UK Hydrocarbons Network

Annual Report for 2015

Report for the Environment Agency

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Executive summary

The UK Hydrocarbons Network comprises automatic and non-automatic systems to measure benzene in compliance with the European Directive 2008/50/EC[1] (AQD). The UK is required to meet the Directive annual mean limit value of 5 μg.m^{-3} as well as achieving compliance with Objectives in the UK Air Quality Strategy[2]. This report details the 2015 data and compares against the UK and EU limit values.

The Directive also requires the measurement of ozone precursor volatile organic compounds (VOCs). The UK Hydrocarbons Network measures 29 of the 31 listed 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 monitoring stations in operation from January to December 2015 was 96.4%. The annual mean concentration across all non-automatic monitoring stations in the UK was 0.75 μg.m^{-3}. All 34 monitoring stations used for non-automatic benzene measurements are situated in urban locations.

The mean data capture for benzene measured by the automatic hydrocarbon network in 2015 was 72.5%. The annual mean across all automatic monitoring stations in the UK was 0.5 μg.m^{-3}, of the 4 automatic monitoring stations used for hourly automatic measurements, two are situated at rural locations.

The results confirm no exceedances of EU or UK limit values and objectives at any of the Rural, Urban Traffic, Centre and Background locations during 2015.

This report also includes some analysis of long terms trends in benzene concentrations.

Box 1: Key findings for 2015

- In 2015 none of the automatic or non-automatic monitoring stations in the UK exceeded either the 5 μg.m^{-3} annual mean Limit Value, the Upper Assessment Threshold of 3.5 μg.m^{-3} or the Lower Assessment Threshold of 2.0 μg.m^{-3} for benzene set out in the EC Air Quality Directive.
- The results confirm no exceedances of EU or UK limit values and objectives at any of the Urban, Traffic and Background monitoring stations during 2015.
- Long term trends from 2002 to 2008 show benzene concentrations have declined significantly. This demonstrates that over this period motor vehicle exhaust catalysts and evaporative canisters have effectively and efficiently controlled vehicular emissions of benzene in the UK. This should have led to reduced health impact on individuals living in the UK as a result of long term exposure to these pollutants. Since 2010, concentrations have remained relatively stable up to and including 2015.

[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 2015 by the UK Hydrocarbon monitoring network.

The 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 a minimum of 34 urban traffic, urban background or urban industrial monitoring stations, and a suggested suite of ozone precursors should be measured at one or more suburban locations in the UK. Up to 29 ozone precursor substances (including 1,3-butadiene) are measured using the automatic system at 4 sites, 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 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 Health 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 Quality Objectives 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 Directive 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 for compliance reporting. 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 benzene measurement uncertainty is ±25% with a minimum data capture of 90%. A further 5% of 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 current automatic hydrocarbon network 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 its 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 Benzene 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 Energy & Environment (Ricardo), 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 2015 there were only four UK sites in operation to satisfy network requirements. 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. The following 29 species are currently measured by the automatic gas chromatographs (Table 3).

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

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. Initial development of such a standard is currently being discussed under CEN Working Group 12.

Automated thermal desorption with in situ gas chromatography and flame ionisation detection (FID) is used to measure hourly hydrocarbon concentrations. During 2015, hydrocarbons at all sites were measured using automatic Perkin Elmer Ozone Precursor Analysers. A known volume of air (800 ml) is dried and drawn through a cold trap, which contains adsorbent material. The cold trap is held at -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 30 component gas mixture.

2 Site Management

2.1 Monitoring Stations during 2015

The monitoring stations operating in the UK Hydrocarbon Network during 2015 are shown in Figure 1. Table 4 provides a full list of the non-automatic monitoring stations and associated Local Site Operators, and Table 5 provides the equivalent information for the automatic monitoring stations

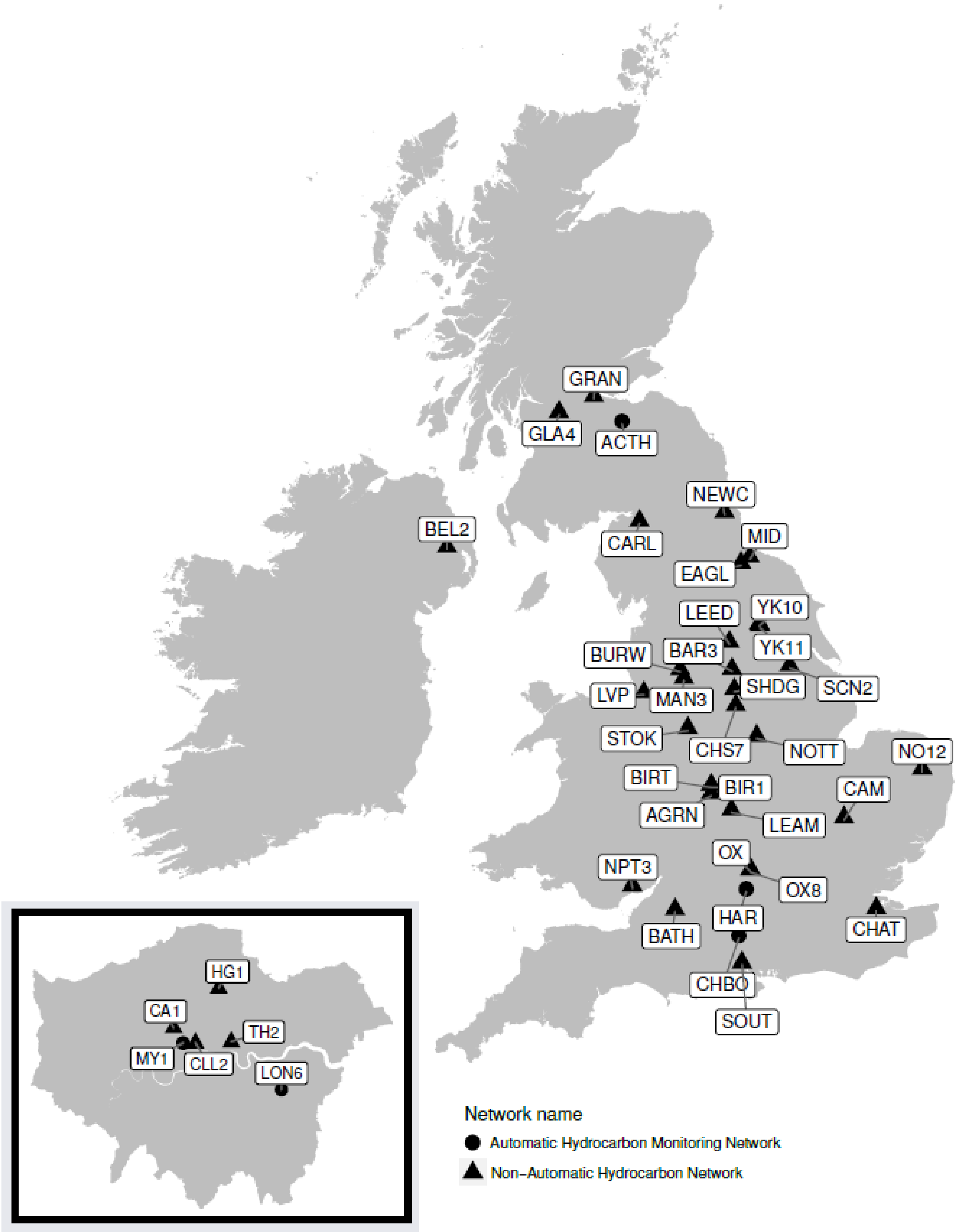

Figure 1 **Map of UK Hydrocarbon Monitoring Stations in 2015**

Table 4 Non-Automatic Hydrocarbon Network monitoring stations in 2015

Site ID	Site	Classification	Zone	Grid Ref Easting / Northing	Local Site Operator
BAR3	Barnsley Gawber	Urban Background	Yorkshire & Humberside	432529, 407472	Barnsley Council
BATH	Bath Roadside	Urban Traffic	South West	375882, 166096	Bath & North Somerset Council
BEL2	Belfast Centre	Urban Background	Belfast Urban Area	333900, 374400	Belfast City Council
BIR1	Birmingham Tyburn	Urban Background	West Midlands Urban Area	411595, 290439	Birmingham City Council
BIRT	Birmingham Tyburn Roadside	Urban Traffic	West Midlands Urban Area	411556, 290456	Ricardo Energy & Environment
BURW	Bury Whitefield Roadside	Urban Traffic	Greater Manchester Urban Area	380637, 406974	Bury Metropolitan Council
CAM	Cambridge Roadside	Urban Traffic	Eastern	545248, 258155	Cambridge Council
CA1	Camden Kerbside	Urban Traffic	Greater London Urban Area	526640, 184433	Ricardo Energy & Environment
CARL	Carlisle Roadside	Urban Traffic	North West & Merseyside	339442, 555956	Carlisle Council
CHAT	Chatham Roadside	Urban Traffic	South East	577435, 166993	Medway Council
CHS7	Chesterfield Roadside	Urban Traffic	East Midlands	436351, 370682	Chesterfield Council
GLA4	Glasgow Kerbside	Urban Traffic	Glasgow Urban Area	258708, 665200	Ricardo Energy & Environment
GRAN	Grangemouth	Urban Industrial	Central Scotland	293837, 681035	Falkirk Council
HG1	Haringey Roadside	Urban Traffic	Greater London Urban Area	533885, 190669	Ricardo Energy & Environment
LEAM	Leamington Spa	Urban Background	West Midlands	431932, 265743	Warwick District Council
LEED	Leeds Centre	Urban Background	West Yorkshire Urban Area	429976, 434268	Leeds City Council
LVP	Liverpool Speke	Urban Background	Liverpool Urban Area	343860, 383598	AECOM
CLL2	London Bloomsbury	Urban Background	Greater London Urban Area	530107, 182041	Bureau Veritas
MAN3	Manchester Piccadilly	Urban Background	Greater Manchester Urban Area	384310, 398325	Manchester City Council
MID	Middlesbrough	Urban Industrial	Teesside Urban Area	450480, 519632	Middlesbrough BC
NEWC	Newcastle Centre	Urban Background	Tyneside	425016, 564940	Newcastle City Council
NPT3	Newport	Urban Background	South Wales	33410, 189604	Newport City Council
NO12	Norwich Lakenfields	Urban Background	Eastern	623637, 306940	Mark Leach
NOTT	Nottingham Centre	Urban Background	Nottingham Urban Area	457420, 340050	Nottingham City Council

Site ID	Site	Classification	Zone	Grid Ref Easting / Northing	Local Site Operator
OX	Oxford Centre Roadside	Urban Traffic	South East	451366, 206152	Oxford City Council
OX8	Oxford St Ebbes	Urban Background	South East	451225, 206009	Oxford City Council
SCN2	Scunthorpe Town	Urban Industrial	Yorkshire & Humberside	490338, 410836	North Lincs CBC
SHDG	Sheffield Devonshire Green	Urban Background	Sheffield Urban Area	434816, 386990	Sheffield City Council
SOUT	Southampton Centre	Urban Background	Southampton Urban Area	442565, 112255	Southampton City Council
EAGL	Stockton-on-Tees - Eaglescliffe	Urban Traffic	North East	441620, 513673	Stockton on Tees BC
STOK	Stoke-on-Trent Centre	Urban Background	The Potteries	388348, 347894	City of Stoke on Trent Council
TH2	Tower Hamlets Roadside	Urban Traffic	Greater London	535927, 182218	Kings College, London
YK10	York Bootham	Urban Background	Yorkshire & Humberside	460024, 452768	City of York Council
YK11	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

Table 5 Automatic Hydrocarbon Network monitoring stations in 2015

Site ID	Site	Classification	Zone	Grid Ref Easting / Northing	Local Site Operator
HAR	Harwell	Rural Background	South West	446772, 186020	Ricardo Energy & Environment
CHBO*	Chilbolton Observatory	Rural Background	South East	439390, 139078	Ricardo Energy & Environment
MY1	Marylebone Road	Urban Traffic	Greater London Urban Area	528120, 182000	Kings College, London
ACTH	Auchencorth Moss	Rural Background	Scotland	322050, 656250	CEH
LON6	London Eltham	Suburban Background	Greater London Urban Area	543978, 174668	Greenwich Borough Council

*The new Chilbolton monitoring station replaced the Harwell monitoring station at the end of 2015, but didn't start making any measurements until January 2016

2.2 Monitoring Regime Assessment

The size and shape of the national monitoring networks is determined principally by the need to make measurements for compliance assessments under the Air Quality Directive. The Directive provides criteria to determine monitoring requirements according to concentrations relative to a Lower Assessment Threshold (LAT) and an Upper Assessment Threshold (UAT) and population by zone. These data inform the number of monitoring stations required by zone. This number is then adjusted according to the Directive due to the application of Supplementary Assessment (modelling) which allows for a reduction in stations by up to 50%. The assessment is based on five years of monitoring and modelling data and must be repeated at least every five years to ensure that the pollution climate of a Member State is being adequately represented by its compliance reporting. The last formal assessment of the national monitoring networks was made using 2006-2010 monitoring data[7]. A revised assessment using 2011 to 2015 monitoring data is currently under way.

