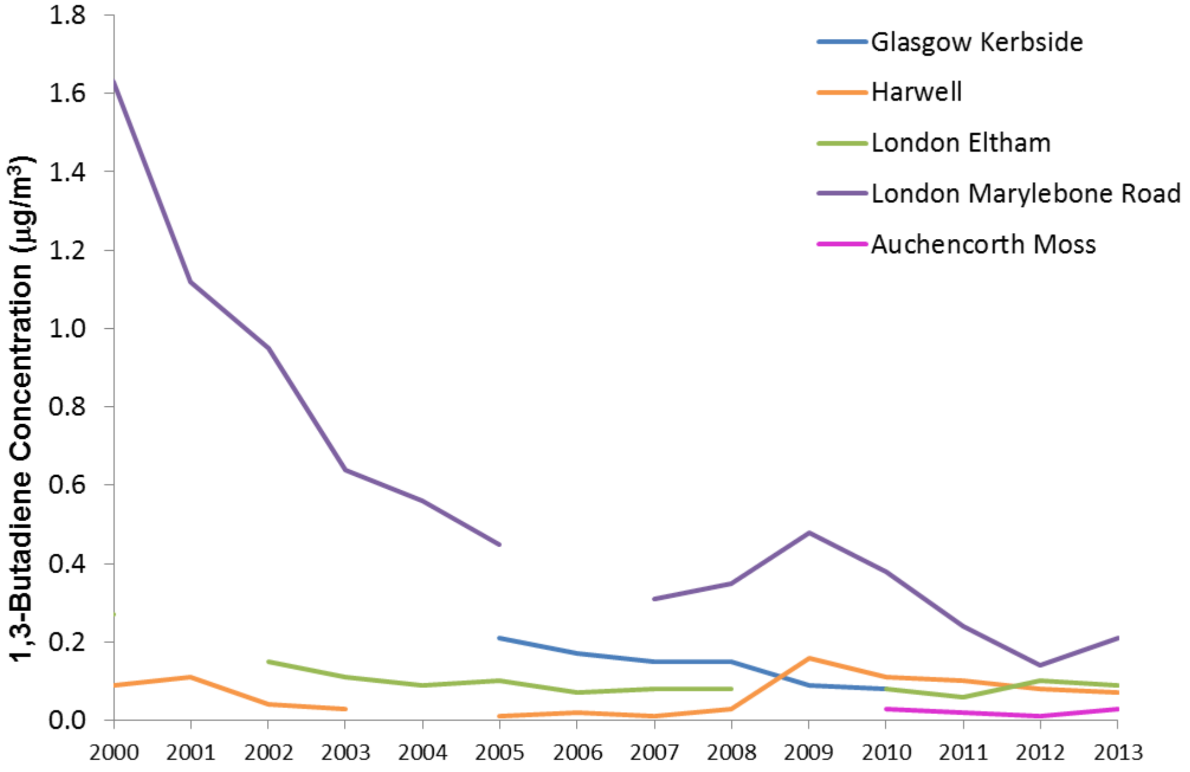


Figure 14 Long term automatic annual mean 1,3-butadiene timeseries



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 data have been excluded where the data capture in the year was less than 75%. A similar downward trend seen for benzene measurements is also seen with 1,3-butadiene. This decrease in concentrations resulted in measurements below the limit of detection using diffusive samplers on the non-automatic network. There is little concern of exceedances of the objectives in the UK AQS and although 1,3 butadiene is no longer measured using diffusive samples continues to be measured using the automatic method. The diffusive 1,3-butadiene measurements were removed from the monitoring programme in 2007 as a result of this decline.

The results conclude no exceedances of the EU or UK criteria at Urban, Traffic or Background locations. One exceedance of the Lower Assessment Threshold at Scunthorpe Town has been seen.

Automatic analyser annual timeseries are provided in Annex 4, Figure 18 to Figure 25. These show the benzene and 1,3 butadiene concentrations were below the LV in the AQD and the objectives in the UK AQS. Indeed London Eltham and Marylebone Road maximum hourly measurements only reach levels comparable to the benzene annual mean limit value in the AQD and only do so on one and five occasions respectively.

Non-automatic annual timeseries are provided in Annex 4 Figure 26 to Figure 59, with the exception of Grangemouth (Figure 38), Middlesbrough (Figure 45) and Scunthorpe Town (Figure 52), the predominant source of benzene is road traffic. Further background industrial emissions are present, for example emissions from power stations. The annual timeseries show the expected elevated levels in winter (Jan, Feb, Dec) and lower measurements in summer.

4 Data Quality

4.1 Butanol contamination

The Marylebone Road and Harwell automatic hydrocarbons systems are co-located with Condensation Particle Counters (CPC) which use n-butanol for the detection technique. The n-butanol is used to 'grow' sub-micron particles so that they can be detected by conventional methods. The butanol had been located within the same room housing the automatic hydrocarbon analysers. The system used to dry the sampled gas for the automatic hydrocarbon analyser (nafion dryer) uses air from within the room. It is suspected that n-butanol ingresses to the hydrocarbon sampling system through the nafion dryer. Observations of the chromatograms have indicated a 'peak' which elutes just after that for benzene. It is possible for the peak integration software to report these two peaks as a single co-eluting measurement. This leads to the over estimation of benzene concentrations and these results must be removed from the dataset. Isolation of the n-butanol feedstock from the room containing the hydrocarbon has been implemented at the Harwell and Marylebone monitoring station and has now resolved this as an issue.

4.2 Intercomparisons

Comparing data from co-located samplers is a good way to validate the data and can help identify issues such as co-elution of n-butanol. Comparisons of data from two sites where both the non-automatic and automatic systems have been operated alongside each other are shown below.

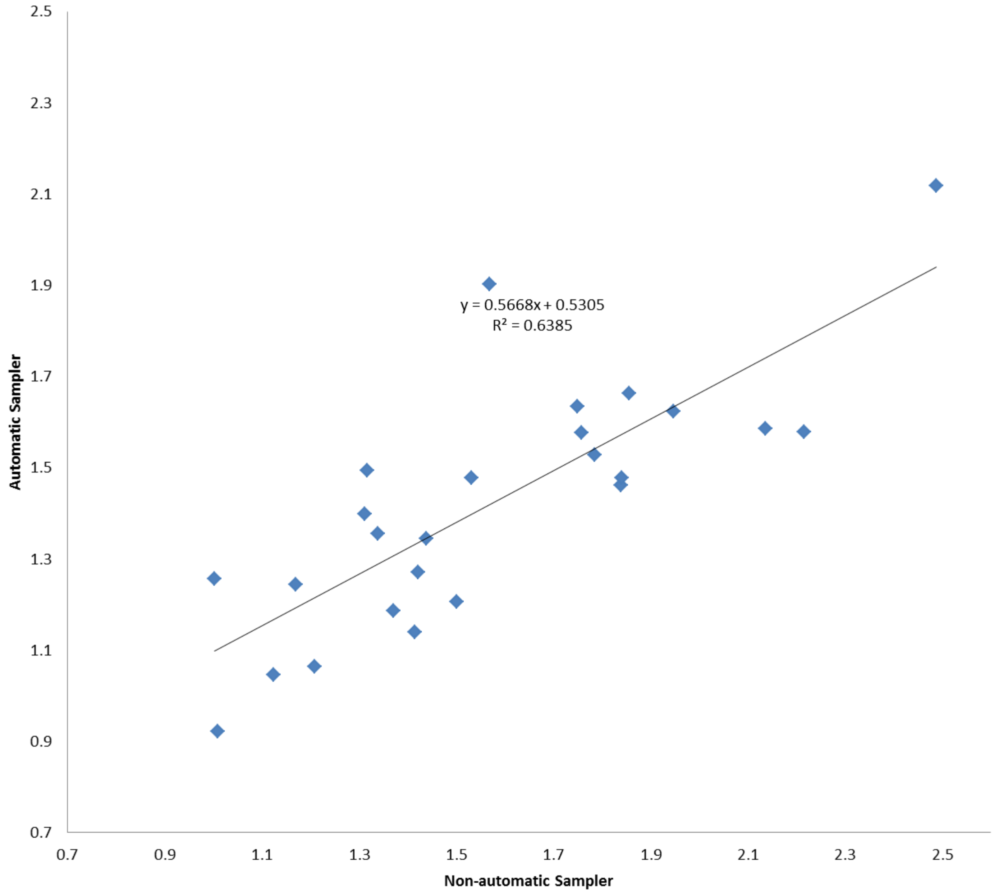
There are two sites at which Non-Automatic samplers and Automatic analysers have been co-located following on from the previous contract; at Marylebone Road, between 14th December 2011 and 21st January 2013 and at London Eltham between 26th April 2011 and 5th July 2012. If further interferences are found, further co-location studies can be undertaken.

4.2.1 Marylebone Road

Data are available from the two co-located samplers at Marylebone Road.

Figure 15 Comparison of collocated samplers at Marylebone Road 14/12/11-21/01/13 and Figure 16 Comparison of collocated samplers at London Eltham 26/04/11-05/07/12 show x,y scatter plots (only where data capture >75% for both methods). These automatic fortnightly means correspond to the dates of sampling with the non-automatic benzene samplers, enabling the data to be directly compared.

Figure 15 Comparison of collocated samplers at Marylebone Road 14/12/11-21/01/13

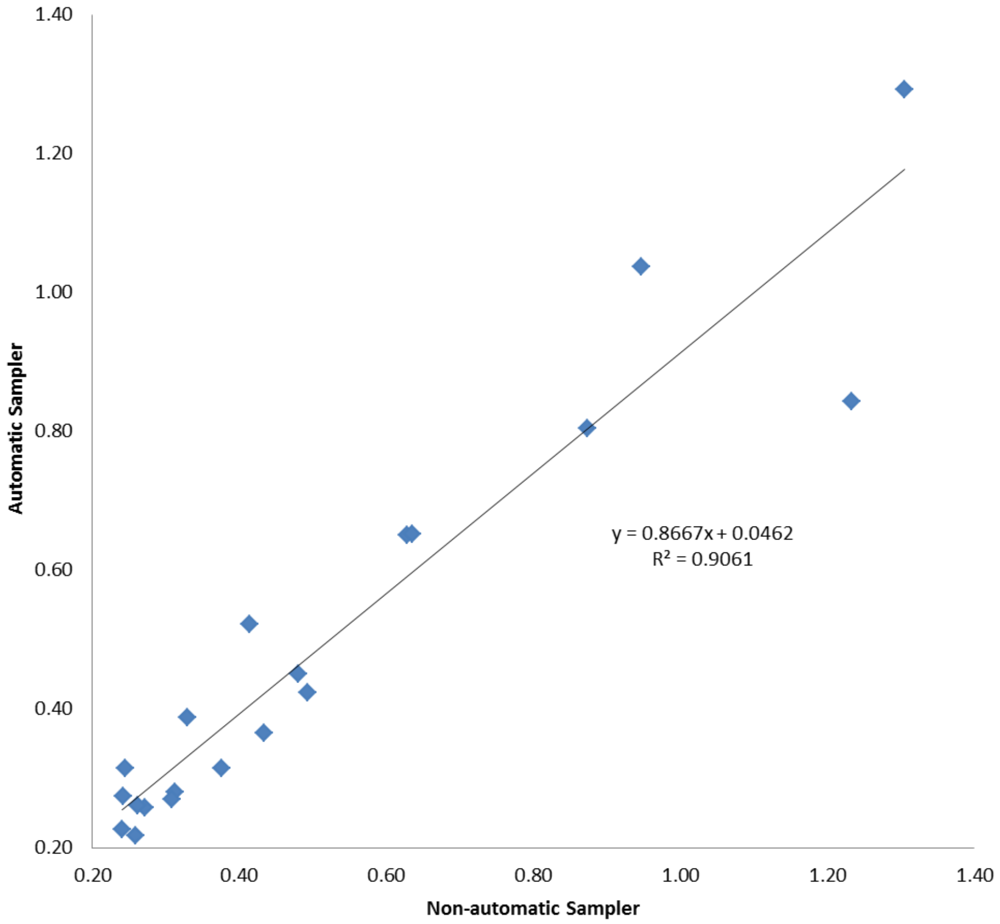


There were 26 measurements when both sampling methods achieved >75% data capture at Marylebone Road (1 outlier was removed) (Figure14). The agreement between the two methods is reasonable but not as close as that shown at Eltham (Figure 15), it is suggested that co-elution of butanol caused this issue at Marylebone Road, Eltham is not exposed to butanol as the site does not include a CPC instrument. It should be noted that the Harwell site, also co-located with a CPC system uses a nitrogen cylinder to supply dry air to the nafion dryer for drying sample gas and as such does not see the same issue.

4.2.2 London Eltham

Data from the co-located samplers at London Eltham have been compared in a similar way and are presented in Figure 16 Comparison of collocated samplers at London Eltham 26/04/11-05/07/12.

__Figure 16__ __Comparison of collocated samplers at London Eltham 26/04/11-05/07/12__



There were 22 samples when data capture exceeded 75%, two of these were outliers and were removed. The regression (R^2) of 0.91 at Eltham (Figure 16) shows a better agreement than 0.64 at Marylebone Road (Figure 15).

It seems likely that co-elution of n-butanol emitted from the Condensation Particle Counter at Marylebone Road affects benzene measurements from the automatic analyser which is in turn affecting the correlation at Marylebone Road. The source of n-butanol used at Marylebone Road has been moved to a separate cabin at the site, the chromatography has not been affected by co-elution since and the intercomparison ceased.

4.3 Estimation of Uncertainty

Calculated uncertainty for the Non-Automatic Hydrocarbon sites in 2013 for benzene is 15%, expressed at a 95% level of confidence. This includes contributions from Ricardo-AEA's flow measurements, desorption efficiency and analysis uncertainty.

The requirement for benzene measurement uncertainty from an automatic hydrocarbon analyser is 25%, expressed at 95% confidence limit. The Perkin-Elmer analyser used in the UK network has not been type tested, so an estimate of the various contributions has been made to assess compliance with the DQO requirement. The main contributions are:

- Repeatability and lack of fit – derived if possible from the manufacturers specifications
- Variation in sample gas pressures , surrounding temperature and electrical voltage – derived if possible from the manufacturers specifications
- Interference from ozone – derived if possible from the manufacturers specifications

- Memory effects – derived if possible from the manufacturers specifications
- Differences between the sample and calibration port – these differences are negligible, the sample and calibration port are in contact with 90% of the same valve. Removing the calibration cylinder to evaluate this will disturb the system and affect sample measurements for some considerable time afterwards.
- Uncertainty in calibration gas – from NPL cylinder certificate
- Reproducibility under field conditions – this could be estimated from the manufacturers specifications
- Long term drift – corrections are made such that this is not applicable to the expanded uncertainty.

