UK Hydrocarbon Network

Annual Report for 2014

Report for Defra and the Devolved Administrations

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Note: In November 2012, Ricardo plc acquired the assets and goodwill of AEA Technology plc and formed a new company, Ricardo-AEA Ltd. The entire capability and resources previously represented by AEA Technology plc were transferred to Ricardo-AEA, as were all employees. Consequently, where specific projects or track record referenced in this proposal were undertaken and completed prior to the acquisition, for contractual reasons, these continue to be identified as AEA Technology plc.

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 5 µg.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 operation from January to December 2014 was 93.1%. The annual mean concentration across all non-automatic measurement sites in the UK was 0.92 µg.m^{-3}.

The mean data capture for benzene measured by the automatic hydrocarbon network in 2014 was 76%.The annual mean across all automatic measurement sites in the UK was 0.6 µg.m^{-3}.

In 2014 none of the automatic and non-automatic monitoring sites in the UK exceeded the 5 µg.m^{-3} annual mean Limit Value or the Upper Assessment Threshold of 3.5 µg.m^{-3} for benzene set out in the AQD. The site located within Scunthorpe, classified as an industrial site, exceeds the Lower Assessment Threshold of 2 µg.m^{-3} defined within the directive with an annual mean of 2.3 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 2014.

Long term trends form 2000 to 2010 show benzene concentrations have declined significantly, this demonstrates that motor vehicle exhaust catalysts and evaporative canisters have effectively and efficiently controlled vehicular emissions of hydrocarbons in the UK. This implies reduced health effects to individuals living in the UK as a result of long term exposure to these pollutants. Since 2010, concentrations have remained relatively stable.

[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

Table of contents

1 Introduction

This report provides a summary of the site management and data produced in 2014 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) monitoring stations.

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 and was re-assessed in 2011 [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/.

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.

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):

[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

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).

Table 2 European Benzene 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 <2% 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 at least one urban or suburban area 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 3. 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] (DD4). 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

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. This methodology currently produces measurements as nominal fortnightly averages at 34 sites.

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 at 10 ml/min for 8 minutes 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 of 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, passive diffusion tubes were also used to measure 1,3-butadiene 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 with passive diffusion tubes.

Currently, 1,3 butadiene is only measured using the automatic method.

1.3.2 Automatic Hydrocarbon Monitoring

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 and in 2014 there were four sites exceeding the single site requirement of the Directive, measuring the following 29 species by automatic gas chromatographs (Table 3).

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

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	

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. During 2014, 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.

2 Site Management

2.1 Network sites during 2014

2.1.1 Non-Automatic Hydrocarbon Network

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

Figure 1 Map of Non-Automatic Hydrocarbon Network sites in 2014

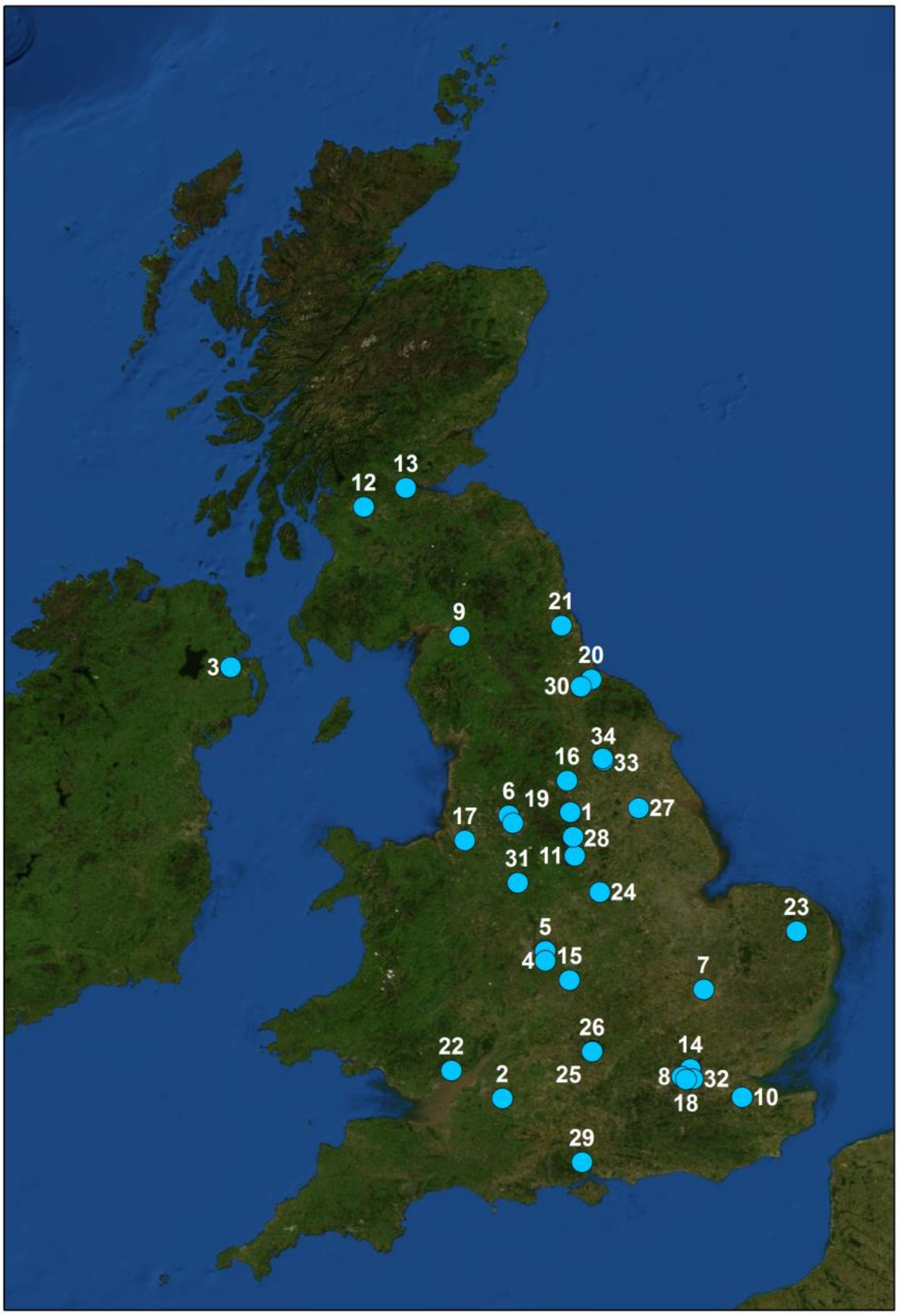


Table 4 Non-Automatic Hydrocarbon Network sites in 2014

	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 Whitefield Roadside	Urban Traffic	Greater Manchester Urban Area	380637, 406974	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 Traffic	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 Industrial	Teesside Urban Area	450480, 519632	Middlesbrough BC

	Site	Classification	Zone	Grid Ref Easting / Northing	Local Site Operator
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
28	Sheffield Devonshire Green	Urban Background	Sheffield Urban Area	434816, 386990	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/networks/search-site-info

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 2014

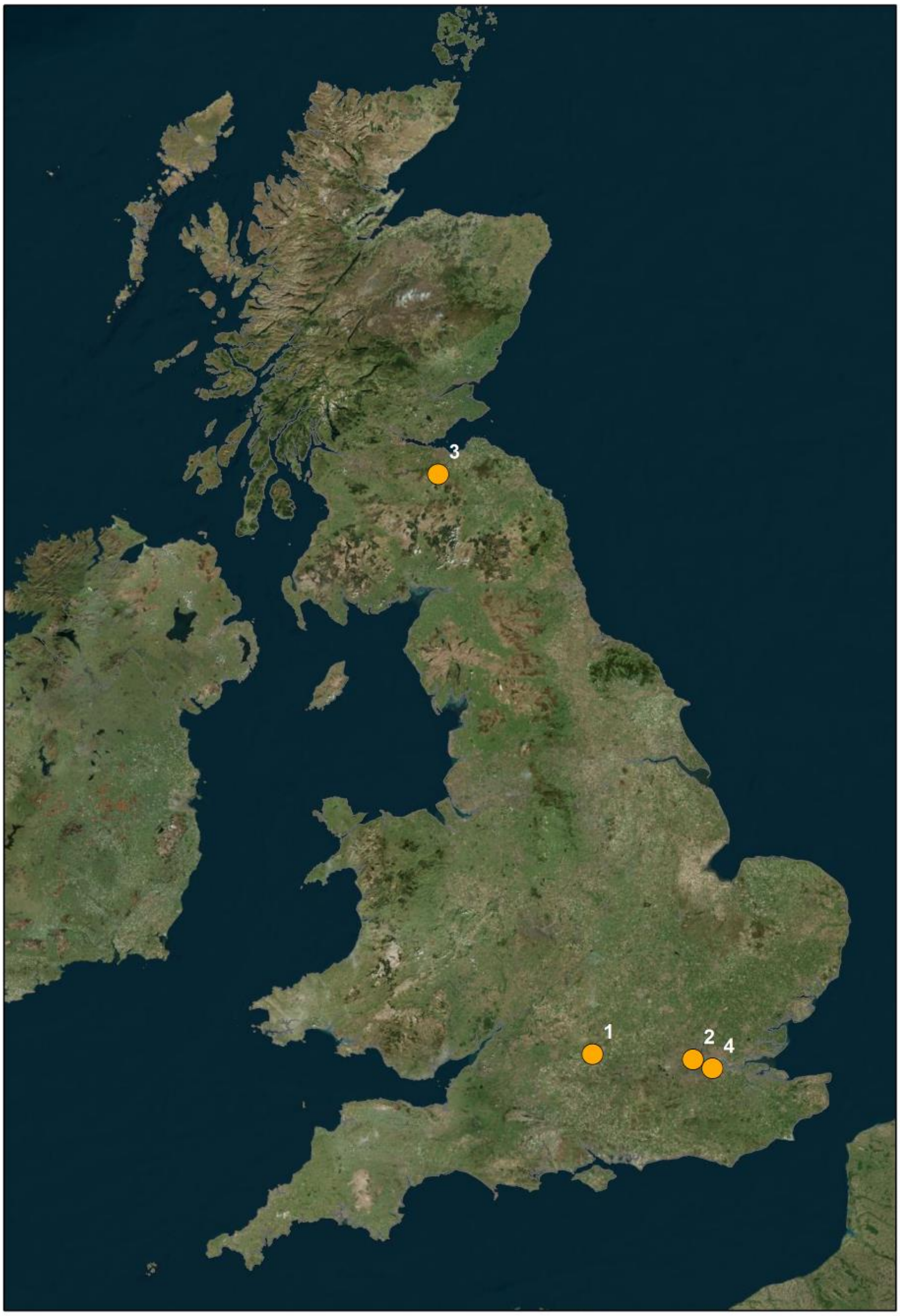


Table 5 Automatic Hydrocarbon Network sites in 2014

	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

The London Eltham site fulfils requirements of DD4 to monitor ozone precursors at an urban background location, Marylebone Road measurements are made to inform research undertaken at the site with regard to roadside emissions and the two rural background sites support the European Monitoring and Evaluation Programme[6] (EMEP) and provide information regarding concentrations at rural locations in the UK.

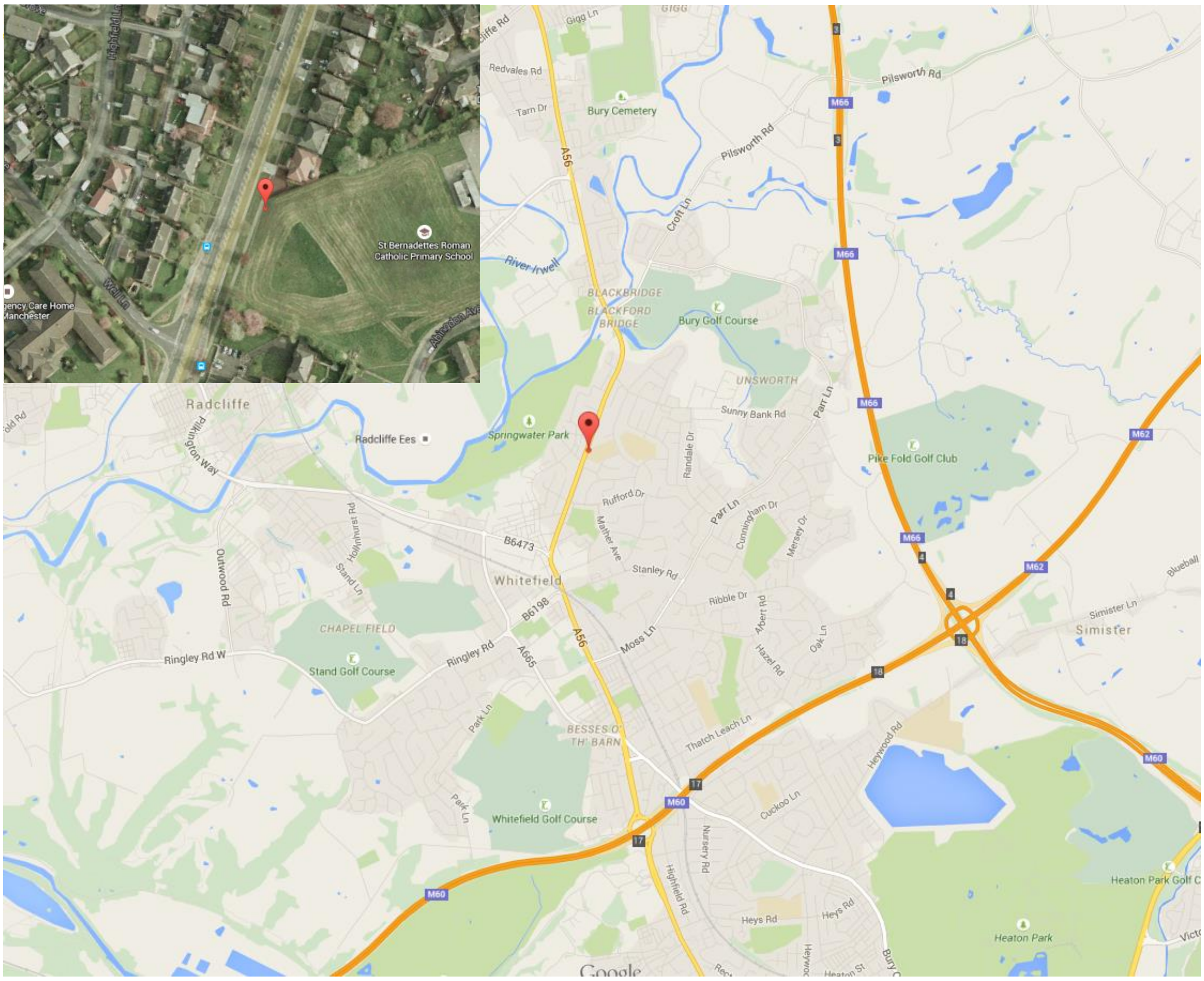
[6] http://www.emep.int/

2.2 Site Changes in 2014

2.2.1 Bury Whitefield Roadside

Following the monitoring regime assessment, the Bury Roadside site was removed on 10th September 2013 due to the site not meeting the strict siting criteria of the Directive and replaced with a new site at Bury Whitefield Roadside (Figure 3 Location of the Bury Whitefield Roadside Site), the first benzene sample started on 11th July 2014 when the new AURN enclosure had been re-commissioned.

Figure 3 Location of the Bury Whitefield Roadside 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 benzene samplers were audited in October 2013, April 2014, October 2014 and April 2015. All of these measurements have been used to calculate sample volumes for the 2014 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.

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
    - Leak check all pneumatic systems
    - Replace all consumables such as filters, gaskets
    - Replace the cold trap
    - Check and condition columns, trimming or replacing as necessary
    - Checking and replacing transfer line if necessary
    - Checking and replacing fused silica lines if necessary

The Central Management and Co-ordination Unit (CMCU) provides an annual reference gas audit in addition to the automatic on site calibrations; these audits use the sample line as opposed to the analyser calibrant port. The sample line is replaced annually.

The operational performance and stability of these types of automated chromatography systems can be affected for a period of time following ad-hoc repairs or power cuts. This means that an analyser that was only off for an hour might produce poor chromatography for a few days subsequent to that issue. This data will not be representative of ambient concentrations at the monitoring location. The ratification team will remove any such erroneous data up until the period when the data demonstrates that the instrument has stabilised and is producing meaningful data.

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 2014

3.1 Comparison with Limit Values and Objectives

The annual mean concentration of benzene and 1,3 butadiene over the calendar year 2014 are provided in Table 6 and Table 8, alongside the data capture statistics. Tables 7, 9, 10,11 and 12 detail reasons behind data loss or data removal. Data capture for non-automatic sites where measurements either started or finished during the year are highlighted in red and will not contribute to the total data capture annual mean for the network.

Annual time weighted mean 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 2014

Site	Annual Mean Benzene (µg.m^{-3})	Maximum Fortnightly Result (µg.m^{-3})	Minimum Fortnightly Result (µg.m^{-3})	Data capture
Barnsley Gawber	0.65	1.3	0.26	99.95%
Bath Roadside	1.6	3.9	0.58	99.97%
Belfast Centre	0.62	1.3	0.16	99.98%
Birmingham Acocks Green	0.65	1.3	0.31	76.59%
Birmingham Tyburn	1.5	2.0	0.94	15.50%
Birmingham Tyburn Roadside	1.1	2.0	0.51	99.96%
Bury Whitefield Roadside	0.77	1.5	0.33	47.56%
Cambridge Roadside	0.84	1.5	0.45	99.98%
Camden Kerbside	1.3	2.2	0.56	60.20%
Carlisle Roadside	0.86	1.8	0.37	87.15%
Chatham Roadside	0.9	2.1	0.51	99.98%
Chesterfield Roadside	0.84	5.8	0.41	92.44%
Glasgow Kerbside	0.87	1.8	0.42	94.79%
Grangemouth	0.97	2.0	0.36	99.97%
Haringey Roadside	1.2	2.1	0.58	99.98%
Leamington Spa	0.65	1.6	0.29	96.07%
Leeds Centre	0.7	1.5	0.29	96.14%
Liverpool Speke	1	1.8	0.3	86.61%
London Bloomsbury	0.84	1.6	0.4	99.95%
Manchester Piccadilly	0.76	1.8	0.23	99.97%

Site	Annual Mean Benzene (µg.m^{-3})	Maximum Fortnightly Result (µg.m^{-3})	Minimum Fortnightly Result (µg.m^{-3})	Data capture
Middlesbrough	1.4	4.5	0.39	73.14%
Newcastle Centre	0.66	1.6	0.27	71.75%
Newport	0.72	1.4	0.36	99.99%
Norwich Lakenfields	0.62	1.4	0.24	96.16%
Nottingham Centre	0.77	1.5	0.35	96.42%
Oxford Centre Roadside	0.77	1.5	0.39	80.78%
Oxford St Ebbes	0.6	1.5	0.27	99.58%
Scunthorpe Town	2.29	5.4	0.51	99.98%
Sheffield Devonshire Green	0.68	1.8	0.28	95.86%
Southampton Centre	0.83	1.5	0.37	99.96%
Stockton-on-Tees Eaglescliffe	0.96	1.7	0.41	96.08%
Stoke-on-Trent Centre	0.74	1.5	0.4	95.88%
Tower Hamlets Roadside	1.2	1.4	0.75	80.16%
York Bootham	0.55	2.2	0.2	92.38%
York Fishergate	0.89	1.2	0.4	88.84%

Table 7 Non-Automatic Sampler Faults and failures in 2014

Site	Start	End	Days	Reason
Camden Kerbside	23/04/2014	01/09/2014	131	Site audit measurement was low, no accurate sample volume could be identified for the period
Carlisle Roadside	05/02/2014	05/03/2014	28	Power failure from 09/02/2014 – 03/03/2014, data deemed erroneous at the quality circle
Carlisle Roadside	15/10/2014	03/11/2014	19	Very low analytical results deemed erroneous by the project team at the quality circle
Chesterfield Roadside	04/12/2014	29/01/2015	56	Very low analytical results, sampler fault. Sampler replaced with a spare 20/01/2015
Glasgow Kerbside	14/03/2014	02/04/2014	19	Low concentrations deemed erroneous by project team at the quality circle
Leamington Spa	02/05/2014	16/05/2014	14	Analytical fault, erroneous data removed by project team at the quality circle
Leeds Centre	30/04/2014	14/05/2014	14	Analytical fault, erroneous data removed by project team at the quality circle
Liverpool Speke	24/04/204	12/06/2014	49	Health and safety risk affecting AURN site, no visitors allowed on site for any reason
Middlesbrough	05/08/2014	11/11/2014	98	Sampling fault found at audit, sampler replaced on 07/10/2014. Erroneous data removed at the quality circle
Newcastle Centre	30/04/2014	14/05/2014	14	Analytical fault, erroneous data removed by project team at the quality circle

Site	Start	End	Days	Reason
Norwich Lakenfields	30/04/2014	14/05/2014	14	Analytical fault, erroneous data removed by project team at the quality circle
Nottingham Centre	02/05/2014	15/05/2014	13	Analytical fault, erroneous data removed by project team at the quality circle
Oxford Centre Roadside	21/05/2014	18/06/2014	42	Analytical results were inconsistent, deemed erroneous by the project team at the quality circle[1]
Oxford Centre Roadside	30/07/2014	27/08/2014	28	Analytical results were inconsistent, deemed erroneous by the project team at the quality circle[1]
Sheffield Devonshire Green	29/04/2014	14/05/2014	15	Analytical fault, erroneous data removed by project team at the quality circle
Stockton-on-Tees Eaglescliffe	30/09/2014	14/10/2014	14	Analytical fault, no data provided
Stoke-on-Trent Centre	29/01/2014	12/02/2014	14	Unusually high data, no correlation found with other pollutants, data deemed erroneous by the project team at the quality circle
Tower Hamlets Roadside	09/12/2013	13/03/2014	95	Sampling fault found at audit, data removed by the project team at the quality circle
York Bootham	05/03/1014	19/03/2014	14	Unusually low data, no correlation found with other pollutants, data deemed erroneous by the project team at the quality circle
York Bootham	30/04/2014	14/05/2014	14	Unusually high data, no correlation found with other pollutants, data deemed erroneous by the project team at the quality circle
York Fishergate	30/04/2014	14/05/2014	14	Analytical fault, erroneous data removed by project team at the quality circle
York Fishergate	26/06/2014	23/07/2014	27	Operator error, one tube sent back un-sampled, another sampled twice. Results deemed erroneous by the project team at the quality circle