2.3 Equipment Maintenance and Audits

All non-automatic monitoring stations were visited by Ricardo field engineers every 6 months during 2015 in order to carry out site audits and to undertake routine maintenance of the equipment. The main functions of these 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 April and October 2015. Routine flow measurements have been used to calculate sample volumes for the 2015 data set by means of interpolation. The schedule and results of 2015 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 stations 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 (Ricardo Energy & Environment) provides an annual reference gas audit in addition to the automatic on site calibrations. These audits use the instrument

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

sample port as opposed to the analyser calibrant port. The sample line is inspected and cleaned/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. Data obtained when the instrument is stabilising following repair 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. The schedule of service and audit visits can be seen in Appendix 2.

3 Data capture and Annual Statistics for 2015

3.1 Comparison with Limit Values and Objectives

The annual mean concentrations of benzene measured using non-automatic samplers over the calendar year 2015 are provided in Table 6, alongside the associated data capture statistics. Table 8 provides similar statistics for the automatic monitoring of benzene and 1,3-butadiene. Tables 7, 9, 10, 11 and 12 detail the reasons behind any significant data loss or removal at each of the network stations.

Annual time weighted mean concentrations at all monitoring stations were below the Limit Value of 5 $\mu g.m^{-3}$ 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 2015

Site	Time Weighted Annual Mean Benzene ($\mu g.m^{-3}$)	Maximum Fortnightly Result ($\mu g.m^{-3}$)	Minimum Fortnightly Result ($\mu g.m^{-3}$)	Data capture
Barnsley Gawber	0.52	1.06	0.29	100%
Bath Roadside	1.50	2.54	0.72	96%
Belfast Centre	0.52	1.13	0.19	100%
Birmingham Tyburn	0.71	1.22	0.33	93%
Birmingham Tyburn Roadside	0.85	1.63	0.44	96%
Bury Whitefield Roadside	0.64	2.28	0.25	100%
Cambridge Roadside	0.70	1.26	0.37	100%
Camden Kerbside	1.02	1.72	0.56	100%
Carlisle Roadside	0.78	1.62	0.21	87%
Chatham Roadside	0.80	1.25	0.54	100%
Chesterfield Roadside	0.66	1.38	0.36	88%
Glasgow Kerbside	0.75	1.54	0.36	96%
Grangemouth	0.72	1.69	0.27	100%
Haringey Roadside	1.00	1.67	0.49	96%
Leamington Spa	0.61	1.14	0.24	97%
Leeds Centre	0.65	1.28	0.30	96%
Liverpool Speke	0.76	1.61	0.35	96%
London Bloomsbury	0.75	1.37	0.39	96%
Manchester Piccadilly	0.67	1.34	0.30	100%
Middlesbrough	0.98	2.09	0.39	100%
Newcastle Centre	0.58	1.09	0.30	100%
Newport	0.62	1.04	0.30	100%
Norwich Lakenfields	0.56	1.13	0.27	100%

Site	Time Weighted Annual Mean Benzene (µg.m^{-3})	Maximum Fortnightly Result (µg.m^{-3})	Minimum Fortnightly Result (µg.m^{-3})	Data capture
Nottingham Centre	0.70	1.29	0.34	100%
Oxford Centre Roadside	0.60	1.17	0.29	100%
Oxford St Ebbes	0.54	1.05	0.24	100%
Scunthorpe Town	1.18	2.77	0.30	95%
Sheffield Devonshire Green	0.69	1.28	0.35	81%
Southampton Centre	0.69	1.36	0.38	100%
Stockton-on-Tees Eaglescliffe	0.66	1.17	0.29	96%
Stoke-on-Trent Centre	0.70	1.22	0.39	96%
Tower Hamlets Roadside	1.09	2.01	0.30	95%
York Bootham	0.50	1.04	0.20	96%
York Fishergate	0.94	1.53	0.45	82%

Table 7 Non-Automatic Sampler Faults and data loss in 2015

Site	Start	End	Days	Reason
Bath Roadside	24/08/2015	09/09/2015	15	Sampler pump failure, pump replaced during call out visit
Birmingham Tyburn	08/04/2015	22/04/2015	14	Suspect analytical results, data nulled following quality circle review
Birmingham Tyburn	23/10/2015	04/11/2015	12	Samples lost by Royal Mail on return
Birmingham Tyburn Roadside	09/09/2015	25/09/2015	16	Suspect analytical results, data nulled following quality circle review
Carlisle Roadside	04/09/2016	16/09/2015	12	Suspect analytical results, data nulled following quality circle review
Carlisle Roadside	25/11/2015	21/04/2016	36*	AURN site flooded, elevated to red on Health and Safety database. Benzene sampler and pump replaced and restarted following recommissioning of site.
Chesterfield Roadside	18/12/2014	29/01/2015	29*	Sampler pump failure, pump replaced during call out visit
Chesterfield Roadside	10/09/2015	24/09/2015	14	Suspect analytical results, data nulled following quality circle review
Glasgow Kerbside	01/10/2015	15/10/2015	14	Analytical laboratory quality control tube failure at end of analysis. Analytical data erroneous, not reported.
Haringey Roadside	02/09/2015	15/09/2015	13	Suspect analytical results, data nulled following quality circle review
Leamington Spa	11/12/2015	23/12/2015	14	Suspect analytical results, data nulled following quality circle review
Leeds Centre	02/09/2015	17/09/2015	13	Suspect analytical results, data nulled following quality circle review
Liverpool Speke	19/11/2015	03/12/2015	14	Suspect analytical results, data nulled following quality circle review
London Bloomsbury	17/09/2015	01/10/2015	14	Suspect analytical results, data nulled following quality circle review
Scunthorpe Town	17/06/2015	06/07/2015	19	AURN Hut replaced, engineer did not switch sampler back on. LSO issued call out. Field team member switched the sampler back on.
Sheffield Devonshire Green	15/04/2015	10/06/2015	56	Site vandalism, elevated to red on Health and Safety database, site switched off until AURN Hut repaired
Sheffield Devonshire Green	06/08/2015	19/08/2015	13	Samples lost by Royal Mail on return

Site	Start	End	Days	Reason
Stockton-on-Tees Eaglescliffe	07/09/2015	21/09/2015	14	Suspect analytical results, data nulled following quality circle review
Stoke-on-Trent Centre	14/10/2015	28/10/2015	14	Suspect analytical results, data nulled following quality circle review
Tower Hamlets Roadside	23/04/2015	12/05/2015	19	Suspect analytical results, data nulled following quality circle review
York Bootham	28/10/2015	11/11/2015	14	Suspect analytical results, data nulled following quality circle review
York Fishergate	23/12/2015	06/01/2016	8*	Analysis indicated the sorbent was contaminated therefore no reportable result

*Days lost during 2015 only

3.1.2 Automatic Hydrocarbon Network Statistics

Table 8 Benzene and 1,3-butadiene Statistics 2015

Site	Pollutant	Annual Mean (µg.m^{-3})	Maximum (µg.m^{-3})	Data capture (%)
Auchencorth Moss	1,3-butadiene	0.014	0.43	41
	benzene	0.15	1.4	38
Harwell	1,3-butadiene	0.066	0.22	86
	benzene	0.32	1.6	86
London Eltham	1,3-butadiene	0.066	0.88	87
	benzene	0.52	4.6	88
London Marylebone Road	1,3-butadiene	0.029	0.49	78
	benzene	1.0	5.4	78

Limit values for benzene and 1,3-butadiene only exist for benzene and 1,3-butadiene, statistics for all ozone precursor VOCs reported can be seen in Appendix 3.

Table 9 Auchencorth Moss Faults and data loss during 2015

Start	End	Days lost	Reason
02/01/2015	14/01/2015	12	TurboMatrix fault. Perkin Elmer call out on 07/01/2015. TD Power control board installed not compatible. Engineer broke the transfer line. Correct board and transfer line delivered and fitted at Engineer visit on 14/01/2016.
14/01/2015	28/01/2015	14	Power cut two hours' afters previous repair. LSO call out to reset system on 19 and 21/01/2015, system not running for more than one hour. Perkin Elmer call out on 28/01/2015 to reset system.
28/01/2015	17/06/2015	140	Data removed following quality circle, following multiple engineer call outs, Ricardo decided there must have been a problem with sample inlet despite function checks being acceptable. Sample line replaced on 10th June 2015.
14/08/2015	02/09/2015	19	Communications failure
24/09/2015	30/09/2015	6	GC Fault, LSO call out to reset system
09/10/2015	20/10/2015	11	Hydrogen generator failure, poor chromatography. Engineer call out. New column fitted for c6-c9 VOCs. replaced electrolyte in generator after flushing palladium cell with deionised water.
08/11/2015	18/11/2015	10	GC Flow error, Hydrogen generator flow is too low. Spare hydrogen generator checked, couriered to site and installed by Engineer.

Table 10 Harwell faults and data loss during 2015

Start	End	Days lost	Reason
29/04/2015	30/04/2015	1	Compressor fault, Engineer Call out
06/05/2015	08/05/2015	2	Poor chromatography. Engineer call out. Replaced Hydrogen generator and re-installed original generator following workshop repair on 13/05/2015.
19/06/2015	22/06/2015	3	Compressor failed, Engineer call out. Repaired at visit
28/06/2015	30/06/2015	2	Power cut, LSO Call out to restart Hydrogen generator
26/07/2015	30/07/2015	4	GC Fault. Engineer call out. Fitted a new Helium regulator and BP1 column. Fused silica transfer line replaced.
01/08/2015	04/08/2015	3	Compressor failed, Engineer Call out. Repaired at visit
14/08/2015	19/08/2015	5	GC Locked up, Daily checker remotely restarted. System failure, Engineer called out, repaired at visit.
21/08/2015	26/08/2015	5	Instrument communication error. System reset
11/09/2015	15/09/2015	4	Nitrogen leak, replaced regulator.
17/09/2015	23/09/2015	6	Nitrogen leak, replaced nitrogen line.
09/12/2015	17/12/2015	8	Preventative maintenance visit on 9th December. System stopped running at midnight, comms error. Engineer call out 16th December, full system reset.
29/04/2015	30/04/2015	1	Compressor fault, Engineer Call out
06/05/2015	08/05/2015	2	Poor chromatography. Engineer call out. Replaced Hydrogen generator and re-installed original generator following workshop repair on 13/05/2015.

Table 11 London Eltham faults and data loss during 2015

Start	End	Days lost	Reason
24/03/2015	31/03/2015	7	Hydrogen generator failure, spare generator couriered and installed on 31/03/2016
20/05/2015	24/05/2015	4	Poor chromatography, multiple engineer call outs to repair fault including new FID head collector and amplifier board (twice), repair compressor and replace jet. Remake all dean switch connections. Found leak on TD, repaired leak and replaced cold trap.
11/09/2015	17/09/2015	6	Power cut to out building containing compressor. Local authority provided electrician to repair fixed electrical fault
15/10/2015	30/10/2015	15	GC locked up and data nulled during ratification following findings at engineer call outs on 26th, 27th, 29th and 30th October. Replaced dryer, rotor, silica transfer line, repaired valve in online system that puts trap in line with pump, replaced rotor turn fitting. Data collected in between was erroneous and has not been reported.