By far the largest components in the uncertainty budget are lack of fit and calibration gas uncertainty. The calibration gas used is of the highest available quality. In the absence of data from type testing, the maximum permissible values stated in the EN Standard have been used as a worst case scenario. Using these values and the known values from the calibration cylinder the uncertainty budget has been calculated. The uncertainty of benzene measurements using a Perkin-Elmer analyser is estimated to be < 24%.

Reliability and intercomparability of UK benzene measurements is regularly assessed through international intercomparisons. Involvement in the Aerosols, Clouds, and Trace gases Research Infrastructure Network (ACTRIS) results showed Harwell +6.5%, AM -7.6% from the reference value.

4.4 Standard Methods

The AQD states that automatic measurements of benzene should be compliant with 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 $\mu g.m^{-3}$. Measurements undertaken by the Automatic Hydrocarbon Network are carried out in accordance with this Standard.

The Standard Method for measurement of benzene using an automatic analyser is in the process of review by CEN Working Group 12. Ricardo-AEA has a presence at CEN meetings, comments of which are summarised and sent to Defra following each meeting. At the time of publication of this report, the proposed revisions include a requirement for more rigorous linearity tests. The proposal states the linearity tests will be performed using at minimum the following concentrations: 0 %, 10 %, 50 % and 90 % of the maximum of the certification range of benzene or the user-defined range. At each concentration (including zero) at least 3 measurements shall be performed, the result of the first shall be discarded. The test shall be repeated at the following intervals:

- Within 1 year of the test at initial installation; subsequently:
- Within 1 year after test if the lack-of-fit is within 2,0 % to 5,0 %;
- Within 3 years if the lack of fit is ≤ 2,0 %;
- After repair

The AQD states that non-automatic measurements of benzene should be compliant with European Standard EN14662-1:2005 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 the National Physical Laboratory in compliance with this standard. Ricardo-AEA contract Environmental Scientifics Groups (ESG) to analyse the samples in accordance with this standard. The non-automatic samplers were built specifically to meet the standard.

The AQD does not specify a standard method for the measurement of ozone pre-cursors (including formaldehyde), with the exception of benzene, as described above.

The Perkin Elmer ozone pre-cursor analyser used for automatic measurements cannot measure formaldehyde. The system used for the measurement of aldehyde has been constructed broadly in-line with the benzene method in EN14662-1:2005 and using the relevant analysis method suggested by the DNPH tube manufacturers (Waters Inc.)[14]. This method follows the guidance of the EMEP manual for aldehyde measurements[15]. The flow rate and sample time have been adjusted to achieve a volume within the upper and lower limit of the DNPH tube limits as specified by the manufacturer.

This method has been tested for sample breakthrough using two in-line tubes. The analytical laboratory has spiked the DNPH tubes with known quantities of acetaldehyde and formaldehyde at levels near the limit of detections and at the highest levels measured during the pilot study. The system uses a mass flow controller, calibrated using Ricardo-AEAs accredited flow measurement system in order to calculate the sample volume.

4.5 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 $\mu g.m^{-3}$ from a 14 day sample period.

The Limit of Detection for each of the 29 species measured by the Perkin Elmer Ozone Precursor Analysers used by the Automatic Hydrocarbon Network is shown in Table 10.

Table 10 Automatic Analyser Detection Limits

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

[14] Sep-Pak XPoSure Aldehyde Sampler Care and Use manual http://www.waters.com/webassets/cms/support/docs/wat047204.pdf
[15] Nilu, 2001. EMEP Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe EMEP manual for sampling and chemical analysis

5 Developments and Recommendations

5.1 EN14662-3:2005

European Standard EN14662-3:2005 is currently under review by CEN Working Group 12, to bring it in line with the other gaseous pollutants' standards. Ricardo-AEA is involved in the review through a representative on the Working Group, and is providing appropriate contributions and feedback to Defra and the Devolved Administrations regarding the potential implications for the Automatic Hydrocarbon Network. The most significant change proposed under the current revision is the inclusion of a linearity audit, by means of reference gas dilution. This might have cost implications for the operation of the network. A current audit of the system using one concentration of known VOCs in a gas mixture requires 4 hourly samples from the reference cylinder. If these changes are implemented, in order to test lack of fit (linearity), 4 concentrations, including 0% should be analysed. Each dilution will be repeated for three hourly samples. This audit will take 2 working days unless an automated, programmable dilution system can be employed.

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 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'.

In 2012, Ricardo-AEA started a pilot study 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.

5.3 Benzene concentrations and emissions

In August 2014, Ricardo-AEA carried out some analysis for Defra under the NAEI, including detailed analysis of a long time-series of hydrocarbon data at Marylebone Road. A strong downward trend in ambient concentrations of HCs known to be emitted from road vehicles was observed. The trends are broadly consistent with emission trends implied by the NAEI, again providing verification of the inventory for petrol vehicle emissions. However, there are some differences in trends for benzene and 1,3-butadiene in recent years that cannot be fully explained by the inventory. Ambient measurements data for 2012 further suggest ratios of benzene/CO_2 and 1,3-butadiene/CO_2 that are lower than the ratios implied by the NAEI. Further work is required to reconcile the benzene and 1,3-butadiene/CO_2 ratios, the recent concentration trends observed for these hydrocarbons and the emission inventory trends.

The analysis in this report goes further. The flat trends at Harwell and Auchencorth Moss shown in Figure 12 may not be relevant because they are not traffic influenced sites, however, London Eltham and Glasgow Kerbside might be showing a pattern similar to Marylebone Rd with a flattening off in concentrations in recent years. However, to really understand these sites, we would need to look at trends in traffic in these areas which haven't been undertaken. It is possible that traffic has been changing at rates different to the UK average and strongly influencing the measurement trends. Ricardo-AEA would have to carry out further analysis to investigate this.

Appendices

Appendix 1: 2013 Audit Schedule

Appendix 2: Data capture, maximum and annual mean values from the Automatic Hydrocarbon Network

Appendix 3 Current Non automatic flow audit certificate

Appendix 4: Benzene and 1, 3-Butadiene Timeseries plots, Automatic and Non automatic data

Appendix 1 – 2013 Audit schedule

Table 11 Non automatic sample flow measurements used for 2013 data

Site	Date	Adjusted flow, ml/min	Date	Measured Flow, ml/min	Adjusted flow, ml/min	Date	Measured Flow, ml/min	Adjusted flow, ml/min	Date	Measured Flow, ml/min
Barnsley Gawber	31/10/2012	10.0	02/04/2013	9.5	9.7	01/10/2013	10.2	10.2	14/04/2014	9.9
Bath Roadside	03/10/2012	10.0	24/04/2013	9.5	10.1	21/10/2013	10.4	10.1	24/04/2014	9.6
Belfast Centre	18/10/2012	10.1	17/04/2013	9.7	10.1	14/10/2013	9.7	10.1	07/04/2014	10.2
Birmingham Acocks Green	10/10/2012	10.0	11/04/2013	10.6	10.0	10/10/2013	9.0	10.0	10/04/2014	10.0
Birmingham Tyburn Roadside	10/10/2012	10.0	11/04/2013	10.3	10.1	10/10/2013	8.9	10.1	10/04/2014	10.0
Bury Roadside	13/11/2012	10.0	03/04/2013	9.6	9.9	10/09/2013	10.4	N/A	N/A	N/A
Cambridge Roadside	17/10/2012	10.0	08/04/2013	9.4	10.0	07/10/2013	9.5	10.0	07/04/2014	9.7
Camden Kerbside	23/10/2012	10.1	16/04/2013	9.6	10.0	22/10/2013	10.5	10.0	15/04/2014	9.3
Carlisle Roadside	03/10/2012	10.0	08/04/2013	9.6	10.0	07/10/2013	10.5	10.2	02/04/2014	10.0
Chatham Roadside	15/10/2012	10.0	04/04/2013	8.6	10.1	02/10/2013	9.9	10.1	29/04/2014	9.7
Chesterfield Roadside	31/10/2012	9.9	22/04/2013	10.8	10.1	01/10/2013	10.1	10.0	28/04/2014	10.2
Glasgow Kerbside	08/10/2012	9.8	15/04/2013	10.1	10.0	30/09/2013	10.1	10.1	25/04/2014	9.7
Grangemouth	08/10/2012	10.0	15/04/2013	10.6	10.0	30/09/2013	9.3	10.1	22/04/2014	10.1
Haringey Roadside	22/10/2012	9.9	19/04/2013	20.3	10.1	23/10/2013	11.3	10.1	16/04/2014	9.2
Leamington Spa	12/10/2012	10.1	18/04/2013	9.4	10.0	17/10/2013	9.7	10.0	15/04/2014	9.2
Leeds Centre	31/10/2012	10.0	02/04/2013	10.2	10.0	23/10/2013	10.0	10.0	14/04/2014	10.2
Liverpool Speke	14/11/2012	10.0	10/04/2013	9.7	10.0	09/10/2013	10.0	10.1	08/04/2014	9.9
London Bloomsbury	24/10/2012	10.1	15/04/2013	10.1	9.9	22/10/2013	10.6	10.0	14/04/2014	8.9
Manchester Piccadilly	11/10/2012	10.1	04/04/2013	9.6	9.9	22/10/2013	9.6	10.0	01/04/2014	9.6
Middlesbrough	02/10/2012	10.0	10/04/2013	9.5	10.0	09/10/2013	9.5	10.0	08/04/2014	10.3

Site	Date	Adjusted flow, ml/min	Date	Measured Flow, ml/min	Adjusted flow, ml/min	Date	Measured Flow, ml/min	Adjusted flow, ml/min	Date	Measured Flow, ml/min
Newcastle	02/10/2012	10.1	09/04/2013	9.8	10.0	02/10/2013	10.0	10.2	09/04/2014	10.1
Newport	31/10/2012	10.1	02/04/2013	10.4	10.0	22/11/2013	9.1	10.0	01/04/2014	10.3
Norwich Lakenfields	16/10/2012	10.0	09/04/2013	9.6	10.1	08/10/2013	9.9	10.0	08/04/2014	9.4
Nottingham Centre	31/10/2012	10.0	15/04/2013	9.6	10.1	14/10/2013	9.9	10.0	09/04/2014	9.6
Oxford Centre Roadside	25/10/2012	10.1	23/04/2013	9.8	10.0	07/10/2013	10.1	10.1	03/04/2014	10.4
Oxford St Ebbes	25/10/2012	10.0	23/04/2013	9.5	10.1	07/10/2013	10.6	10.1	03/04/2014	10.0
Scunthorpe Town	13/11/2012	10.0	08/04/2013	9.9	10.1	07/10/2013	9.8	10.2	14/04/2014	10.0
Sheffield Centre	31/10/2012	10.0	23/04/2013	9.7	10.0	29/08/2013	10.1	N/A	N/A	N/A
Sheffield Devonshire Green	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	29/04/2014	9.7
Southampton	02/10/2012	10.2	22/04/2013	9.7	10.1	25/10/2013	10.4	10.1	10/04/2014	9.2
Stockton-on-Tees Eaglescliffe	29/08/2012	10.0	10/04/2013	9.8	10.0	09/10/2013	9.8	10.0	09/04/2014	9.5
Stoke-on-Trent Centre	09/10/2012	10.0	24/04/2013	9.9	10.0	23/10/2013	9.9	10.0	30/04/2014	10.1
Tower Hamlets Roadside	05/11/2012	10.1	18/04/2013	9.9	10.0	24/10/2013	10.1	10.0	13/03/2014	9.7
York Bootham	06/11/2012	10.0	09/04/2013	10.3	10.1	08/10/2013	9.8	10.0	15/04/2014	9.8
York Fishergate	30/10/2012	10.0	09/04/2013	9.8	10.1	08/10/2013	9.8	10.0	15/04/2014	9.8

2013 Audit Schedule of the Automatic Hydrocarbon Network

Table 12 Audit and service schedule of the automatic hydrocarbon analysers

Site	Service/Audit Date	Service/ Audit Date	Service/Audit Date	Service/Audit Date	Service/Audit Date
Auchencorth Moss	18/05/2011	27/10/2011	28/03/2012	16/01/2013	TBC
Harwell	14/03/2011	27/06/2011	12/04/2012	11/09/2013	25/06/2014
Eltham	16/03/2011	22/11/2011	22/03/2012	15/10/2013	27/06/2014
Marylebone Road	15/03/2011	15/03/2011	20/03/2012	22/04/2013	26/06/2014

Appendix 2

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, in a change from previous years, data below the limit of detection has been reported as half of the limit of detection.

Table 13 Auchencorth Moss statistics, 2013

Compound	% Data capture	Maximum hourly concentration (µg.m^{-3})	Annual Mean concentration (µg.m^{-3})
1,2,3-trimethylbenzene	90	0.02	0.02
1,2,4-trimethylbenzene	90	0.02	0.02
1,3,5-trimethylbenzene	90	0.02	0.02
1,3-butadiene	93	0.56	0.03
1-butene	93	2.21	0.04
1-pentene	93	0.01	0.01
2-methylpentane	93	9.37	0.06
benzene	90	4.99	0.25
ethane	91	5.73	0.02
ethylbenzene	90	20.02	1.97
ethene	93	2.41	0.16
ethyne	93	7.05	0.04
isoprene	93	0.96	0.12
propane	93	21.85	0.34
propene	93	7.35	0.03
toluene	90	51.55	0.20
cis-2-butene	93	12.89	0.15
iso-butane	93	14.10	0.08
iso-octane	90	53.37	0.62
iso-pentane	93	8.94	0.04
m+p-xylene	90	5.36	0.06
n-butane	93	7.49	0.03
n-heptane	90	19.34	0.15
n-hexane	93	7.18	0.04
n-octane	90	66.39	1.30
n-pentane	93	4.54	0.11
o-xylene	90	8.64	0.18
trans-2-butene	93	1.79	0.02
trans-2-pentene	93	0.01	0.01

Percentage data capture, maximum and annual mean values of ratified data from the Harwell site of the Automatic Hydrocarbon Network. Note that, in a change from previous years, data below the limit of detection has been reported as half of the limit of detection.