3.1.2 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	0.35	2.4	98
	1,3-Butadiene	0.067	0.29	97
Marylebone Road	Benzene	1.25	6.1	83
	1,3-Butadiene	0.33	3.1	41
Auchencorth Moss	Benzene	0.26	1.6	39
	1,3-Butadiene	0.027	0.52	63
London Eltham	Benzene	0.58	31	82
	1,3-Butadiene	0.084	3.0	82

Table 9 Auchencorth Moss Faults during 2014

Start	End	Days lost	Reason
27/01/2014	29/01/2014	2	GC locked up
03/03/2014	12/03/2014	9	Potential system artefact on one column, affecting baseline and resolution of peaks. Baseline poor on other column. Data removed at the quality circle.
02/06/2014	04/06/2014	2	Site, power off for maintenance, Helium empty, helium cylinder replaced
25/06/2014	09/07/2014	14	Helium empty, internal system leak not found by engineer, Helium replaced
02/10/2014	20/10/2014	18	Concentrations appeared to be dropping. New cold trap and heater sensor installed
27/10/2014	29/10/2014	2	Power cut, hydrogen generator reset by LSO

Table 10 Harwell faults during 2014

Start	End	Days lost	Reason
15/07/2014	18/07/2014	3	Compressor leak, repaired

Table 11 London Eltham faults during 2014

Start	End	Days lost	Reason
20/01/2014	28/01/2014	8	Power cut, FID not relit properly
31/03/2014	31/03/2014	1	GC/PC Comms error
22/04/2014	25/04/2014	3	Compressor fault, engineer repair
01/07/2014	03/07/2014	2	Compressor fault, engineer repair
12/09/2014	15/09/2014	3	Helium pipe broken at cylinder change, helium transfer line replaced
04/10/2014	10/10/2014	6	Compressor fault, engineer repair

Start	End	Days lost	Reason
22/10/2014	28/10/2014	6	Valco valve fault, valco valve repaired

Table 12 London Marylebone Road faults during 2014

Start	End	Days lost	Reason
01/01/2014	09/01/2014	8	Compressor fault, engineer repair
05/04/2014	06/04/2014	1	Power Cut
08/05/2014	21/05/2014	13	Turbomatrix Valco valve problem
01/07/2014	15/07/2014	14	Hydrogen generator fault, generator changed
07/08/2014	12/08/2014	5	Hydrogen generator fault, generator repaired
17/11/2014	21/11/2014	4	Hydrogen generator fault, generator replaced
19/12/2014	22/12/2014	3	Turbomatrix failure, Engineer repaired

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

Urban traffic and urban background non-automatic measurements are plotted on one timeseries from the same local urban area where possible. Where benzene measurement sites are more isolated, the best data comparison can be made against co-located AURN Carbon Monoxide, followed by co-located AURN Oxides of Nitrogen (where CO is unavailable) because:

1. Benzene emissions are more significant from petrol vehicles
2. CO is present in petrol vehicle exhaust
3. NO_x emissions are more significant from diesel powered vehicles

Grangemouth, Scunthorpe Town and Middlesbrough are classified as industrial sites and are subject to a wider variety of benzene sources (than roadside locations) and do not tend to show a relationship with CO or NOx as a result.

The 2011 Implementing Provisions Regulations[7] (Commission Implementing Decision 2011/850/EU) has changed how the UK reports statutory air quality data to Europe. For VOCs, IPR requires measurements below the instruments 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:

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

- 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.

3.1.3 Long Term Trends

The following figures show the benzene concentration (µg.m^{-3}) timeseries since the start of monitoring for each Non-automatic site (Figures 4 – 9) and each automatic site (Figure 12 - 15).

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

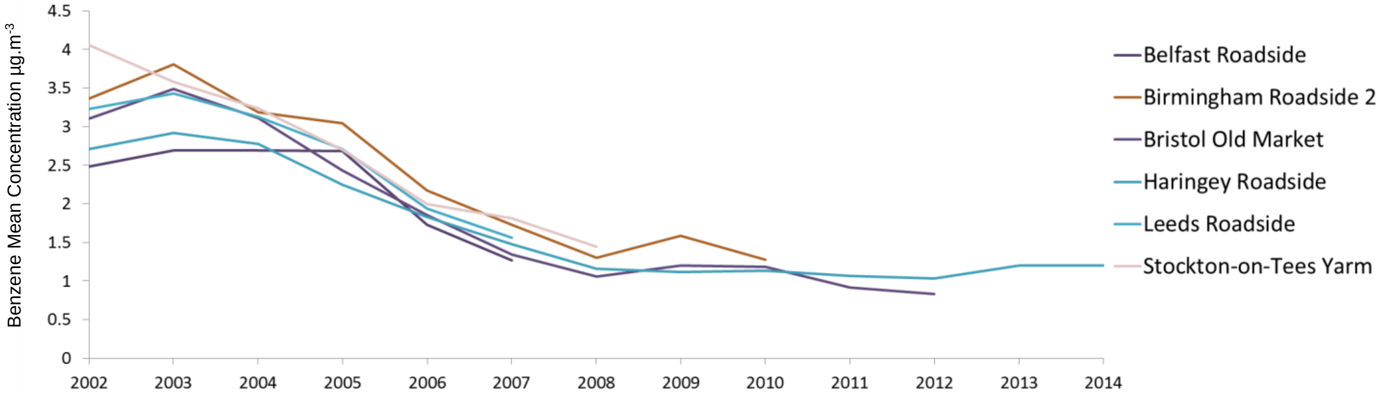


Figure 5 Long term Non-Automatic benzene annual mean timeseries

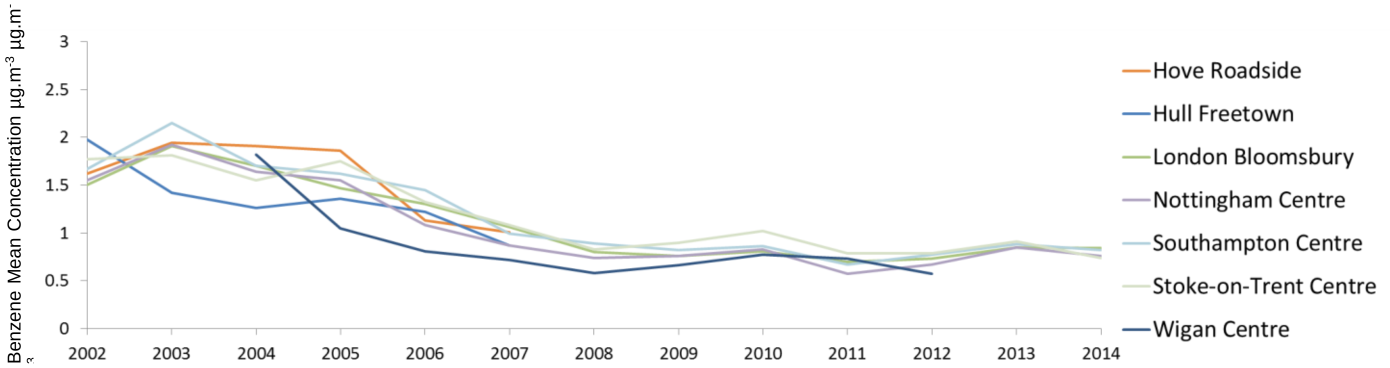


Figure 6 Long term Non-Automatic benzene annual mean timeseries

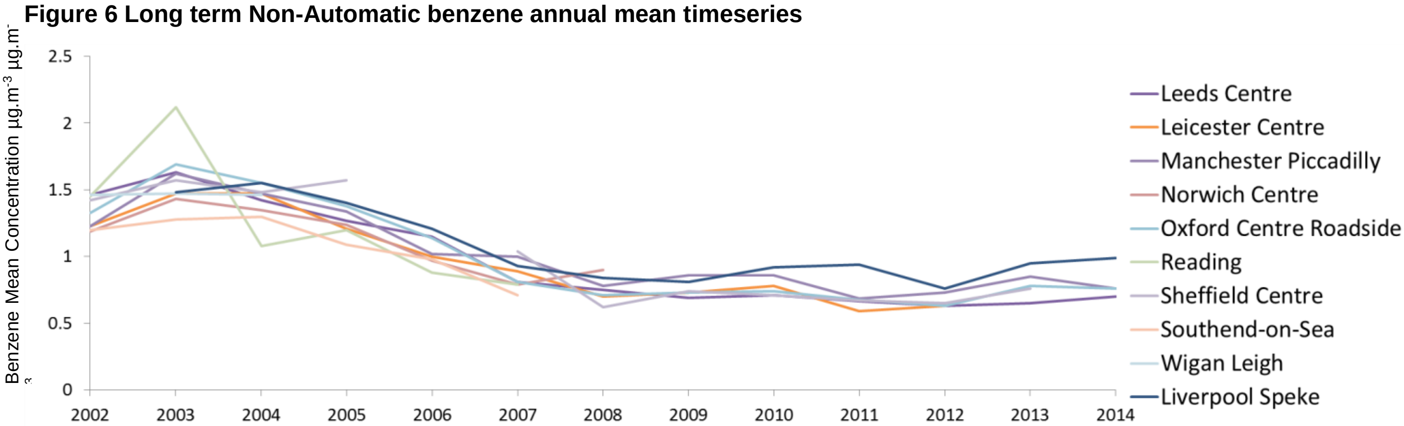
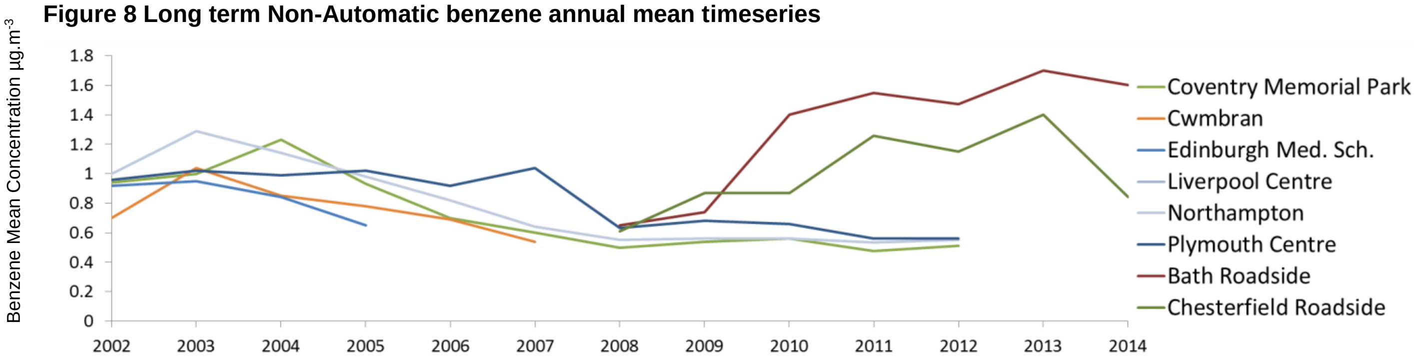


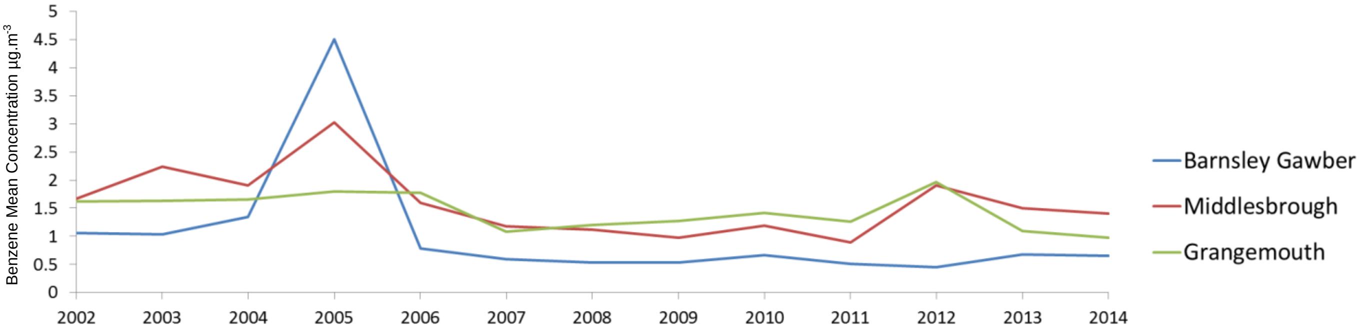
Figure 7 Long term Non-Automatic benzene annual mean timeseries

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 decrease negligibly for most sites from 2013 to 2014.

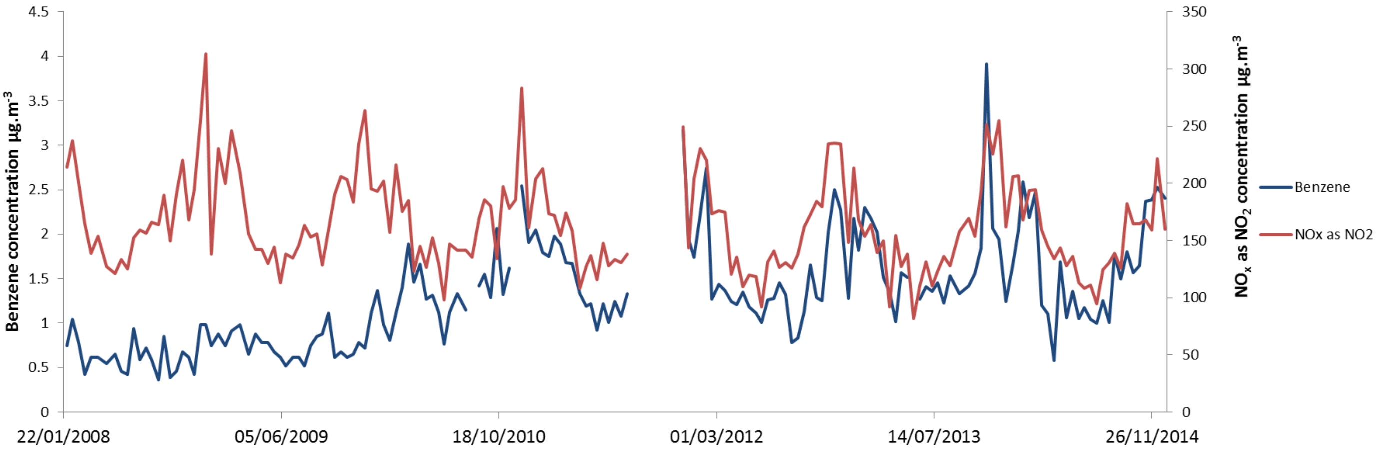
Figure 9 Long term Non-Automatic benzene annual mean timeseries



In Figure 8 (see trends for 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 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, as such the data has not been removed. In 2014, the annual mean has dropped at both sites, the concentrations at Chesterfield drop back down to similar concentrations seen in 2008 and 2009. The drop at Bath is less significant, however, less benzene measured during November 2014 (compared with November 2013) which could be associated with bonfire night. The monitoring station is situated on the A4, a major route in and out of Bath.

Unusual trends in (Grangemouth and Middlesbrough) in 2012 have been discussed in the network report for 2012[8]. 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 benzene and AURN NOx Timeseries



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

Figure 11 Chesterfield Roadside long term fortnightly benzene and AURN NOx Timeseries

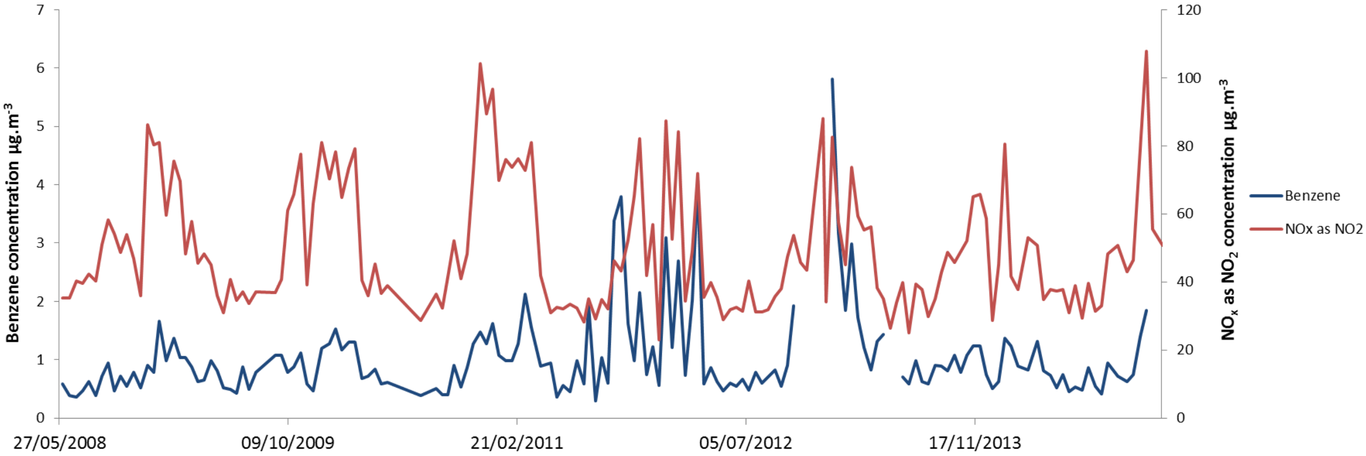
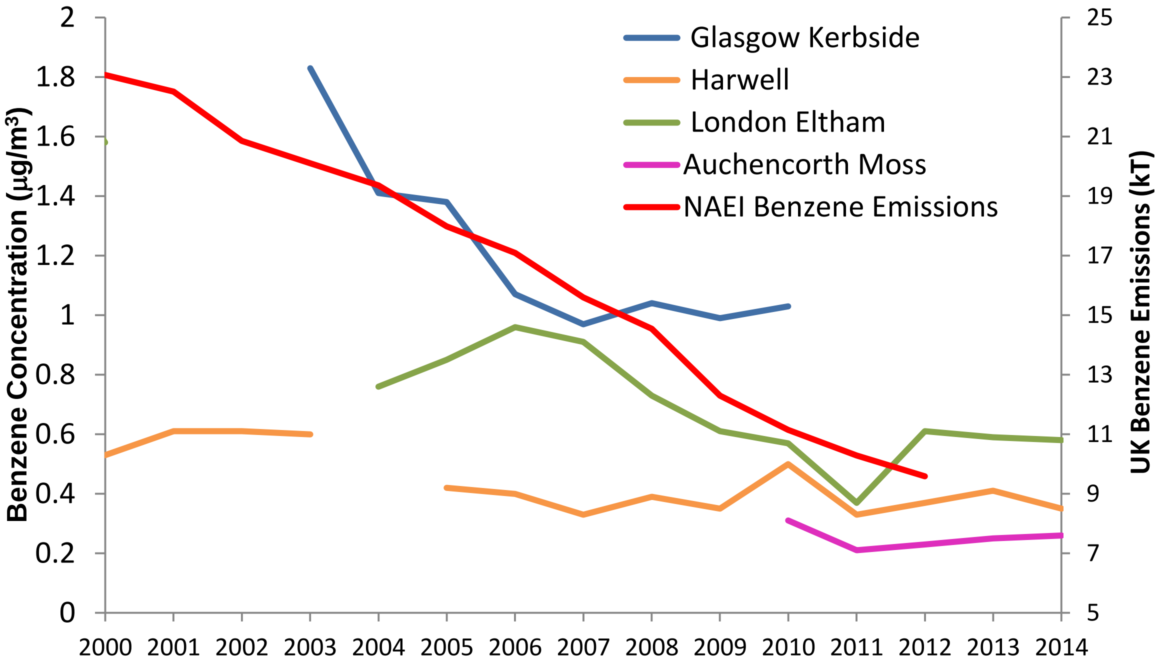


Figure 12 Long term automatic annual mean benzene to Figure 15 show the long-term timeseries of the annual mean concentrations of benzene and 1,3-butadiene at the four sites measuring ozone precursors with long running datasets within the Automatic Hydrocarbon Network. Note that in 2010 and 2011 annual 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. These declines demonstrate that motor vehicle exhaust catalysts and evaporative canisters have effectively and efficiently controlled vehicular emissions of hydrocarbons in the UK[9]. 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 concentrations plateau from 2010 to 2014.

Figure 12 Long term automatic annual mean benzene timeseries and emissions



[9] 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

The source of benzene emissions on Marylebone road is predominantly from traffic. Figure 13 demonstrates there is some relationship between the national NAEI benzene traffic emission data and the Marylebone benzene measurements from 2000 until 2012.