Table 12 London Marylebone Road faults and data loss during 2015

Start	End	Days lost	Reason
20/02/2015	27/02/2015	7	Hydrogen Generator not reset following a power cut, engineer call out, issued LSO call out. LSO unable to restart system. Engineer called out. Engineer restarted generator. LSO retrained in line with manuals.
16/03/2015	25/03/2015	9	Compressor failure, spare compressor installed temporarily on 25th March.
08/04/2015	10/04/2015	2	Turbomatrix fault, LSO call out, reset Turbomatrix.
07/05/2015	14/05/2015	7	Poor chromatography identifed, LSO found no problem at call out. Zero air generator had been switched off by site visitor by mistake. Data nulled for period. Zero air generator plugged into different location and re-labelled.
10/06/2015	16/06/2015	6	GC Fault, LSO call out for system reset, some poor chromatography providing erroneous data prior to system shutdown nulled.
21/06/2015	22/06/2015	1	Power cut, LSO call out to restart Hydrogen generator
25/09/2015	04/11/2015	40	Trap temperature failure, trap not cooling properly. Parts ordered from USA and installed on 30th September. No peaks in chromatography following visit. Further engineer call outs on 10th and 14th October, stripped down the ATD, replace fused silica line, remade all dean switch connections, replaced cold trap. System not starting, Engineer call out 19th October, repair sample pump and replaced filters in online system. Chromatography erroneous for a few days before settling down. Data only reported after 4th November.

The 2011 Implementing Provisions Regulations[8] (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 with a specific data flag. 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.

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

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

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's 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.

3.2 Long term trends

With so many sites it is difficult to show the trends by individual site for all 62 locations used since the start of monitoring in 2000. The plot below (Figure 2) does however provide an indication of the variation in trends split by site type.

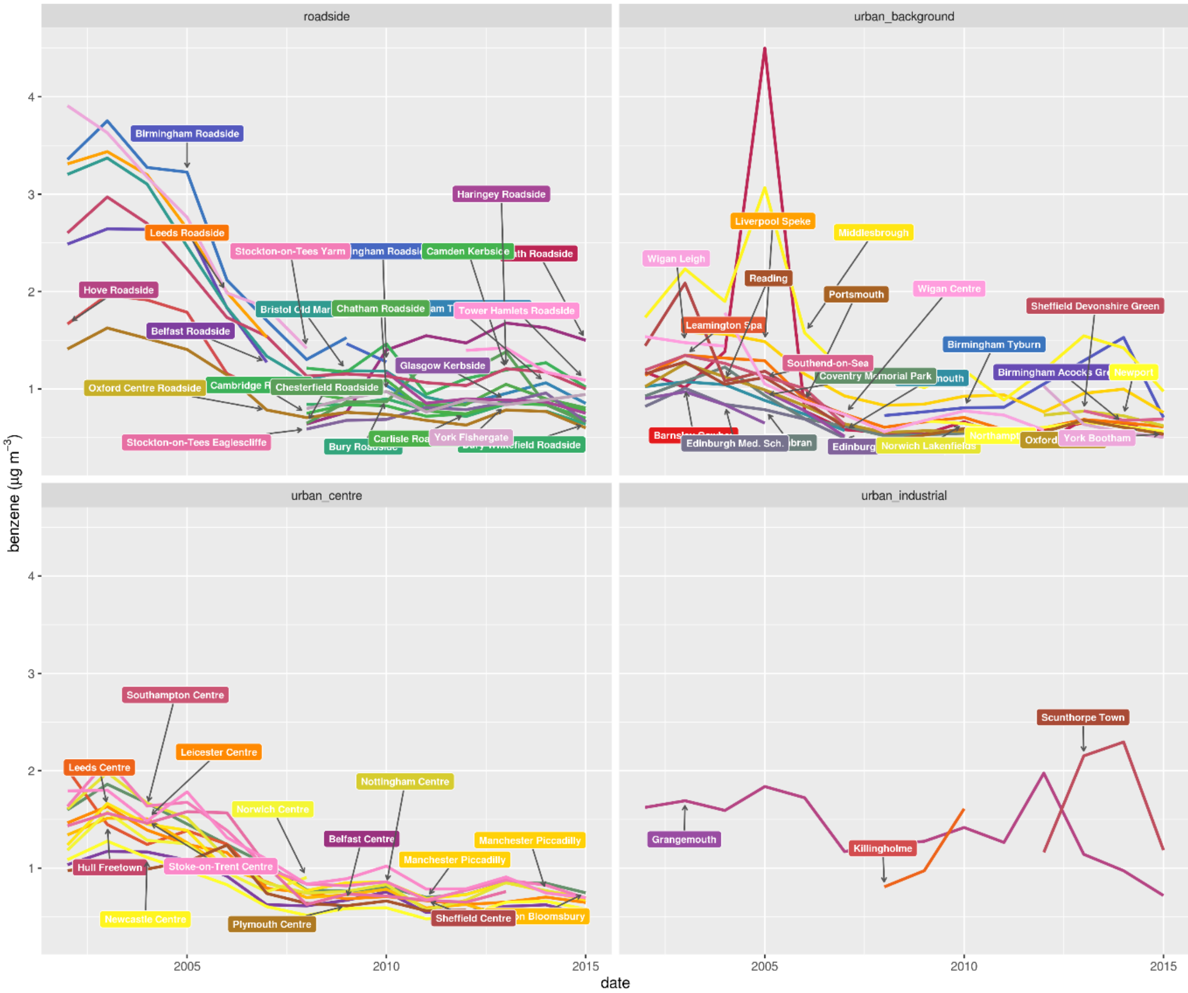

Figure 2 Non-Automatic Benzene Long term trends 2002 – 2015 (µg.m^{-3})

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

Trend estimates using robust statistical techniques in openair provide a way of quantifying the trends over time as a percentage change in benzene concentration per year. To help with interpretation the trends are ordered and a dashed line is shown for zero change. The plot below shows that almost all sites showed a decrease in benzene concentration over the period 2002 to 2015. Note that the error bars relate to the 95% confidence intervals, which reveals that the trends at some sites are relatively uncertain.

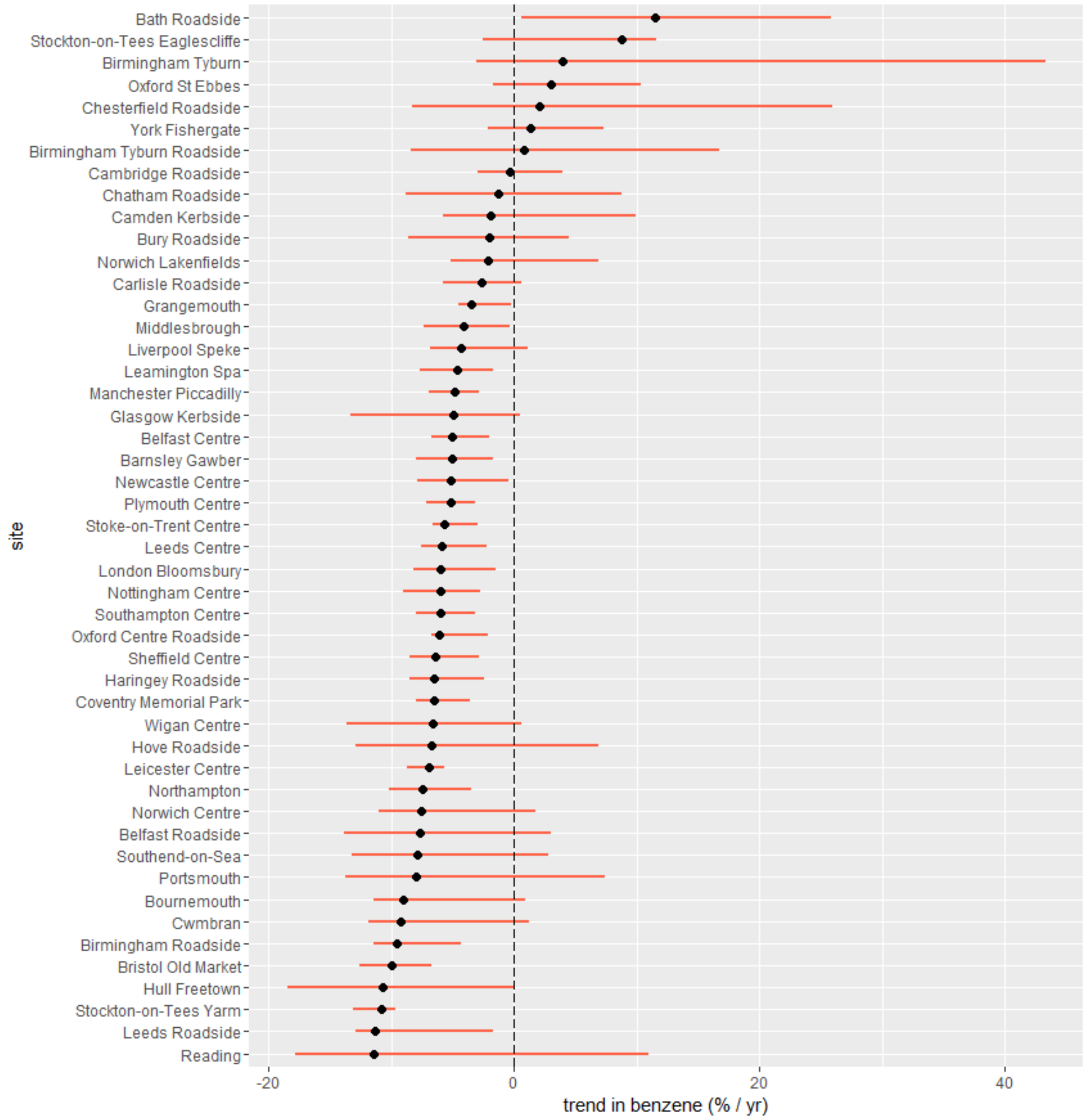

Figure 3 Non-Automatic Trend analysis plot % / yr benzene change at all Non-Automatic sites 2002 - 2015

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

The trends in benzene concentration have been averaged across the four main site types, as shown in Figure 4 – and a smooth trend line fitted. The plot reveals that the highest concentrations are generally observed at roadside sites. Note that there are only two industrial sites and these trends are noisier than for other site types. What is clear from the trend analysis is that concentrations of benzene decreased sharply from 2002 to 2008, which reflects better emissions control on vehicles (both for exhaust and evaporative). For 2015, roadside concentrations are on average much closer to background concentrations than they were in the early 2000s.

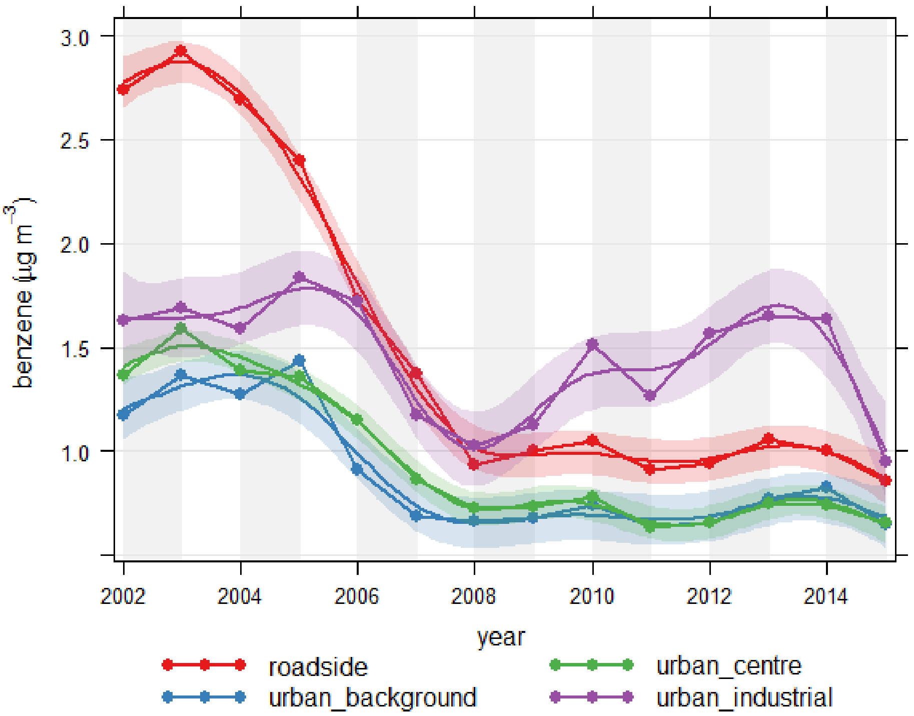

Figure 4 Average Non Automatic network benzene means by site type 2002 -2015 (µg.m^{-3})

The trends have generally shown two characteristics: a decrease from 2002 to 2008 and then a period of stabilisation from 2008 to 2015. The plot below separately considers the trends for these two periods. None of the site types have shown a statistically significant change in benzene concentration since 2008, suggesting there is strong evidence that benzene concentrations have now stabilised. The drop in concentrations from the three urban industrial monitoring stations is likely to be due to a drop in activity at the steel works in Scunthorpe measured at the Scunthorpe Town monitoring station.