Table 14 Harwell statistics 2013

Compound	% Data capture	Maximum hourly concentration ($\mu g.m^{-3}$)	Annual Mean concentration ($\mu g.m^{-3}$)
1,2,3-trimethylbenzene	88	0.90	0.07
1,2,4-trimethylbenzene	88	2.34	0.10
1,3,5-trimethylbenzene	88	0.60	0.04
1,3-butadiene	88	0.31	0.06
1-butene	88	0.51	0.12
1-pentene	88	0.01	0.01
2-methylpentane	88	1.39	0.10
benzene	88	3.08	0.39
ethane	88	0.14	0.03
ethylbenzene	88	14.96	2.79
ethene	88	20.55	0.50
ethyne	88	0.97	0.08
isoprene	88	17.10	0.35
propane	88	5.28	0.47
propene	88	0.81	0.06
toluene	88	4.64	0.35
cis-2-butene	88	0.62	0.03
iso-butane	88	2.73	0.18
iso-octane	88	8.08	0.79
iso-pentane	88	2.58	0.08
m+p-xylene	88	2.75	0.11
n-butane	88	2.80	0.04
n-heptane	88	2.48	0.19
n-hexane	88	1.45	0.10
n-octane	88	10.12	1.64
n-pentane	88	3.35	0.19
o-xylene	88	5.85	0.42
trans-2-butene	88	0.21	0.04
trans-2-pentene	88	0.01	0.01

Percentage data capture, maximum and annual mean values of ratified data from the London Eltham site of the Automatic Hydrocarbon Network. Note that, in a change from previous years, data below the limit of detection has been reported as half of the limit of detection.

Table 15 London Eltham statistics 2013

Compound	% Data capture	Maximum hourly concentration (µg.m^{-3})	Annual Mean concentration (µg.m^{-3})
1,2,3-trimethylbenzene	80	3.74	0.29
1,2,4-trimethylbenzene	80	3.39	0.30
1,3,5-trimethylbenzene	80	1.60	0.10
1,3-butadiene	80	1.53	0.09
1-butene	80	1.65	0.09
1-pentene	80	0.99	0.04
2-methylpentane	80	13.27	0.42
benzene	80	6.29	0.59
ethane	75	0.88	0.05
ethylbenzene	80	71.01	5.57
ethene	80	28.30	0.70
ethyne	80	3.48	0.23
isoprene	80	3.31	0.34
propane	80	41.07	1.47
propene	80	5.92	0.16
toluene	80	56.34	1.70
cis-2-butene	80	7.55	0.26
iso-butane	80	12.56	0.60
iso-octane	80	57.35	2.68
iso-pentane	80	4.03	0.25
m+p-xylene	80	14.02	0.32
n-butane	80	1.28	0.08
n-heptane	80	23.47	0.87
n-hexane	80	3.31	0.30
n-octane	80	41.00	2.93
n-pentane	80	6.01	0.34
o-xylene	80	21.11	1.05
trans-2-butene	80	1.16	0.06
trans-2-pentene	80	3.06	0.06

Percentage data capture, maximum and annual mean values of ratified data from the Marylebone Road site of the Automatic Hydrocarbon Network. Note that, in a change from previous years, data below the limit of detection has been reported as half of the limit of detection.

Table 16 Marylebone Road statistics 2013

Compound	% Data capture	Maximum hourly concentration ($\mu g.m^{-3}$)	Annual Mean concentration ($\mu g.m^{-3}$)
1,2,3-trimethylbenzene	97	4.24	0.29
1,2,4-trimethylbenzene	97	8.78	0.51
1,3,5-trimethylbenzene	97	8.13	0.37
1,3-butadiene	96	1.66	0.21
1-butene	96	2.31	0.43
1-pentene	96	2.85	0.19
2-methylpentane	96	12.76	1.13
benzene	97	8.37	1.15
ethane	96	1.56	0.15
ethylbenzene	97	83.58	8.98
ethene	96	43.88	2.37
ethyne	96	5.91	0.63
isoprene	96	8.68	1.13
propane	96	28.09	2.98
propene	96	4.60	0.47
toluene	97	76.03	4.38
cis-2-butene	96	0.01	0.01
iso-butane	96	18.51	1.88
iso-octane	97	51.15	5.08
iso-pentane	96	8.56	0.47
m+p-xylene	97	7.12	0.69
n-butane	96	3.37	0.16
n-heptane	97	18.89	1.86
n-hexane	96	6.74	0.76
n-octane	97	93.74	5.80
n-pentane	96	15.68	1.17
o-xylene	97	38.63	3.26
trans-2-butene	96	1.75	0.20
trans-2-pentene	96	3.84	0.22

Appendix 3

Figure 17 Current non-automatic audit certificate

UKAS CALIBRATION

0401

RICARDO-AEA

Certificate of Calibration

Ricardo-AEA,The Gemini Building, Fermi Avenue, Harwell, Didcot, Oxon, OX11 0QR 01235 753000

Certificate Number: 2964

Page 1 of 2

Approved Signatories:	S Eaton B Stacey	D Hector S Stratton
Signed:		
Date of issue:	2 May 2014	
Customer Name and Address:	Dr Daniel Waterman 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 non-automatic benzene samplers in the UK Hydrocarbons Network	

Measured flowrates

Site	Date of measurement	Flow A (mlmin-^{1})	Flow B (mlmin^{-1})	Difference (mlmin^{-1})	Uncertainty (mlmin^{-1})
Barnsley Gawber	14/04/2014	10.21	10.22	0.01	0.002
Bath Roadside	24/04/2014	9.91	9.91	0.00	0.002
Belfast Centre	07/04/2014	10.09	10.04	0.05	0.003
Birmingham Acocks Green	10/04/2014	10.02	10.01	0.01	0.002
Birmingham Tyburn Roadside	10/04/2014	10.09	10.03	0.07	0.003
Cambridge Roadside	07/04/2014	9.97	10.02	0.06	0.003
Camden Kerbside	15/04/2014	10.07	10.02	0.05	0.003
Carlisle Roadside	02/04/2014	10.02	10.08	0.06	0.003
Chatham Centre Roadside	29/04/2014	10.06	10.07	0.01	0.002
Chesterfield Roadside	28/04/2014	10.00	10.06	0.06	0.003
Glasgow Kerbside	25/04/2014	10.03	10.05	0.03	0.002
Grangemouth	22/04/2014	10.05	9.93	0.12	0.004
Haringey Roadside	16/04/2014	10.12	10.13	0.00	0.002
Leamington Spa	15/04/2014	10.04	9.99	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.

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Certificate Number: 2964

0401

Site	Date of measurement	Flow A (mlmin-^{1})	Flow B (mlmin^{-1})	Difference (mlmin^{-1})	Uncertainty (mlmin^{-1})
Leeds Centre	14/04/2014	10.25	10.30	0.04	0.003
Liverpool Speke	08/04/2014	9.96	9.96	0.00	0.002
London Bloomsbury	14/04/2014	10.10	10.04	0.06	0.003
Manchester Piccadilly	01/04/2014	9.91	9.89	0.02	0.002
Middlesbrough	08/04/2014	10.14	10.11	0.02	0.002
Newcastle Centre	09/04/2014	10.20	10.17	0.04	0.003
Newport	01/04/2014	10.01	10.02	0.00	0.002
Norwich Lakenfields	08/04/2014	10.03	10.02	0.02	0.002
Nottingham Centre	09/04/2014	9.98	9.96	0.02	0.002
Oxford Centre Roadside	03/04/2014	10.19	10.20	0.00	0.002
Oxford St Ebbes	03/04/2014	10.11	10.14	0.04	0.003
Scunthorpe Town	14/04/2014	10.24	10.27	0.03	0.003
Sheffield Devonshire Green	29/04/2014	10.05	10.07	0.03	0.002
Southampton Centre	10/04/2014	10.06	10.06	0.00	0.002
Stockton-on-Tees Eaglescliffe	09/04/2014	10.10	9.98	0.12	0.004
Stoke-on-Trent Centre	30/04/2014	10.01	10.04	0.03	0.002
Tower Hamlets Roadside	13/03/2014	9.98	9.99	0.01	0.002
York Bootham	15/04/2014	10.26	10.27	0.02	0.002
York Fishergate	15/04/2014	10.24	10.15	0.09	0.004

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^{o}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 4