Figure 14 Long term automatic annual mean benzene timeseries and emissions, Marylebone Road

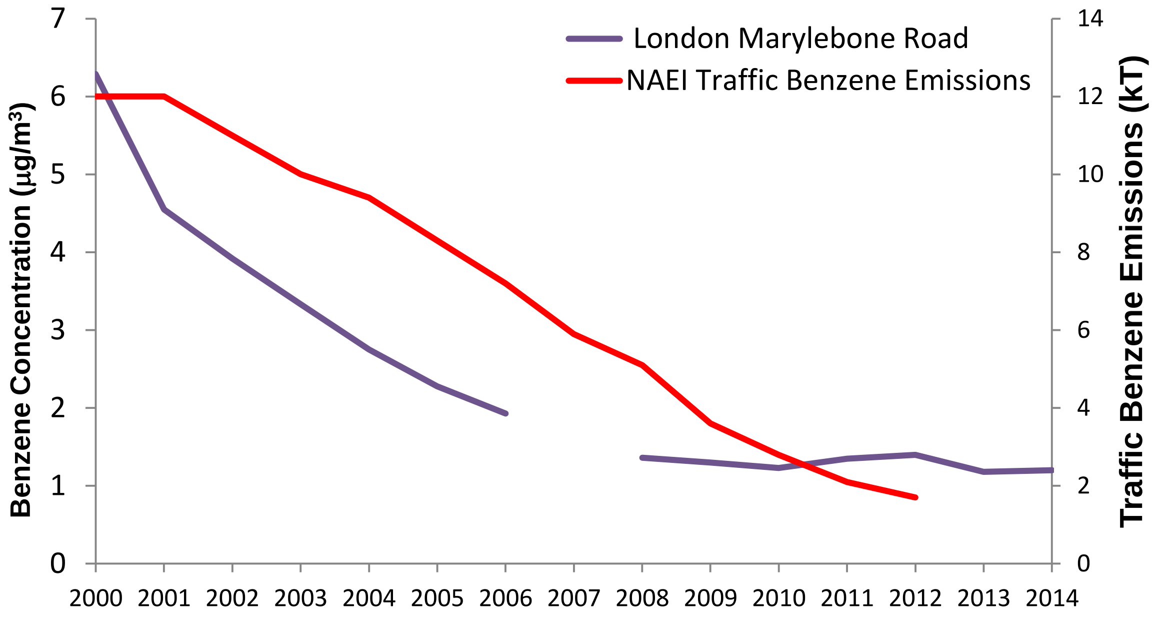
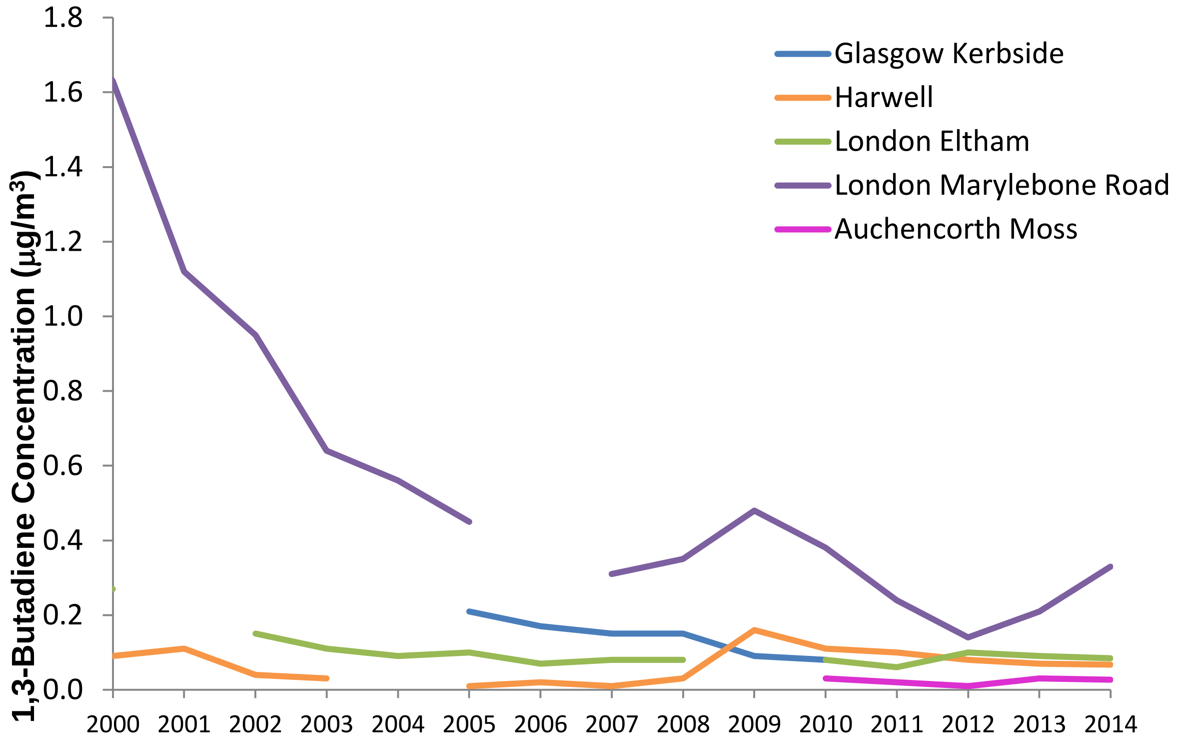


Figure 15 Long term automatic annual mean 1,3-butadiene timeseries



4 Data Quality

4.1 Estimation of Uncertainty

Calculated uncertainty for the Non-Automatic Hydrocarbon sites in 2014 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, as there is no reference method comparator 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.

The largest components in the uncertainty budget are lack of fit and calibration gas uncertainty, although 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 assessed through international intercomparisons. During March 2013, involvement in the Aerosols, Clouds, and Trace gases Research Infrastructure Network (ACTRIS) round robin showed Harwell +6.5%, Auchencorth Moss -7.6% from the reference cylinder concentrations.

4.2 Standard Methods

The AQD states that automatic measurements of benzene should be compliant with European Standard EN14662-3:2005 – Part 3: Automated pumped sampling with in-situ gas chromatography which is determined as the Ambient Air Quality Standard method for the measurements of benzene concentrations. 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 µg.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.

4.3 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 µg.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 13.

Table 13 Automatic Analyser Limits of Detection

Compound	Limit of Detection µg.m^{-3}	Compound	Limit of Detection µg.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		

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 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. 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. Data for was not available at the time of this assessment. 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 flat trends at Harwell and Auchenworth Moss shown in Figure 12 may not be relevant because they are not traffic influenced sites, 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 done, it's possible that traffic has been changing at rates different to the UK average. Ricardo-AEA would have to carry out further analysis to investigate this.

Appendices

Appendix 1: 2014 Audit Schedule

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

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

Appendix 1 - Title Appendix 1 – 2014 Audit schedule

Table 14 Non automatic sample flow measurements used for 2014 data

Site	Date	Final measurement	Date	Initial Measurement	Final Measurement	Date	Initial Measurement	Final Measurement	Date	Initial Measurement
Barnsley Gawber	01/10/2013	10.24	14/04/2014	9.86	10.21	08/10/2014	10.47	10.07	21/04/2015	10.50
Bath Roadside	21/10/2013	10.08	24/04/2014	9.55	9.91	22/10/2014	9.53	10.13	29/04/2015	10.12
Belfast Centre	14/10/2013	10.08	07/04/2014	10.24	10.09	24/10/2014	9.38	10.04	09/04/2015	9.81
Birmingham Acocks Green	10/10/2013	10.00	10/04/2014	10.01	10.02	28/10/2014	9.89	-	-	-
Birmingham Tyburn	-	-	-	-	-	28/10/2014	-	10.00	21/04/2015	8.83
Birmingham Tyburn Roadside	10/10/2013	10.10	10/04/2014	9.96	10.09	29/10/2014	9.87	10.05	21/04/2015	9.60
Bury Whitefield Roadside	-	-	11/07/2014	9.84	10.02	21/10/2014	10.07	-	08/04/2015	10.17
Cambridge Roadside	07/10/2013	9.98	07/04/2014	9.73	9.97	06/10/2014	10.24	10.00	07/04/2015	8.34
Carlisle Roadside	07/10/2013	10.24	02/04/2014	10.02	10.02	09/10/2014	10.59	10.00	16/04/2015	9.81
Chatham Centre Roadside	02/10/2013	10.06	29/04/2014	9.68	10.06	01/10/2014	9.79	9.90	01/04/2015	9.84
Chesterfield Roadside	01/10/2013	10.04	28/04/2014	10.19	10.00	07/10/2014	10.01	10.00	21/04/2015	10.06
Glasgow Kerbside	30/09/2013	10.06	25/04/2014	9.74	10.03	29/09/2014	10.59	10.29	30/04/2015	9.77
Grangemouth	30/09/2013	10.08	22/04/2014	10.09	10.05	29/09/2014	10.26	10.08	22/04/2015	9.82

Site	Date	Final measurement	Date	Initial Measurement	Final Measurement	Date	Initial Measurement	Final Measurement	Date	Initial Measurement
Leamington Spa	17/10/2013	10.03	15/04/2014	9.22	10.04	16/10/2014	10.61	9.97	16/04/2015	9.38
Leeds Centre	23/10/2013	10.04	14/04/2014	10.23	10.25	06/10/2014	10.08	10.00	22/04/2015	8.95
Liverpool Speke	09/10/2013	10.06	08/04/2014	9.87	9.96	01/10/2014	9.64	10.02	31/03/2015	9.61
London Bloomsbury	22/10/2013	10.05	14/04/2014	8.91	10.10	06/10/2014	10.56	10.05	08/04/2015	9.06
London Camden Kerbside	22/10/2013	10.05	15/04/2014	9.29	10.07	05/09/2014	10.11	10.02	09/04/2015	9.00
London Haringey Roadside	23/10/2013	10.10	16/04/2014	9.22	10.12	09/10/2014	10.75	10.11	16/04/2015	9.53
Manchester Piccadilly	22/10/2013	9.97	01/04/2014	9.63	9.91	20/10/2014	10.24	10.25	09/04/2015	9.55
Middlesbrough	09/10/2013	10.03	08/04/2014	10.35	10.14	07/10/2014	9.89	10.01	14/04/2015	9.60
Newcastle Centre	02/10/2013	10.18	09/04/2014	10.09	10.20	08/10/2014	10.05	10.02	15/04/2015	9.67
Newport	22/11/2013	10.05	01/04/2014	10.27	10.01	22/10/2014	9.23	10.08	01/05/2015	10.50
Norwich Lakenfields	08/10/2013	9.99	08/04/2014	9.42	10.03	07/10/2014	10.64	10.04	08/04/2015	8.88
Nottingham Centre	14/10/2013	9.96	09/04/2014	9.57	9.98	13/10/2014	10.09	10.04	13/04/2015	9.40
Oxford Centre Roadside	07/10/2013	10.07	03/04/2014	10.39	10.19	11/09/2014	9.76	9.99	07/04/2015	9.20
Oxford St Ebbes	07/10/2013	10.07	03/04/2014	10.03	10.11	18/11/2014	9.95	10.04	07/04/2015	9.24
Scunthorpe Town	07/10/2013	10.20	14/04/2014	9.96	10.24	08/10/2014	10.55	10.14	20/04/2015	9.65
Sheffield Devonshire Green	31/10/2013	9.97	29/04/2014	9.70	10.05	06/10/2014	10.42	10.04	21/04/2015	9.24

Site	Date	Final measurement	Date	Initial Measurement	Final Measurement	Date	Initial Measurement	Final Measurement	Date	Initial Measurement
Southampton Centre	25/10/2013	10.07	10/04/2014	9.23	10.06	16/10/2014	10.69	10.01	23/04/2015	9.03
Stockton-on-Tees Eaglescliffe	09/10/2013	9.98	09/04/2014	9.53	10.10	08/10/2014	10.85	10.01	13/04/2015	9.66
Stoke-on-Trent Centre	23/10/2013	10.03	30/04/2014	10.13	10.01	30/10/2014	10.01	9.99	22/04/2015	9.06
Tower Hamlets Roadside	24/10/2013	10.01	13/03/2014	9.74	9.98	17/10/2014	9.83	10.02	10/04/2015	9.07
York Bootham	08/10/2013	9.98	15/04/2014	9.80	10.26	09/10/2014	10.68	10.15	22/04/2015	9.71
York Fishergate	08/10/2013	10.00	15/04/2014	9.79	10.24	09/10/2014	10.81	10.02	12/02/2015	8.95

2014 Audit Schedule of the Automatic Hydrocarbon Network

Table 15 Audit and service schedule of the automatic hydrocarbon analysers

Site	Service/Audit Date	Service/ Audit Date	Service/Audit Date
Auchencorth Moss	16/01/2013	03/12/2014	09/01/2015
Harwell	11/09/2013	25/06/2014	-
Eltham	15/10/2013	27/06/2014	-
Marylebone Road	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 16 Auchencorth Moss statistics, 2014 (µg.m^{-3})

Compound	Mean	Maximum	Data Capture
ethane	2.2	120	60%
ethene	0.15	7	63%
ethyne	0.12	0.67	63%
propane	1.2	60	63%
propene	0.098	4.2	63%
iso-butane	0.27	8.4	63%
n-butane	0.49	14	63%
1-butene	0.051	1.7	63%
trans-2-butene	0.018	1.4	63%
cis-2-butene	0.018	1	63%
iso-pentane	0.14	13	63%
n-pentane	0.083	6.8	63%
1,3-butadiene	0.027	0.52	63%
trans-2-pentene	0.015	0.015	63%
1-pentene	0.015	0.015	63%
2-methylpentane	0.037	3.8	63%
isoprene	0.03	2.1	63%
n-hexane	0.034	2.9	63%
n-heptane	0.04	0.46	39%
iso-octane	0.035	0.66	39%
n-octane	0.036	0.95	39%
benzene	0.26	1.6	39%
toluene	0.17	3.9	39%
ethylbenzene	0.04	1.1	39%
m+p xylene	0.066	3.4	39%
o-xylene	0.052	1.5	39%
1,2,3-trimethylbenzene	0.025	0.025	39%
1,2,4-trimethylbenzene	0.025	0.025	39%
1,3,5-trimethylbenzene	0.025	0.025	39%

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 17 Harwell statistics 2014 (µg.m^{-3})

Compound	Mean	Maximum	Data Capture
ethane	2.7	24	97%
ethene	0.44	6.3	97%
ethyne	0.22	2.2	97%
propane	1.6	29	97%
propene	0.26	7.5	97%
iso-butane	0.44	18	97%
n-butane	0.75	41	97%
1-butene	0.1	0.61	97%
trans-2-butene	0.036	0.26	97%
cis-2-butene	0.025	0.21	97%
iso-pentane	0.36	5	97%
n-pentane	0.19	2.6	97%
1,3-butadiene	0.067	0.29	97%
trans-2-pentene	0.014	0.17	97%
1-pentene	0.015	0.015	97%
2-methylpentane	0.11	33	97%
isoprene	0.022	0.37	97%
n-hexane	0.1	3.8	97%
n-heptane	0.064	1.3	98%
iso-octane	0.057	1.3	98%
n-octane	0.035	0.38	98%
benzene	0.35	2.4	98%
toluene	0.34	5.9	98%
ethylbenzene	0.069	1.2	98%
m+p xylene	0.15	4.1	98%
o-xylene	0.085	1.8	98%
1,2,3-trimethylbenzene	0.065	1	98%
1,2,4-trimethylbenzene	0.094	1.6	98%
1,3,5-trimethylbenzene	0.04	1	98%

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 18 London Eltham statistics 2014 ($\mu g.m^{-3}$)

Compound	Mean	Maximum	Data Capture
ethane	5.6	68	74%
ethene	0.73	110	82%
ethyne	0.48	11	82%
propane	3	110	82%
propene	0.39	33	82%
iso-butane	1.6	32	82%
n-butane	3	55	82%
1-butene	0.11	5.1	82%
trans-2-butene	0.071	1.9	82%
cis-2-butene	0.056	1.2	82%
iso-pentane	1.6	26	82%
n-pentane	0.93	14	82%
1,3-butadiene	0.084	3	82%
trans-2-pentene	0.069	1.4	82%
1-pentene	0.05	1.1	82%
2-methylpentane	0.37	5	82%
isoprene	0.23	6.7	82%
n-hexane	0.29	7.7	82%
n-heptane	0.18	2.1	82%
iso-octane	0.14	1.5	82%
n-octane	0.085	0.9	82%
benzene	0.58	31	82%
toluene	1	13	82%
ethylbenzene	0.21	4.8	82%
m+p xylene	0.6	17	82%
o-xylene	0.28	5.7	82%
1,2,3-trimethylbenzene	0.3	65	82%
1,2,4-trimethylbenzene	0.23	4.9	82%
1,3,5-trimethylbenzene	0.077	1.6	82%

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 19 Marylebone Road statistics 2014 (µg.m^{-3})

Compound	Mean	Maximum	Data Capture
ethane	8.8	74	82%
ethene	2.5	15	83%
ethyne	1.1	8	83%
propane	5.6	230	83%
propene	1.3	38	83%
iso-butane	3.3	59	83%
n-butane	5.4	52	83%
1-butene	0.54	6	34%
trans-2-butene	0.31	3.2	41%
cis-2-butene	0.25	2.5	41%
iso-pentane	4.2	60	83%
n-pentane	2	17	83%
1,3-butadiene	0.33	3.1	41%
trans-2-pentene	0.32	3.3	41%
1-pentene	0.25	4.5	41%
2-methylpentane	1.1	49	83%
isoprene	0.054	6.1	83%
n-hexane	0.72	9.7	83%
n-heptane	0.48	4.3	83%
iso-octane	0.47	4.5	83%
n-octane	0.17	3.1	83%
benzene	1.2	6.1	83%
toluene	3.4	30	83%
ethylbenzene	0.7	5.4	83%
m+p xylene	2.1	19	83%
o-xylene	0.86	7.8	83%
1,2,3-trimethylbenzene	0.41	3.5	83%
1,2,4-trimethylbenzene	0.65	6.8	83%
1,3,5-trimethylbenzene	0.4	4.9	83%