Annual average concentrations for all of the monitoring stations for the calendar year 2015 are all below the level of the Lower Assessment Threshold (LAT).

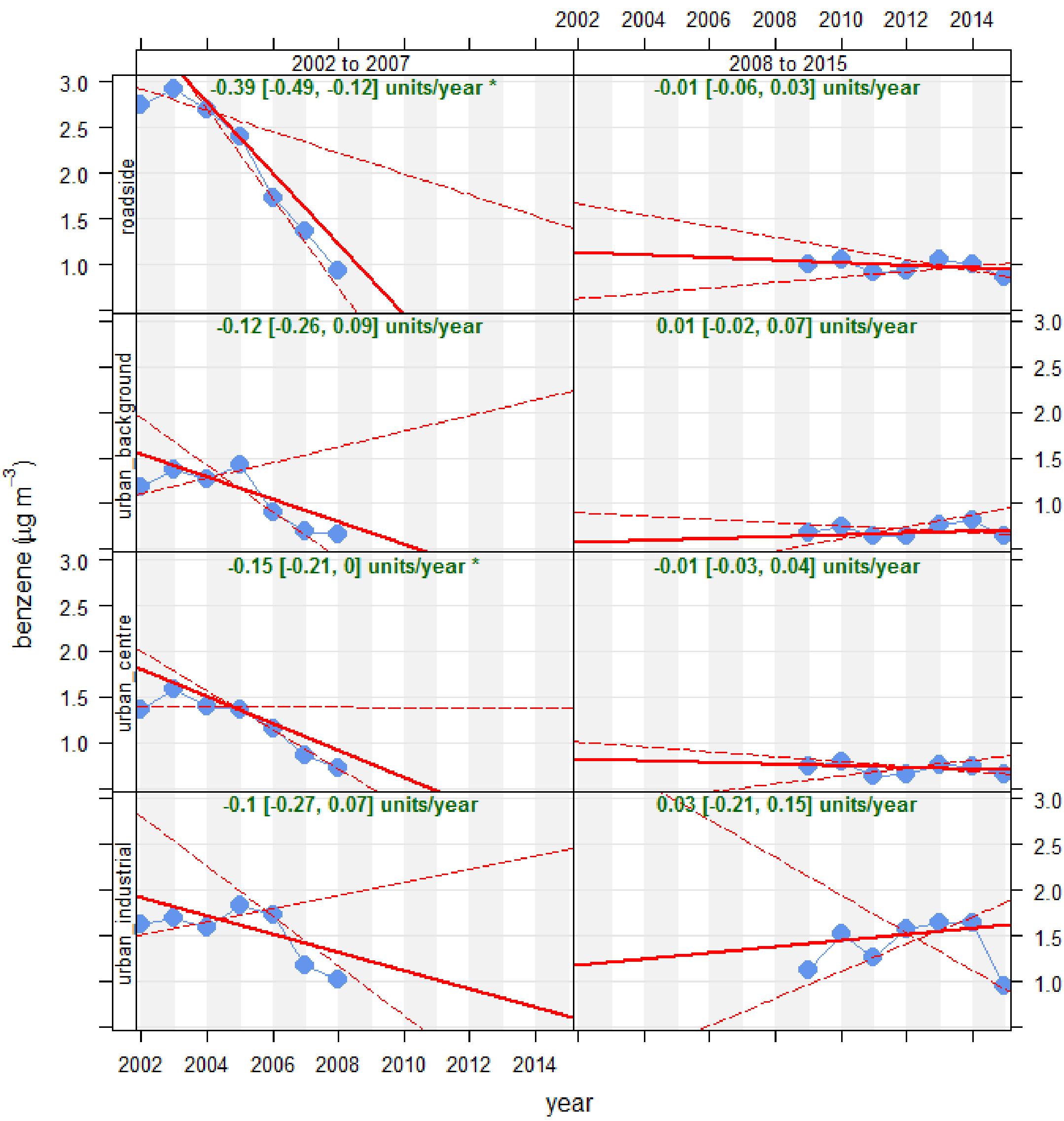

Figure 5 Non Automatic benzene rate of change 2002-2007 and 2008 2015

Data obtained from the National Atmospheric Emissions Inventory can be used to see if there is a relationship between emissions and measurements (Figure 6). The NAEI urban benzene emissions data agrees with the monitoring data, where a sharp decline can be seen up to the year 2000, the emissions data is steadily decreasing since 2000, but the monitoring data has stabilised, possibly due to additional urban sources of benzene, such as use of wood burning appliances for domestic and commercial space and water heating. The NAEI trend has been added to the plot as the bold, black line.

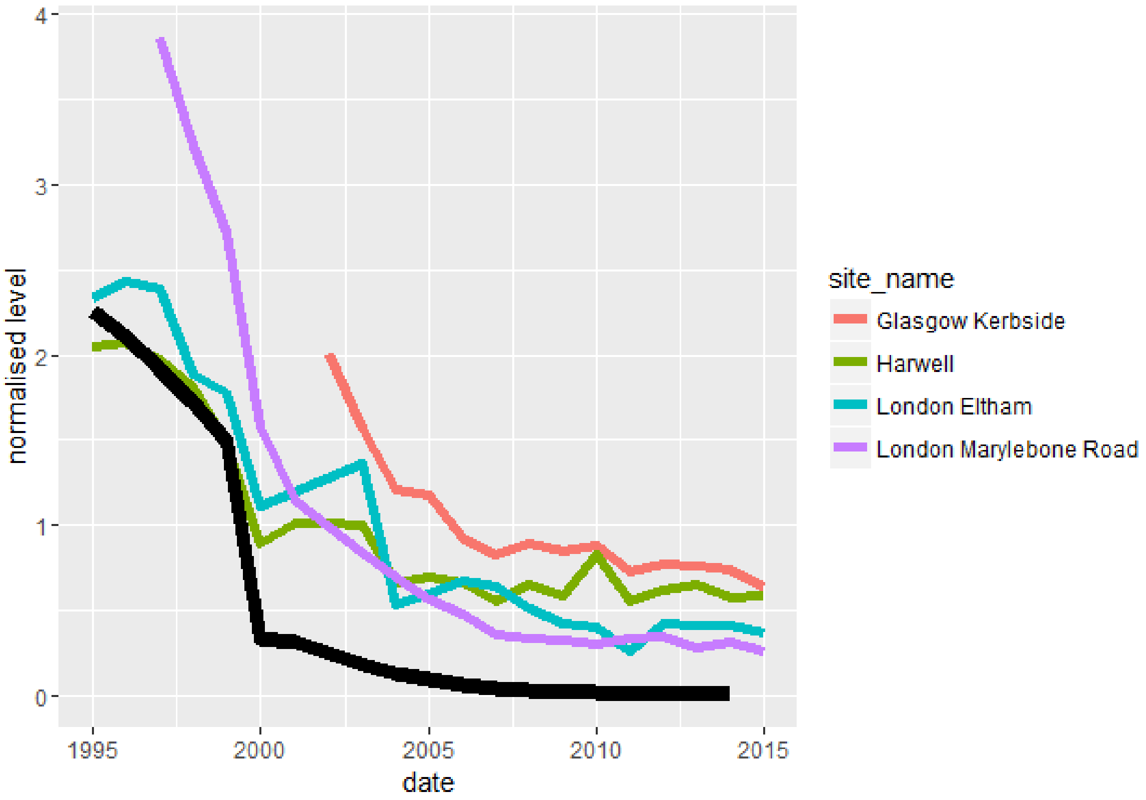

Figure 6 Normalised automatic monitoring and NAEI urban benzene data

3.3 Benzene Modelling

Ricardo undertakes compliance modelling activities on behalf of Defra under contract AQ0650. These activities use the national hydrocarbons network measurements to support the benzene model. The model results, in combination with the measurements from the hydrocarbons network, then form the basis of the annual compliance assessment for benzene submitted to the European Commission each September under the Air Quality Directive.

The latest report available detailing the modelling methodology and compliance results is presented on Defra's UK-Air website for 2013[10], subsequent annual update reports will follow.

There were no exceedances of the 5 µg m^{-3} annual mean LV modelled in 2014. However, a single 1km square at Port Talbot (Swansea Urban Area) was modelled to be 4.98 µg m^{-3}. The model source apportionment shows that almost 80% of this was due to combustion in industry. Currently, there are no benzene measurements carried out in this area. The modelled results will help inform the review of monitoring networks to be undertaken during 2016.

[10] https://uk-air.defra.gov.uk/assets/documents/reports/cat09/1511251423_AQ0650_2013_MAAQ_technical_report.pdf

4 Data Quality

4.1 Estimation of Uncertainty

Calculated uncertainty for the Non-Automatic Hydrocarbon sites in 2015 for benzene is 15%, expressed at a 95% level of confidence. This includes contributions from Ricardo'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%.

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 5ng. This is equivalent to about 0.05 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 EN14662-3:2015

European Standard EN14662-3:2005 has now been superseded by a 2015 version by CEN Working Group 12, to bring it in line with the other gaseous pollutants' standards. Ricardo was involved in the review through a representative on the Working Group, and provided appropriate contributions and feedback to Defra and the Devolved Administrations regarding the potential implications for the Automatic Hydrocarbon Network. The most significant change under the current revision is the inclusion of a linearity audit, by means of reference gas dilution. Ricardo have developed a dilution system with which to carry out such a linearity, this will be tested during 2016.

5.2 Standard Method for Ozone Precursors

In Europe, there has never been a standard method for the measurement of ozone precursors to date. Under Working Group 12, funding from the European Commission has been requested in order to start a five-year process for development of such a standard. Working Group 12 are aware that the US EPA are also currently developing a new standard, including measurement of additional target analytes such as oxygenated compounds. The main driver for this is the use of bioethanol in petrol vehicles, causing a potential rise in emission of carbonyl compounds such as acetaldehyde and formaldehyde. The current state of the art machines are not capable of measuring these compounds due to the means by which moisture is removed from the sample gas resulting in any polar compounds being removed, including the oxygenates. Systems for measuring these are under development, in line with development of the new standards, both in the US and Europe.

5.3 Conclusions

The annual mean concentration across all non-automatic monitoring stations in the UK for 2015 was 0.75 µg.m^{-3}. All 34 monitoring stations used for non-automatic benzene measurements are situated in urban locations. The mean data capture for benzene measured at the non-automatic hydrocarbon monitoring stations in operation from January to December 2015 was 96.4%.

The annual mean across all automatic monitoring stations in the UK was 0.5 µg.m^{-3}, of the 4 automatic monitoring stations used for hourly automatic measurements, two are situated at rural locations. The mean data capture for benzene measured by the automatic hydrocarbon network in 2015 was 72.5%.

Monitoring and data capture statistics for other measured pollutants can be seen in Appendix 3.

In 2015 none of the automatic or non-automatic monitoring stations in the UK exceeded either 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 EC Air Quality Directive. The results confirm no exceedances of EU or UK limit values and objectives at any of the Urban, Traffic and Background monitoring stations during 2015. The highest concentrations observed during 2015 have been seen at roadside and industrial locations. The trends from sites classified as urban traffic, centre and background do show similar trends, indicating that benzene sources in these urban areas are typically from road traffic. Industrial locations do not share the same trend, most likely due to additional sources of benzene from industrial processes and combustion from point sources and fugitive emissions.