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

Figure 18 Auchencorth Moss 1,3-Butadiene hourly mean concentrations 2013

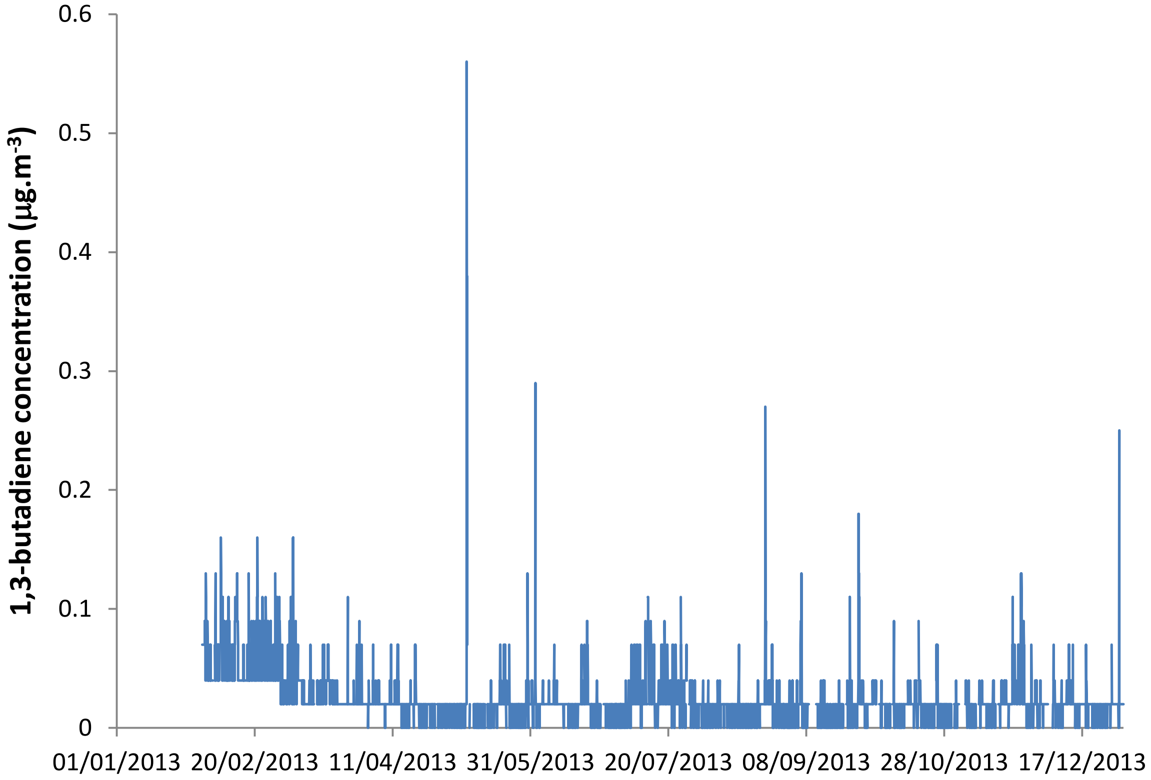


Figure 19 Auchencorth Moss Benzene hourly mean concentrations 2013

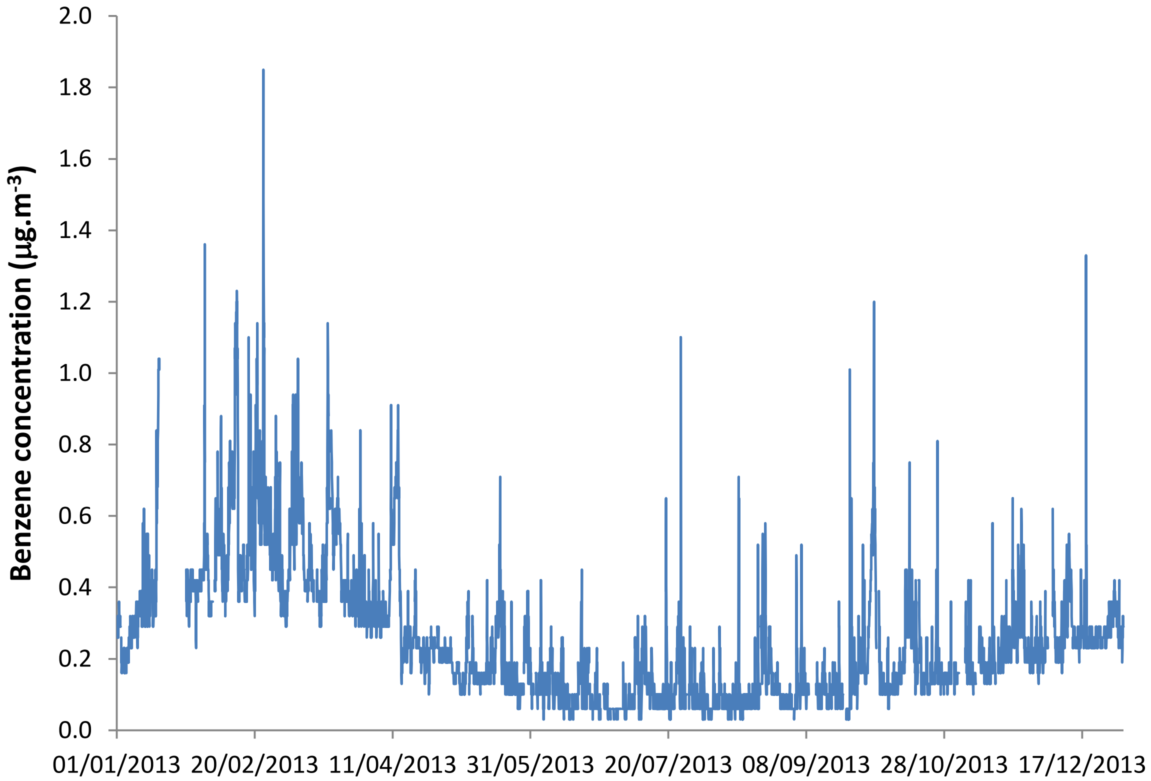


Figure 20 Harwell 1,3-Butadiene hourly mean concentrations 2013

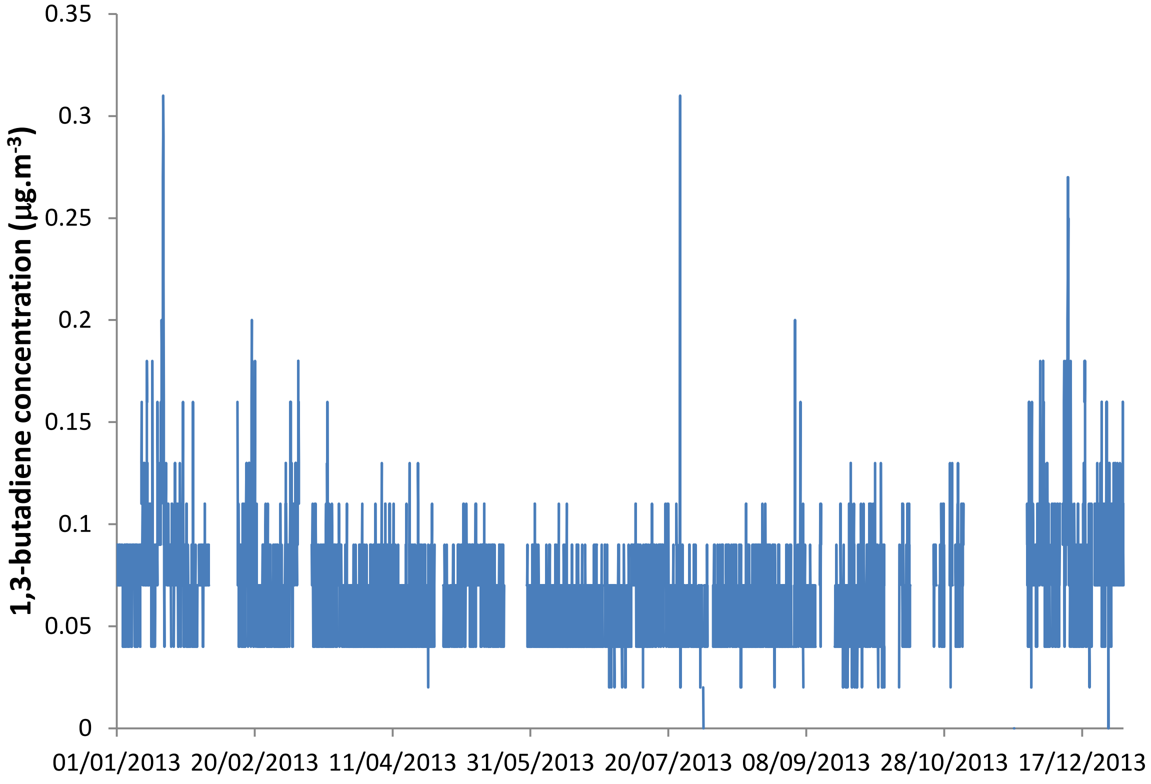


Figure 21 Harwell Benzene hourly mean concentrations 2013

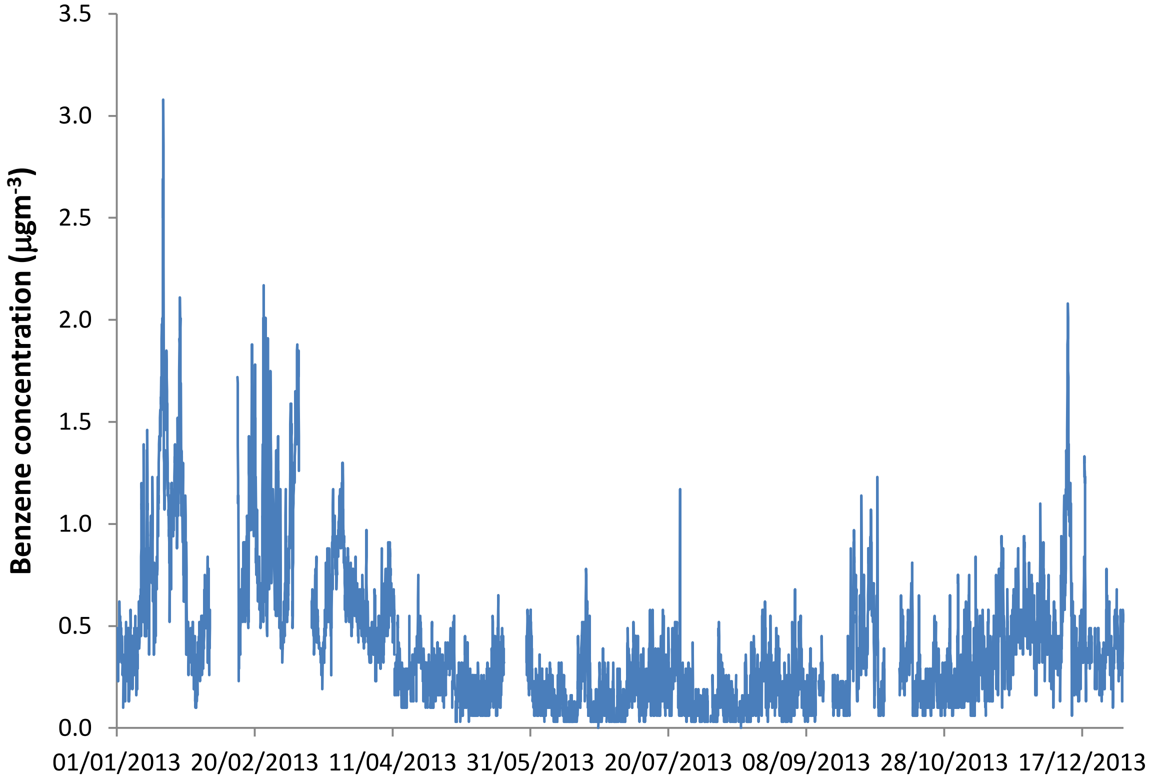


Figure 22 London Eltham 1,3-Butadiene hourly mean concentrations 2013

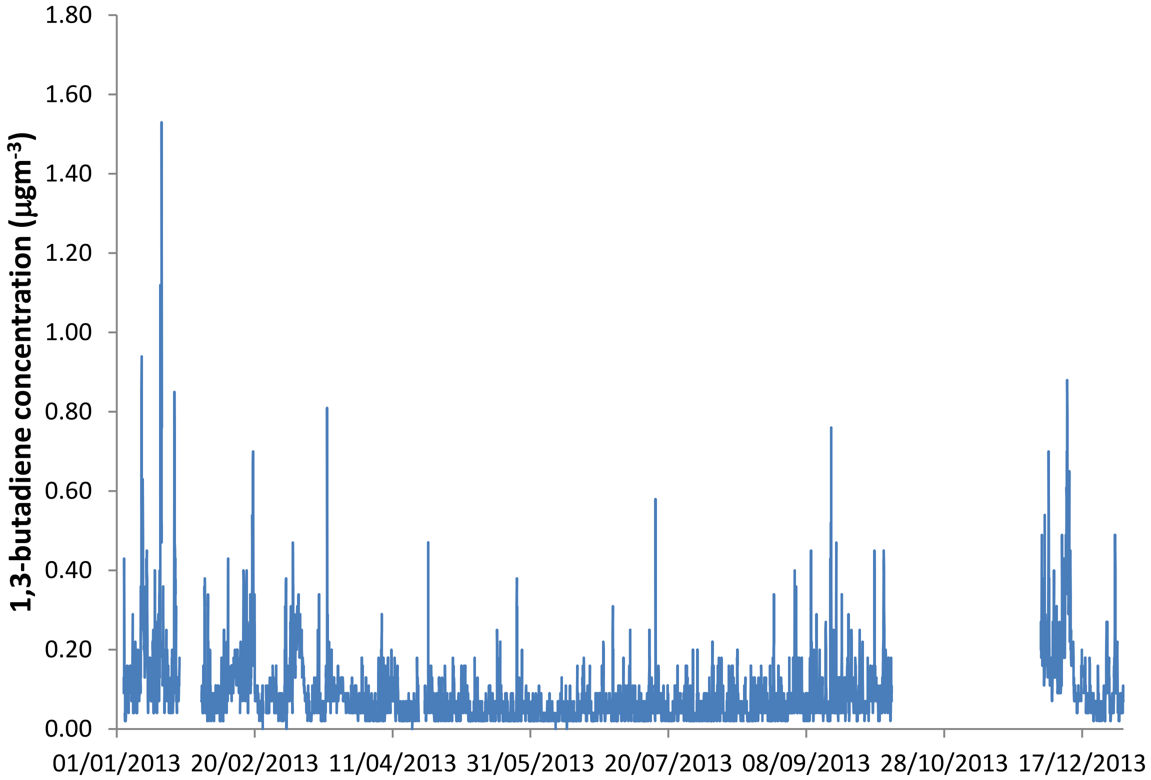


Figure 23 London Eltham Benzene hourly mean concentrations 2013

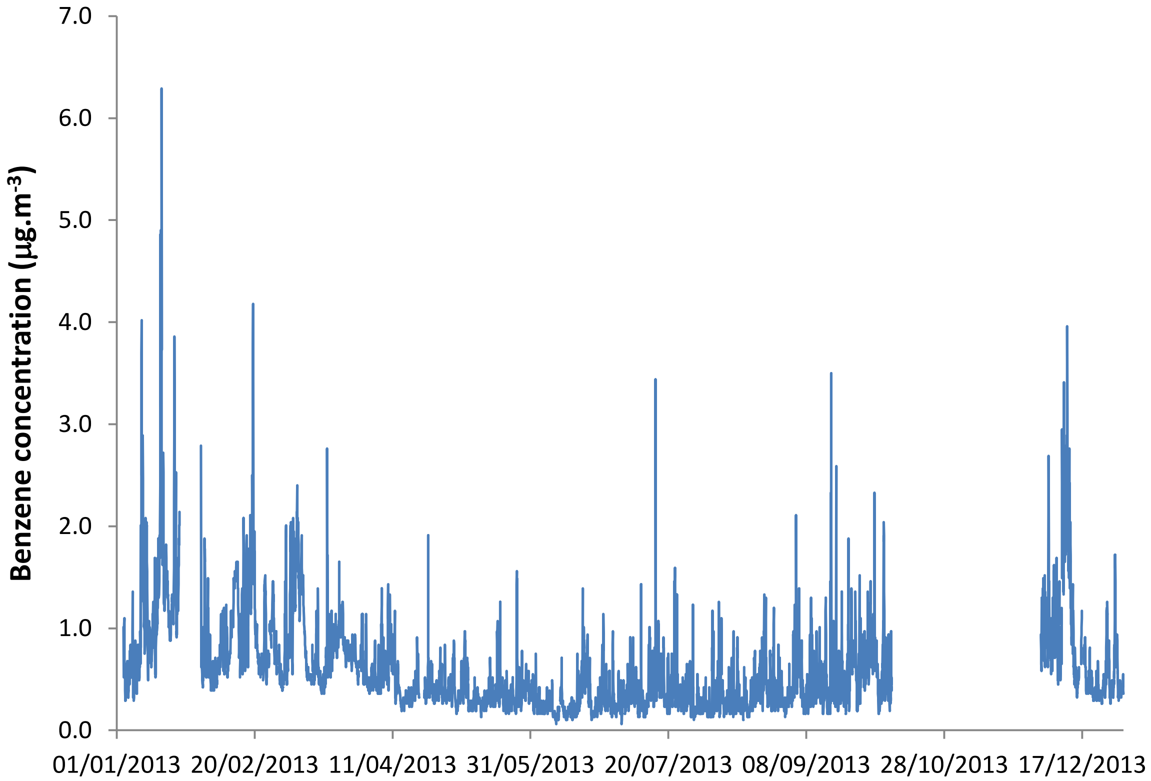


Figure 24 London Marylebone Road 1,3-Butadiene hourly mean concentrations 2013

