UK Hydrocarbons Network

Annual Report for 2020

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 (AQD) (EC, 2008). 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 (Defra, 2007). This report details the 2020 data and compares against the UK and EU limit values.

The Directive sets data capture requirements of 90% for benzene. The mean data capture for benzene measured at the non-automatic hydrocarbon monitoring stations in operation from January to December 2020 was 93%. The annual mean concentration across all non-automatic monitoring stations in the UK was 0.55 µg m^{-3}. All 34 monitoring stations used for non-automatic benzene measurements are situated in urban locations.

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. There are two urban stations, an urban traffic station on the Marylebone Road, London and a suburban station in Eltham, Greenwich.

Rural automatic stations at Chilbolton Observatory, Hampshire and Auchencorth Moss, Midlothian are used to support The European Monitoring and Evaluation Programme (EMEP) to Level 2. EMEP is a scientifically based and policy driven programme under the Convention on Long-range Transboundary Air Pollution (CLRTAP) for international co-operation to solve transboundary air pollution problems.

The mean data capture for benzene measured by the automatic hydrocarbon network in 2020 was 72%. The annual mean across all automatic monitoring stations in the UK was 0.42 µg m^{-3}.

The results for both automatic and non-automatic monitoring confirm no exceedances of EU or UK limit values and objectives at any of the Rural, Urban Traffic, Centre and Background locations during 2020.

This report also includes some more in-depth analysis of:

- Long term trends in benzene concentrations;
- Ozone creation potential for different VOC species.

Key findings for 2020:

- In 2020, none of the automatic or non-automatic monitoring stations 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 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 2020.

Measurements made at the Chilbolton observatory indicate that, of the 29 species measured, ethene, Meta + Para-Xylene, nbutane, propane and toluene are the largest contributors to regional O$_3$ increment during daylight hours in summer.

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1 Introduction

This report provides a summary of the site management activities and data produced in 2020 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 2011 (Defra, 2013).

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 data set if future audits and calibrations identify a need to correct the data. Latest data can always be accessed from UK-AIR.

1.1 Sources of NMVOCs

Figure 1 shows source data from the National Atmospheric Emissions Inventory (NAEI) for Non-Methane Volatile Organic Compounds (NMVOCs) from 1990 to 2019. VOC emissions from road vehicles and fuel use predominated emissions until around 2001. However, the predominant source today is solvent use (Figure 1).
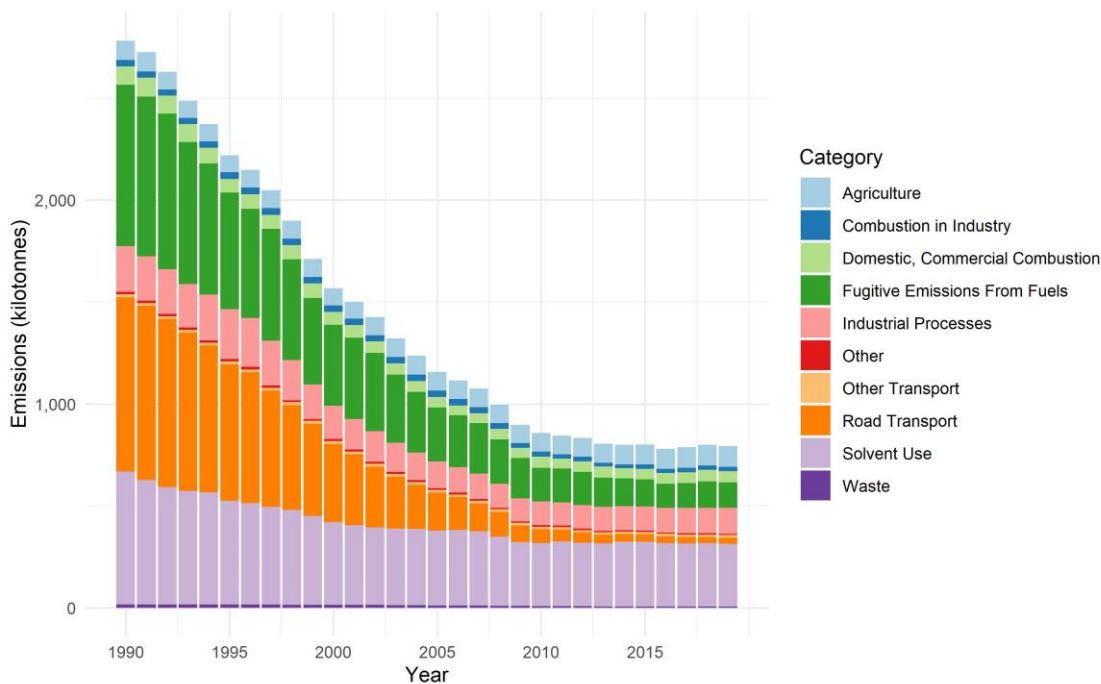
Figure 1: NAEI estimated NMVOCs emission from 1990.

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).

Table 1: UK Air Quality Objectives

Pollutant	Applicable to	Concentration (μg m^{-3})	Measured As	To be achieved by
Benzene	All authorities	16.25	Running annual mean	31-Dec-03
Benzene	England and Wales Only	5.00	Annual mean	31-Dec-10
Benzene	Scotland and N. Ireland	3.25	Running annual mean	31-Dec-10
1,3-Butadiene	All authorities	2.25	Running annual mean	31-Dec-03

1.2.2 European Directive Limit Values

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 (µg m^{-3})	Measured As
Limit Value	5.0	Annual mean
Upper assessment threshold	3.5	Annual mean
Lower assessment threshold	2.0	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 (EC, 2008) lists 31 other Volatile Organic Compounds (VOCs) which are ozone precursors and which must 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%.

1.2.3   The European Monitoring and Evaluation Programme

The European Monitoring and Evaluation Programme (EMEP) is a scientifically based and policy driven programme under the Convention on Long-range Transboundary Air Pollution (CLRTAP) for international co-operation to solve transboundary air pollution problems. Defra have supported the programme, providing two sites to Level 2 status, which includes the measurement of ozone precursor measurements. The same system used to support the AQD is used at two Rural locations; Chilbolton Observatory, Hampshire and Auchencorth Moss, Midlothian. In addition, data are also reported to and used by the Aerosol, Clouds and Trace Gases Research Infrastructure (ACTRIS) pan-European initiative to consolidate trace gas measurements. EMEP and ACTRIS data are both held within the EBAS database maintained by the Norwegian Institute for Air Research (NILU).

1.3 Network background and methods

The UK Hydrocarbon Network is one of several air quality monitoring networks operated by the Environment Agency on behalf of Defra to fulfill 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 (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' using the sorbent carbopack-X and based on a study by Martin et al. (2003). This methodology currently produces measurements as nominal fortnightly averages at 34 stations.

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 the analyte is able to travel through the sorbent and be lost causing 'sample breakthrough'.

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:

• 1,3-butadiene levels at all the sites were well below the objective.
• 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 from 2015 there were only four UK sites in operation to

satisfy network requirements. The London Eltham site fulfils requirements of AQD 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 EMEP and ACTRIS programmes 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). Table 3 also lists the photochemical ozone creation potential (POCP) for individual VOCs. These values are used to study the contribution of each VOC to the regional ozone formation in section 4.3.

Table 3: Species measured by the automatic chromatographs. Note that m-xylene and p-xylene are reported as a single measurement. The main sources for each VOC are taken from Malley et.al (2015). The "main source" column gives the Selected Nomenclature for Air Pollution (SNAP) sector with the largest contribution of that VOC to UK annual anthropogenic emissions in 2011, with the exception of isoprene which is mainly of biogenic origin. The POCP values are taken from Derwent et al. (2007). The listed SNAP sectors are SNAP 2, non-industrial combustion plants; SNAP 4, production processes; SNAP 5, extraction and distribution of fossil fuels; SNAP 6, solvent use; SNAP 7, road transport; and SNAP 8, non-road transport.