Annual means of less than 1 µg.m^{-3} have been observed at urban centre and urban background locations, whereas some roadside monitoring stations have exceeded 1 ug.m^{-3} at Bath Roadside, Camden Kerbside, Haringey Roadside and London Marylebone Road.

Non-automatic monitoring stations have measured a general decline, almost all sites showed a decrease in benzene concentration over the period 2002 to 2015. Long term trends from 2002 to 2008 show benzene concentrations have declined significantly. This demonstrates that over this period motor vehicle exhaust catalysts and evaporative canisters have effectively and efficiently controlled vehicular emissions of benzene in the UK. This should have led to reduced health impact on individuals living in the UK as a result of long term exposure to these pollutants. Since 2010, concentrations have remained relatively stable up to and including 2015. Benzene emissions data provided by the National Atmospheric Emissions Inventory shows a steady decline in benzene emissions from 2010 to 2015, conversely, the stability seen in benzene monitoring data could be from an alternative source of benzene, such as from increased use of wood-burning appliances used for domestic and commercial space and water heating.

Further analysis of automatic data has been provided in Appendix 4, 5 and 6 to analyse the relationship between ozone precursor VOCs, investigate when highest concentrations have been observed and changes in concentration depending on wind speed and direction.

5.4 Recommendations

There are currently no known requirements to change monitoring station locations, however, since the results of the 2014 annual benzene modelling assessment suggests there may be elevated levels of benzene in the Swansea urban area, particularly near the steel works in Port Talbot, the results will be used to inform the review of all monitoring networks to be conducted during 2016.

Appendices

Appendix 1	Schedule and results of the Non-Automatic Calibration Visits
Appendix 2	Schedule of the Automatic Audits
Appendix 3	Automatic Hydrocarbon Statistics for all VOC species
Appendix 4	Automatic Correlation Analysis Plots
Appendix 5	Automatic Time Variation Analysis Plots
Appendix 6	Polar Plots for Automatic Benzene and 1,3-Butadiene

Appendix 1 – Schedule and results of the Non-Automatic Calibration Visits

Table 14 - April 2015 Benzene sampler flow calibrations (* inc. call outs)

Site	Audit Date	Tube A	Tube B	Difference (ml/min)	Uncertainty (ml/min)
Barnsley Gawber	21/04/2015	10.03	10.02	0.01	0.37
Bath Roadside	29/04/2015	10.00	10.02	0.02	0.37
Belfast Centre	09/04/2015	9.99	9.98	0.01	0.37
Birmingham Tyburn Roadside	21/04/2015	10.02	10.05	0.03	0.37
Birmingham Tyburn	21/04/2015	10.01	10.03	0.01	0.37
Bury Whitefield Roadside	08/04/2015	10.03	10.04	0.01	0.37
Cambridge Roadside	07/04/2015	10.01	10.01	0.00	0.37
Carlisle Roadside	16/04/2015	10.01	10.00	0.01	0.37
Chatham Centre Roadside	01/04/2015	10.03	10.01	0.02	0.37
Chesterfield Roadside	21/04/2015	10.02	10.03	0.01	0.37
Glasgow Kerbside	30/04/2015	10.03	10.01	0.02	0.37
Grangemouth	22/04/2015	9.95	9.97	0.01	0.37
Leamington Spa	16/04/2015	10.06	10.02	0.04	0.37
Leeds Centre	22/04/2015	10.03	10.07	0.04	0.37
Liverpool Speke	31/03/2015	10.03	10.04	0.01	0.37
London Bloomsbury	08/04/2015	10.03	10.03	0.00	0.37
London Camden Kerbside	09/04/2015	10.10	10.06	0.04	0.37
London Haringey Roadside	16/04/2015	10.01	10.08	0.07	0.37
Manchester Piccadilly	09/04/2015	9.99	10.00	0.01	0.37
Middlesbrough	14/04/2015	10.00	9.99	0.01	0.37
Middlesbrough*	02/12/2014*	10.00	9.92	0.08	0.37
Newcastle Centre	15/04/2015	10.00	10.02	0.02	0.37
Newport	01/05/2015	10.02	10.05	0.02	0.37
Norwich Lakenfields	08/04/2015	9.96	9.99	0.03	0.37
Norwich Lakenfields	20/04/2015	10.05	9.99	0.06	0.37
Nottingham Centre	13/04/2015	10.02	10.03	0.02	0.37
Oxford Centre Roadside	07/04/2015	10.01	10.00	0.01	0.37
Oxford St Ebbes	07/04/2015	10.08	10.07	0.01	0.37
Scunthorpe Town	20/04/2015	10.02	10.01	0.02	0.37
Sheffield Centre	21/04/2015	10.05	10.06	0.01	0.37
Southampton Centre	23/04/2015	10.00	10.02	0.02	0.37
Stockton-on-Tees Eaglescliffe	13/04/2015	10.01	10.02	0.01	0.37
Stoke-on-Trent Centre	22/04/2015	9.98	10.02	0.04	0.37
Tower Hamlets Roadside	10/04/2015	10.01	10.05	0.04	0.37
York Bootham	22/04/2015	10.02	9.97	0.05	0.37
York Fishergate*	12/02/2015*	10.00	10.03	0.03	0.37
York Fishergate	23/04/2015	10.03	10.03	0.00	0.37

Table 15 - October 2015 Benzene sampler flow calibrations (* inc. call outs)

Site	Audit Date	Tube A	Tube B	Difference (ml/min)	Uncertainty (ml/min)
Barnsley Gawber	27/10/2015	10.02	10.06	0.04	0.37
Bath Roadside	21/10/2015	10.02	10.01	0.01	0.37
Bath Roadside*	11/09/2015*	10.03	10.01	0.02	0.37
Belfast Centre	07/10/2015	9.99	10.06	0.08	0.37
Birmingham Tyburn Roadside	27/10/2015	10.05	10.00	0.04	0.37
Birmingham Tyburn	27/10/2015	10.04	9.97	0.07	0.37
Bury Whitefield Roadside	20/09/2015	10.05	10.01	0.05	0.37
Cambridge Roadside	05/10/2015	10.00	9.97	0.04	0.37
Carlisle Roadside	05/10/2015	9.98	10.00	0.02	0.37
Chatham Centre Roadside	30/09/2015	10.04	10.09	0.04	0.37
Chesterfield Roadside	27/10/2015	10.00	10.04	0.04	0.37
Glasgow Kerbside	29/10/2015	10.04	10.00	0.03	0.37
Grangemouth	19/10/2015	10.02	9.97	0.05	0.37
Leamington Spa	15/10/2015	10.00	9.98	0.02	0.37
Leeds Centre	27/10/2015	10.07	10.09	0.02	0.37
Liverpool Speke	29/09/2015	9.98	9.99	0.01	0.37
London Bloomsbury	14/10/2015	10.03	10.01	0.02	0.37
Manchester Piccadilly	30/09/2015	10.10	10.06	0.04	0.37
Middlesbrough	07/10/2015	9.96	9.96	0.00	0.37
London Camden Kerbside	06/10/2015	10.10	10.13	0.03	0.37
London Haringey Roadside	07/10/2015	10.05	10.04	0.01	0.37
Tower Hamlets Roadside	08/10/2015	9.98	9.98	0.00	0.37
Newcastle Centre	08/10/2015	10.03	10.07	0.03	0.37
Newport	21/10/2015	10.06	10.01	0.06	0.37
Norwich Lakenfields	06/10/2015	10.00	9.98	0.02	0.37
Nottingham Centre	12/10/2015	9.95	9.95	0.00	0.37
Oxford Centre Roadside	29/10/2015	10.07	10.01	0.07	0.37
Oxford St Ebbes	29/10/2015	10.00	10.03	0.03	0.37
Scunthorpe Town	28/10/2015	10.00	9.98	0.02	0.37
Sheffield Centre	27/10/2015	10.06	10.06	0.00	0.37
Southampton Centre	28/10/2015	10.03	10.00	0.02	0.37
Stockton-on-Tees Eaglescliffe	07/10/2015	10.06	10.03	0.03	0.37
Stoke-on-Trent Centre	28/10/2015	9.98	9.98	0.00	0.37
York Bootham	28/10/2015	10.02	10.01	0.01	0.37
York Fishergate	29/10/2015	10.03	10.01	0.01	0.37
Bury Whitefield Roadside	20/09/2015	10.05	10.01	0.05	0.37
Cambridge Roadside	05/10/2015	10.00	9.97	0.04	0.37

Appendix 2 – Schedule of the Automatic Audits

Annual preventative maintenance services

Harwell	9th April 2015
London Marylebone Road Service	9th January 2015
London Eltham	17th November 2015
Auchencorth Moss	17th November 2015

Site Audits

Harwell	14th September 2015
London Marylebone Road	25th September 2015
London Eltham	24th September 2015
Auchencorth Moss	18th March 2015

Appendix 3 Automatic Hydrocarbon Statistics for all VOC species

Table 16 – Auchencorth Moss Statistics 2015 (2 sig. fig.)

VOC Species	Annual mean µg.m^{-3}	Maximum hourly measurement µg.m^{-3}	Annual data capture (%)
ethane	1.8	8.4	37
ethene	0.13	3.3	41
ethyne	0.061	0.62	41
propane	0.97	24	41
propene	0.092	3.1	41
iso-butane	0.27	17	41
n-butane	0.55	40	41
1-butene	0.029	1.2	41
trans-2-butene	0.023	1.0	41
cis-2-butene	0.012	0.16	41
iso-pentane	0.23	31	41
n-pentane	0.17	12	41
1,3-butadiene	0.014	0.43	41
trans-2-pentene	0.015	0.015	41
1-pentene	0.015	0.015	41
2-methylpentane	0.034	4.3	41
isoprene	0.033	1.8	41
n-hexane	0.041	2.8	41
n-heptane	0.024	0.54	38
iso-octane	0.025	0.66	38
n-octane	0.024	0.19	38
benzene	0.15	1.4	38
toluene	0.082	5.7	38
ethylbenzene	0.028	0.88	38
m+p-xylene	0.035	2.9	38
o-xylene	0.026	1.1	38
1,2,3-trimethylbenzene	0.025	0.025	38
1,2,4-trimethylbenzene	0.025	0.025	38
1,3,5-trimethylbenzene	0.025	0.025	38

Table 17 – Harwell Statistics 2015 (2 sig. fig.)

VOC Species	Annual mean µg.m^{-3}	Maximum hourly measurement µg.m^{-3}	Annual data capture (%)
ethane	2.7	16	85
ethene	0.39	4.5	86
ethyne	0.21	2.9	86
propane	1.5	9.9	86
propene	0.26	1.5	86
iso-butane	0.38	5.1	86
n-butane	0.65	9.2	86
1-butene	0.12	1.3	86
trans-2-butene	0.014	0.14	86
cis-2-butene	0.019	0.07	86
iso-pentane	0.3	4	86
n-pentane	0.16	2.8	86
1,3-butadiene	0.066	0.22	86
trans-2-pentene	0.014	0.15	86
1-pentene	0.015	0.087	86
2-methylpentane	0.089	1.2	86
isoprene	0.02	0.23	86
n-hexane	0.09	1.3	86
n-heptane	0.062	0.62	86
iso-octane	0.05	0.57	86
n-octane	0.037	0.38	86
benzene	0.32	1.6	86
toluene	0.31	4.3	86
ethylbenzene	0.062	0.88	86
m+p-xylene	0.13	2.6	86
o-xylene	0.071	2.1	86
1,2,3-trimethylbenzene	0.053	0.7	86
1,2,4-trimethylbenzene	0.082	1.5	86
1,3,5-trimethylbenzene	0.037	1.3	86

Table 18 – London Marylebone Road Statistics 2015 (2 sig. fig.)