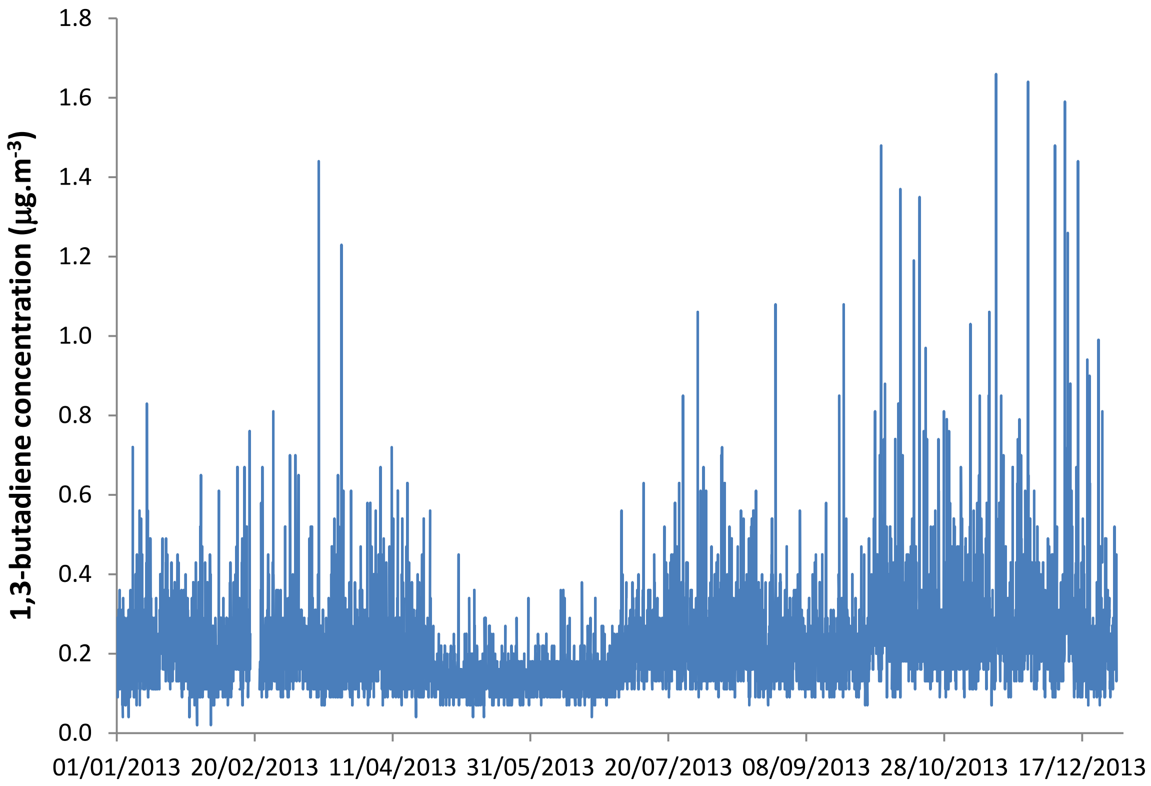
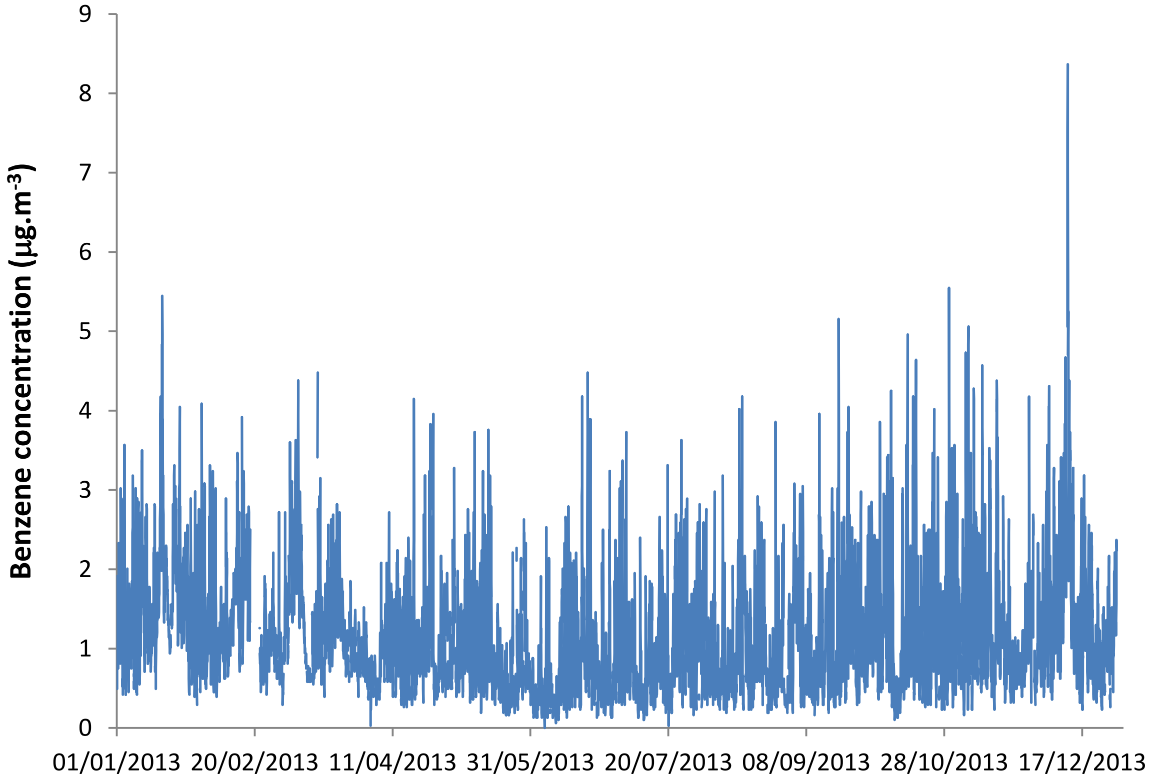


Figure 25 London Marylebone Road Benzene hourly mean concentrations 2013



Non Automatic Fortnightly Mean Graphs for Benzene 2013

Figure 25 to 58 show 2013 annual timeseries plots at each of the non-automatic sites. We would expect higher benzene measurements in winter. Middlesbrough and Scunthorpe Town have local industrial sources of benzene where elevated levels of benzene can be seen at varying times of the year. It's unclear why Barnsley, Stoke, Stockton and Nottingham show elevated levels in summer. A spike in November can be seen for many sites, this could be as a result of bonfire night (5th November) and is most significant at Bath Roadside.