VOC	Class	Chemical formula	Main source	POCP
ethane	alkane	C_2H_6	SNAP5 (65%)	8
propane	alkane	C_3H_8	SNAP5 (36%)	14
n-butane	alkane	C_4H_{10}	SNAP6 (44%)	31
isobutane	alkane	C_4H_{10}	SNAP5 (61%)	28
n-pentane	alkane	C_5H_{12}	SNAP5 (42%)	40
isopentane	alkane	C_5H_{12}	SNAP5 (41%)	34
n-hexane	alkane	C_6H_{14}	SNAP6 (42%)	40
2-methylpentane	alkane	C_6H_{14}	SNAP6 (43%)	41
n-heptane	alkane	C_7H_{16}	SNAP5 (43%)	35
n-octane	alkane	C_8H_{18}	SNAP5 (64%)	34
isooctane	alkane	C_8H_{18}	SNAP4 (100%)	25
ethene	alkene	C_2H_4	SNAP8 (27%)	100
propene	alkene	C_3H_6	SNAP4 (36%)	117
1-butene	alkene	C_4H_8	SNAP7 (26%)	104
cis-2-butene	alkene	C_4H_8	SNAP5 (87%)	113
trans-2-butene	alkene	C_4H_8	SNAP5 (90%)	116
1,3-butadiene	alkene	C_4H_6	SNAP8 (57%)	89
isoprene	alkene	C_5H_8	biogenic	114
ethyne	alkyne	C_2H_2	SNAP7 (46%)	7
1-Pentene	alkyne	C_5H_{10}		95
trans-2-pentene	alkyne	C_5H_{10}		111

VOC	Class	Chemical formula	Main source	POCP
benzene	aromatic	C6H6	SNAP2 (35%)	10
toluene	aromatic	C7H8	SNAP6 (63%)	44
ethylbenzene	aromatic	C8H10	SNAP6 (54%)	46
o-xylene	aromatic	C8H10	SNAP6 (50%)	78
m-xylene	aromatic	C8H10	SNAP6 (71%)	86
p-xylene	aromatic	C8H10	SNAP6 (50%)	72
1,2,3-trimethylbenzene	aromatic	C9H12	SNAP6 (79%)	105
1,2,4-trimethylbenzene	aromatic	C9H13	SNAP6 (74%)	110
1,3,5-trimethylbenzene	aromatic	C9H14	SNAP6 (71%)	107

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 2020, hydrocarbons at all sites were measured using automatic Perkin Elmer Ozone Precursor Analysers. A known volume of air (600 ml) is dried and drawn through a cold trap, which contains adsorbent material. The cold trap is held at -30°C to ensure that all the ozone precursor target analytes are retained. Following a 40-minute period of sampling, components are desorbed from the cold trap and are transferred to the capillary column where they are separated using gas-chromatography 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 2020

The monitoring stations operating in the UK Hydrocarbon Network during 2020 are shown in Figure 2. Full names of the monitoring stations and their coordinates can be found in Appendix I. Further details on the sites can be found on the UK Automatic Urban and Rural Network Site Information Archive.
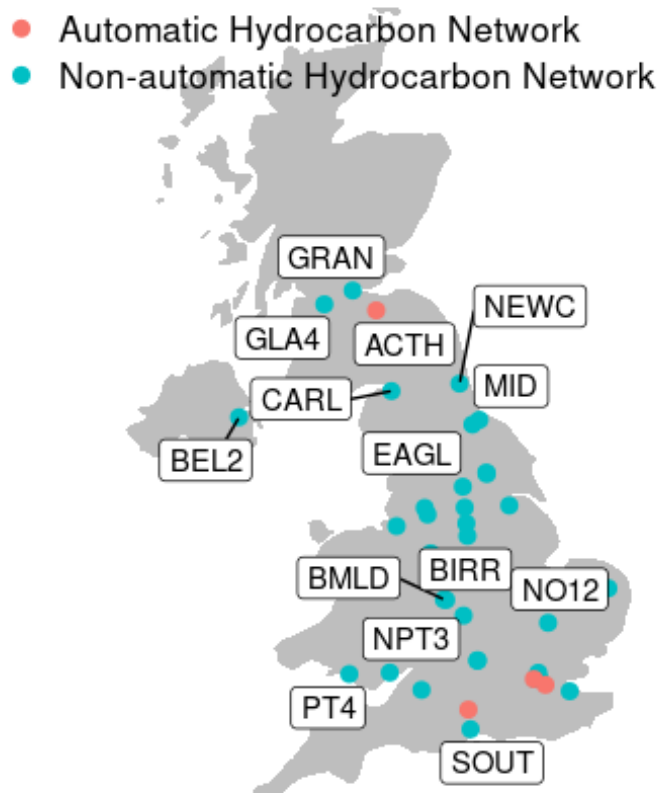

Figure 2: Map of UK Hydrocarbon Monitoring stations in 2020

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 (Defra, 2013). The last formal assessment of the national monitoring networks was made using 2006-2010

monitoring data. This analysis is periodically reviewed and updated as requested by Defra to inform the design of the national networks.

2.3 Equipment Maintenance and Audits

All non-automatic monitoring stations were visited by Ricardo field engineers every 6 months during 2020 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 certified flow measurements 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 2020. Routine flow measurements have been used to calculate sample volumes for the 2020 data set by means of interpolation. 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
- Replacing the nafion dryer 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 sample port as opposed to the analyser calibration 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.

3 Data Quality

3.1 Estimation of Uncertainty

Calculated uncertainty for the Non-Automatic Hydrocarbon sites in 2020 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 measurement uncertainty calculations for the individual hourly measurements are as defined in the standard operating procedures adopted under the ACTRIS project.

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%. Measurements reported to EMEP and ACTRIS are required to be reported with hourly uncertainty figures for each hour. The calculation used is provided in ACTRIS standard operating procedures:

$$\chi_{sample,i} = (A_{sample,i} - A_{blank,i})/V_{sample} * f_{cal,i}$$

Equation 1: Calculation of mole fractions.

$$f_{cal,i} = (V_{cal,i} * \chi_{cal,i})/(A_{cal,i} - A_{blank,i}) = 1/(C_{num}^i * C_{resp,i})$$

Equation 2: Calculation of calibration factor.

Where

- $A_{sample,i}$ = peak area of sample measurement of compound i
- $A_{cal,i}$ = peak area of calibration gas measurement of compound i
- $A_{blank,i}$ = possible blank value of compound i determined in zero gas measurements
- $\chi_{cal,i}$ = certified mole fraction of calibration gas standard
- V_{cal} = sample volume of calibration gas
- V_{sample} = sample volume of sample
- C_{num}^i = Number of C atoms in the molecule i (e.g. for i = n-Pentane, C_{num} = 5)
- $C_{resp,i}$ = mean C-response factor of compound i

3.2 Determination of precision

Precision covers random errors of peak integration, volume determination and blank variation.

Precision ($\delta_{\chi prec}$) is determined as the standard deviation of a series of sample measurements ($\sigma_{\chi sample}$)

$$\Delta_{\chi prec} = \sigma \chi_{sample}$$

Equation 3: Definition of instrument precision.

This represents the instrument precision at the concentration level and complexity of the sample gas. Because the instrument is subjected to variable peak areas in ambient air, a more general description is applied:

$$\Delta_{\chi prec} = \sqrt{(1/3DL)^2 + (\chi * \sigma^{rel}\chi_{sample})^2}$$

Equation 4: Formula for calculating instrument precision.

Where

- DL = detection limit (described below)
- χ = mole fraction of the ambient peak
- $\sigma^{rel}\chi_{sample}$ = relative standard deviation of the sample (from the reference standard)

The detection limit is the dominant factor for small peaks, while reproducibility becomes more important for larger peaks.

3.3 Uncertainty calculations

The total uncertainty $\Delta_{\chi_{unc}^2}$ of a single measurement does not only include the random errors described by the precision but also systematic errors $\Delta_{\chi_{sys}^2}$ of the measurement.

$$\Delta_{\chi^2_{unc}} = \Delta_{\chi^2_{prec}} + \Delta_{\chi^2_{sys}}$$

Equation 5: Calculation of total measurement uncertainty.

Errors included in the UK network calculations include:

- Uncertainty in the standard gas mole fraction $\delta_{\chi_{cal}}$
- Systematic errors (for example peak overlay/poor separation) $\delta_{A_{int}}$
- Sample volume error δv
- Other (system artefacts) $\delta_{\chi_{instrument}}$

The overall systematic error is described as:

$$\Delta_{\chi^2_{sys}} = |\Delta_{\chi^2_{cal}} + \Delta_{\delta^2_{int}} + \Delta_{\chi^2_{vol}} + \Delta_{\chi^2_{instrument}}|$$

Equation 6: Calculation of overall systematic error.

Referring to Equation 1 and Equation 2, the single error contribution is determined for each measurement:

$$\Delta_{\chi_{cal}} = (A_{sample} * v_{cal})/(v_{sample} * A_{cal}) * \delta_{\chi_{cal}}$$

Equation 7: Calculation of calibration error?

Where $\delta_{\chi_{cal}}$ includes the certified relative uncertainty of the standard gas and possible drift.

$$\Delta_{\chi^2_{int}} = (f_{cal}/v_{sample} * \delta_{A_{int.sample}})^2 + (A_{sample} * v_{cal} * \chi_{cal}/(v_{sample} * A^2_{cal}) * \delta_{A_{int.cal}})^2$$

Equation 8: Calculation of relative uncertainty.