VOC Species	Annual mean µg.m^{-3}	Maximum hourly measurement µg.m^{-3}	Annual data capture (%)
ethane	7.7	81	77
ethene	2.1	13	78
ethyne	0.89	6.1	78
propane	4.6	72	78
propene	1	4.4	78
iso-butane	2.2	21	78
n-butane	3.8	34	78
1-butene	0.25	2.1	78
trans-2-butene	0.033	1.9	78
cis-2-butene	0.027	0.84	78
iso-pentane	3.2	43	78
n-pentane	1.4	12	78
1,3-butadiene	0.029	0.49	78
trans-2-pentene	0.076	3.8	78
1-pentene	0.049	1.1	78
2-methylpentane	1	19	78
isoprene	0.014	0.014	78
n-hexane	0.47	4.6	78
n-heptane	0.4	11	78
iso-octane	0.38	18	78
n-octane	0.15	1.8	78
benzene	1	5.4	78
toluene	3	57	78
ethylbenzene	0.6	7.1	78
m+p-xylene	1.9	27	78
o-xylene	0.78	10	78
1,2,3-trimethylbenzene	0.32	2.7	78
1,2,4-trimethylbenzene	0.66	9.5	78
1,3,5-trimethylbenzene	0.35	3.4	78

Table 19 – London Eltham Statistics 2015 (2 sig. fig.)

VOC Species	Annual mean µg.m^{-3}	Maximum hourly measurement µg.m^{-3}	Annual data capture (%)
ethane	5.2	71	85
ethene	0.7	10	87
ethyne	0.43	3.8	87
propane	2.9	44	87
propene	0.31	3.8	87
iso-butane	1.4	48	87
n-butane	2.6	77	87
1-butene	0.15	2	87
trans-2-butene	0.059	2.5	87
cis-2-butene	0.048	1.8	87
iso-pentane	1.3	27	87
n-pentane	0.75	21	87
1,3-butadiene	0.066	0.88	87
trans-2-pentene	0.053	2.3	87
1-pentene	0.043	0.81	87
2-methylpentane	0.25	6.7	87
isoprene	0.18	4.1	87
n-hexane	0.24	12	87
n-heptane	0.16	2.2	88
iso-octane	0.13	2.7	88
n-octane	0.072	0.81	88
benzene	0.52	4.6	88
toluene	0.98	59	88
ethylbenzene	0.19	3.3	88
m+p-xylene	0.55	9.6	88
o-xylene	0.23	4	88
1,2,3-trimethylbenzene	0.19	2.7	88
1,2,4-trimethylbenzene	0.29	4.8	88
1,3,5-trimethylbenzene	0.11	1.5	88

Appendix 4 - Automatic Hydrocarbon Data Correlation Analysis

The plots (Figure 7 - Figure 10) below show a ‘correlation matrix’ for the hydrocarbon measurements. Hierarchical cluster analysis has also been applied to the correlation coefficients such that pollutants that are next to each other behave most similarly. A very close relationship can be identified by colour and shape. A straight diagonal line shows a perfect relationship, the shape widens into an elliptical shape becoming more circular as the correlation decreases. The colours change from red (good relationship) through orange (some relationship) to yellow (limited/no relationship). Green indicates a negative relationship, also these are shown with an elipse in the opposite direction. In addition, a perfect relationship can be seen by 100, through to -100 if a perfect negative relationship exists.

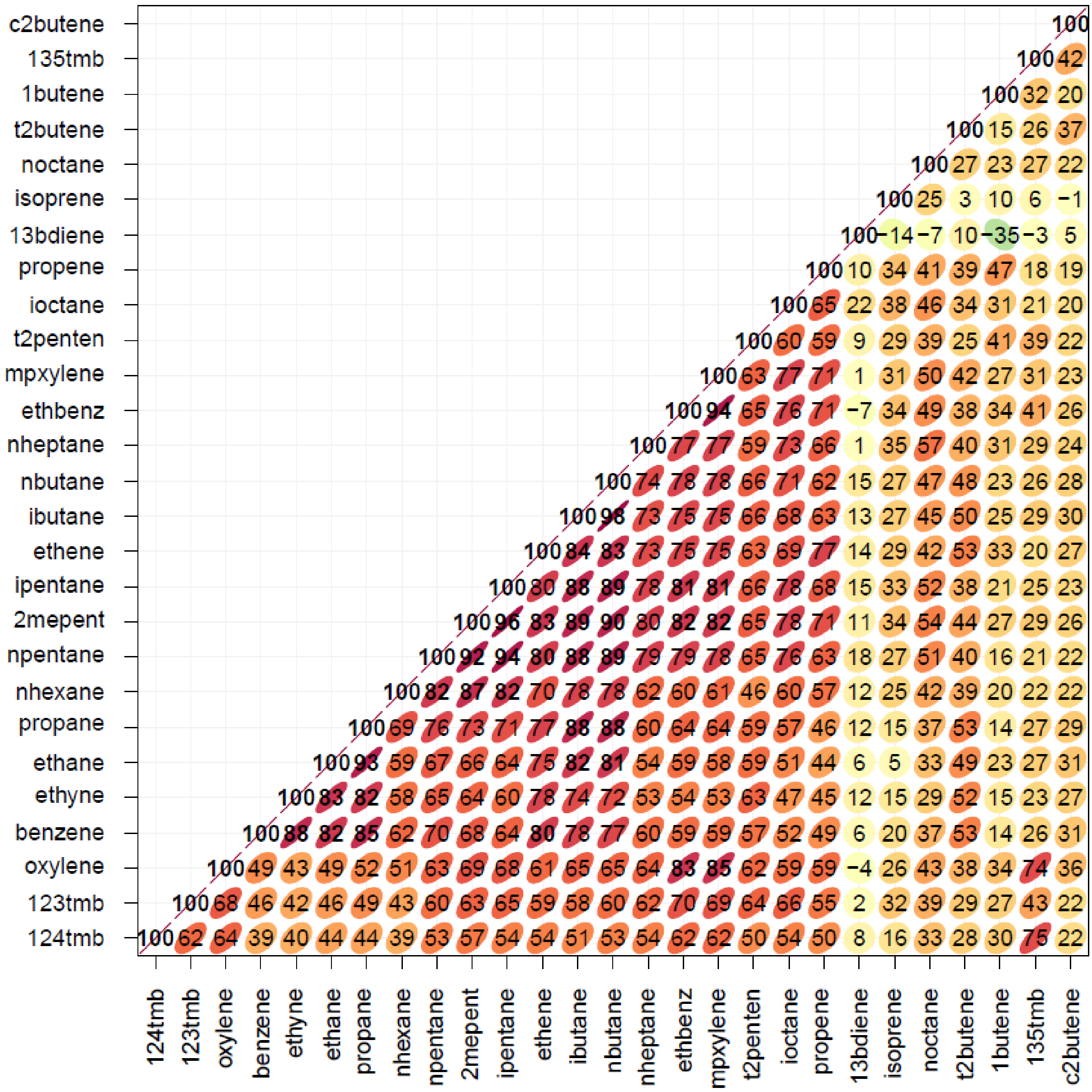

Figure 7 - Harwell correlation matrix

At Harwell, its less correlation with typical vehicle exhaust related compounds and more reactive compounds such as 1,3-butadiene, butane isomers, n-octane and 1,2,3-trimethylbenzene. Isoprene has a biogenic source (trees, grass) so this is not expected to correlate well with the other compounds.

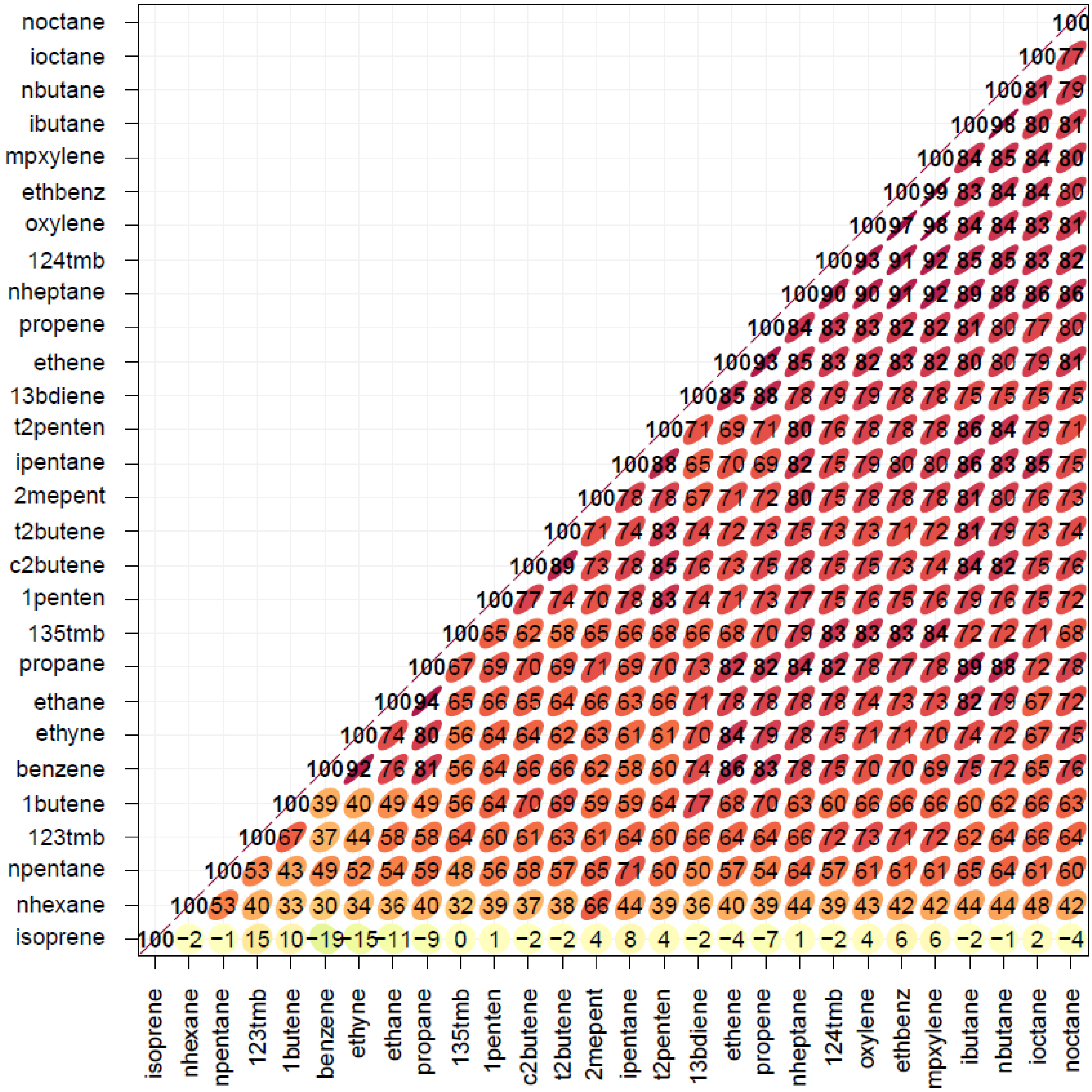

Figure 8 – London Eltham correlation matrix

At Eltham the strong correlation between all compounds suggests the main source of all pollutants except isoprene is vehicle emissions.