Appendix 3

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

Figure 16 Auchencorth Moss 1,3-Butadiene hourly mean timeseries 2014

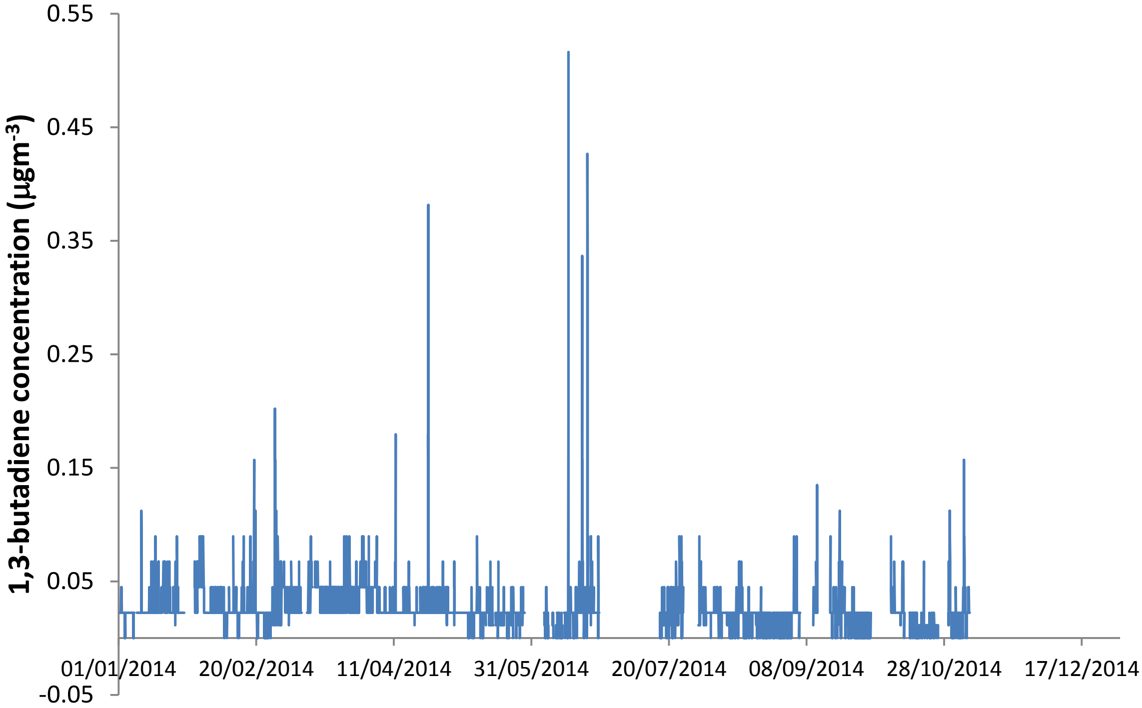


Figure 17 Auchencorth Moss Benzene hourly mean timeseries 2014

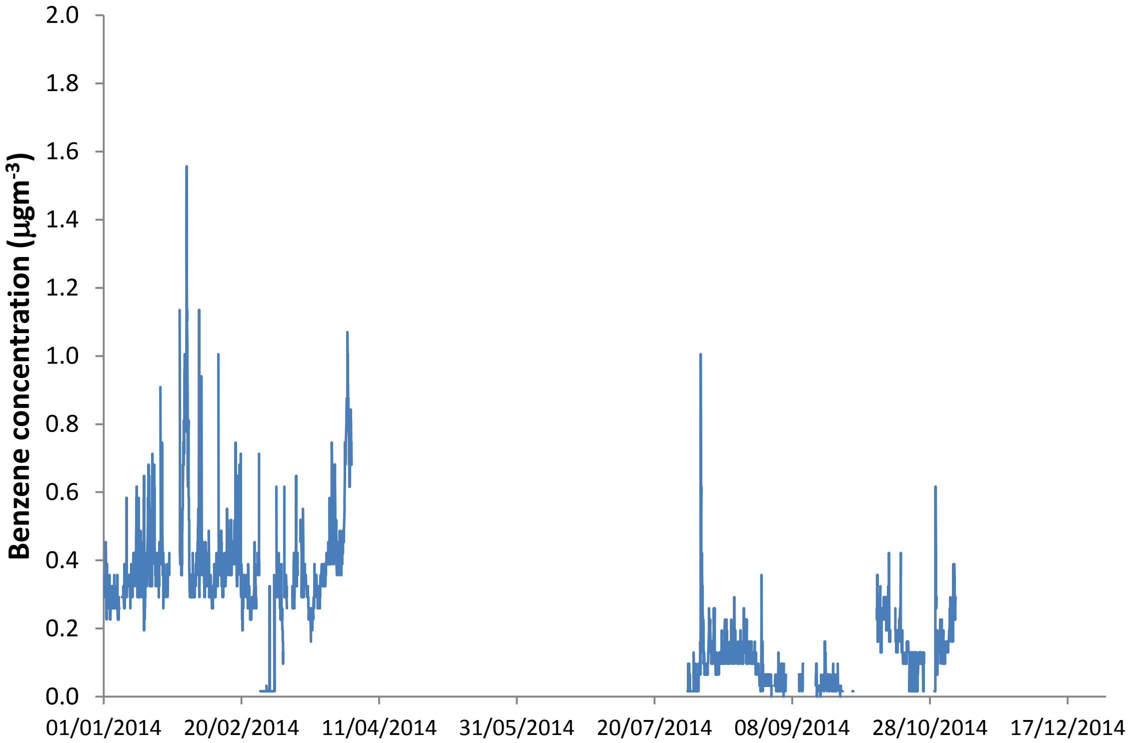


Figure 18 Harwell 1,3-Butadiene hourly mean timeseries 2014

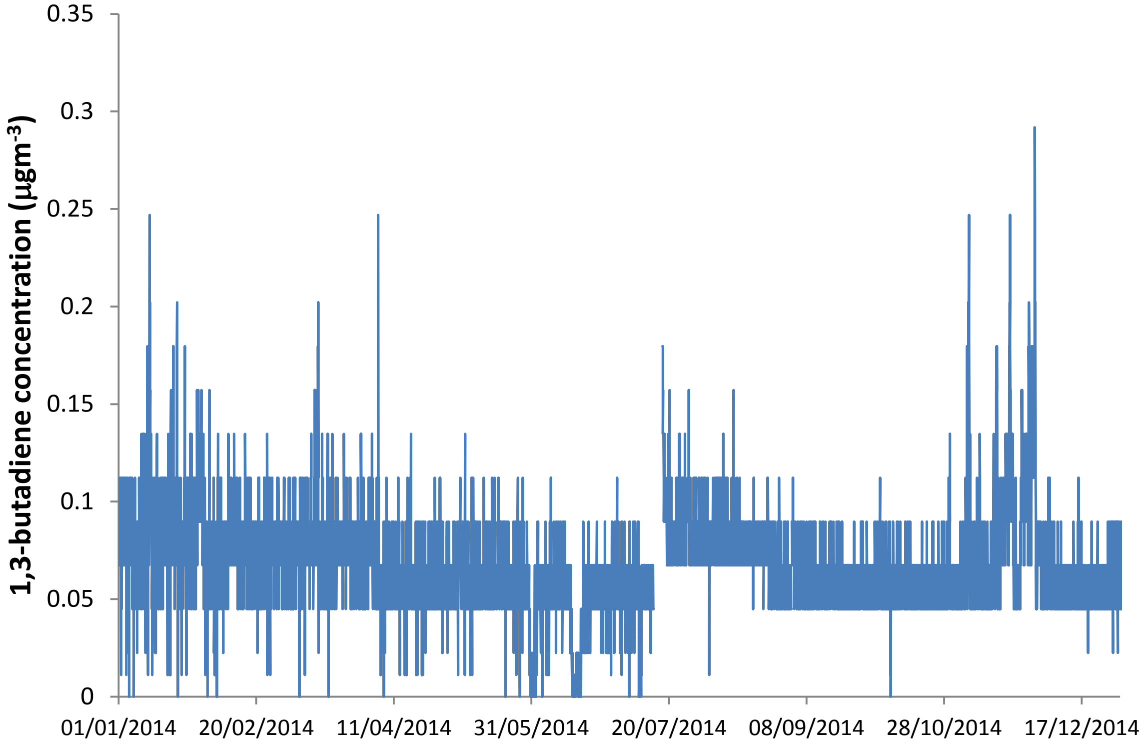


Figure 19 Harwell Benzene hourly mean timeseries 2014

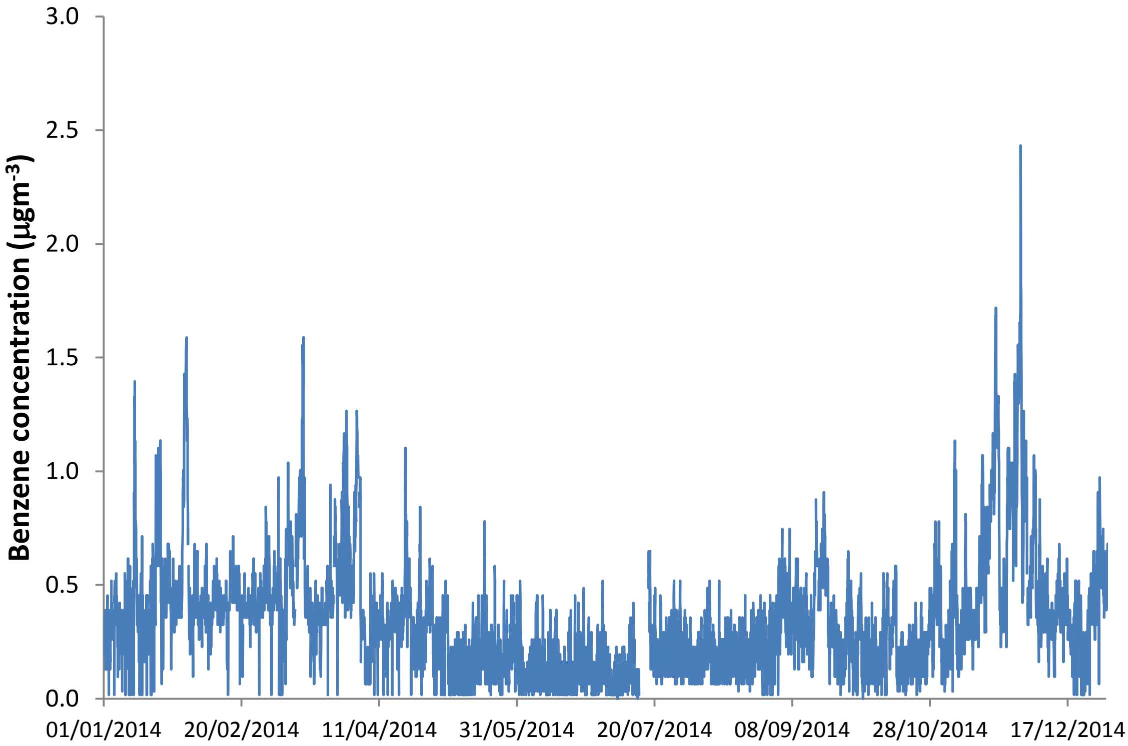


Figure 20 London Eltham 1,3-Butadiene hourly mean timeseries 2014

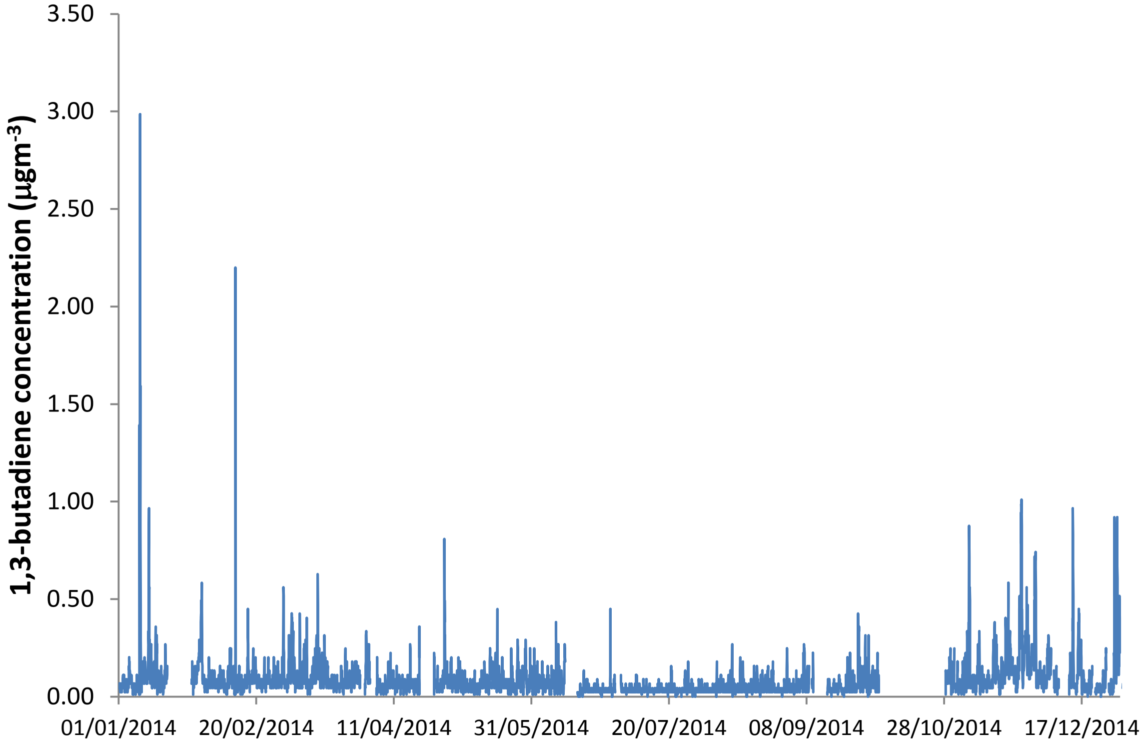


Figure 21 London Eltham Benzene hourly mean timeseries 2014

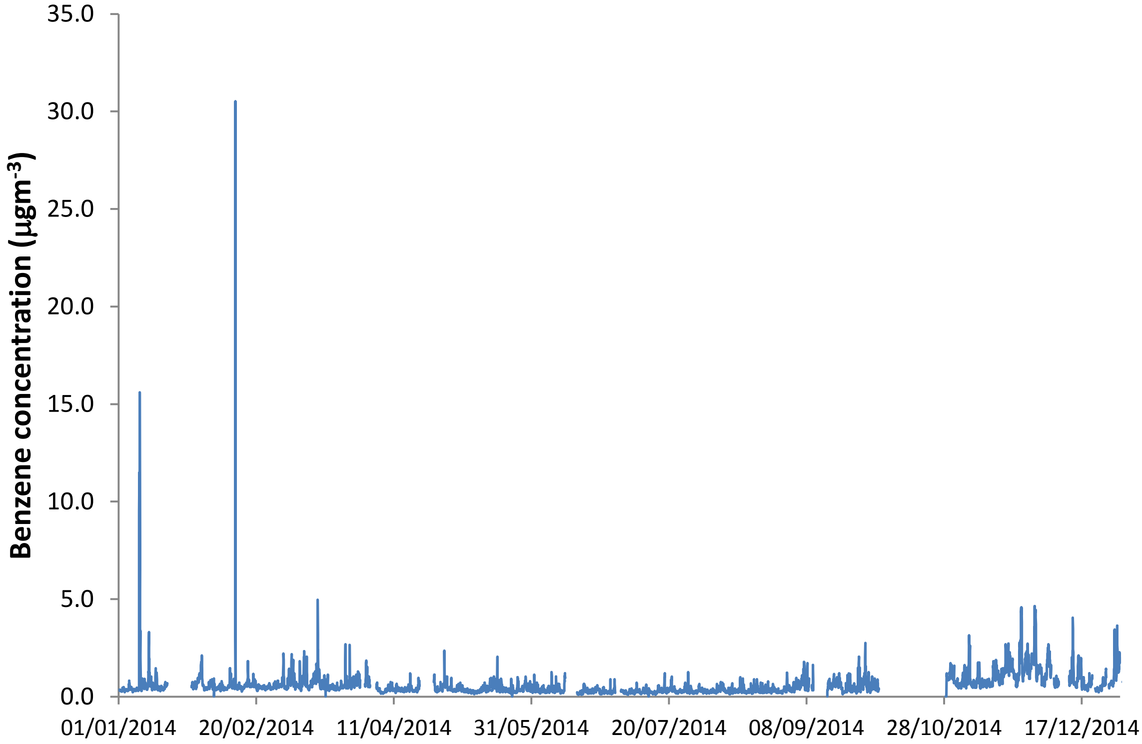


Figure 22 London Marylebone Road 1,3-Butadiene hourly mean timeseries 2014

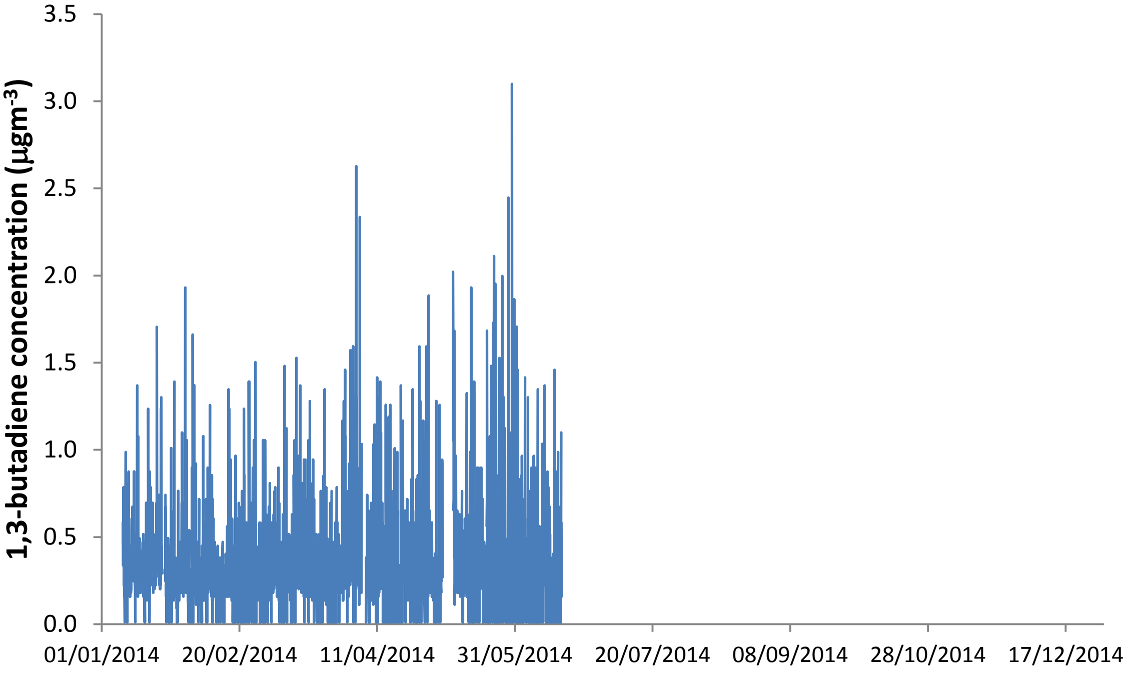
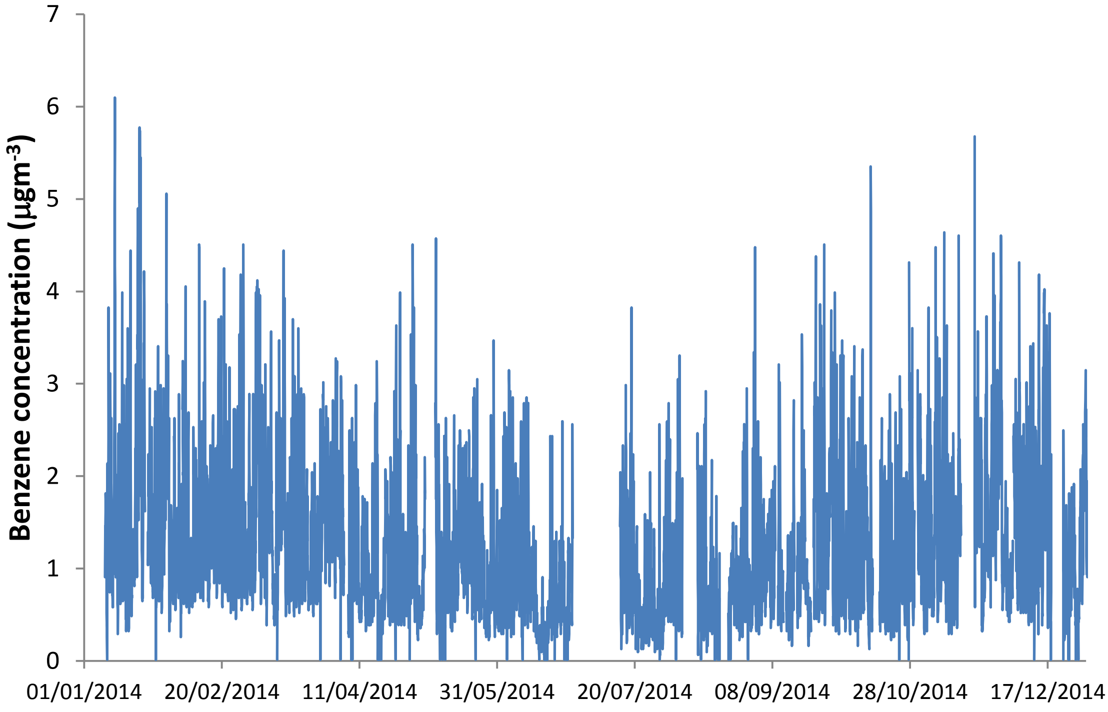


Figure 23 London Marylebone Road Benzene hourly mean timeseries 2014



Non Automatic Fortnightly Mean Graphs for Benzene 2014

Figure 24 to 56 show 2014 annual timeseries plots at each of the non-automatic sites. We would expect higher benzene measurements in winter. Grangemouth, Middlesbrough and Scunthorpe Town have local industrial sources of benzene where elevated levels of benzene can be seen at varying times of the year. Benzene sites within the same urban area are plotted together. Benzene sites that are isolated are compared with CO or NOx data calculated as an average of the same period used for each benzene sample.

Timeseries plots where benzene is measured at two locations within the same urban area

Figure 24 Benzene Timeseries plot of Birmingham measurements during 2014

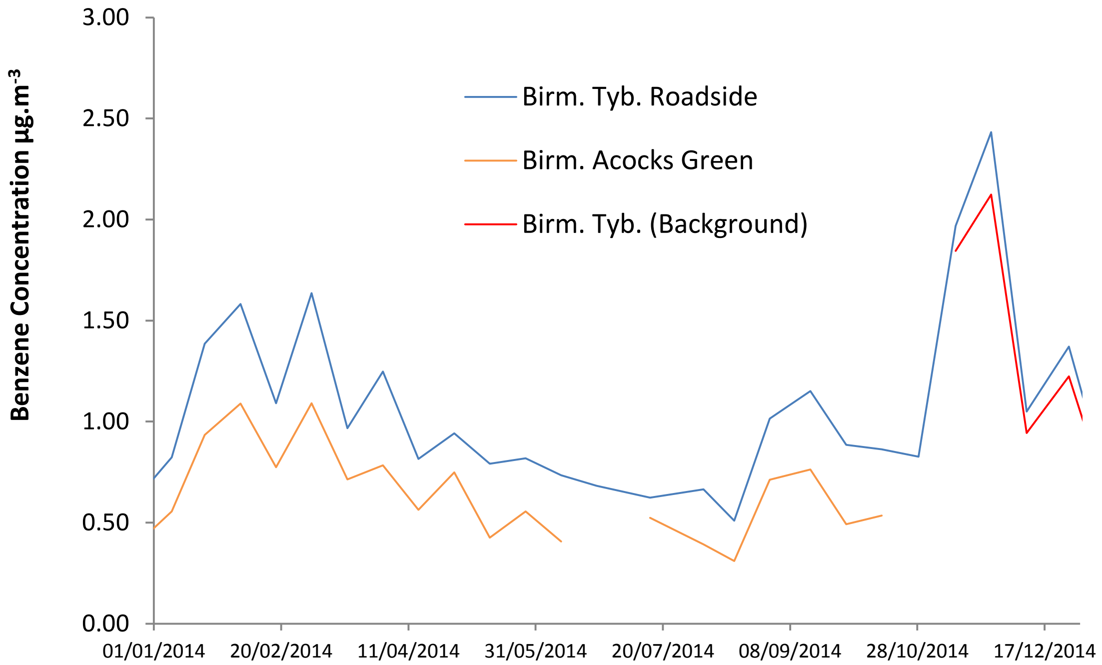


Figure 25 Benzene Timeseries plot of Oxford measurements during 2014

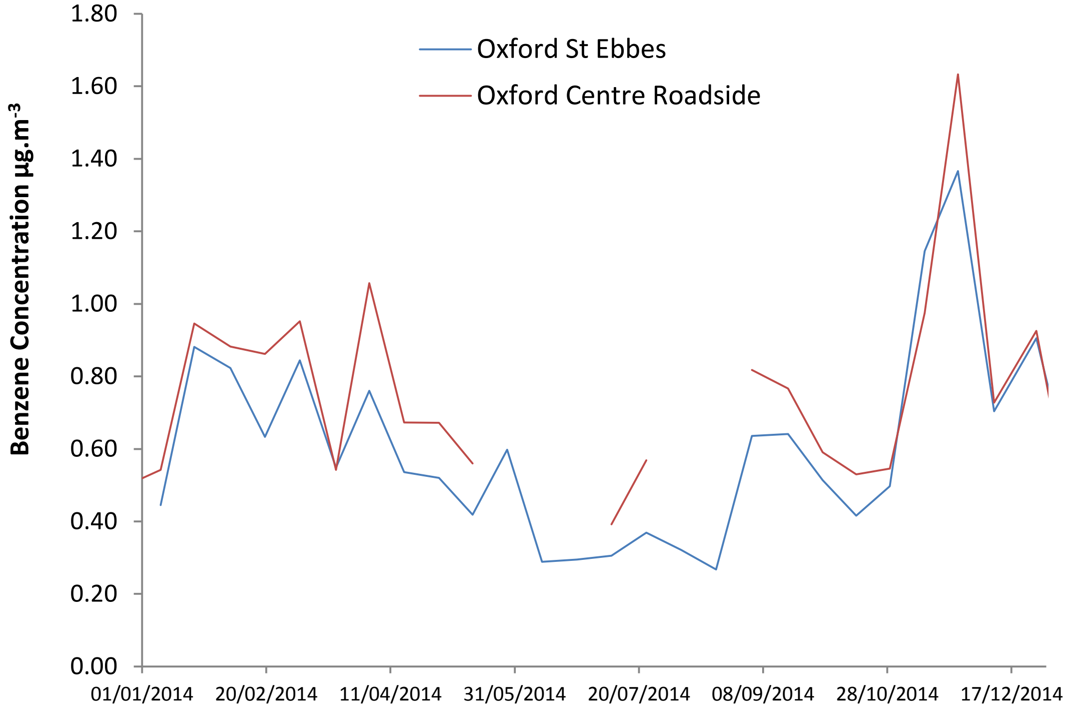
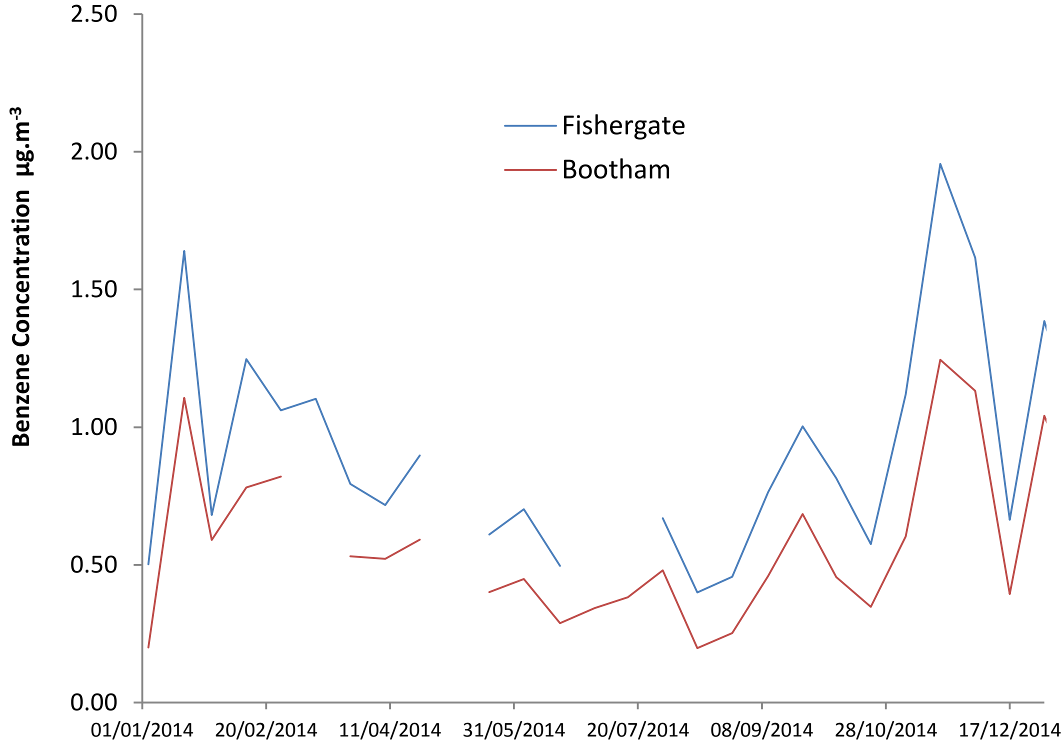