Figure 26 Barnsley Gawber Non Automatic fortnightly Benzene 2013

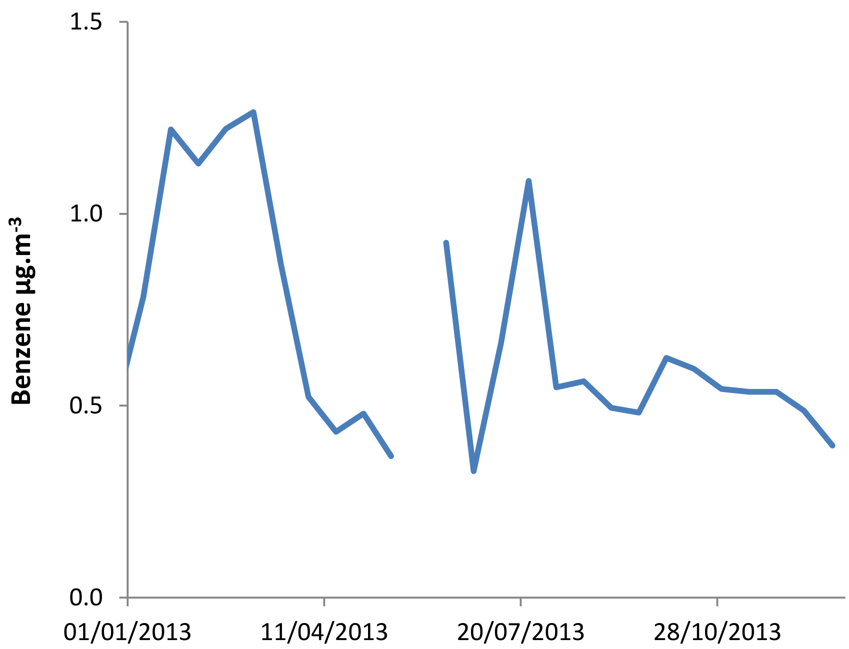


Figure 27 Bath Roadside Non Automatic fortnightly benzene 2013

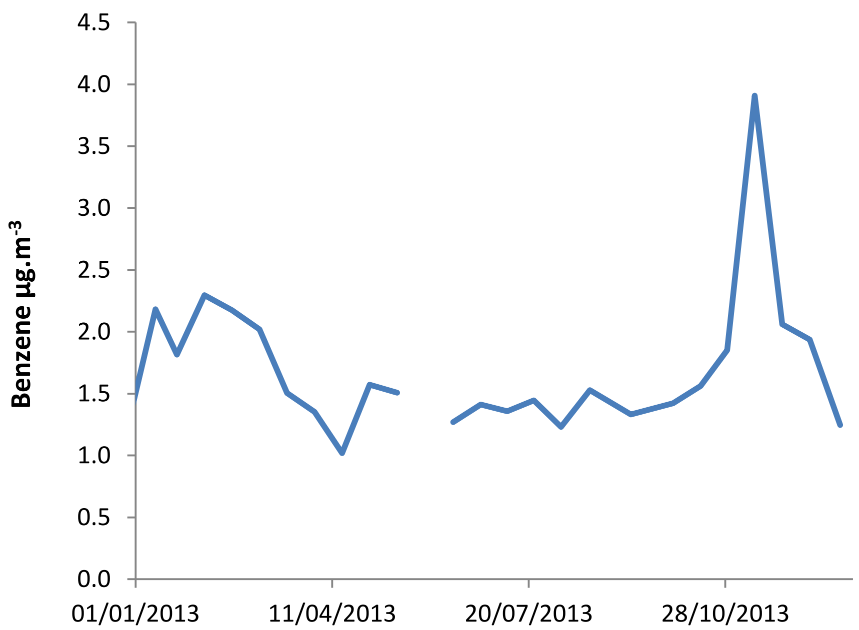


Figure 28 Belfast Centre Non Automatic fortnightly Benzene 2013

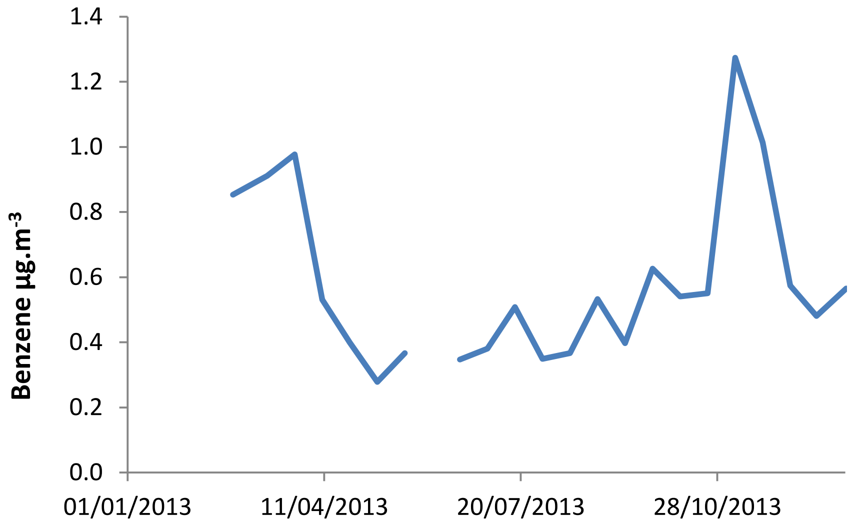


Figure 29 Birmingham Acocks Green Non Automatic fortnightly Benzene 2013

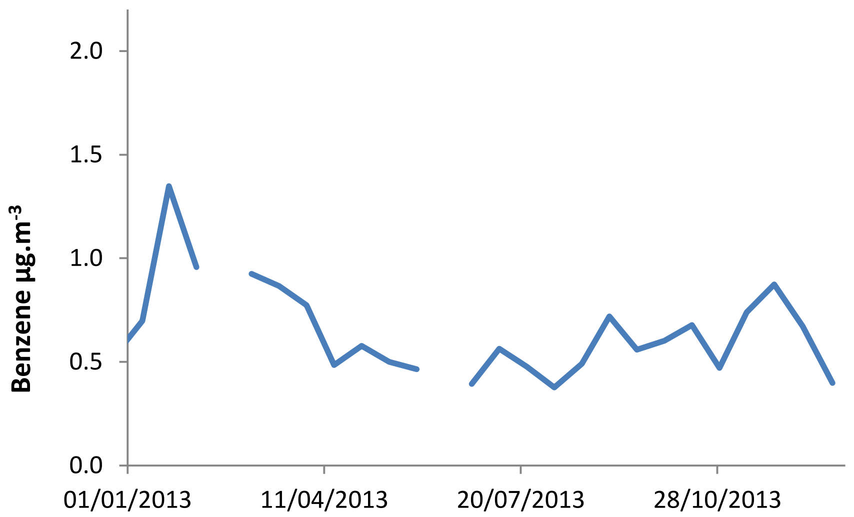


Figure 30 Birmingham Tyburn Roadside Non Automatic fortnightly Benzene 2013

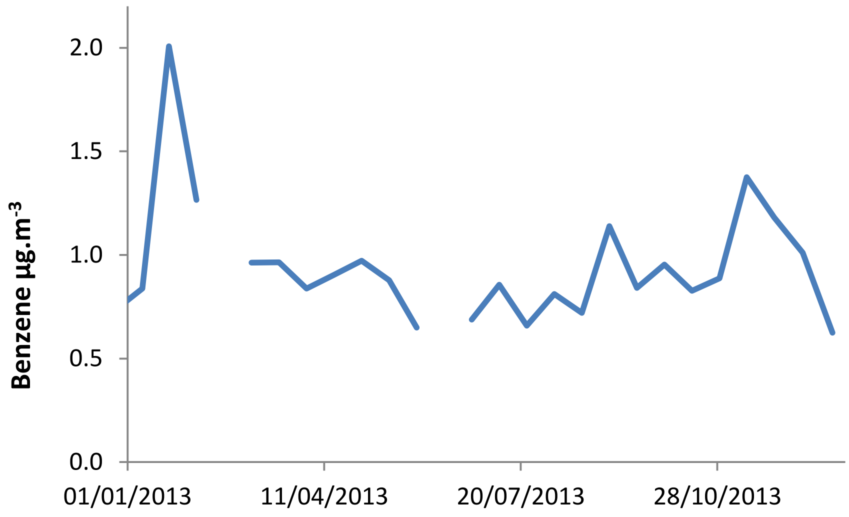


Figure 31 Bury Roadside Non Automatic fortnightly Benzene 2013

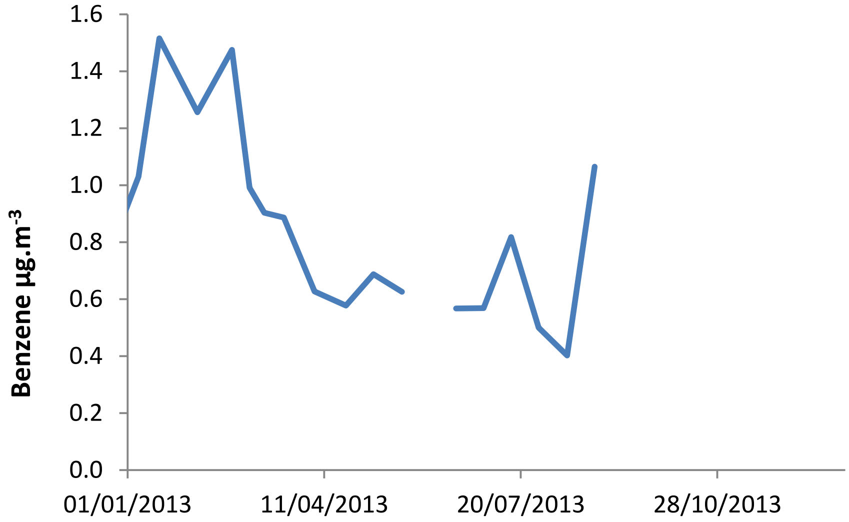


Figure 32 Cambridge Roadside Non Automatic fortnightly Benzene 2013

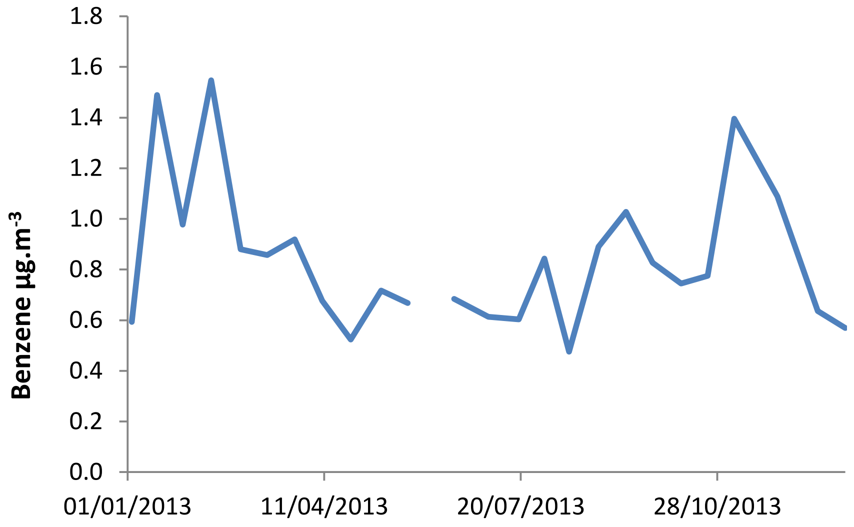


Figure 33 Camden Kerbside Non Automatic fortnightly Benzene 2013

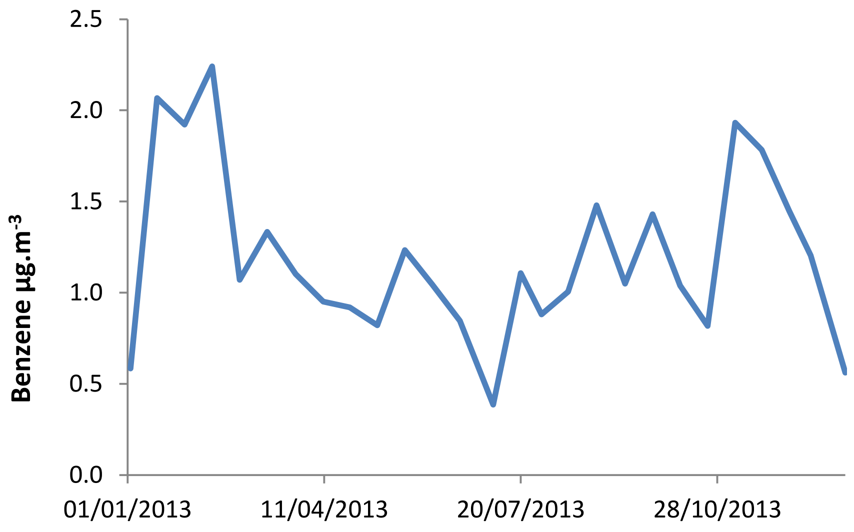


Figure 34 Carlisle Roadside Non Automatic fortnightly Benzene 2013

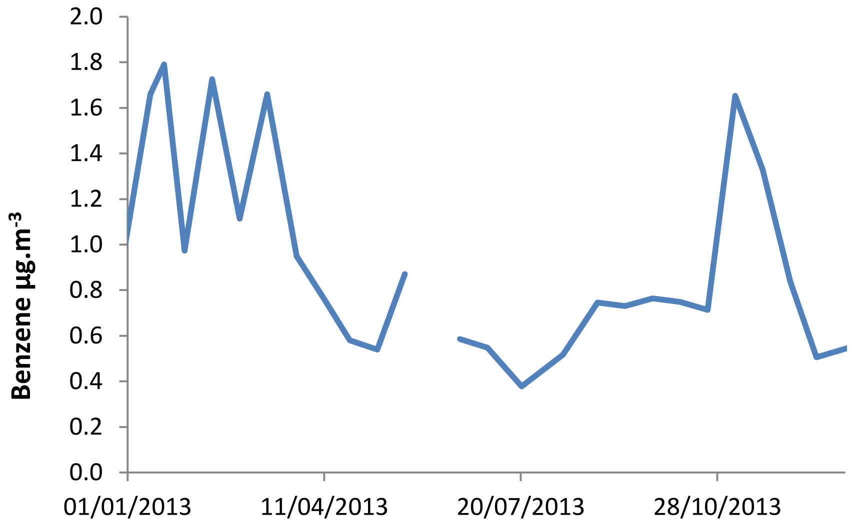


Figure 35 Chatham Roadside Non Automatic fortnightly Benzene 2013

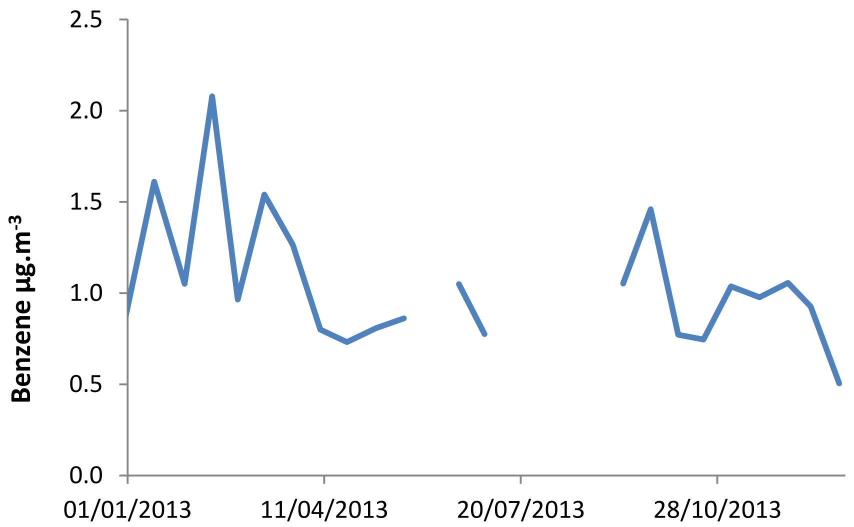


Figure 36 Chesterfield Roadside Non Automatic fortnightly Benzene 2013

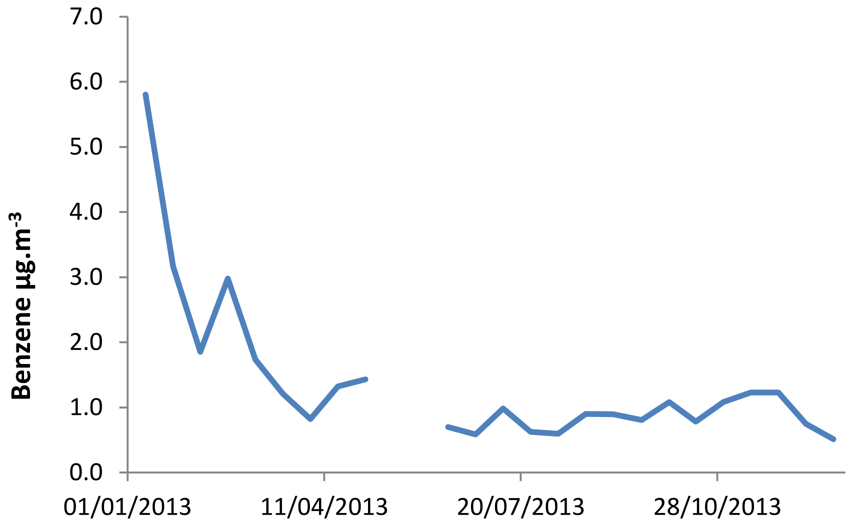


Figure 37 Glasgow Kerbside Non Automatic fortnightly Benzene 2013