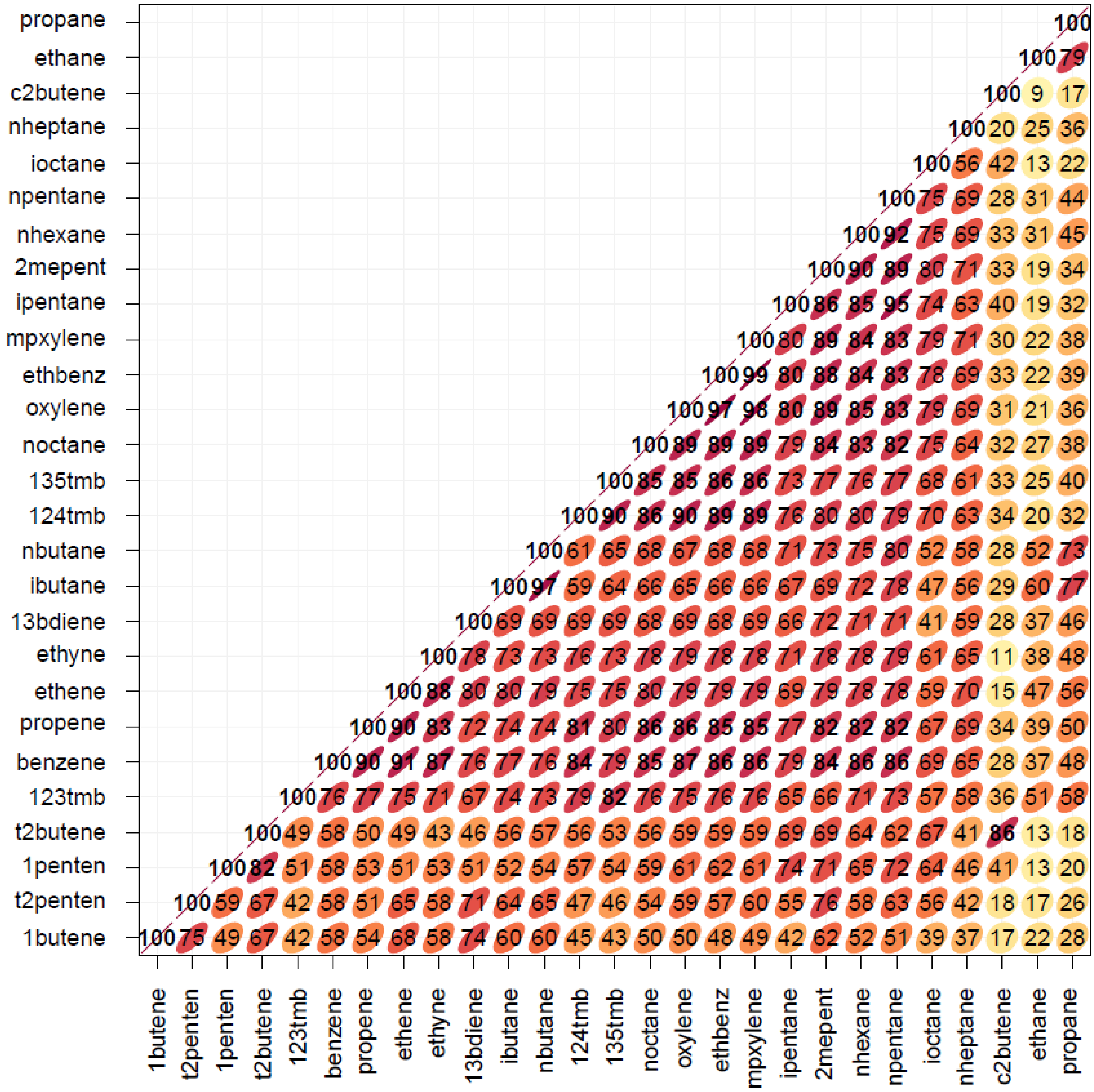

Figure 9 – London Marylebone Road correlation matrix

These results for Marylebone Road show for example, that iso-butane, n-butane, ethane and propane tend not to behave like most other species. This is because these species are associated with local natural gas leakage rather than vehicle emissions. Also, some of the more reactive compounds, such as the butene and pentene isomers tend not to correlate as well as the more stable compounds.

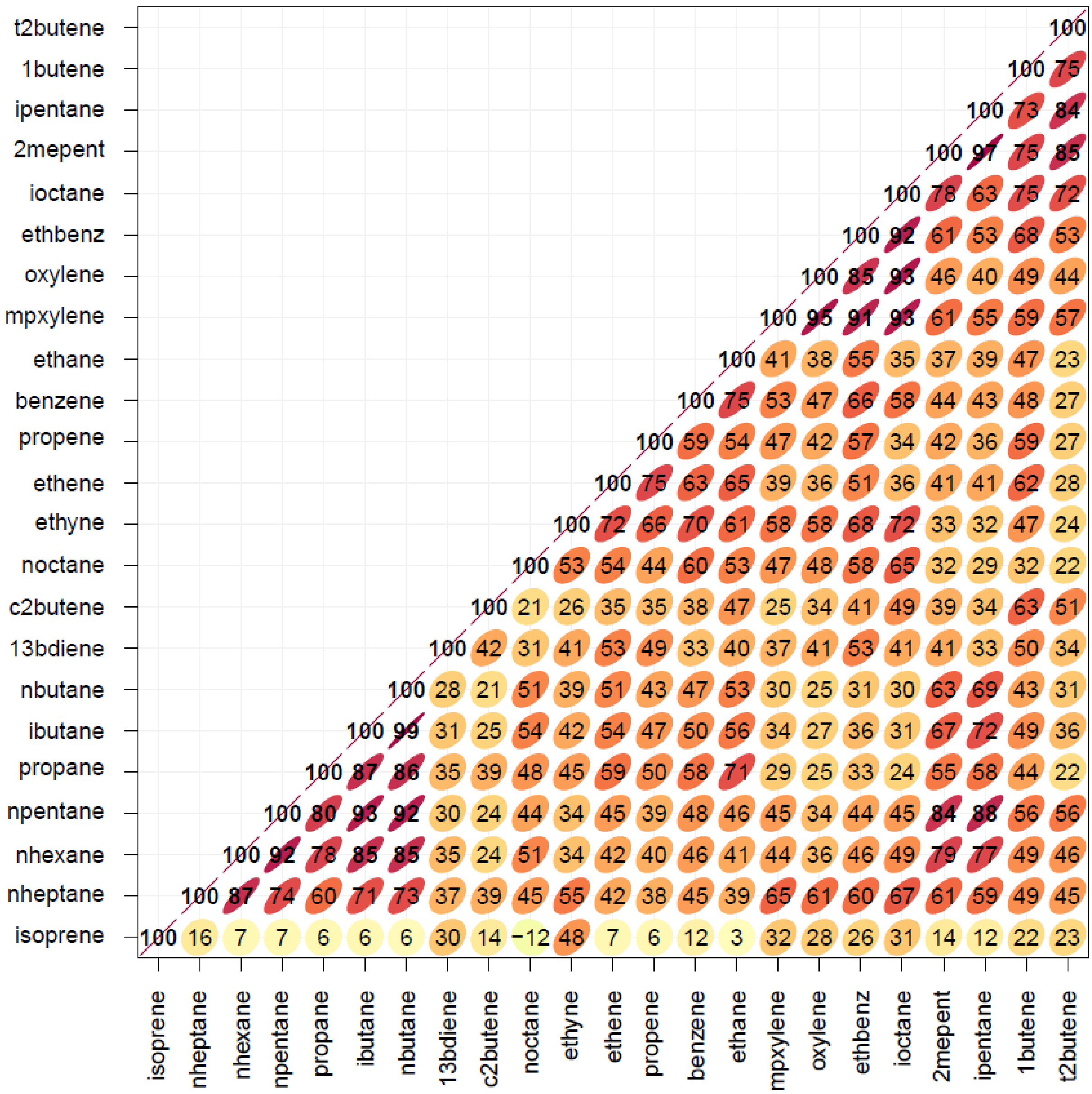

Figure 10 – Auchencorth Moss correlation matrix

Auchencorth Moss is located in a very remote location in Scotland, less compounds are detectable, compounds correlate less well, possibly due to the greater distance travelled from source as well as higher variation in measurement uncertainty at or near the instruments detection limit. The plot is useful for checking the instrument is working correctly, for example by checking that isomers such as n-butane and i-butane correlate well.

Appendix 5 - Automatic Data Time Variations for Benzene and 1,3-Butadiene

The plots in this section analyse trends by day of week, hour of the day, month of the year and day of the week. The scales are normalised such that comparisons can be made between species.

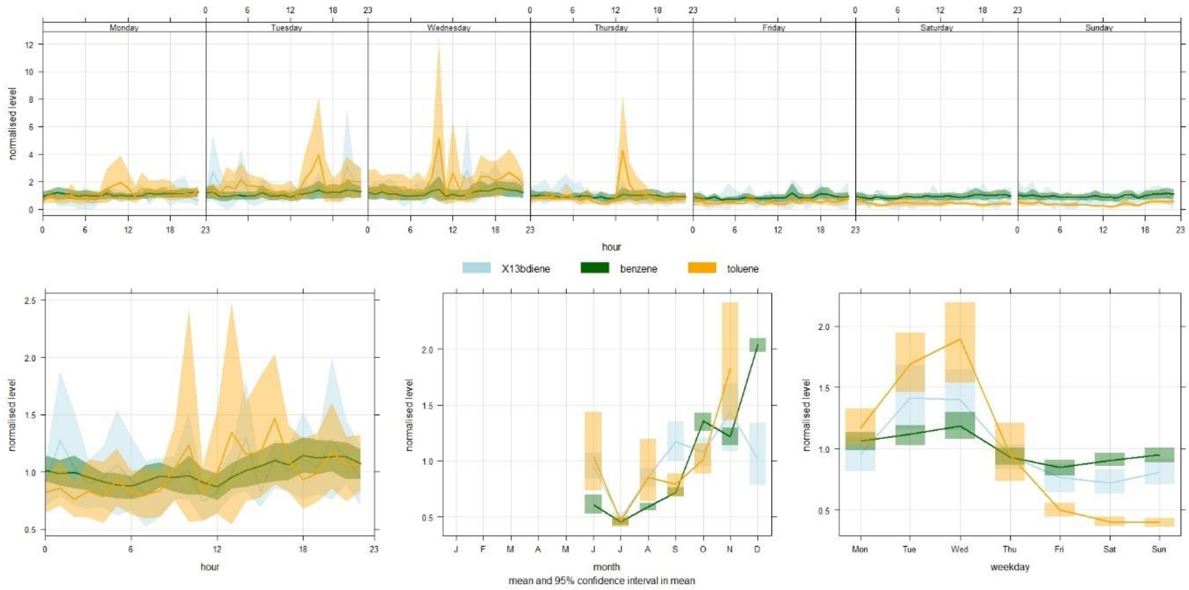

Figure 11 - Auchencorth Moss Time Variations, Benzene, Toluene and 1,3-Butadiene

Due to a problem with the inlet, there's only limited data reported for Auchencorth Moss. Concentrations were highest for benzene in December. Highest concentrations for all pollutants can be seen around midday and afternoons on Tuesday to Thursday, but particularly Wednesday for Benzene and Toluene as the site operator visits in an off road 8-wheel vehicle.

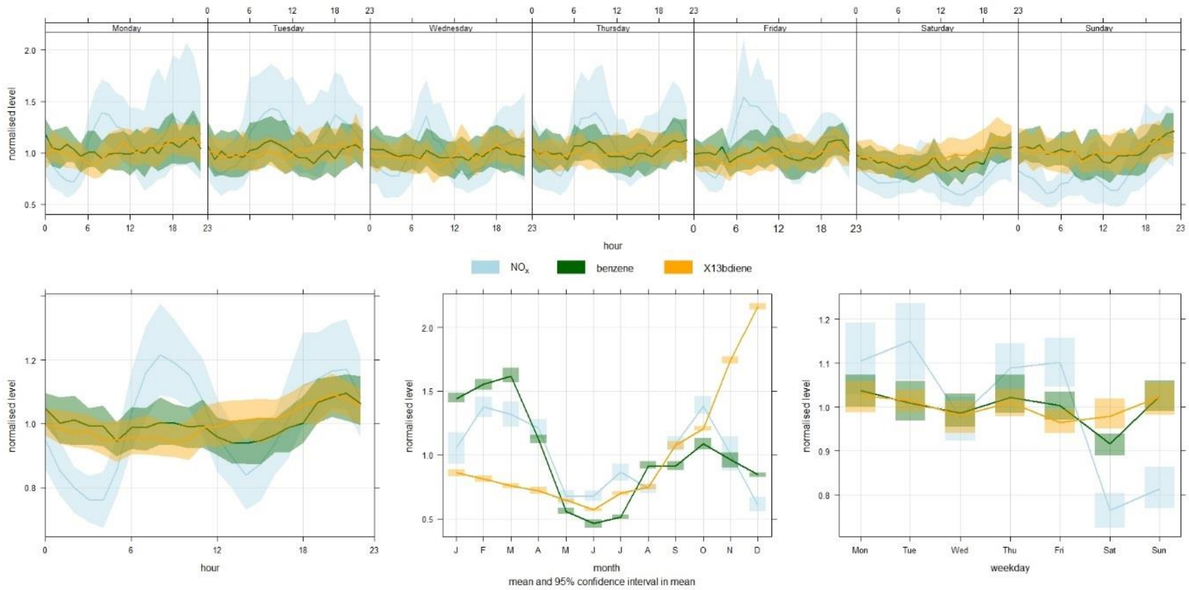

Figure 12 - Harwell Time Variations, AURN NOx, Benzene and 1,3-Butadiene

Typically, daily trends at Harwell appear to show slightly higher levels during the working week with an increase in concentrations towards midnight on Sundays. In general, the sam elevation in concentrations towards midnight has been seen. March shows the highest benzene concentrations, whereas 1,3-butadiene levels were highest in December.