Where $\delta_{A_{int.cal}}$ represents the reference gas standard deviation and the $\delta_{A_{int.sample}}$ represents the sample gas standard deviation respectively.

Sample volume error cancels from Equation 1 as sample and calibration volume are identical.

3.4 Standard Methods

The AQD states that automatic measurements of benzene should be compliant with European Standard EN14662-3:2015 – Part 3 (CEN, 2015): 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 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

Currently the first three of these were already implemented on the UK network.

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 contract SOCOTEC 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.

3.5 Limit of Detection

The Limit of Detection for the mass of benzene on a desorption tube from the Non-Automatic Hydrocarbon Network is approximately 5 ng. 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 is 10 ppt. These are converted to µg m^{-3} and shown in Table 4.

Table 4: Automatic analyser limit of detection

VOC	Limit of detection (µg m^{-3})
Ethane	0.10
Ethene	0.01
Propane	0.02
Propene	0.02
Ethyne	0.01
i-Butane	0.02
n-Butane	0.02
trans-2-Butene	0.02
1-Butene	0.02
cis-2-Butene	0.02

VOC	Limit of detection (µg m^{-3})
i-Pentane	0.03
n-Pentane	0.03
1,3-Butadiene	0.02
trans-2-Pentene	0.03
1-Pentene	0.03
2-Methylpentane	0.04
Isoprene	0.03
n-Hexane	0.04
Benzene	0.03
i-Octane	0.05
n-Heptane	0.04
n-Octane	0.05
Toluene	0.04
Ethylbenzene	0.04
(m+p)-Xylene	0.04
o-Xylene	0.04
1,3,5-Trimethylbenzene	0.05
1,2,4-Trimethylbenzene	0.05
1,2,3-Trimethylbenzene	0.05

4 Data Analysis

4.1 Comparison with Limit Values and Objectives

The annual mean concentrations of benzene measured using non-automatic samplers over the calendar year 2020 are summarised in Figure 3, alongside the associated data capture rate. Figure 4 provides similar statistics for the automatic monitoring of benzene and 1,3-butadiene. Figure 5 shows the data capture rate for other automatically measured VOC species. Summary statistics for other measured pollutants can be seen in Appendix II. Some valid high measurements from industrial and local sources can be seen at Scunthorpe Town. These have not persisted, nor do these have a significant impact on the annual mean causing an exceedance.

The sampler at Camden Kerbside was removed on 20th January 2020. This sampler was installed at the Port Talbot Margam station on 23rd January 2020. The infrastructure used at the Liverpool Speke station was deemed unsafe as of September 2020, the benzene sampler was removed on 7th September 2020, the replacement cabin was not installed during the Calendar year 2020.

1,3-Butadiene at Marylebone Road is affected by contamination and has been rejected by the data ratification team as a result.
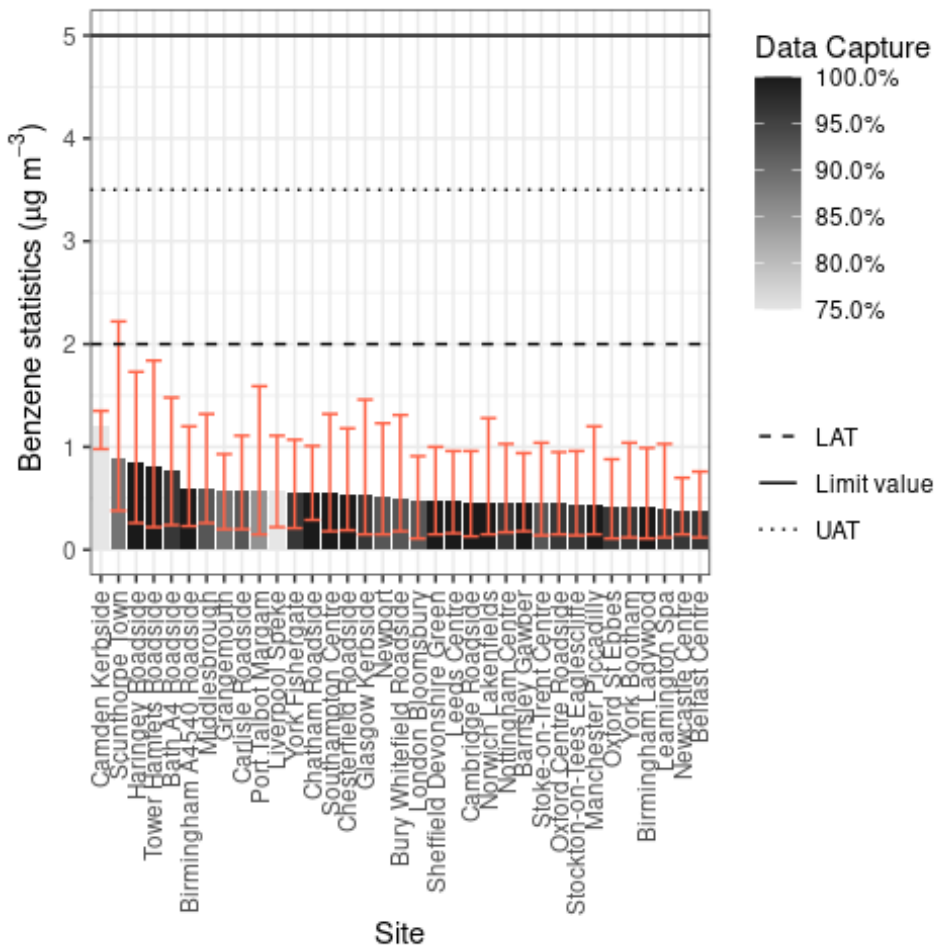
Figure 3: Non-Automatic Benzene annual statistics for 2020. Range shows the annual minimum and maximum nominal fortnightly measurement.
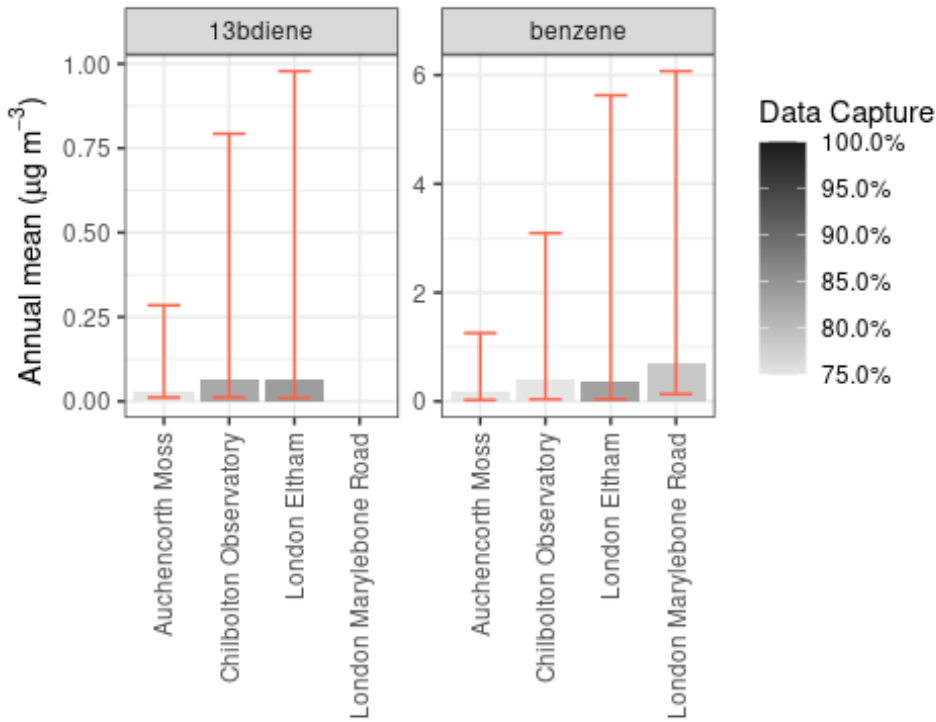
Figure 4: Benzene and 1,3-butadiene annual statistics for 2020. Range shows the annual minimum and maximum hourly measurement.
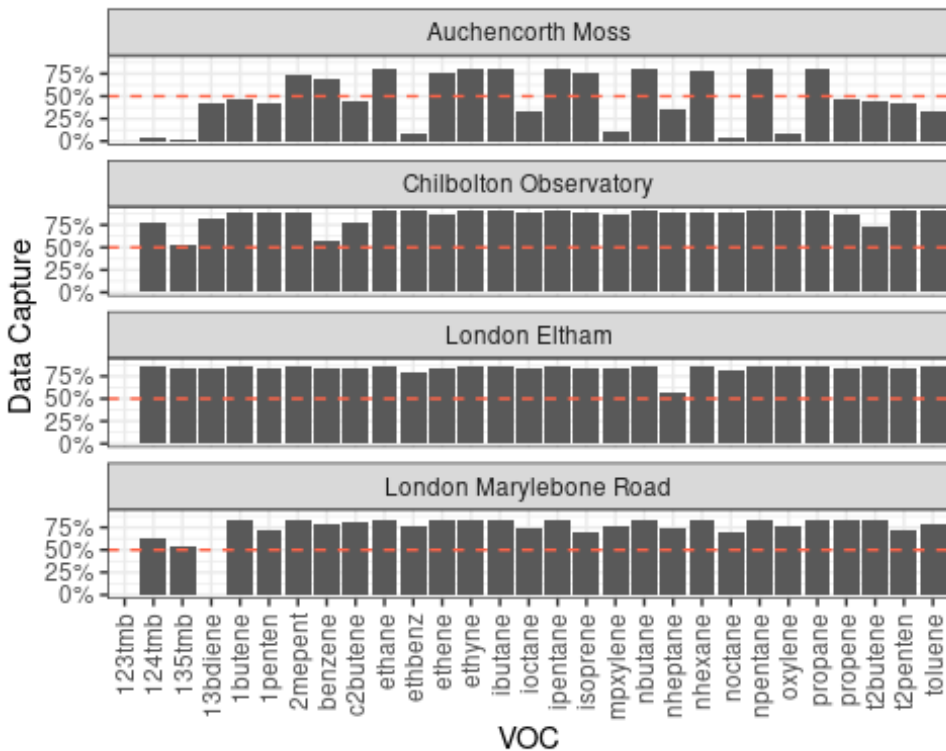