Figure 26 Benzene Timeseries plot of York measurements during 2014



Timeseries plots comparing fortnightly benzene measurements against Carbon Monoxide AURN data averages

Figure 27 Belfast Centre Benzene Measurements and CO Averages 2014

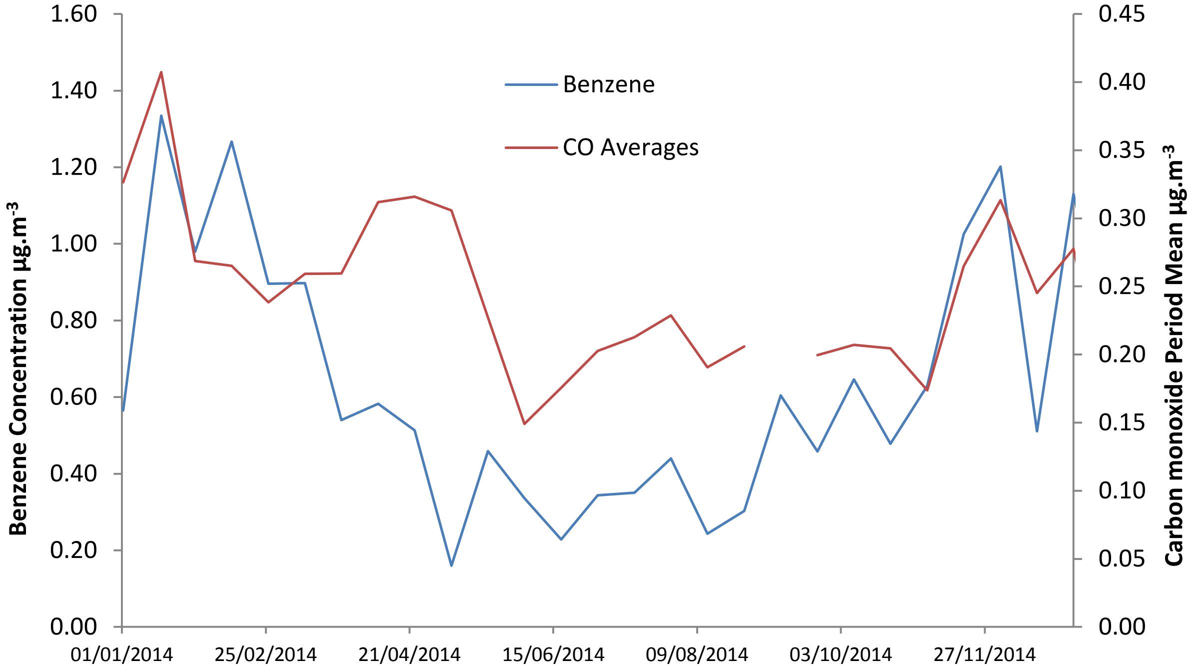
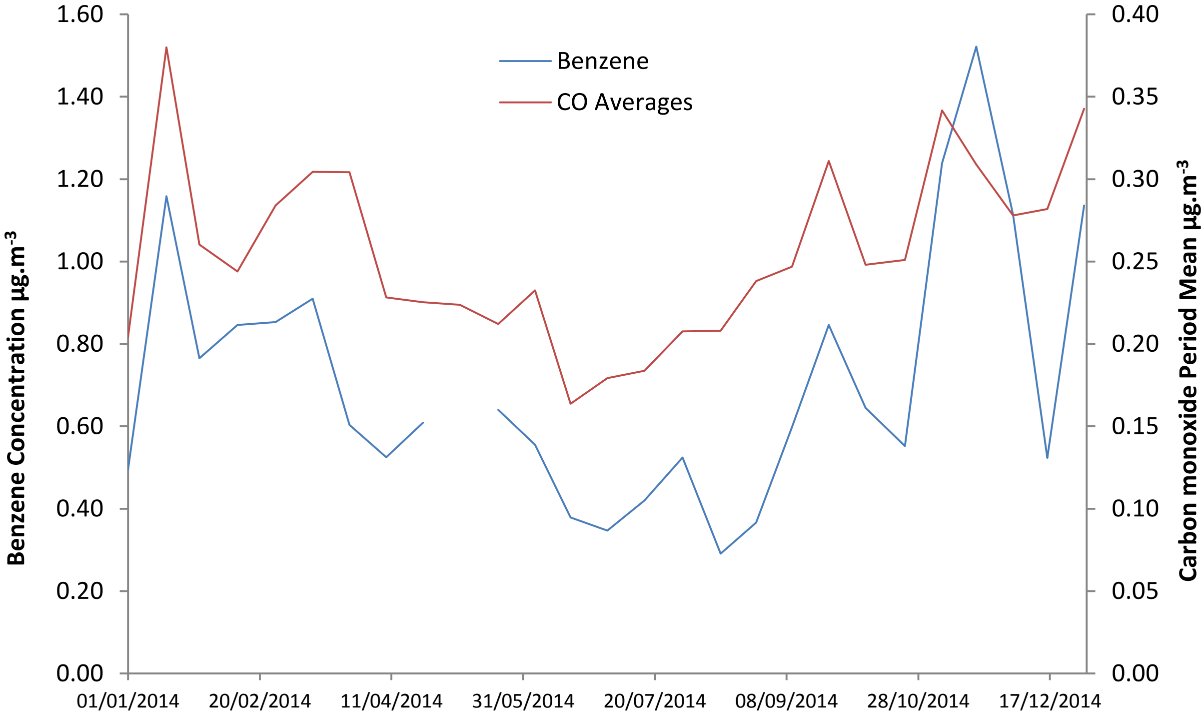


Figure 28 Leeds Centre Benzene Measurements and CO Averages 2014



Timeseries plots comparing fortnightly benzene measurements against Oxides of Nitrogen (NOx) AURN data averages