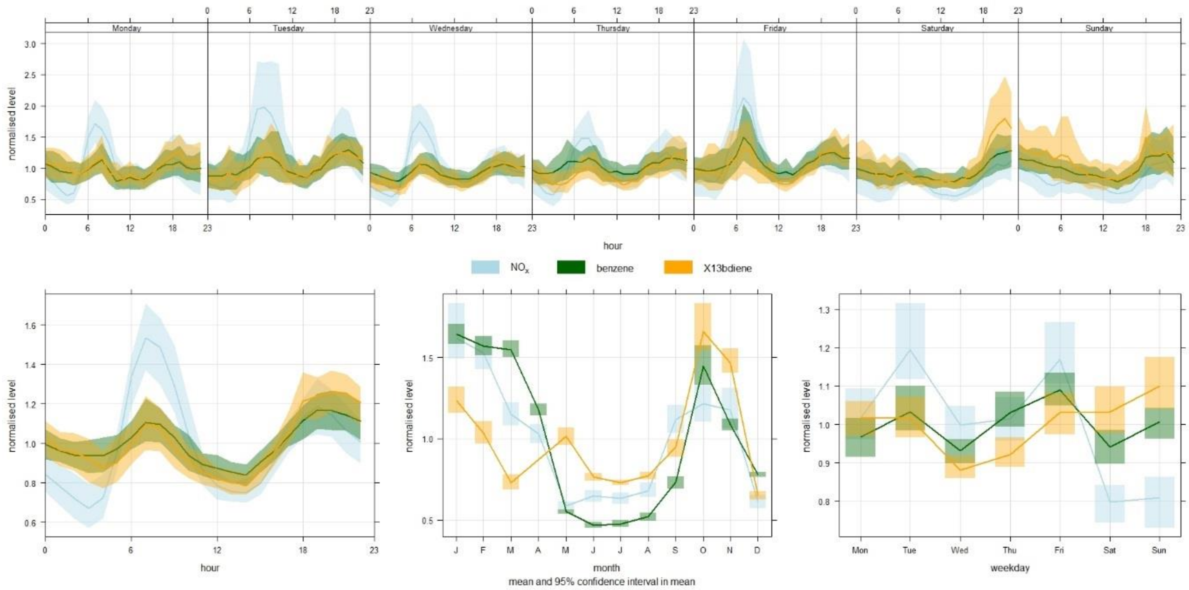

Figure 13 - London Eltham Time Variations. AURN NOx, Benzene and 1,3-Butadiene

At London Eltham, the highest benzene concentrations during 2015 were typically higher on Fridays, with 1,3-butadiene levels typically being highest on a Sunday. Highest benzene levels were seen throughout January to March, with elevated levels for both benzene and 1,3-butadiene especially prominent in October 2015.

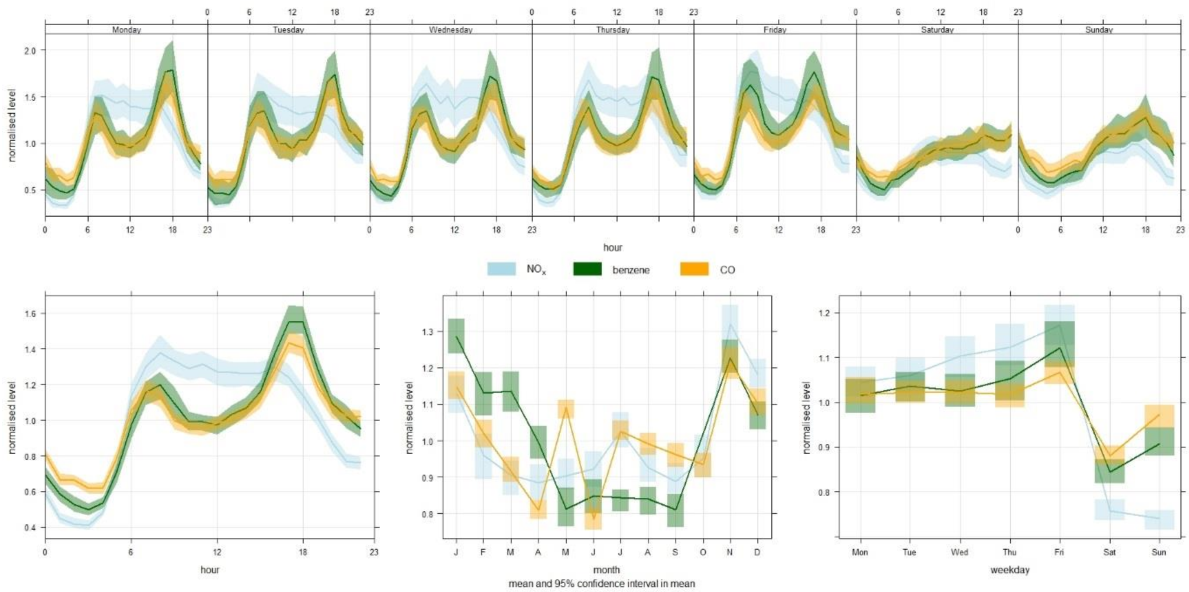

Figure 14 - London Marylebone Road Time Variations, AURN NOx, Benzene and CO

There are very clearly defined elevated benzene concentrations during the ‘rush hours’ from Monday to Friday, particularly at 18:00 hours. In 2015, the highest concentrations of benzene have been seen in January, with the lowest observed concentrations between May and September.

Appendix 6 – Polar Plots for Benzene and 1,3-Butadiene

Polar plots are useful for checking the direction of high concentrations of pollutants of interest using modelled wind speed and direction available from UK-AIR. Figure 15 to Figure 18 show polar plots for benzene and 1,3-butadiene measured at the automatic analysers on the network during 2015.

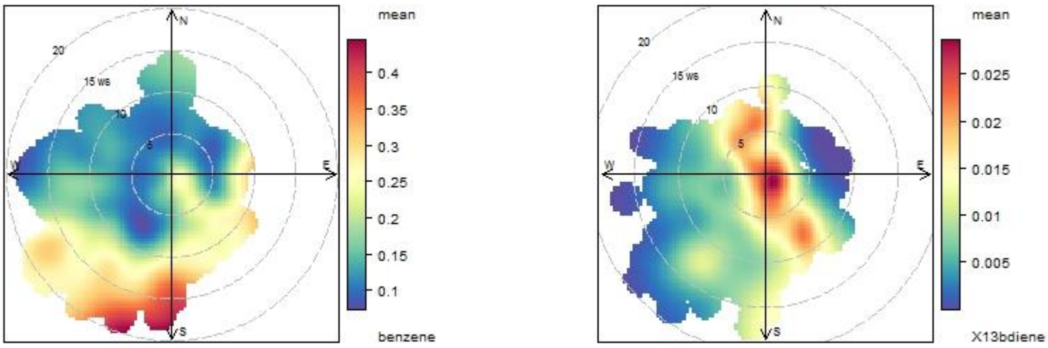

Figure 15 – Auchencorth Moss Polar plots for benzene and 1,3-butadiene

The plots suggest the predominant benzene source at Auchencorth Moss comes from a southerly direction, conversely the predominant source of 1,3-butadiene appears to be mainly local

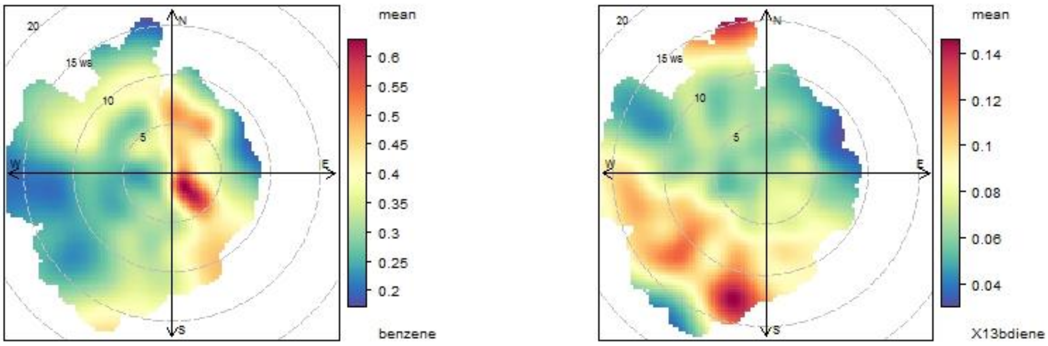

Figure 16 - Harwell Polar plots for benzene and 1,3-butadiene

The sources of benzene and 1.3-butadiene show various sources, with benzene being mainly local and 1,3-butadiene concentrations increasing from Southerly and Northerly directions.

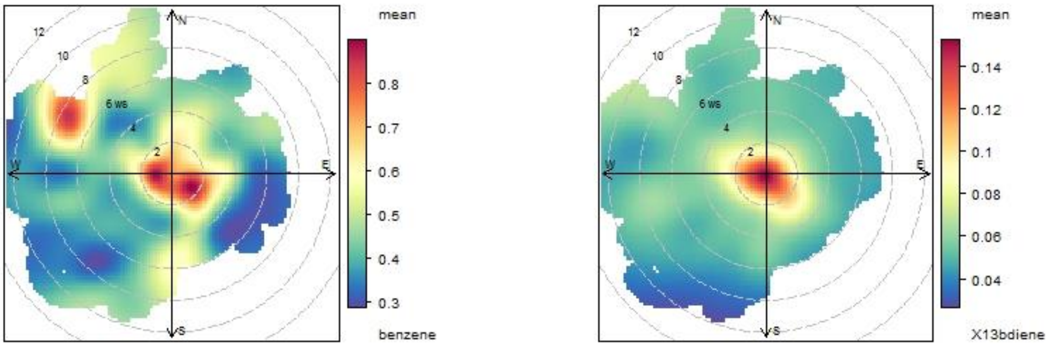

Figure 17 – London Eltham Polar plots for benzene and 1,3-butadiene

The London Eltham monitoring station is located in a suburban area of Greenwich. For both benzene and 1,3-butadiene there are strong local sources of hydrocarbons from vehicles, evaporative emission of VOCs from petrol stations and domestic wood burning. The closest main road is located to the west of the site, high concentrations have been measured from this direction.

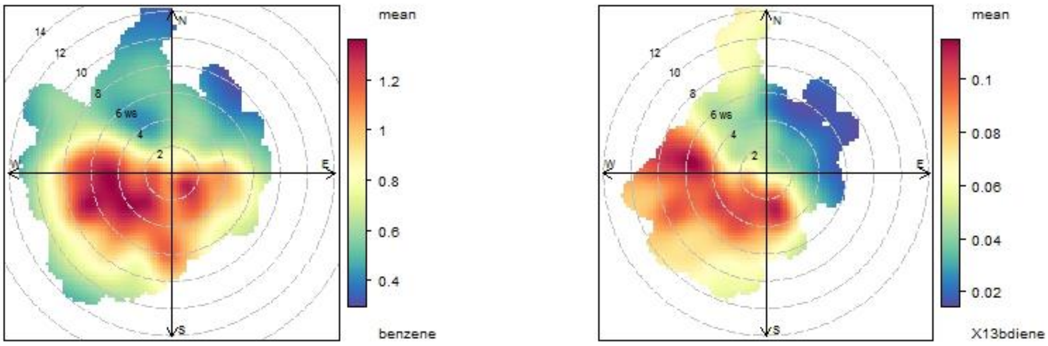

Figure 18 - London Marylebone Road Polar plots for benzene and 1,3-butadiene

London Marylebone Road is situated on the edge, but outside of, the London congestion charging zone. The monitoring station is situated on the South side of the Marylebone Road, City of Westminster. The predominant concentrations can be seen local to the monitoring station, the predominant source is as expected, from vehicles.

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