Figure 5: VOCs annual statistics for 2020. Dashed line shows the objective data capture rate.

Annual time weighted mean concentrations at all monitoring stations 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.

The 2011 Implementing Provisions Regulations (EC, 2011) 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. In previous years, flags recorded less than LoD were reported as 'not measured'.

These 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 µg m^{-3}. These measurements will be reported with a '<' symbol to clarify this for data users. The revised data capture calculation also includes an allowance of 5% for planned maintenance and calibration. This decreases the data capture target for benzene from 90% to 85%.

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

4.2 Instrumental Impacts on Data Capture

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 (including a fan)
- Site PC including Totalchrom software

These components are checked by local site operators on a fortnightly basis. The system manufacturer (Perkin Elmer) carries 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 engineers 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. In addition, specific peaks can be affected by co-elution with a system artefact or other unknown hydrocarbons resulting in reduced data capture for individual species.

4.3 Long term trend of benzene concentration

Figure 6 shows the trends in benzene concentration averaged across four main site types with a smooth trend line fitted. The plot reveals that the highest concentrations were generally observed at roadside sites until 2008. Note that there are only two industrial sites, 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 (exhaust and evaporative emissions). For 2020, roadside concentrations are on average much closer to background concentrations than they were in the early 2000s.
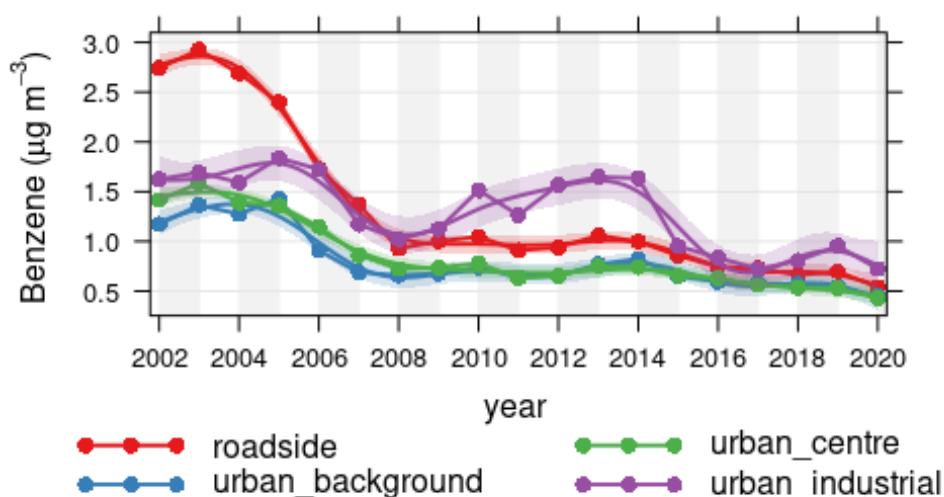

Figure 6: Average Non-Automatic network benzene means by site type from 2002 to 2020.

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. The trends have generally shown two characteristics: a decrease from 2002 to 2008 and then a period of stabilisation from 2008 to 2020. Figure 7 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.
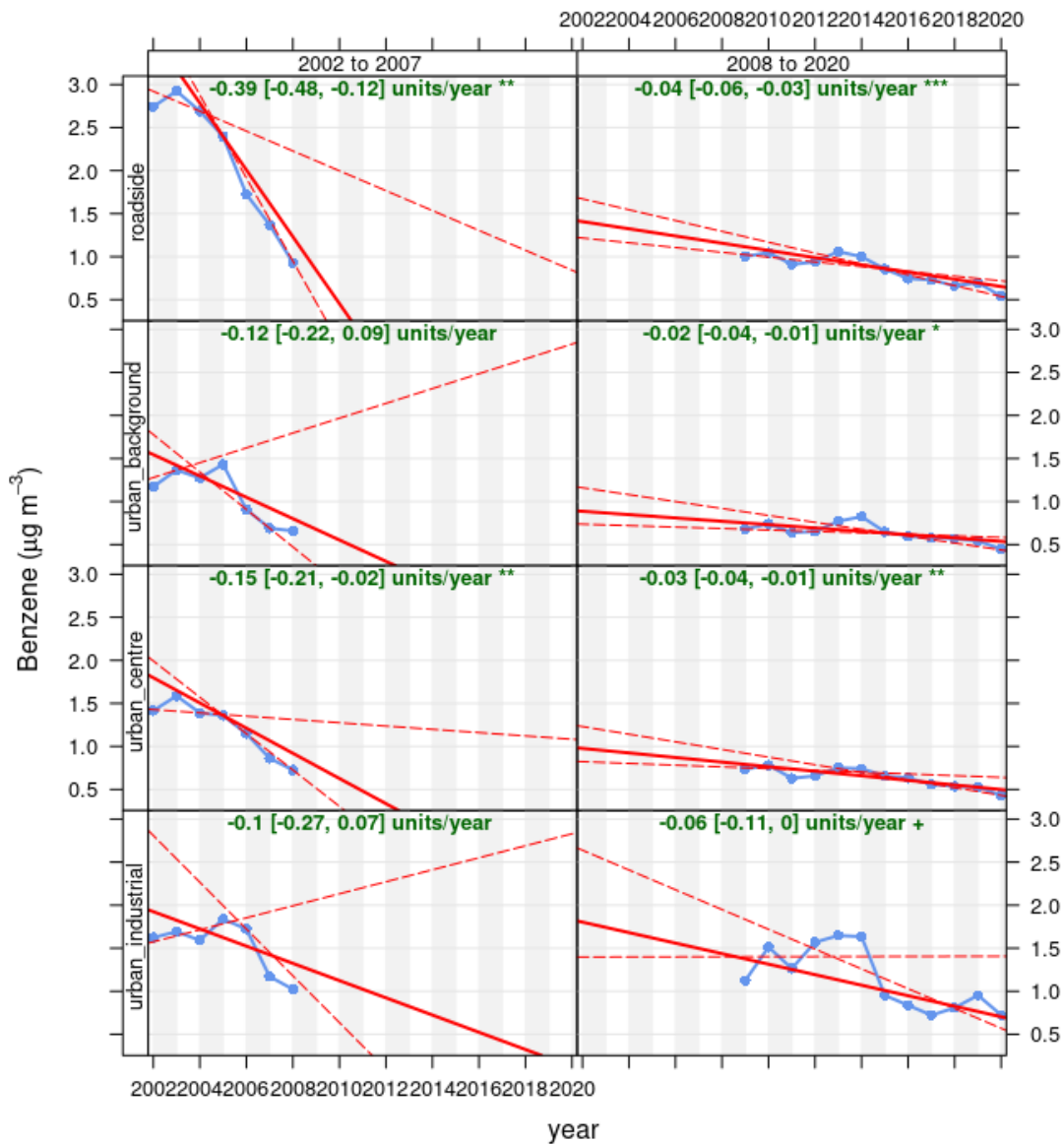
Figure 7: Non-automatic benzene rate of change for 2002-2007 and 2008-2020.

To compare trend in benzene concentrations across all measurement sites, Figure 8 shows the trend in annual average benzene concentrations at non-automatic monitoring sites from 2002 to 2020. To help with interpretation the trends are ordered and a dashed line is shown for zero change.