Figure 29 Barnsley Gawber Benzene Measurements and NOx AURN Averages 2014

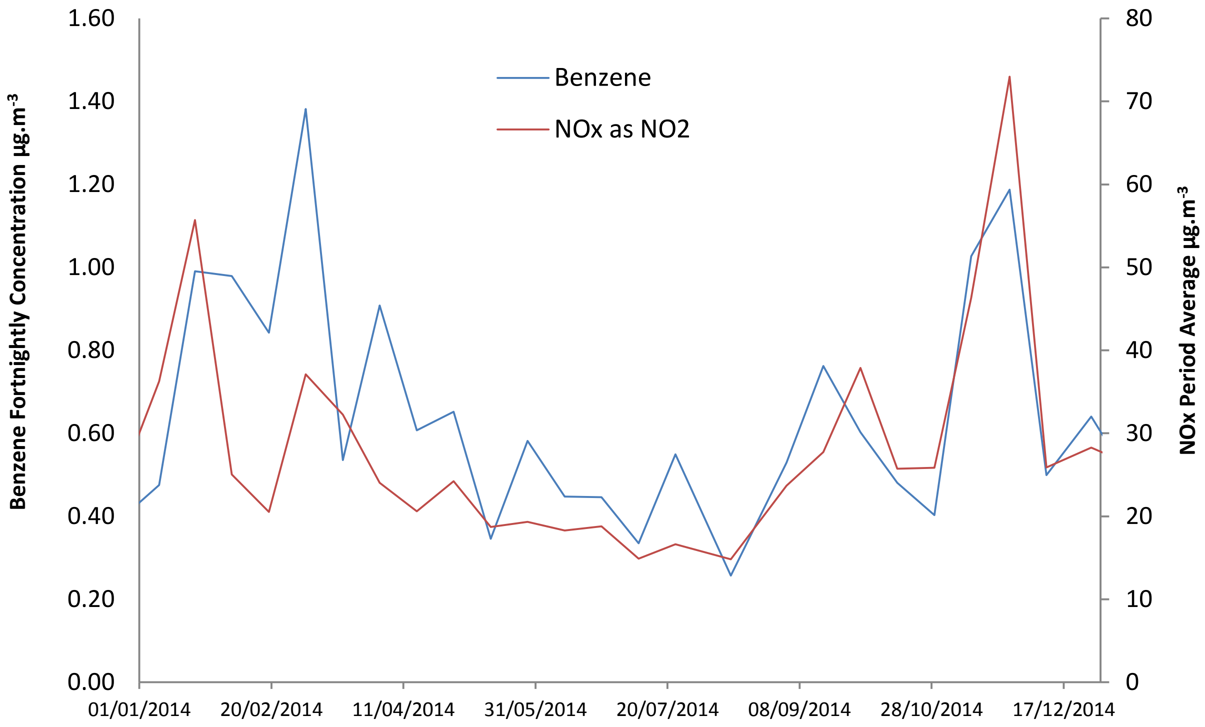


Figure 30 Bath Roadside Benzene Measurements and NOx AURN Averages timeseries

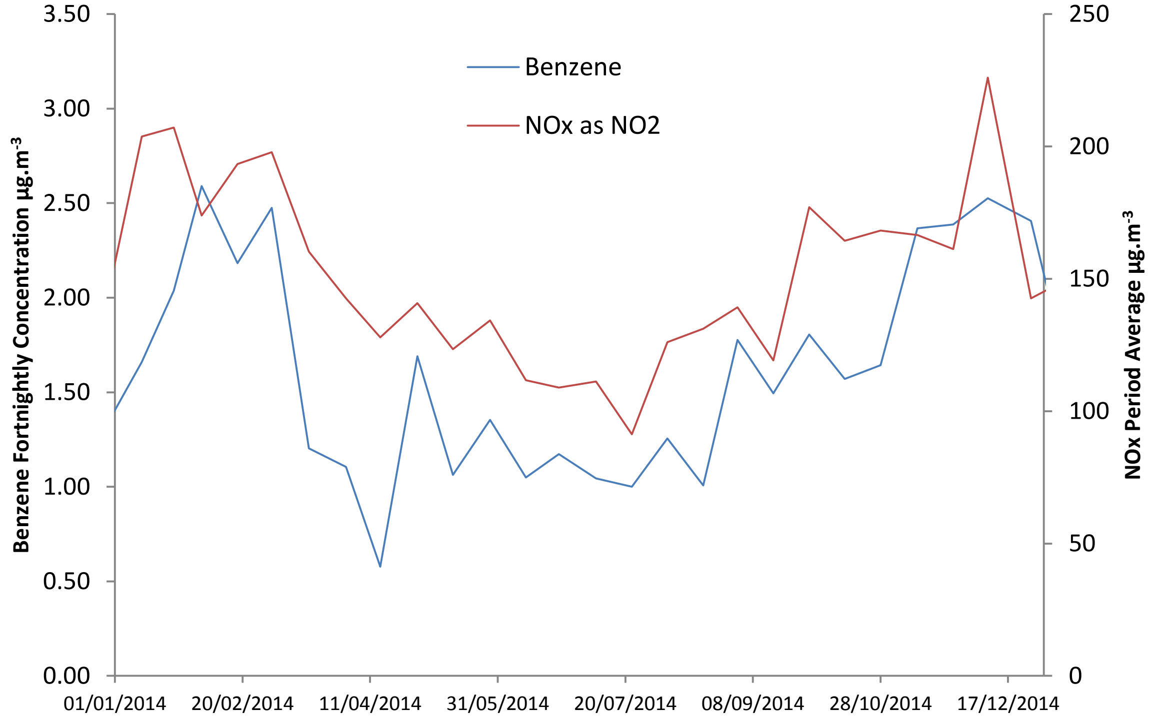


Figure 31 Belfast Centre Benzene Measurements and NOx AURN average timeseries

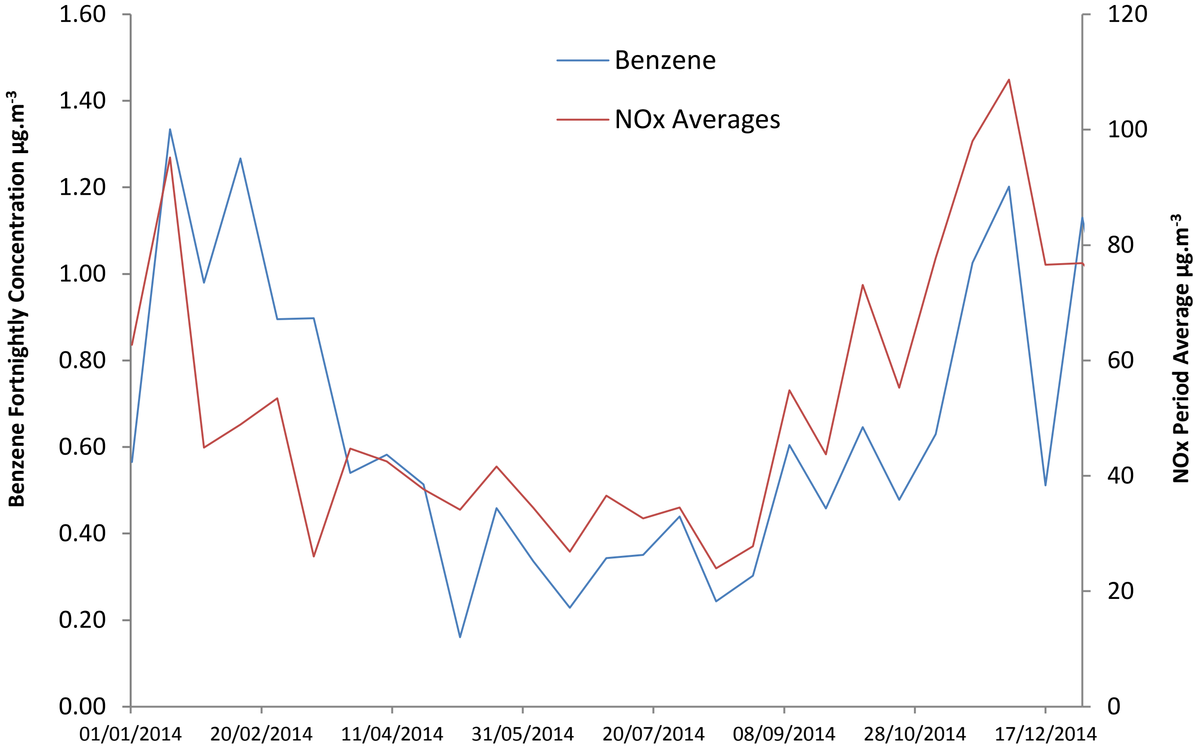


Figure 32 Cambridge Roadside Centre Non Automatic fortnightly Benzene 2014

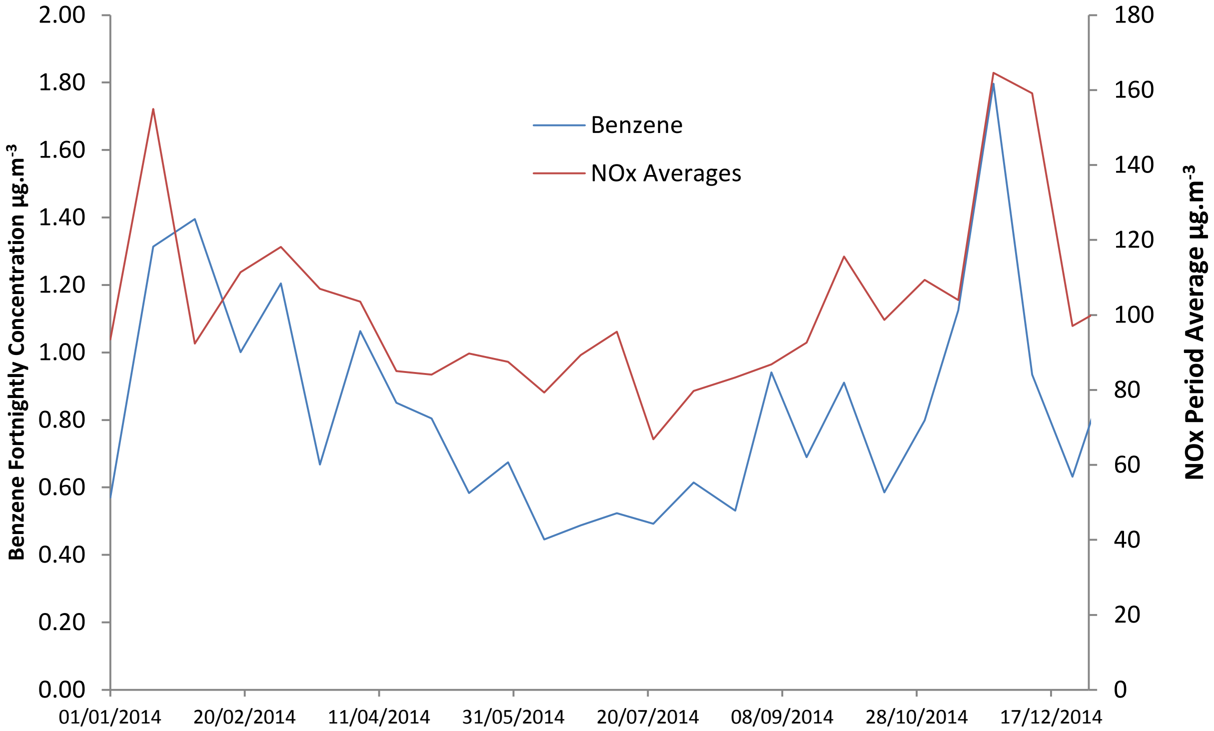


Figure 33 – Camden Kerbside Benzene measurements and NOx averages 2014

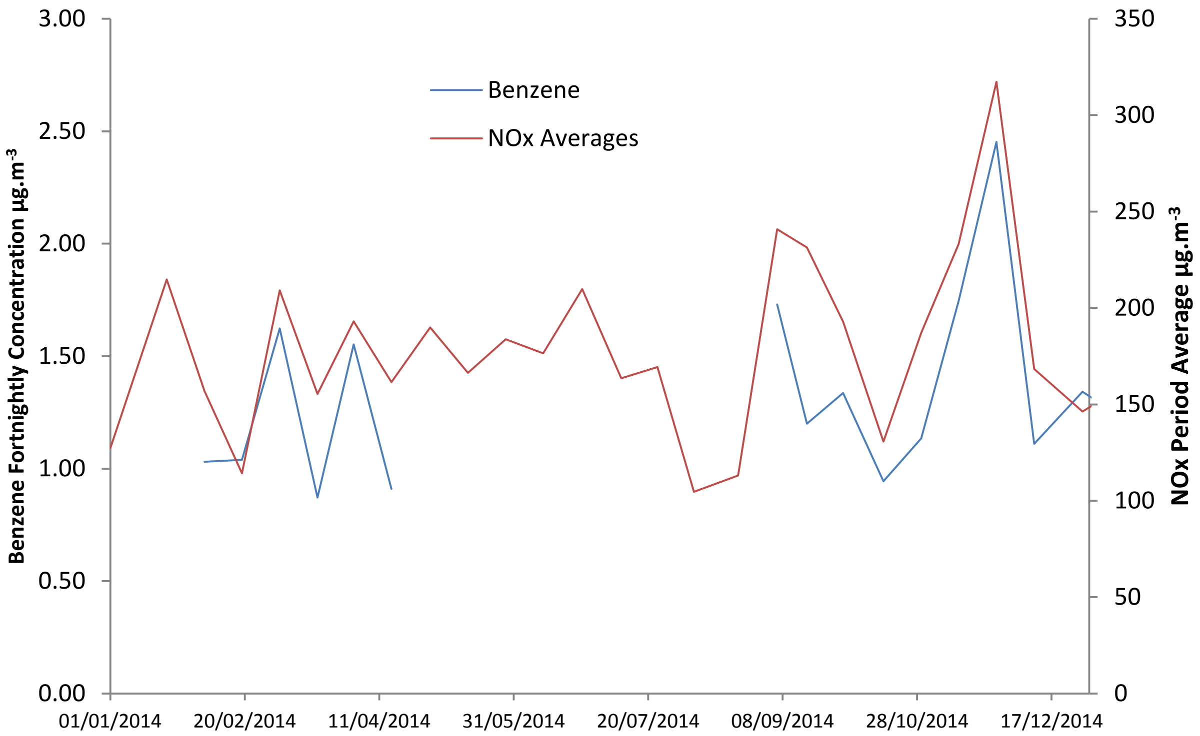


Figure 34 – Carlisle Roadside Benzene measurements and NOx averages 2014

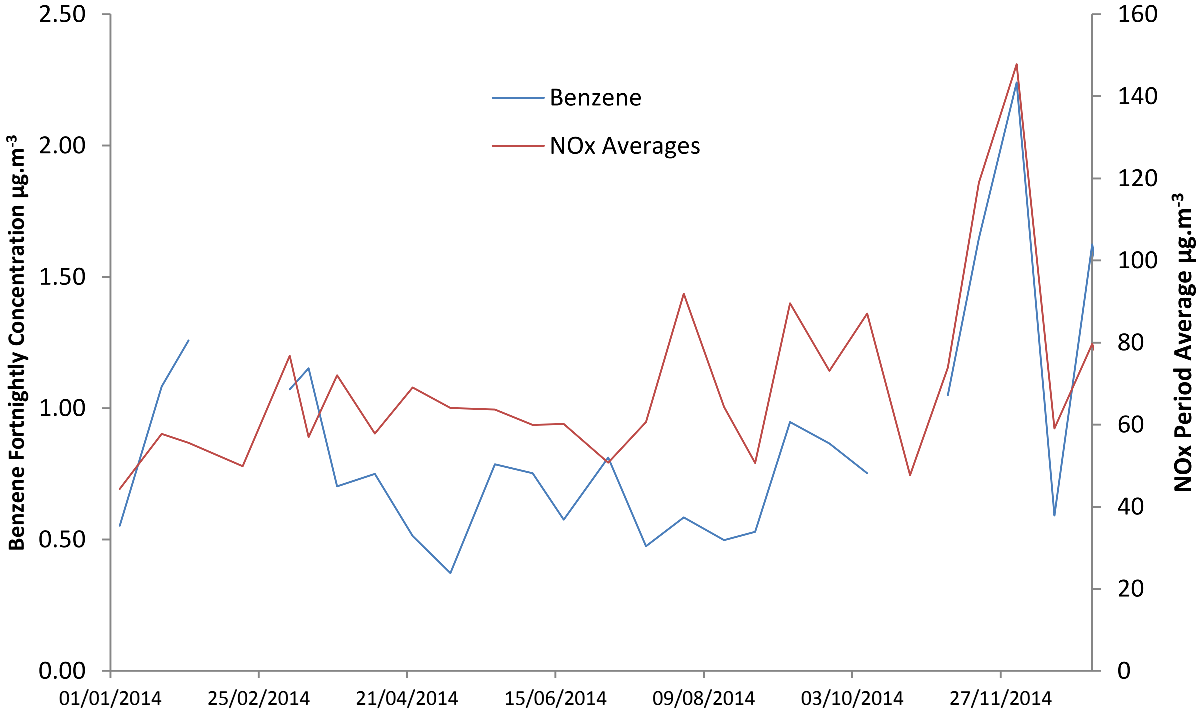


Figure 35 – Chatham Roadside Benzene measurements and NOx averages 2014

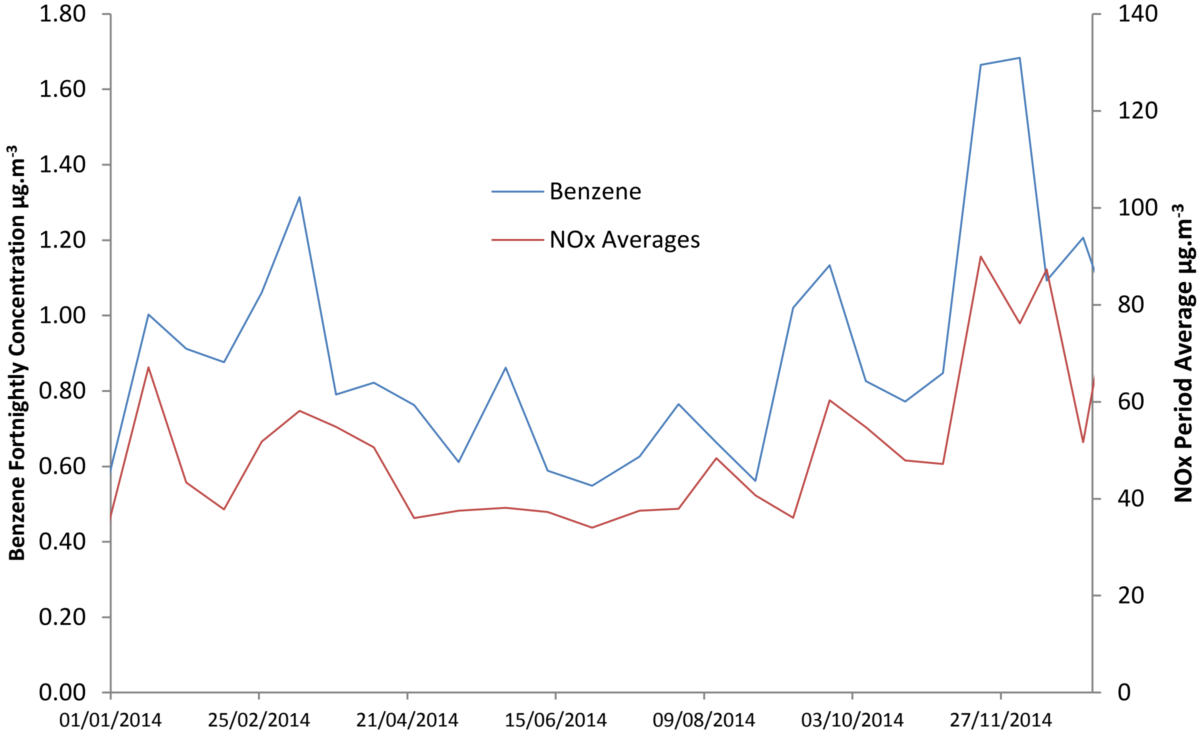


Figure 36- Chesterfield Roadside Benzene measurements and NOx averages 2014

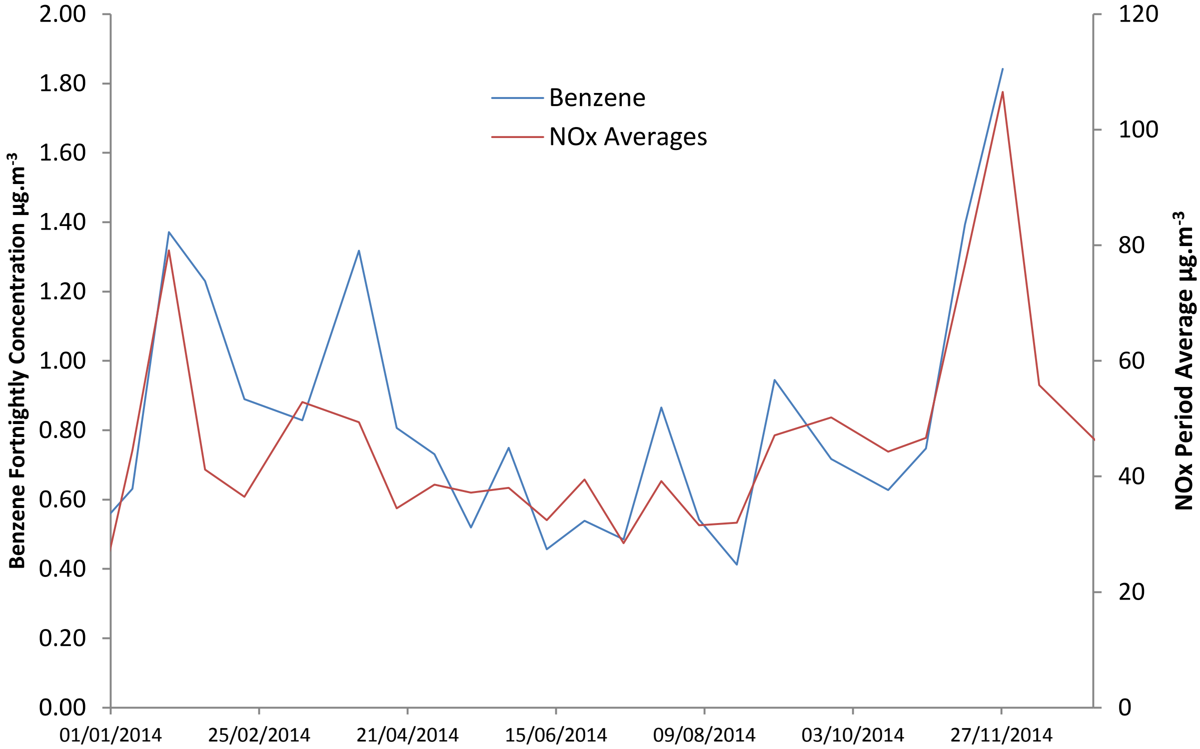


Figure 37- Glasgow Kerbside Benzene measurements and NOx averages 2014

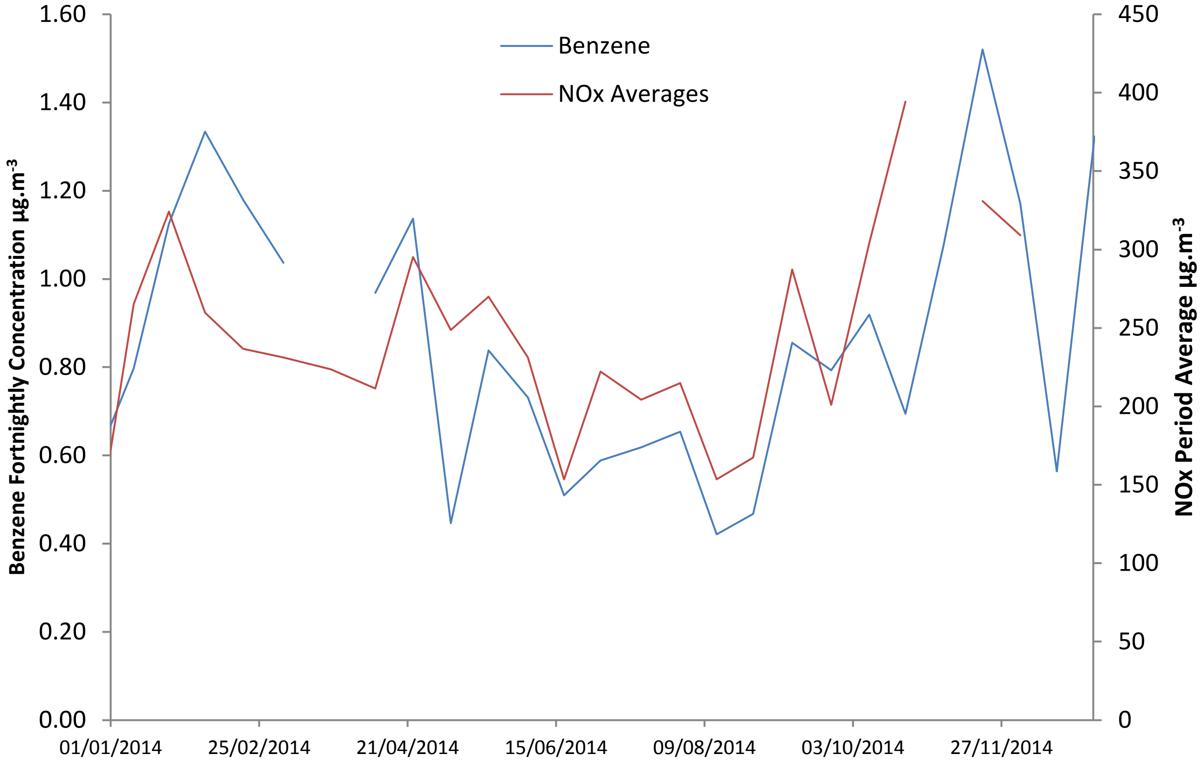


Figure 38 – Grangemouth Benzene measurements and NOx averages 2014