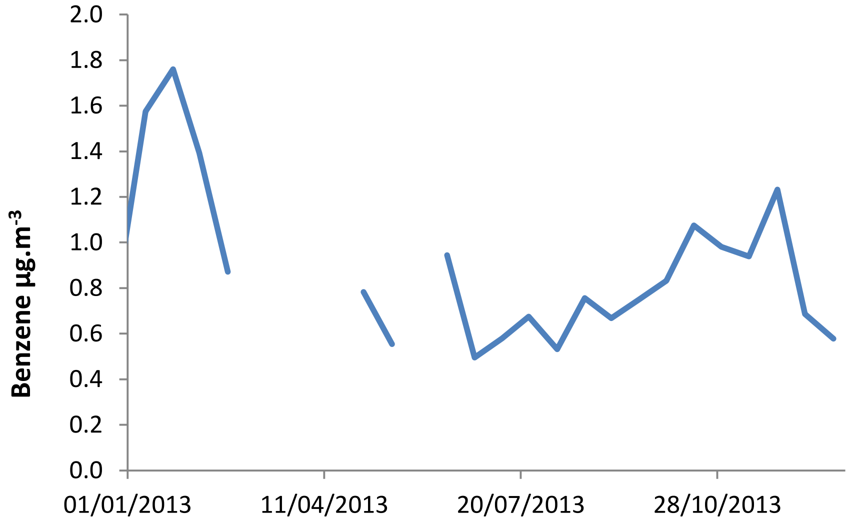


Figure 38 Grangemouth Non Automatic fortnightly Benzene 2013

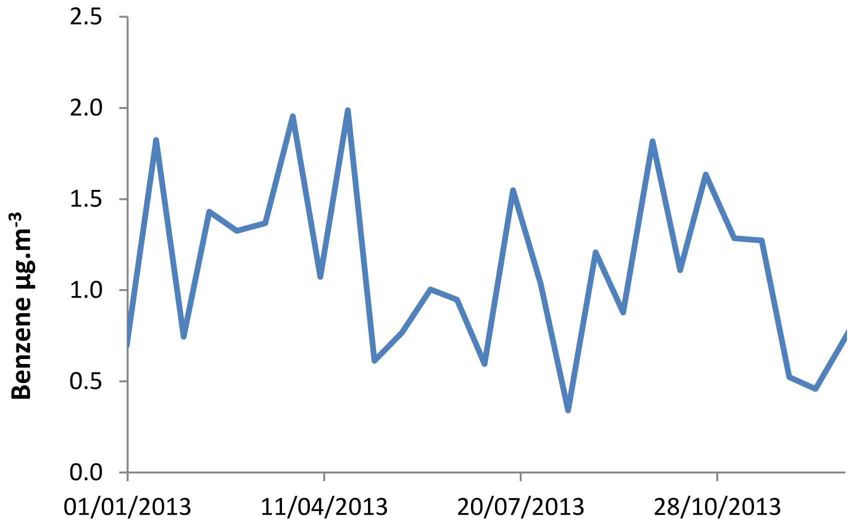


Figure 39 Haringey Roadside Non Automatic fortnightly Benzene 2013

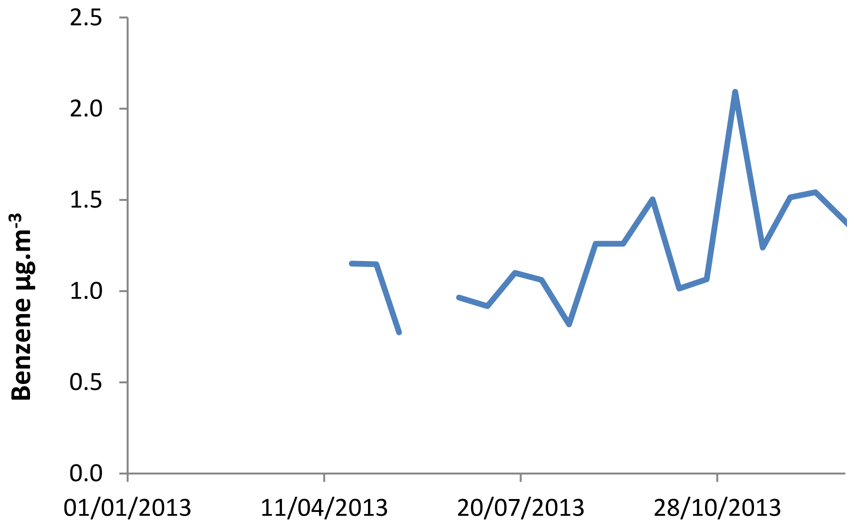


Figure 40 Leamington Spa Non Automatic fortnightly Benzene 2013

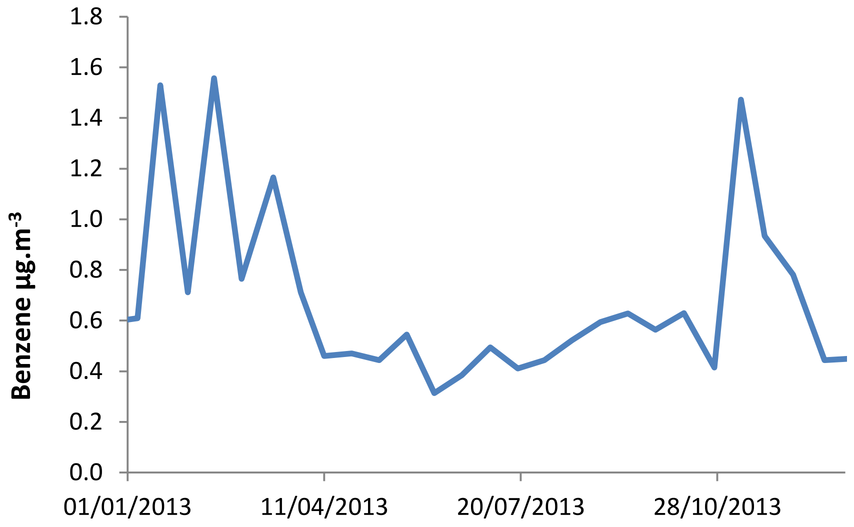


Figure 41 Leeds Centre Non Automatic fortnightly Benzene 2013

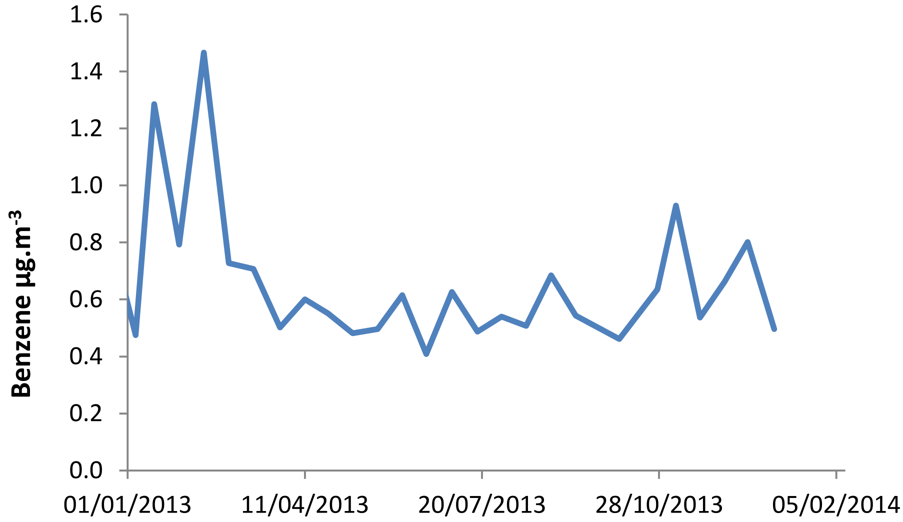


Figure 42 Liverpool Speke Non Automatic fortnightly Benzene 2013

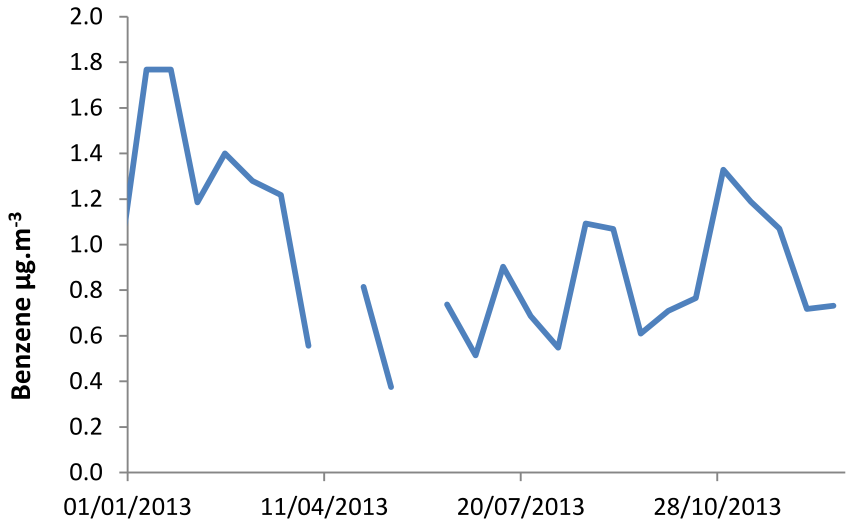


Figure 43 London Bloomsbury Non Automatic fortnightly Benzene 2013

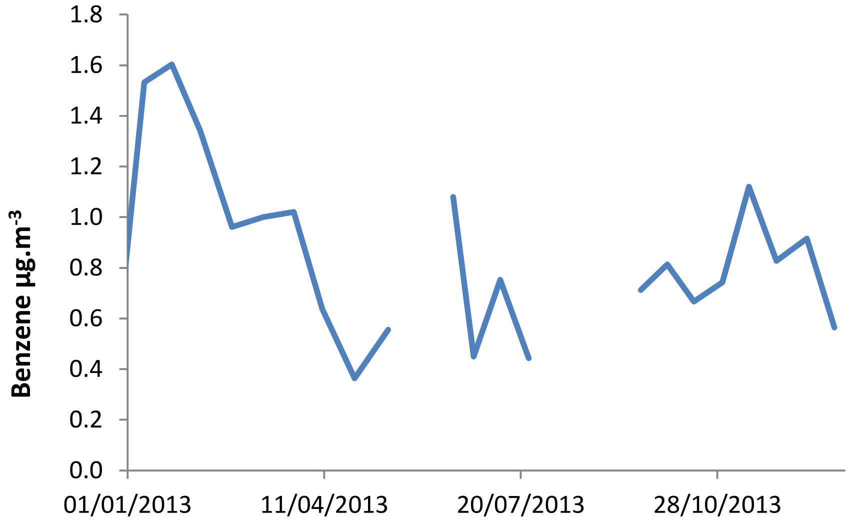


Figure 44 Manchester Piccadilly Non Automatic fortnightly Benzene 2013

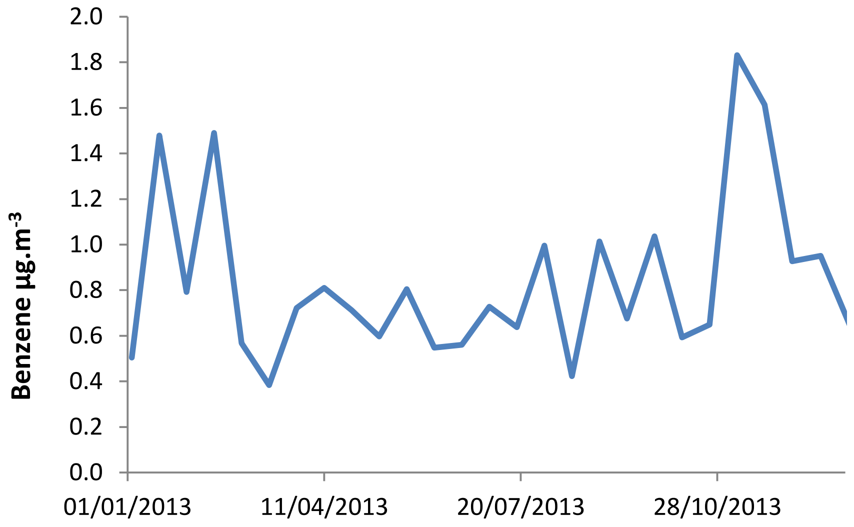


Figure 45 Middlesbrough Centre Non Automatic fortnightly Benzene 2013

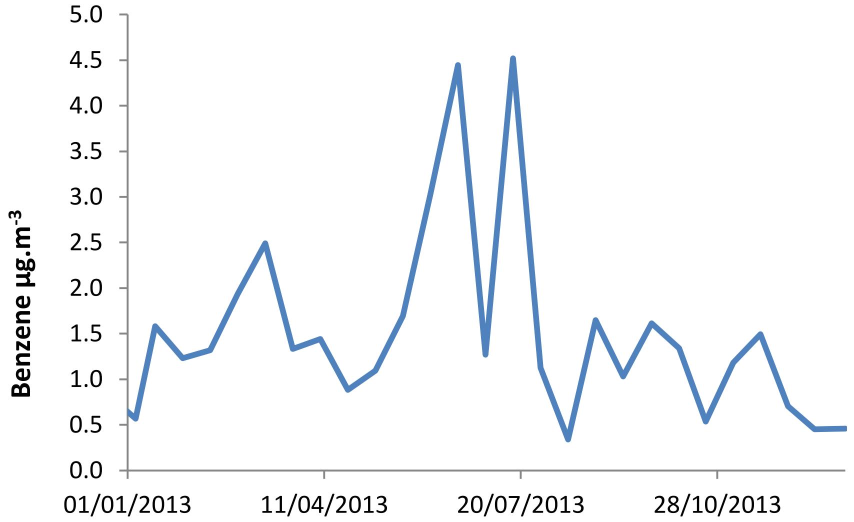


Figure 46 Newcastle Centre Non Automatic fortnightly Benzene 2013

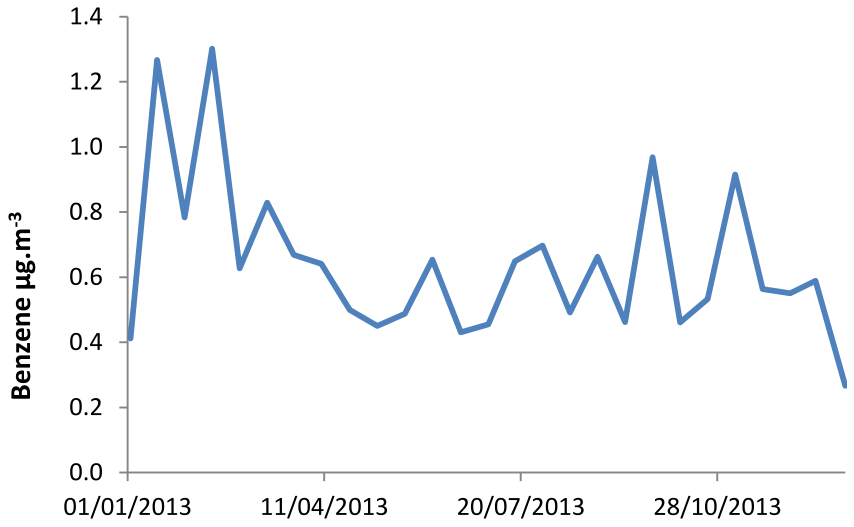


Figure 47 Newport Non Automatic fortnightly Benzene 2013

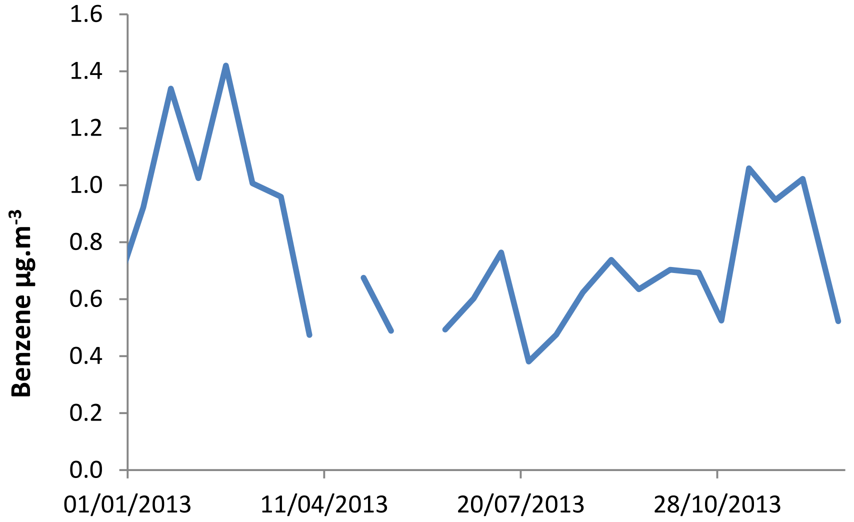


Figure 48 Norwich Lakenfields Non Automatic fortnightly Benzene 2013

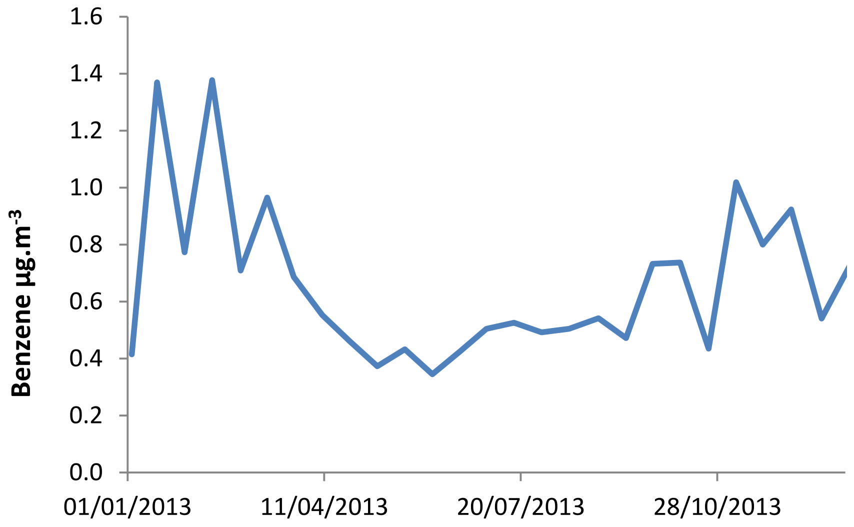