The plot below shows that all sites showed a decrease in benzene concentration over the period 2002 to 2020. The magnitude of the decrease is larger between 2002 and 2007 compared to more recent years. Note that the error bars relate to the 95% confidence intervals, which reveals that the trends at some sites are relatively uncertain.
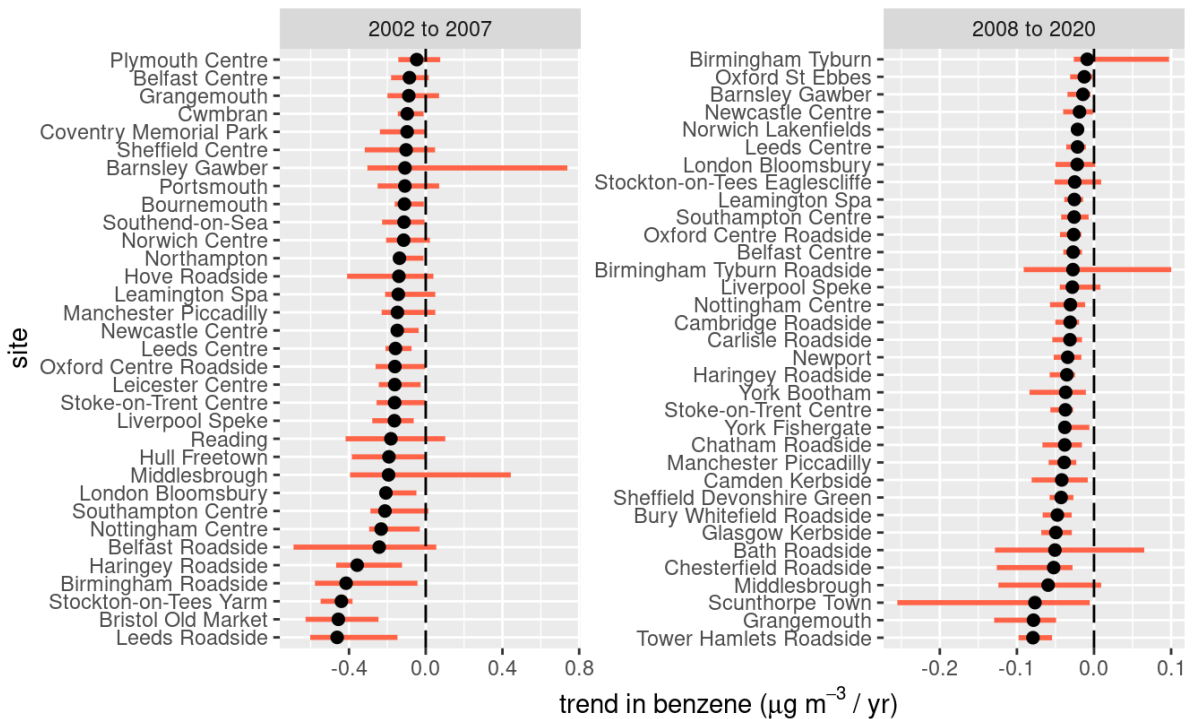
Figure 8: Benzene concentration trend (μg m⁻³ / yr) at non-automatic sites from 2002 to 2020.

Data obtained from the National Atmospheric Emissions Inventory (NAEI) can be used to see if there is a long-term relationship between emissions and measurements (Figure 9). Normalisation involved dividing the annual means by the mean value for the whole time series. The NAEI urban benzene emissions data agrees with the monitoring data, where a sharp decline can be seen from 1995 up to the year 2000 where petrol benzene additives were replaced by toluene for the purposes of maintaining the required octane value, 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. NAEI benzene data for 2020 is not yet available.
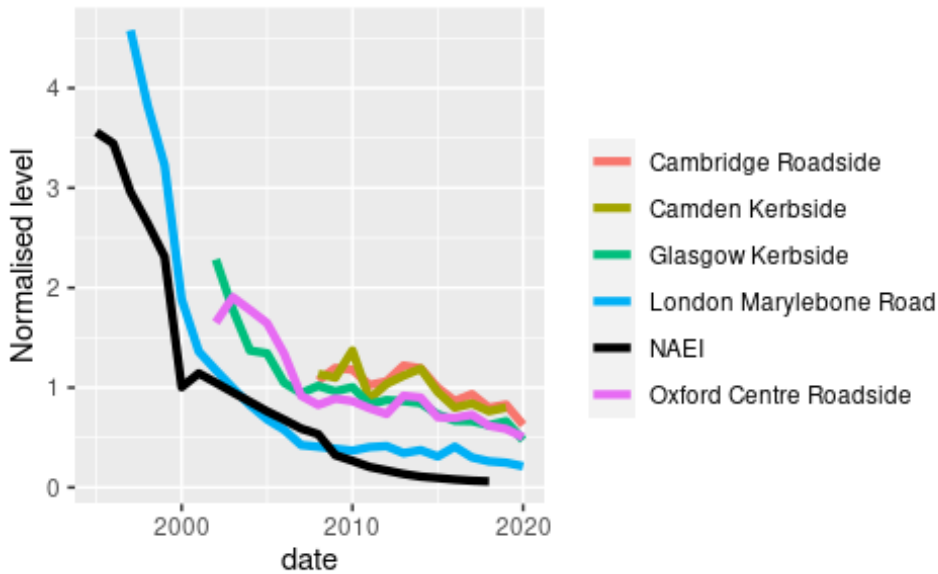
Figure 9: Normalised annual average benzene concentration and NAEI benzene emission estimate (1995 - 2020).

4.4 Impact of VOCs on regional O$_3$ formation

4.4.1 Regional O$_3$ increment

The UK measures different species of VOCs due to their ozone creation potential. To understand the contribution of individual VOCs to the O$_3$ production at the UK (regional) scale, we first need to quantify the O$_3$ increment at the UK level. This section presents evidence of the regional ozone formation and the relative contribution from each VOC. The methodology of the analysis in this section follows that set out by Malley et al. (2015).

In this report, the regional O$_3$ production is defined as the O$_3$ concentration measured at Chilbolton minus the northern hemispheric background O$_3$ concentration. Chilbolton is a rural monitoring site generally representing the regional background O$_3$ in southern England. The hemispheric background O$_3$ concentrations were derived from measurements at Mace Head coupled with air-mass back trajectory analysis. 96h air-mass back trajectories arriving daily at Mace Head were modelled with the Hysplit model and were grouped into 4 clusters based on the similarity of the angle of each trajectory from the origin (Mace Head) (Figure 10). The hours corresponding to trajectory clusters from the west and southwest (C1 and C3) are considered to be "clean" air masses, and therefore representing the hemispheric background O$_3$ concentration.
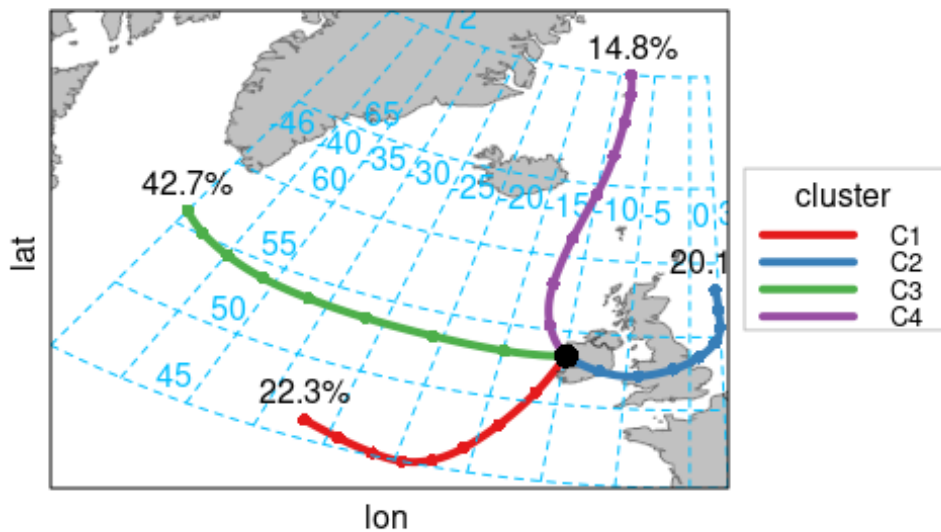
Figure 10: Air mass back trajectories arriving at Mace Head in 2020

To quantify the regional O_3 increment, 288 month-hourly average O_3 concentrations were calculated at Chilbolton and for the "clean" air masses at Mace Head. The difference between the two is shown in Figure 11. In general, we would expect higher concentrations for the hemispheric background O_3, i.e. negative values in Figure 11. However, elevated regional background O_3 concentrations due to photochemical reactions were evident especially during the summer day hours.