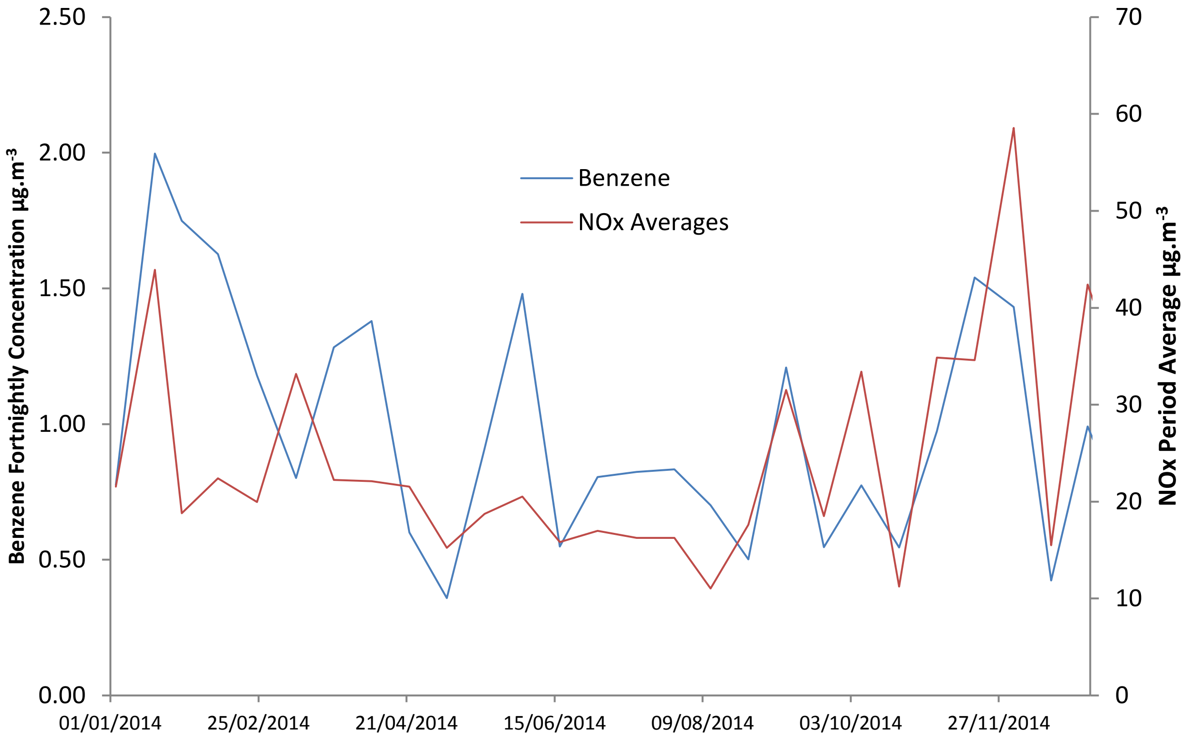


Figure 39 – Haringey Roadside Benzene measurements and NOx averages 2014

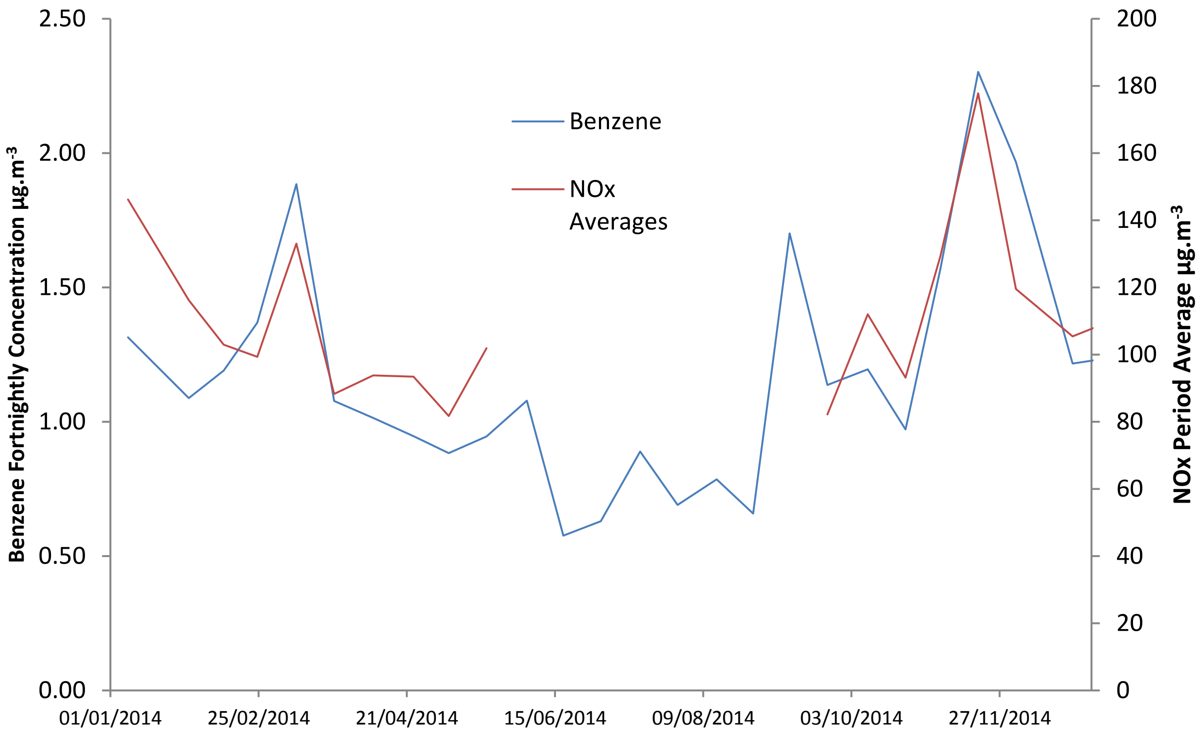


Figure 40 – Leamington Spa Benzene measurements and NOx averages 2014

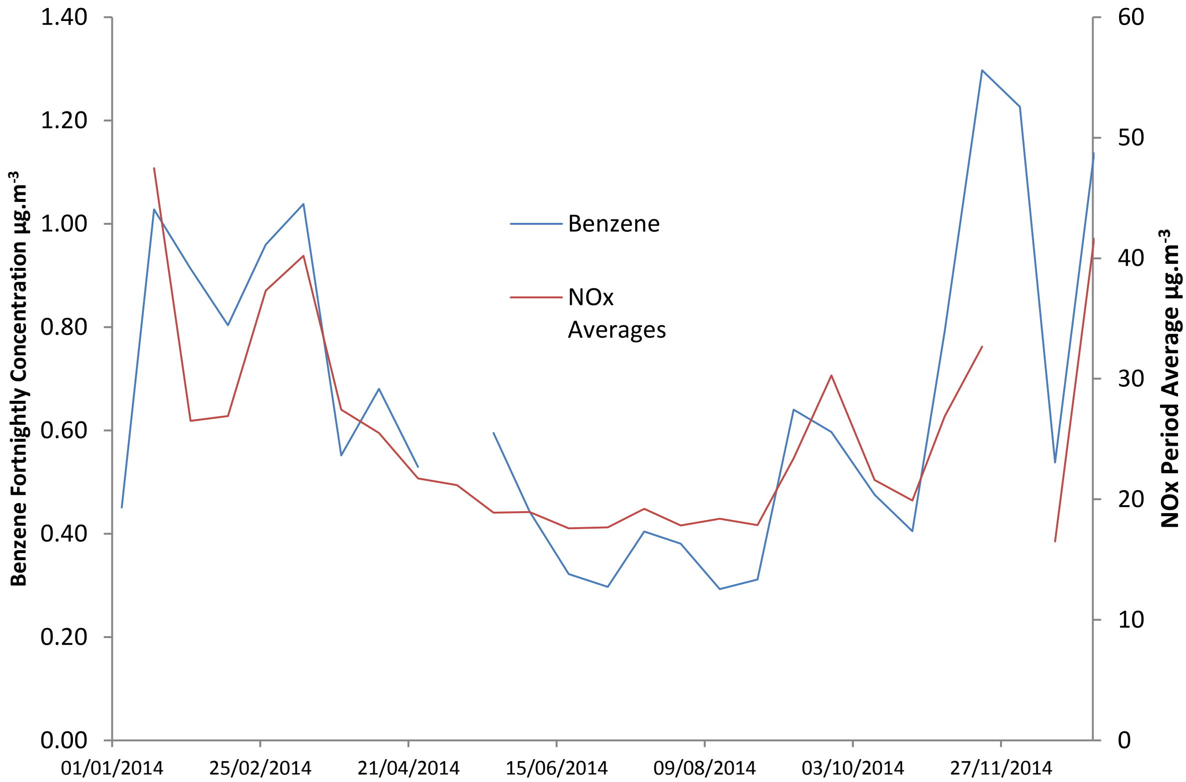


Figure 41 – Liverpool Speke Benzene measurements and NOx averages 2014

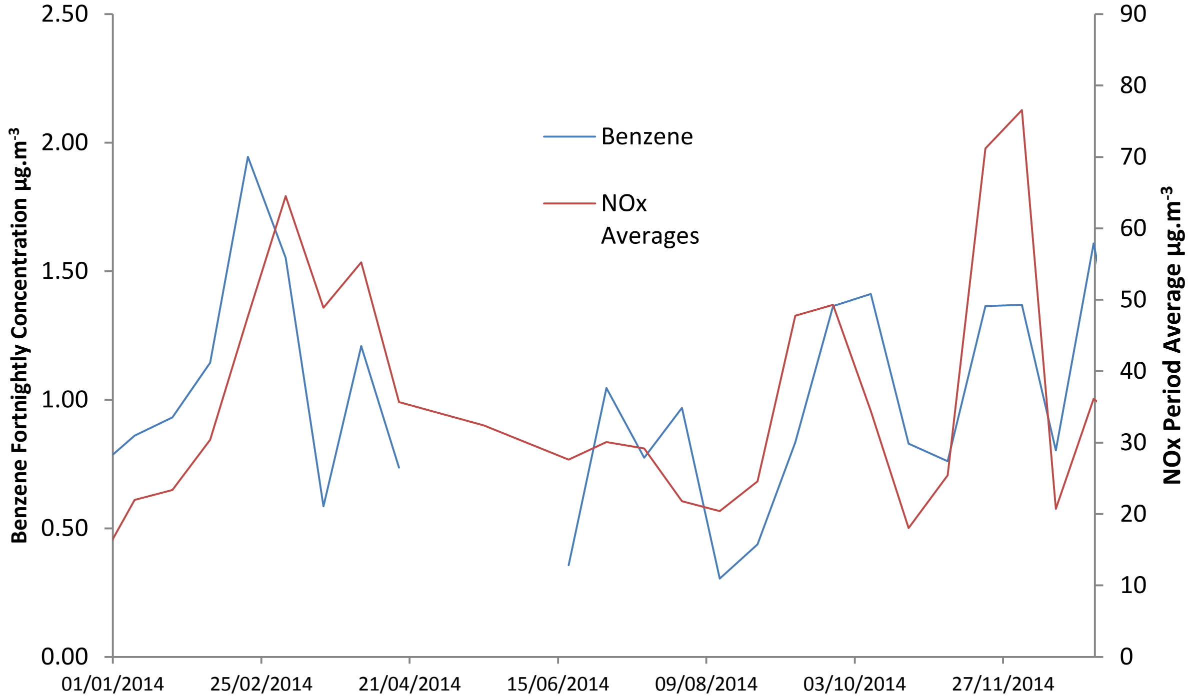


Figure 42 – London Bloomsbury Benzene measurements and NOx averages 2014

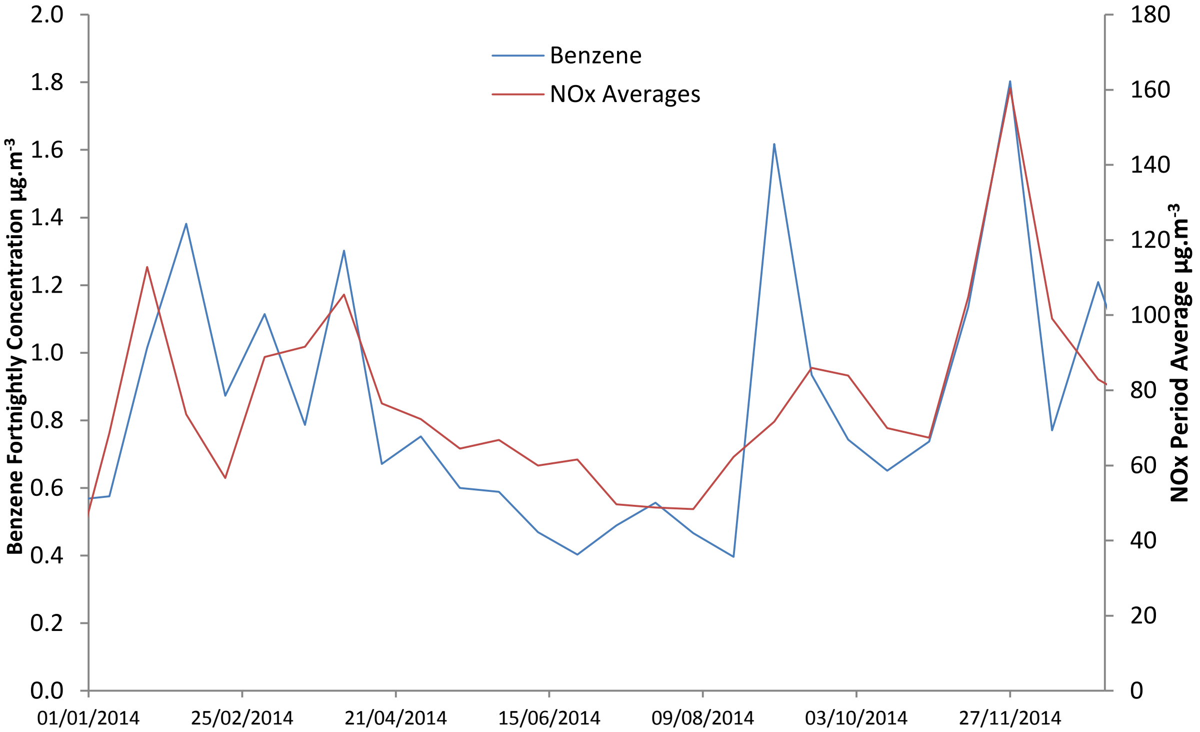


Figure 43 – Manchester Piccadilly Benzene measurements and NOx averages 2014

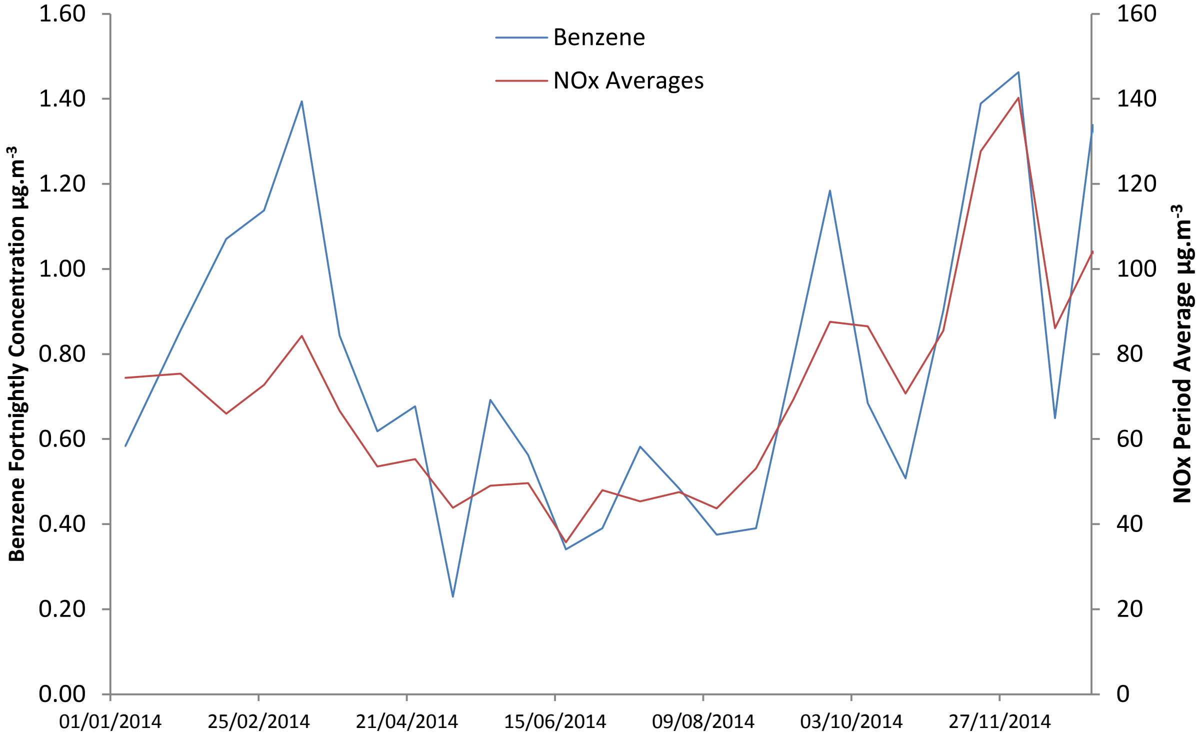


Figure 44 – Middlesbrough Benzene measurements and NOx averages 2014

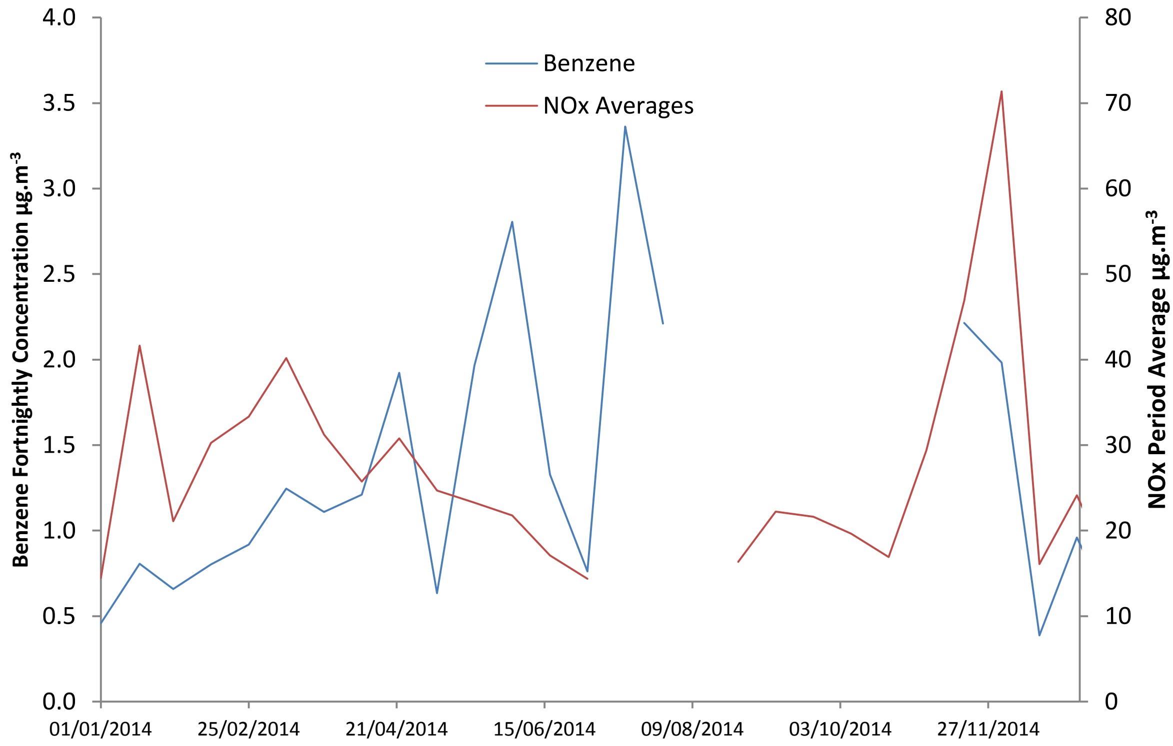


Figure 45 Newcastle Centre Benzene measurements and NOx averages 2014

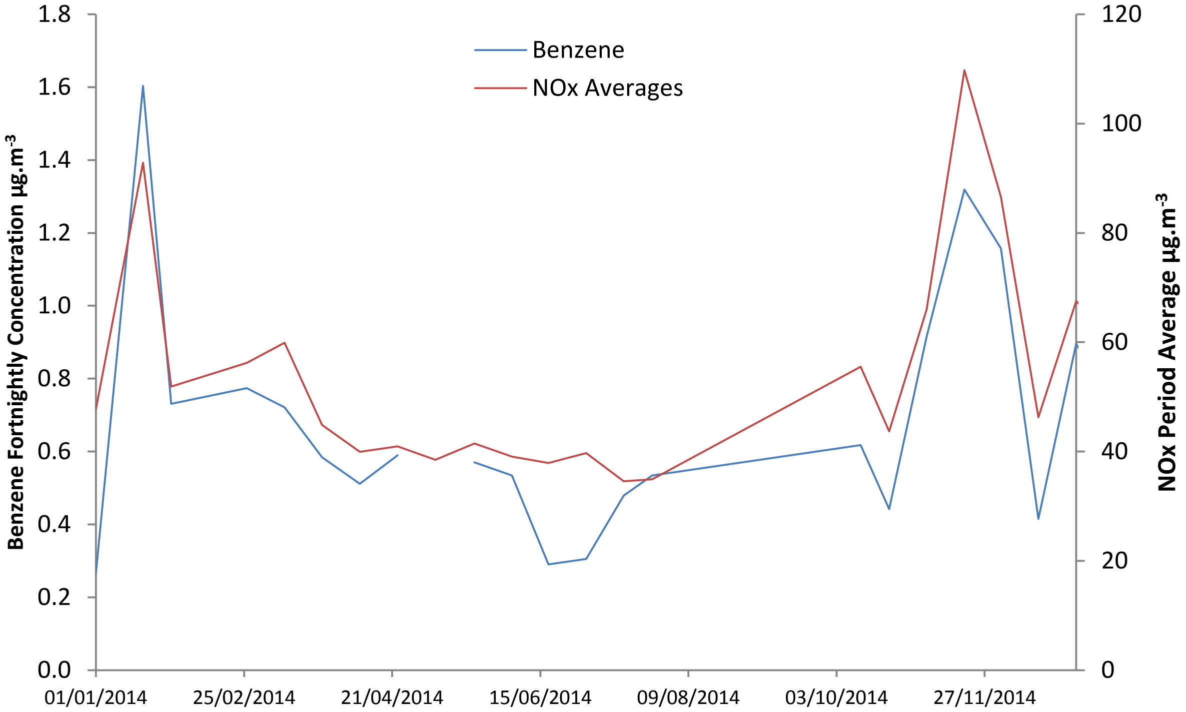


Figure 46 – Newport Benzene measurements and NOx averages 2014

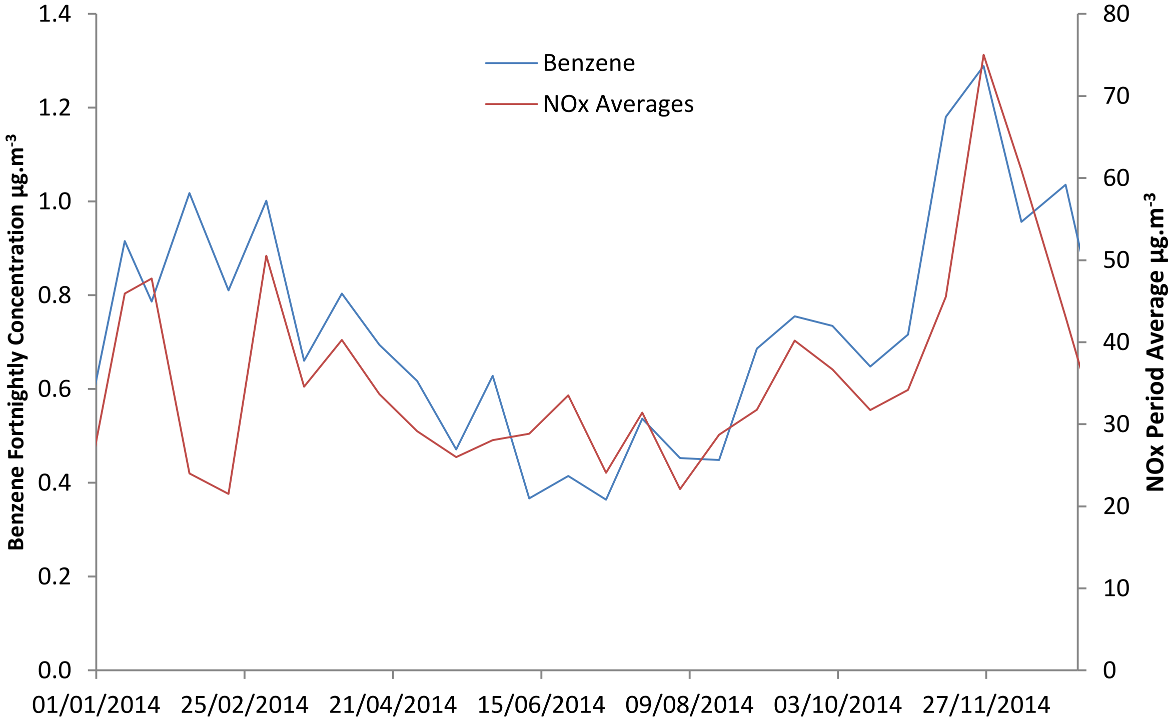


Figure 47 – Norwich Lakenfields Benzene measurements and NOx averages 2014

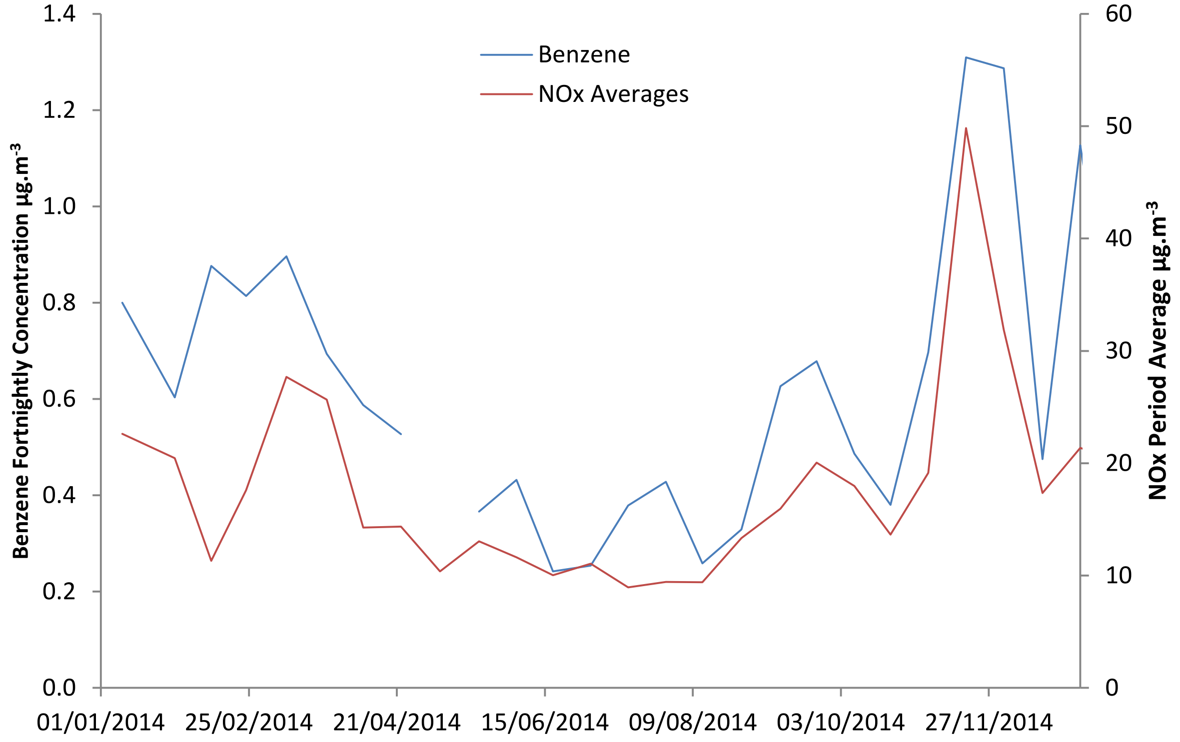