Figure 49 Nottingham Centre Non Automatic fortnightly Benzene 2013

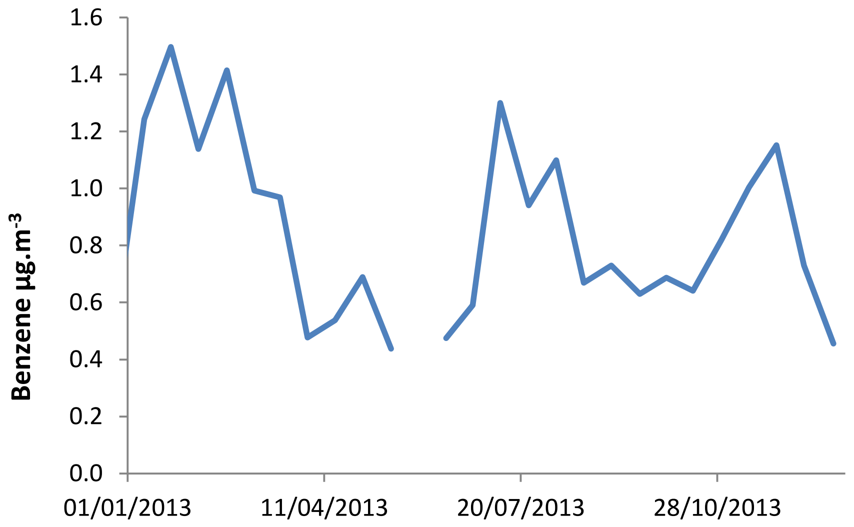


Figure 50 Oxford Centre Roadside Non Automatic fortnightly Benzene 2013

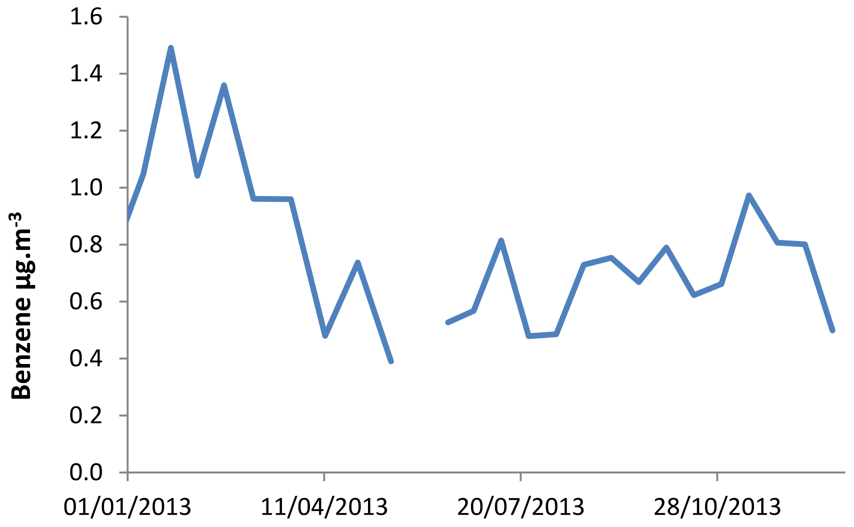


Figure 51 Oxford St Ebbes Non Automatic fortnightly Benzene 2013

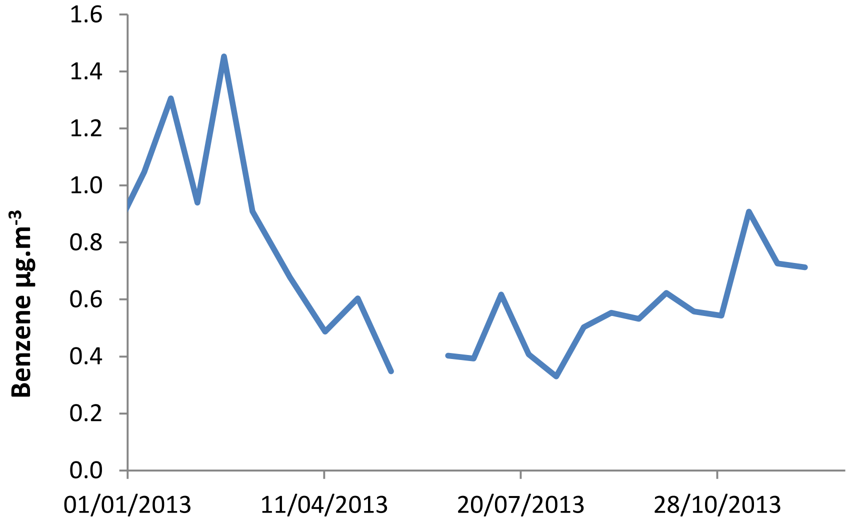


Figure 52 Scunthorpe Town Non Automatic fortnightly Benzene 2013

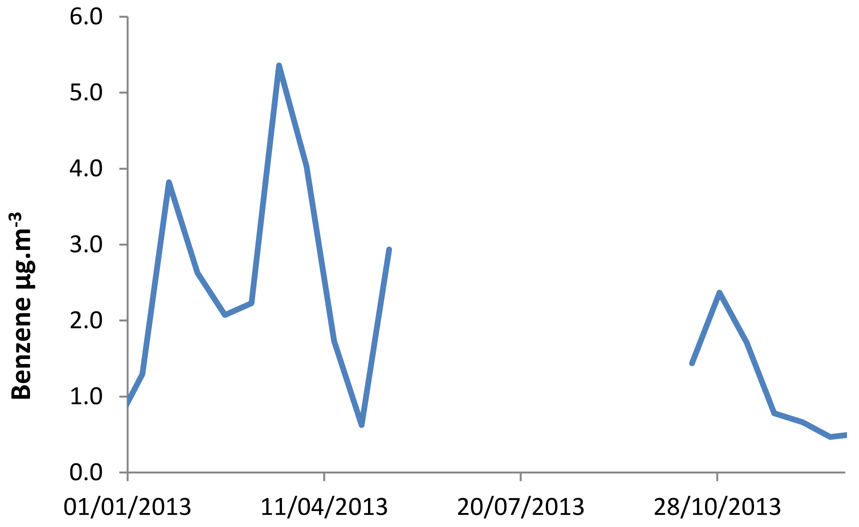


Figure 53 Sheffield Centre Non Automatic fortnightly Benzene 2013

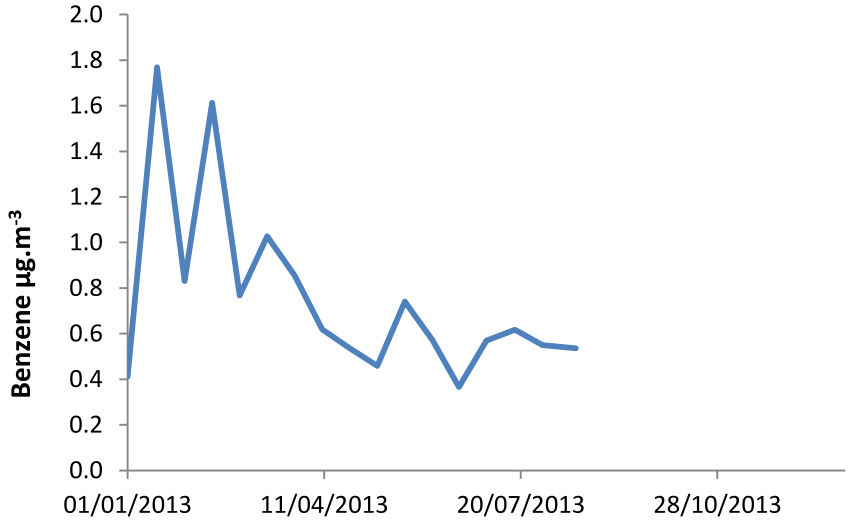


Figure 54 Sheffield Devonshire Green Non Automatic fortnightly Benzene 2013

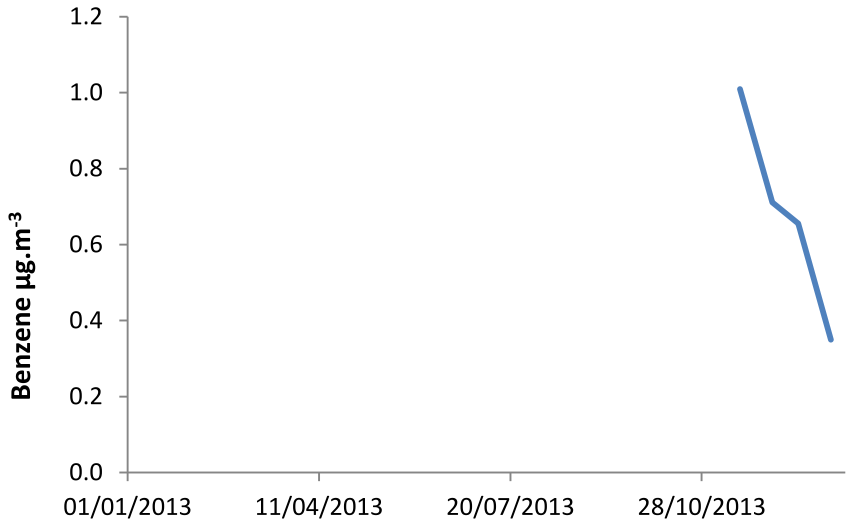


Figure 55 Southampton Non Automatic fortnightly Benzene 2013

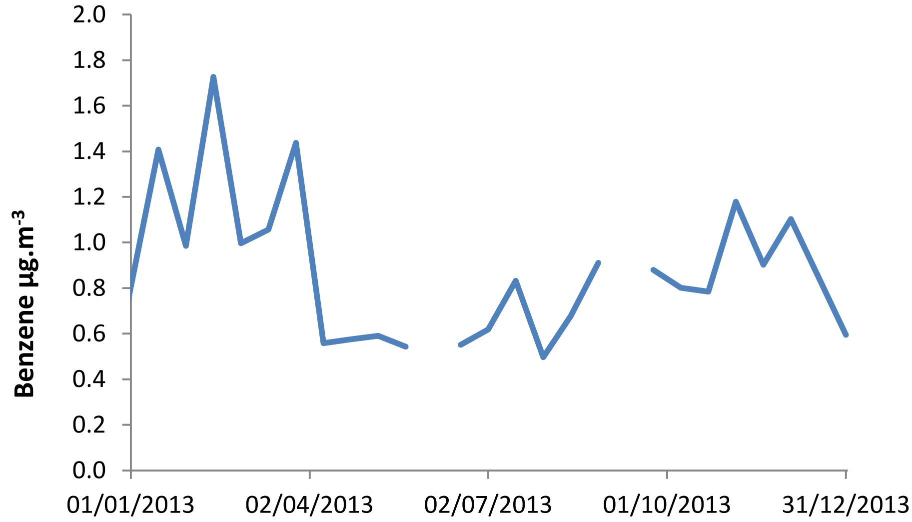


Figure 56 Stockton-on-Tees Eaglescliffe Non Automatic fortnightly Benzene 2013

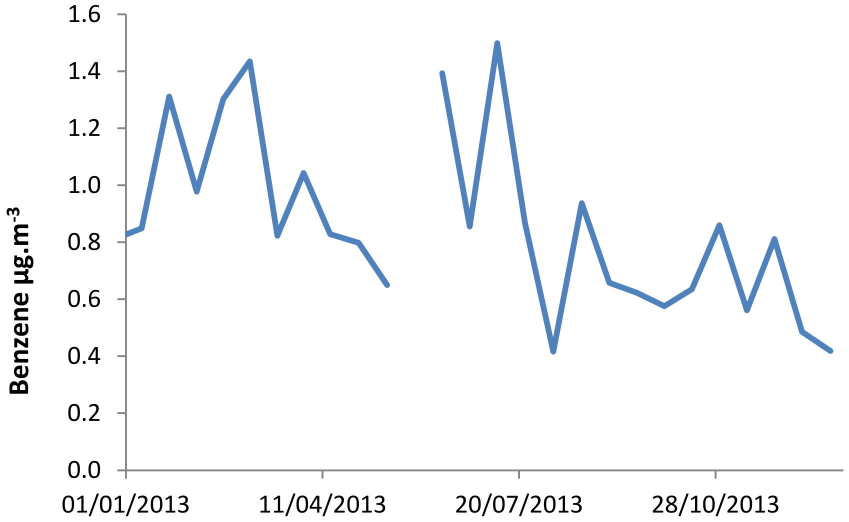


Figure 57 Stoke-on-Trent Centre Non Automatic fortnightly Benzene 2013

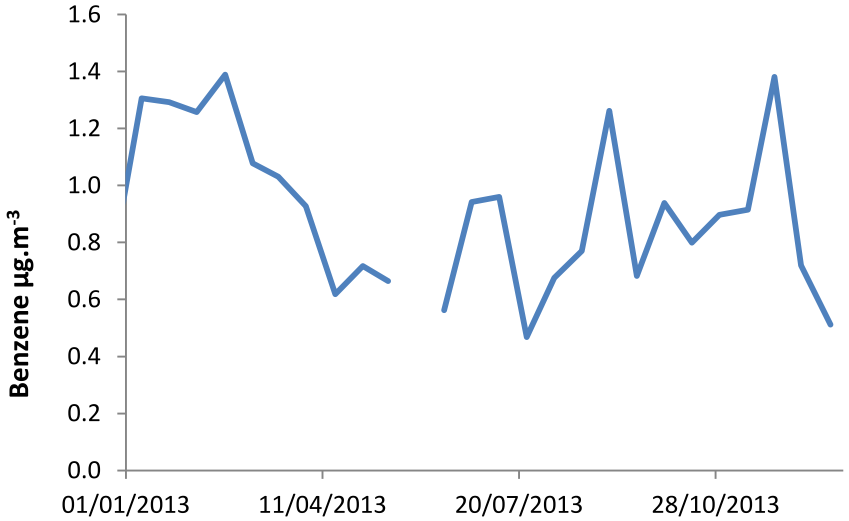


Figure 58 York Bootham Non Automatic fortnightly Benzene 2013

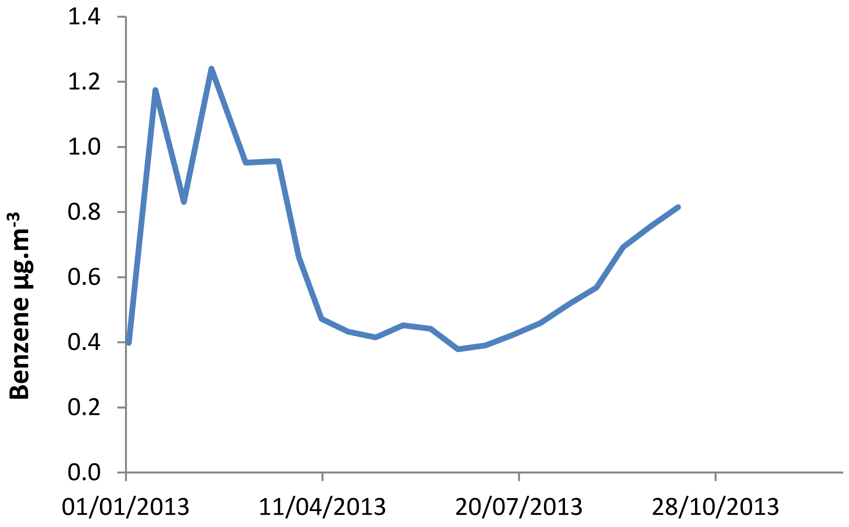
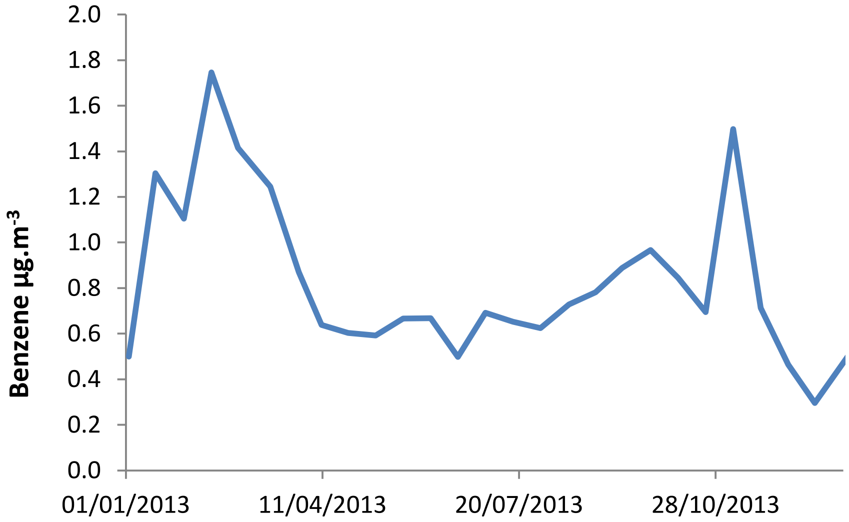


Figure 59 York Fishergate Non Automatic fortnightly Benzene 2013



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