Year
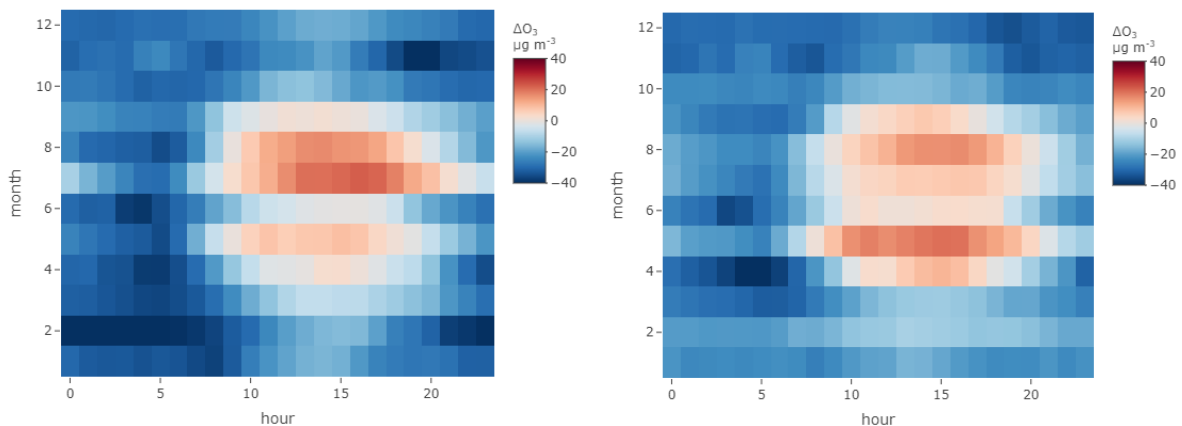
Figure 11: Month–hourly average differences between regional and hemispheric background O_3 for 2019 (left) and 2020 (right) at Chilbolton Observatory.

4.4.2   Photochemical ozone creation potential

Multiple studies have tried to quantify the propensity of each VOC to produce O_3 and derived the photochemical ozone creation potential (POCP) (Derwent et al., 2007; Hakami et al., 2004; Luecken and Mebust, 2008). The POCPs derived by Derwent et al. (2007) are used in this analysis as they were calculated under simulated north-western European conditions, which is most relevant in the UK context. In Derwent et al. (2007), a VOC POCP

was defined as the ratio (multiplied by 100) of the increase in O_3 due to increased emissions of the VOC simulated in a Lagrangian model along a trajectory traversing from central Europe to the UK, relative to the modelled increase in O_3 from the same mass increase in emissions of ethene (the reference POCP VOC assigned a value of 100). Hourly VOC concentrations were multiplied by the corresponding POCPs to weight their potential to create O_3. Diurnal variation of the weighted VOC concentrations at Chilbolton represents the extent of photochemical depletion that occurred in the southern England, and in turn leads to the regional O_3 creation. It is acknowledged that part of the diurnal variation in VOC concentrations is due to changes in the boundary layer mixing depth. To eliminate this effect, hourly POCP-weighted VOC concentrations were normalised by the corresponding POCP-weighted ethane concentrations. Ethane was chosen because it has the second smallest POCP of the measured VOCs (Table 3) and has previously been used to estimate photochemical loss of VOCs (Malley et al., 2015; Yates et al., 2010). The VOC diurnal photochemical depletion is then calculated as the difference between the average POCP-weighted VOC/ethane ratio at night (00:00 – 04:00) and in the afternoon (12:00 – 16:00). A positive value indicates daytime photochemical depletion of the VOC relative to ethane. The median of the VOC diurnal photochemical depletion for each month is summarised in Figure 12. The seasonal pattern of VOC diurnal photochemical depletion matches the seasonal pattern of regional O_3 increment as observed in (Figure 11), i.e. largest VOC diurnal photochemical depletion and regional O_3 increment in the summer months. The magnitude of the VOC diurnal photochemical depletion indicates relative contribution of each VOC to total VOC photochemical depletion, which in turn represents the relative contribution to the production of regional O_3.
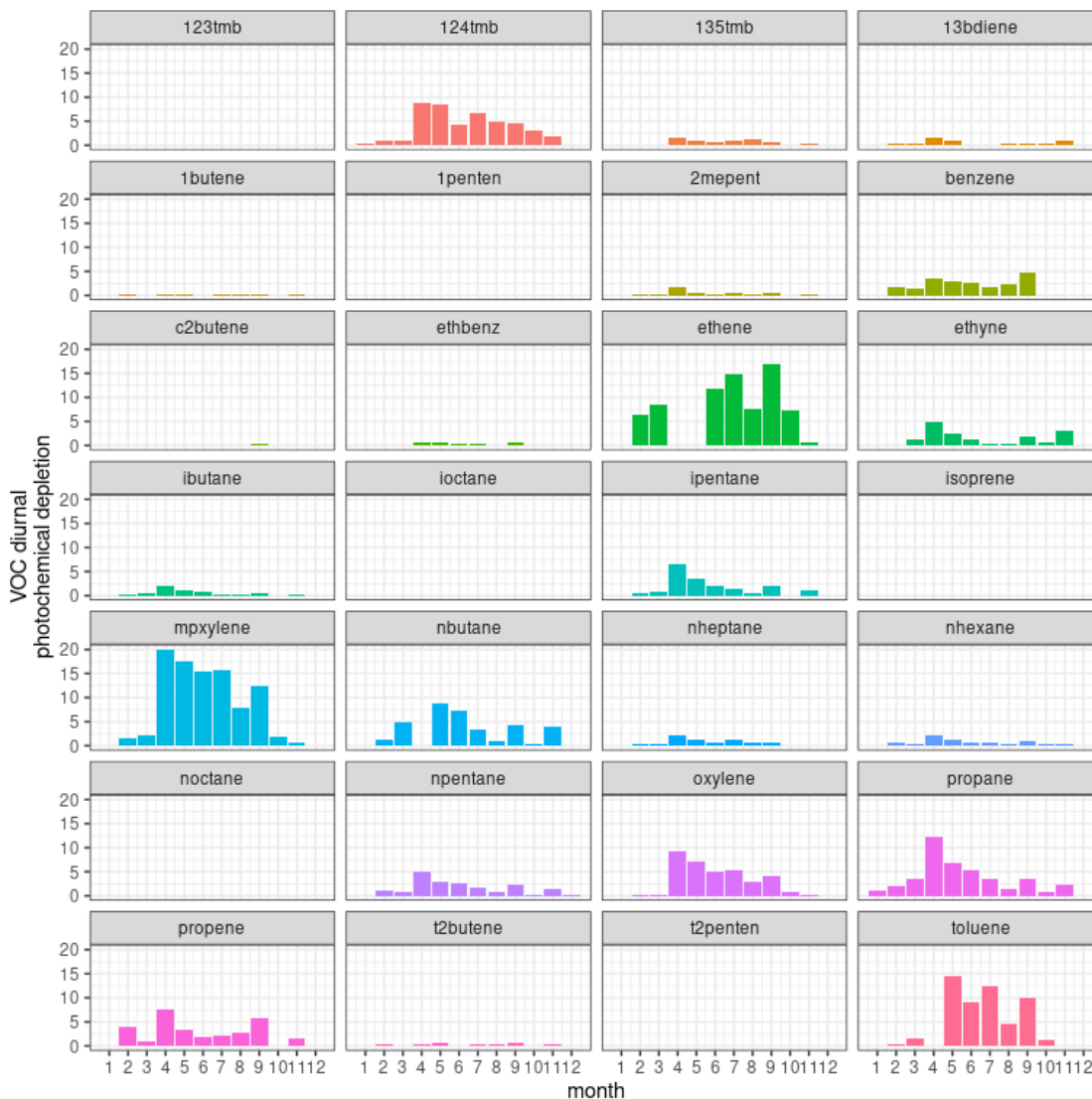
Figure 12: Median of the diurnal VOC photochemical depletion at Chilbolton for each month in 2020.