Figure 48 – Nottingham Centre Benzene measurements and NOx averages 2014

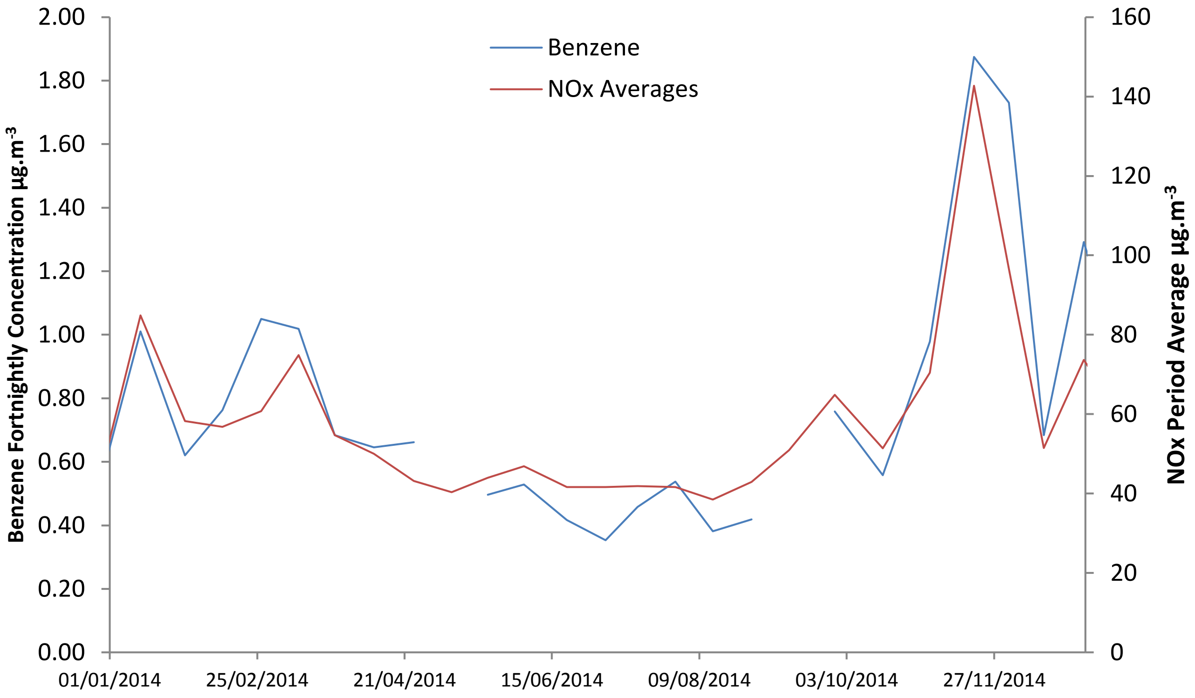


Figure 49 – Oxford Centre Roadside Benzene measurements and NOx averages 2014

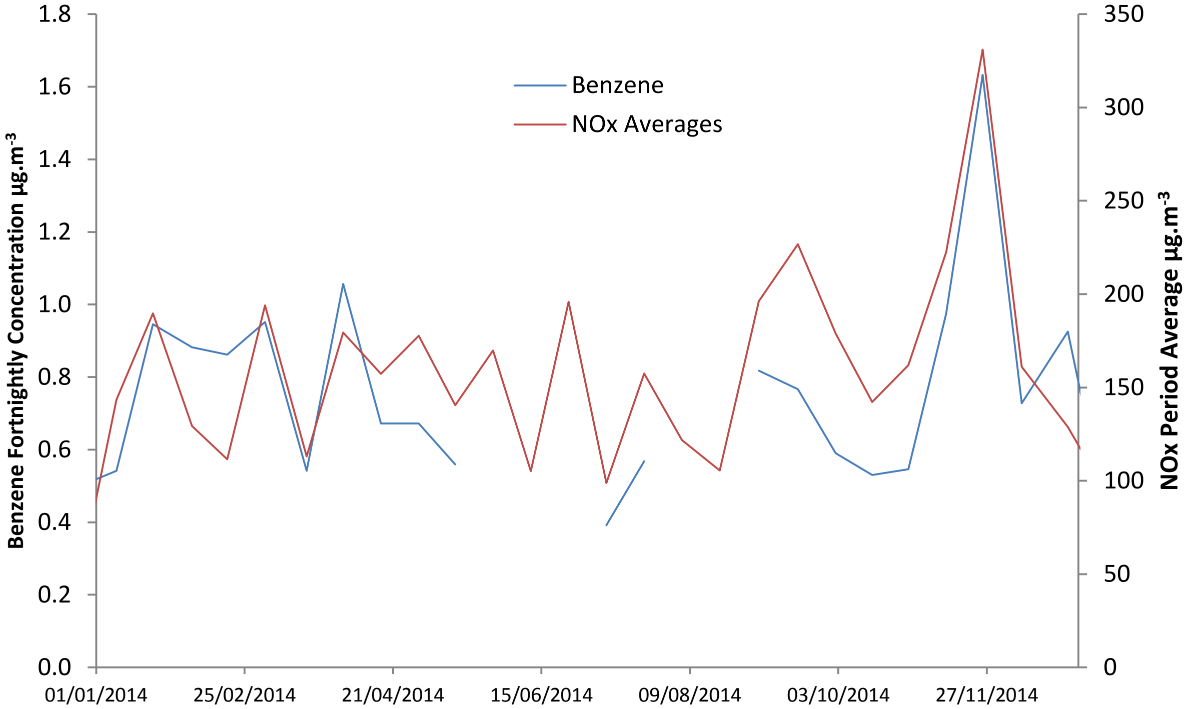


Figure 50 – Oxford St Ebbes Benzene measurements and NOx averages 2014

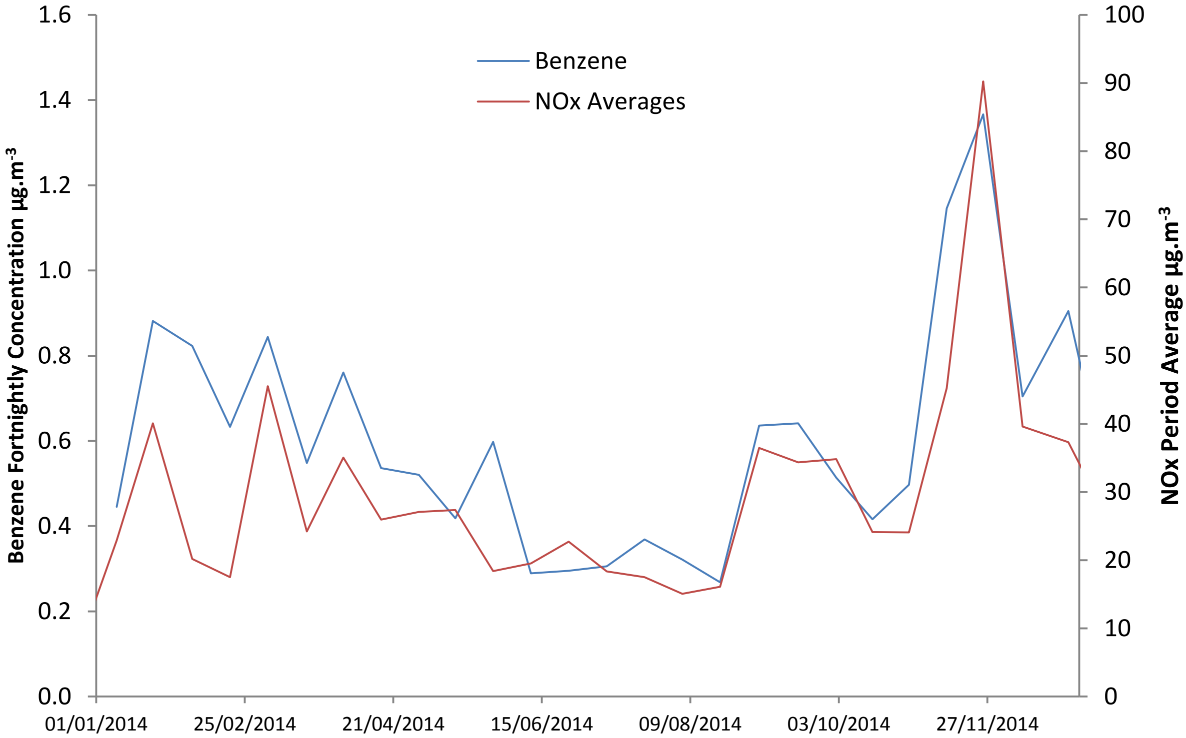


Figure 51 – Scunthorpe Town Benzene measurements compared against 2008/50/EC limit values for 2014

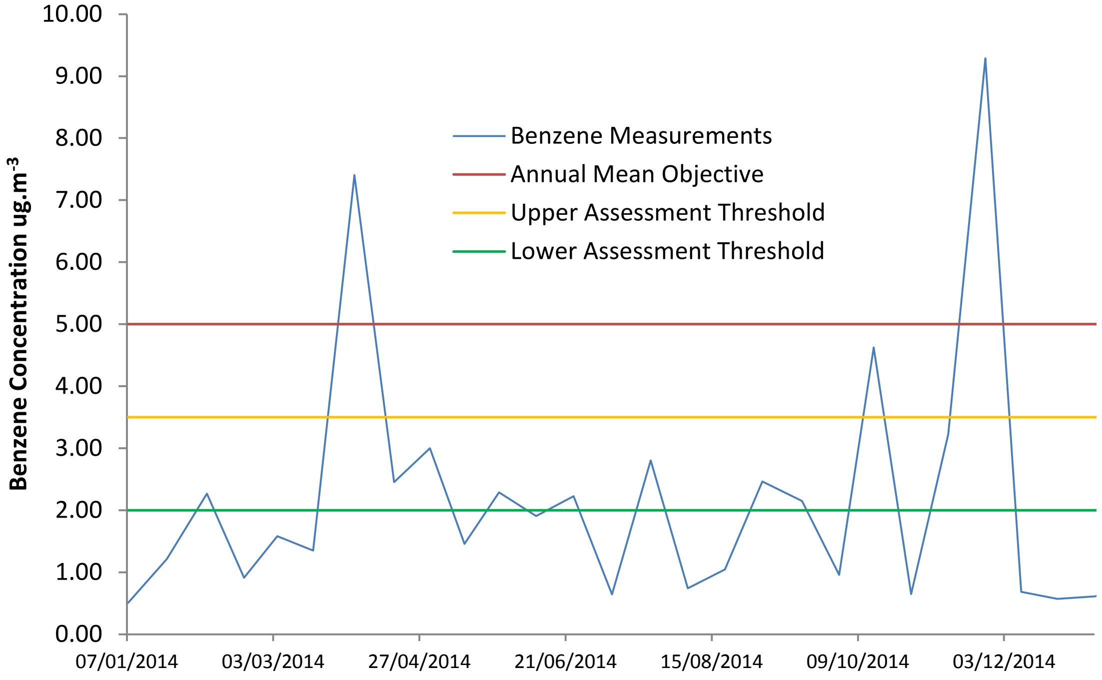


Figure 52 – Sheffield Devonshire Green Benzene measurements and NOx averages 2014

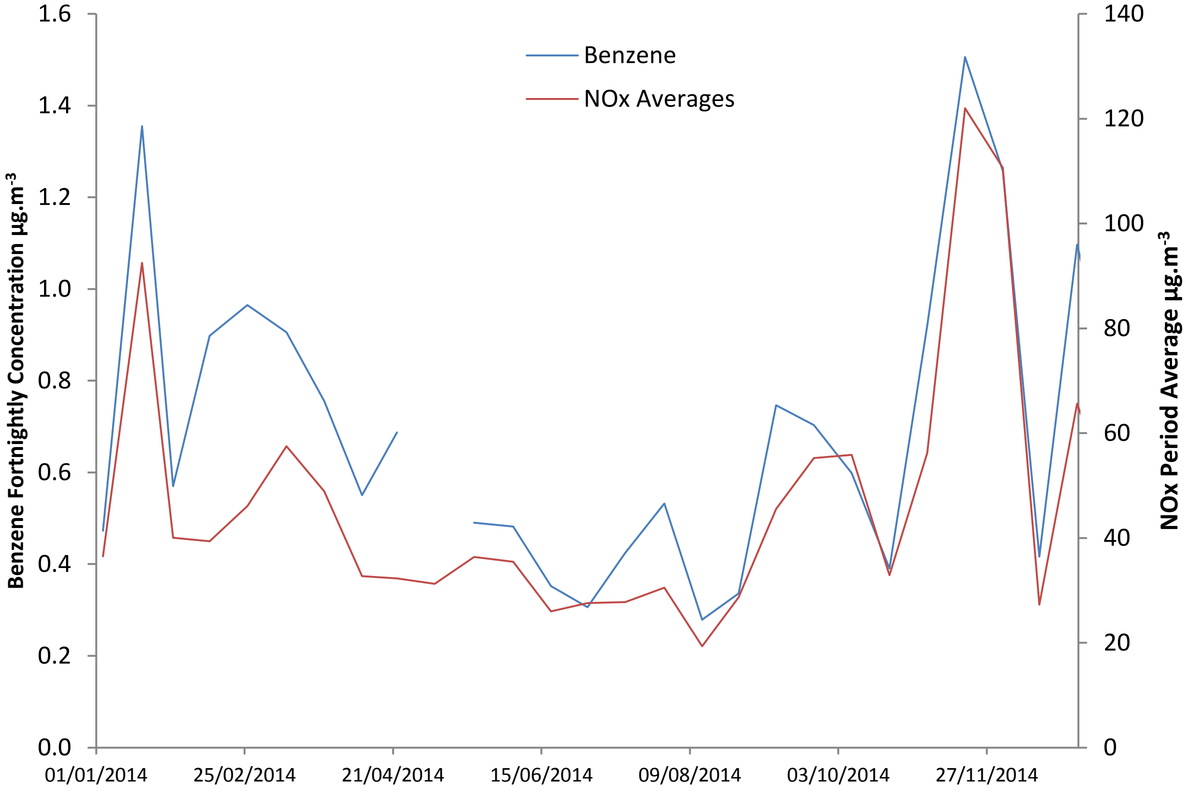


Figure 53 – Southampton Benzene measurements and NOx averages 2014

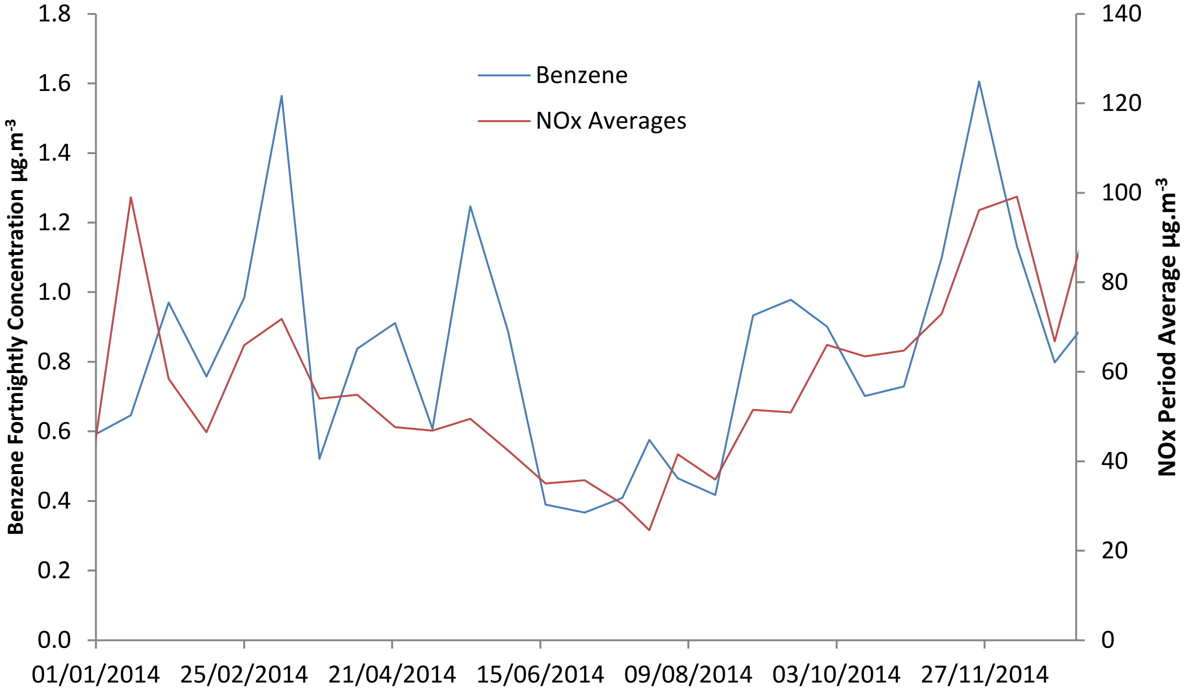


Figure 54 – Stockton-on-Tees Eaglescliffe Benzene measurements and NOx averages 2014

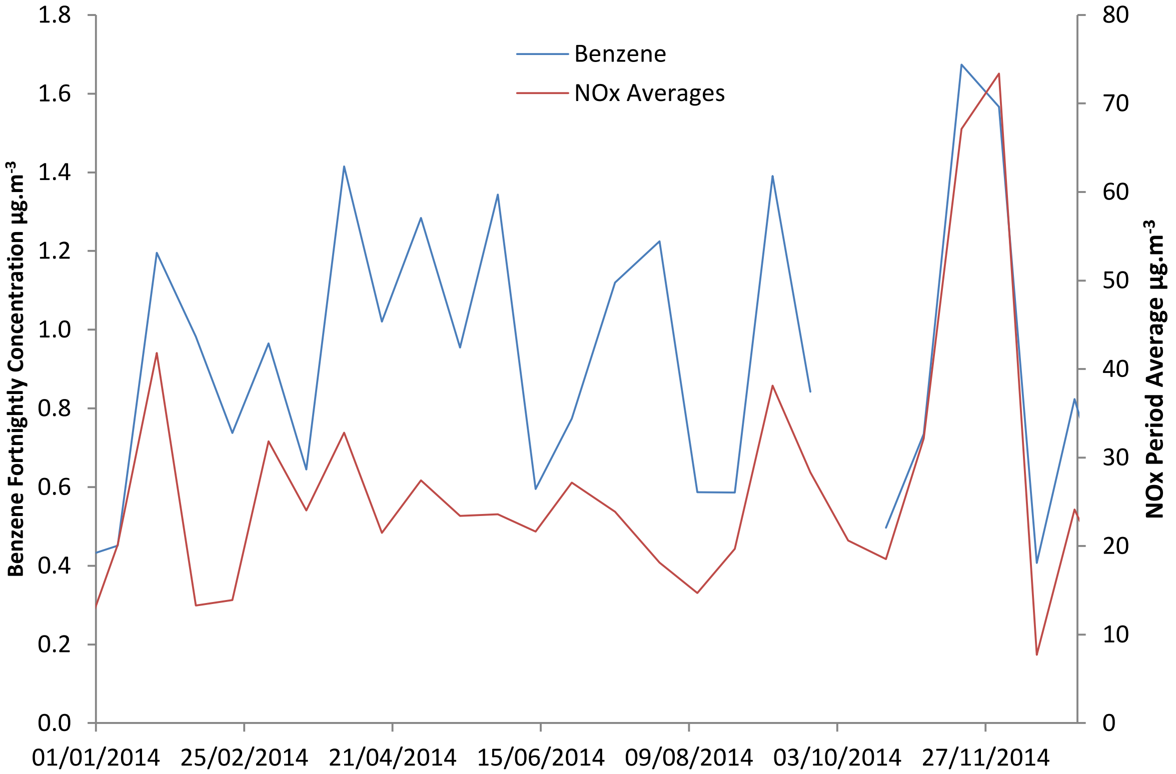


Figure 55 – Stoke-on-Trent Centre Benzene measurements and NOx averages 2014

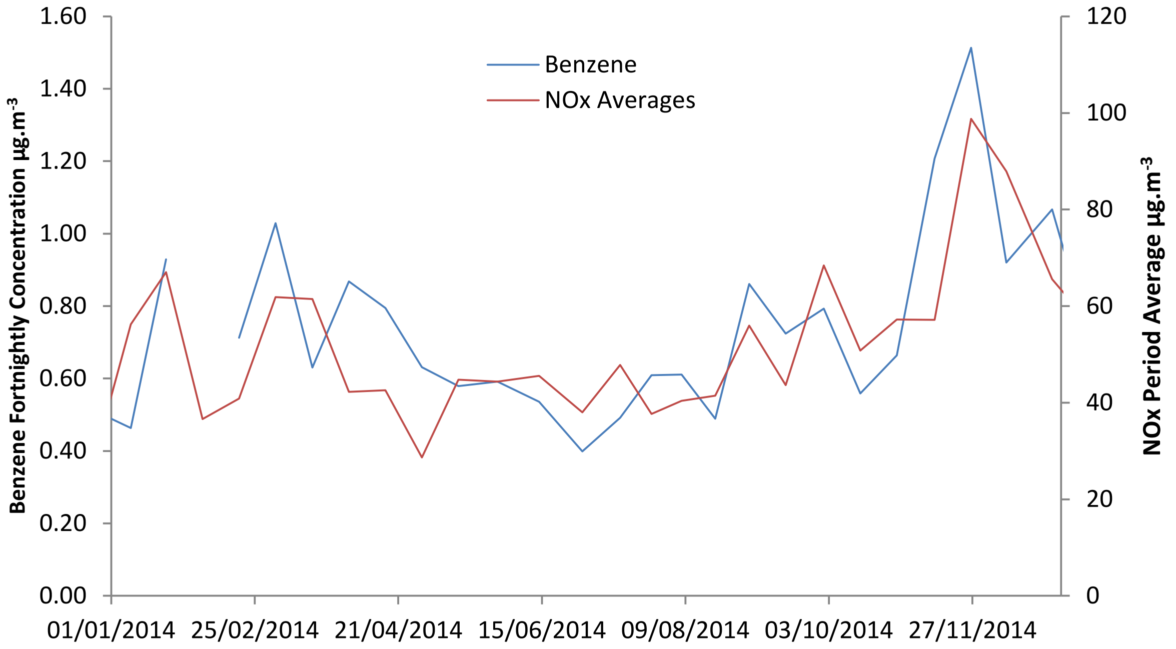
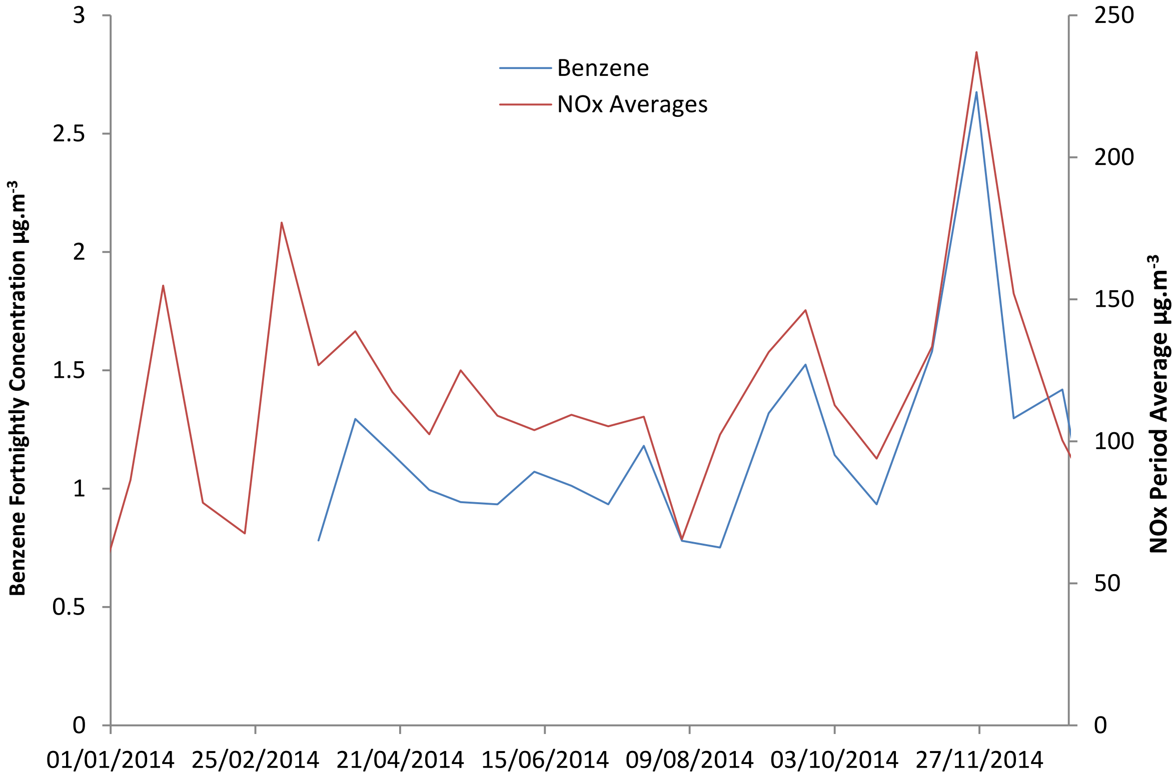


Figure56 – Tower Hamlets Roadside Benzene measurements and NOx averages 2014



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