To compare the relative contribution of each VOC to the regional O_3 increment, Figure 13 shows the median VOC diurnal photochemical depletion values in descending order for the months when regional O_3 increment was observed. Ethene consistently showed the largest contribution to regional O_3 increment during these months. Mpxylene, toluene, 124tmb, nbutane also had similar contribution to the regional O_3 creation and were comparatively larger than other VOC species. The result might suggest that, of the measured VOCs, reduction in emission of ethene, Meta + Para-Xylene, toluene, 1,2,4-trimethylbenzene and nbutane emissions would be most effective in reducing regional O_3 increment. This reflects a small but insignificant change to the same analysis performed in 2019.
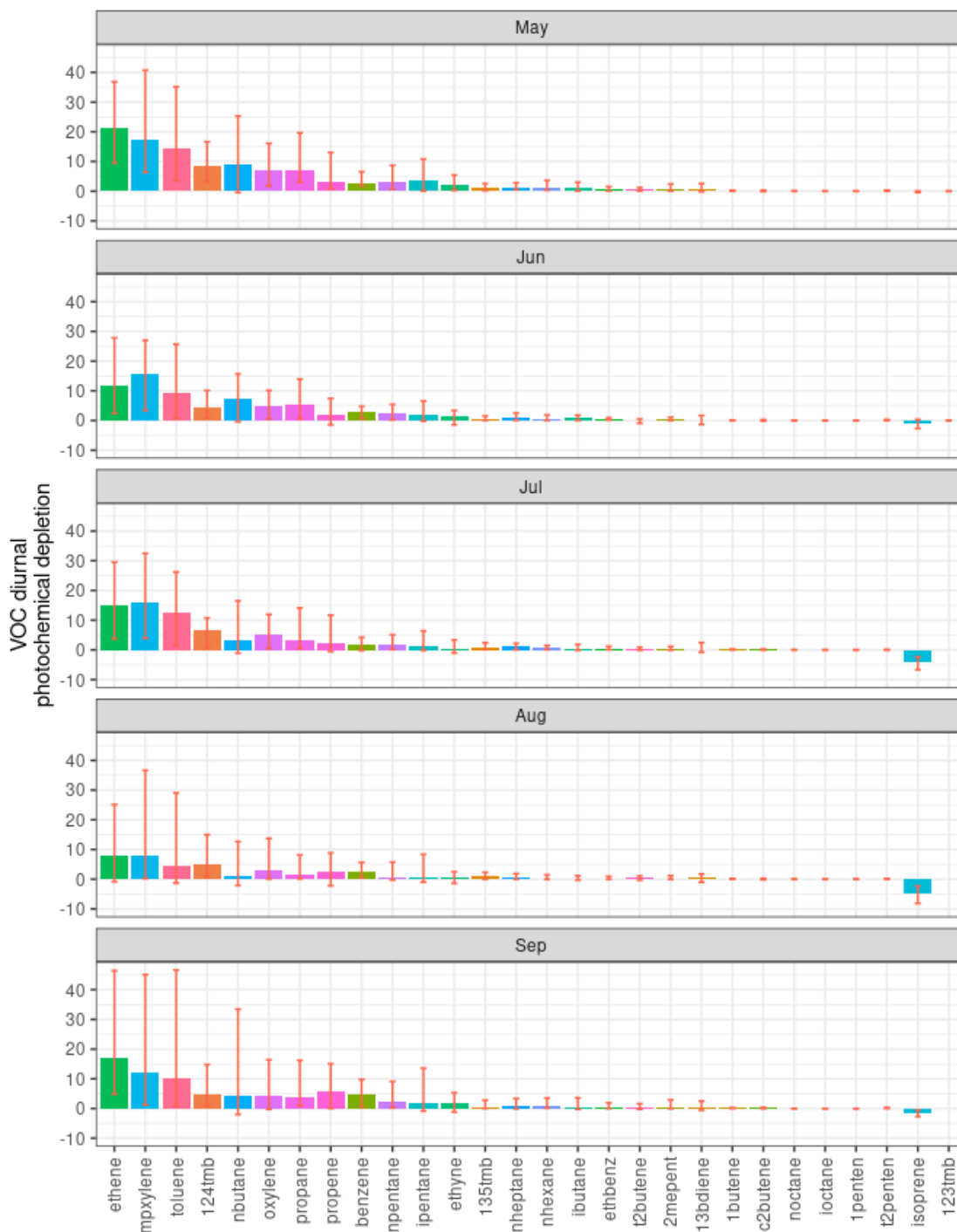
Figure 13: Median of the VOC diurnal photochemical depletion at Chilbolton between May and September in 2020. Error bar indicates the 25 and 75% percentile of the VOC diurnal photochemical depletion for a that VOC in the relevant month.

4.5 Impact of COVID-19 on benzene

The effect of lockdown due to COIVD-19 on the VOC concentrations are presented in this section. Benzene is selected as the pollutant of interest because of its high correlation with many other VOCs and due to the fact that it has a limit value.

4.5.1 Simulated normal concentration

A perennial problem when comparing air pollution data before and after certain interventions is the effect of the weather. To counteract the effect of weather, we use a model to simulate pollutant concentrations using wind speed/direction, temperature, hour of the day, weekday, unix date and Julian day as predictors. The model is trained using 2018 and 2019 data and then used to predict concentrations from 2020, which can be seen as the normal concentrations expected if no intervention had taken place.

The simulated and measured daily average benzene concentrations are shown below. Before 23rd March, when lockdown was enforced, the modelled benzene tracks closely with the measured at Marylebone road, suggesting that the measured concentrations are comparable to the usual levels at this time of the year and under normal business activities. It is noted that the modelled benzene tracks less well at other non-roadside locations before 23rd March. This is expected as the model tries to predict pollutant concentrations using only the diurnal profile and weather conditions, which are thought to have a stronger influence closer to the traffic source.

The modelled [i.e. 'business as usual'(BAU)] benzene concentrations are predominately higher than the measured concentrations from 23rd March to July at all sites, which suggests that reduced emissions from traffic and industry are being seen in the measurements. During the restriction period from June to November the measured benzene concentration are still lower than the 'normal' modelled concentrations. Interestingly, during the second lockdown from November to the end of 2020, the measured benzene are at a similar level to the modelled concentrations.

4.5.1.1 Benzene
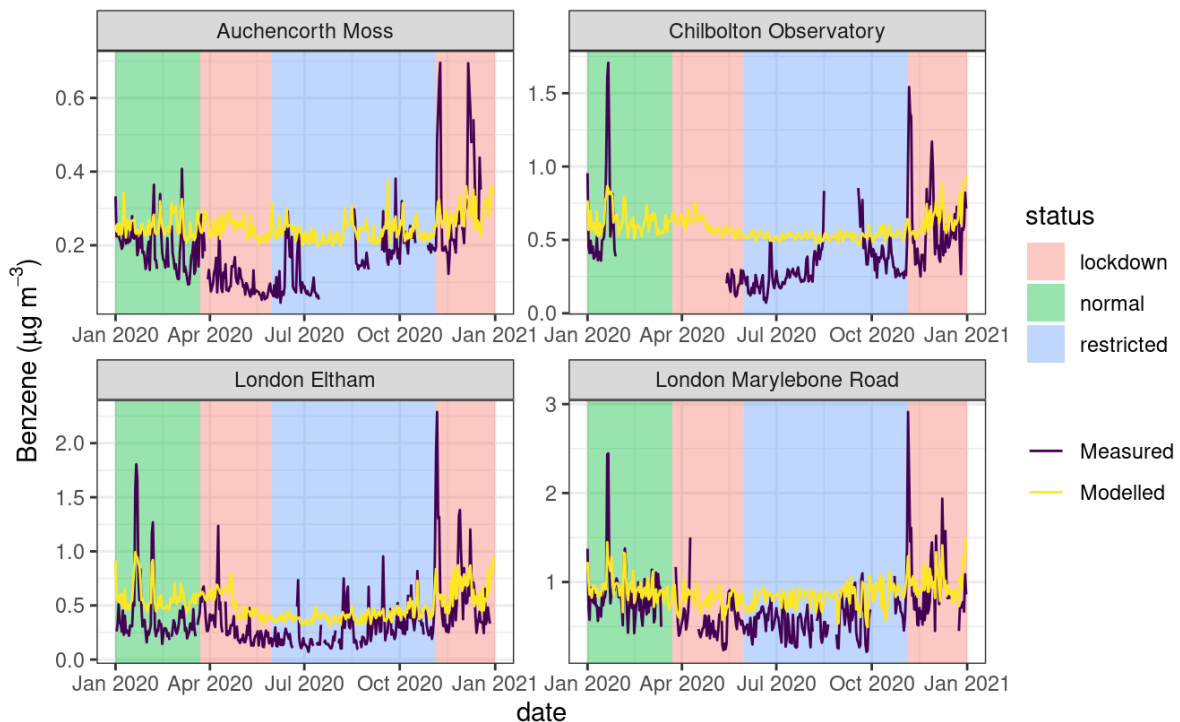
4.5.1.2 Ethane

Unlike benzene, ethane which has limited contributions from exhaust emissions showed less difference between measured and modelled concentration throughout 2020 at two London sites.
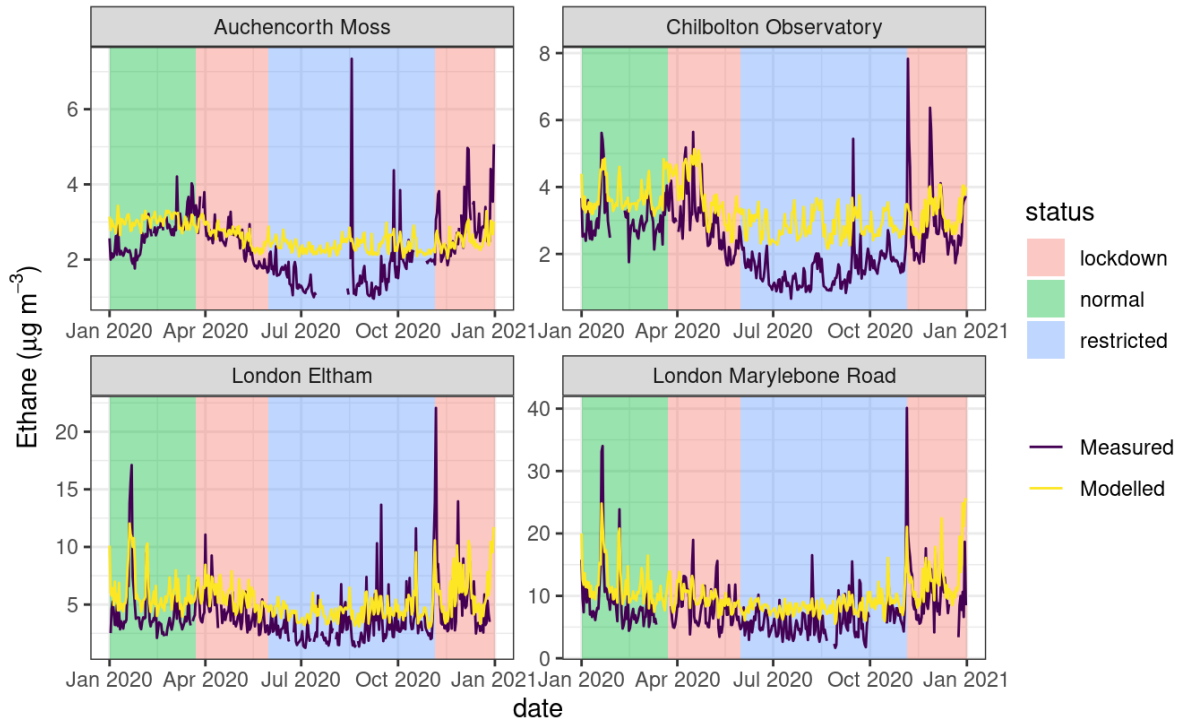
4.5.1.3 NOx

Similar to benzene, NOx measured at the available sites are predominately lower than the BAU concentrations during the first lockdown and restricted periods. However, they compare similarly during the second lockdown especially for the background and rural sites.
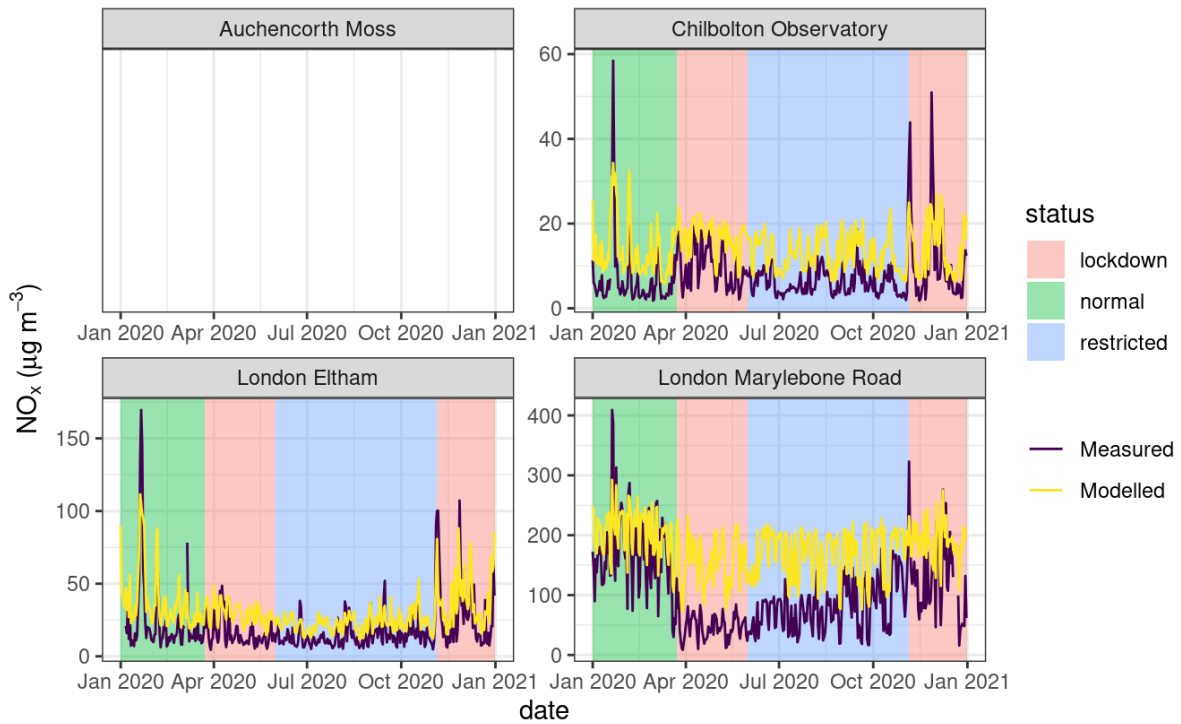
4.5.2 Monthly variation between measured and BAU concentrations

To smooth out any noise in the simulated BAU concentrations, monthly average concentrations for benzene, ethane and NOx with their 95% confidence intervals are shown below. The most notable pattern here is that NOx clearly showed different distributions between measured and modelled concentrations at Marylebone Road during April, May and June. Whereas benzene and ethane did not show significant difference between measured and modelled distributions at Marylebone Road throughout the year.

4.5.2.1 Benzene
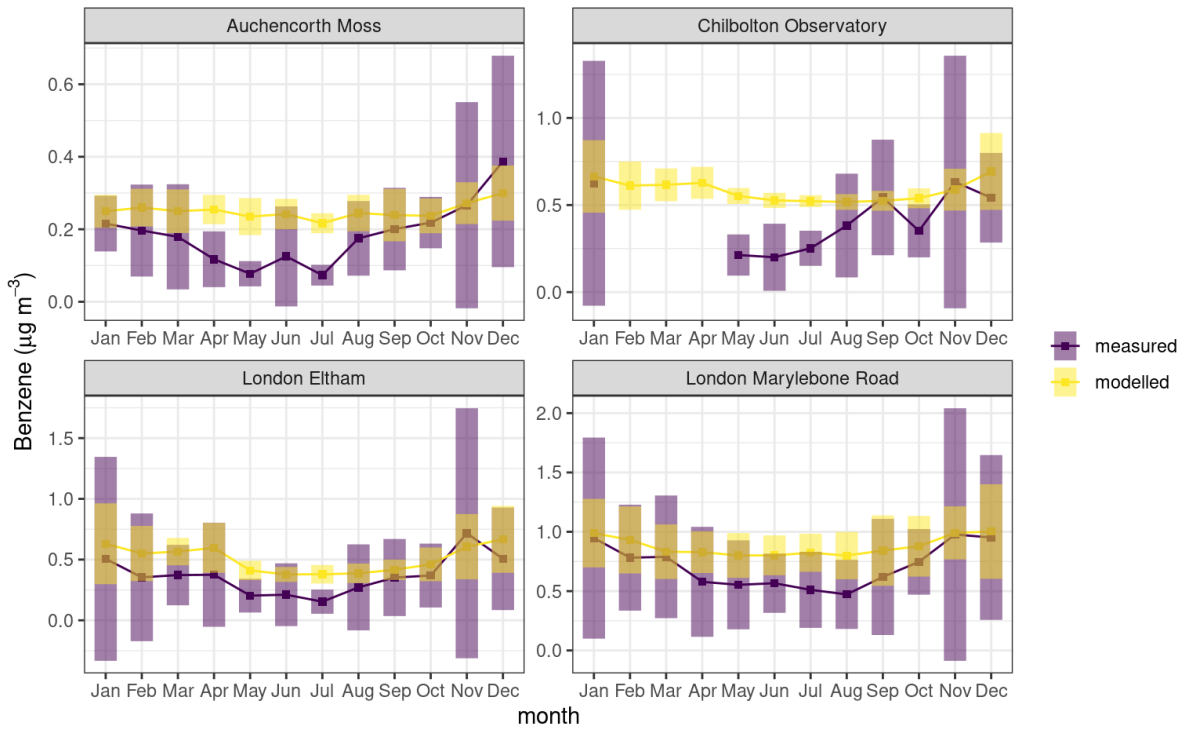
4.5.2.2 Ethane
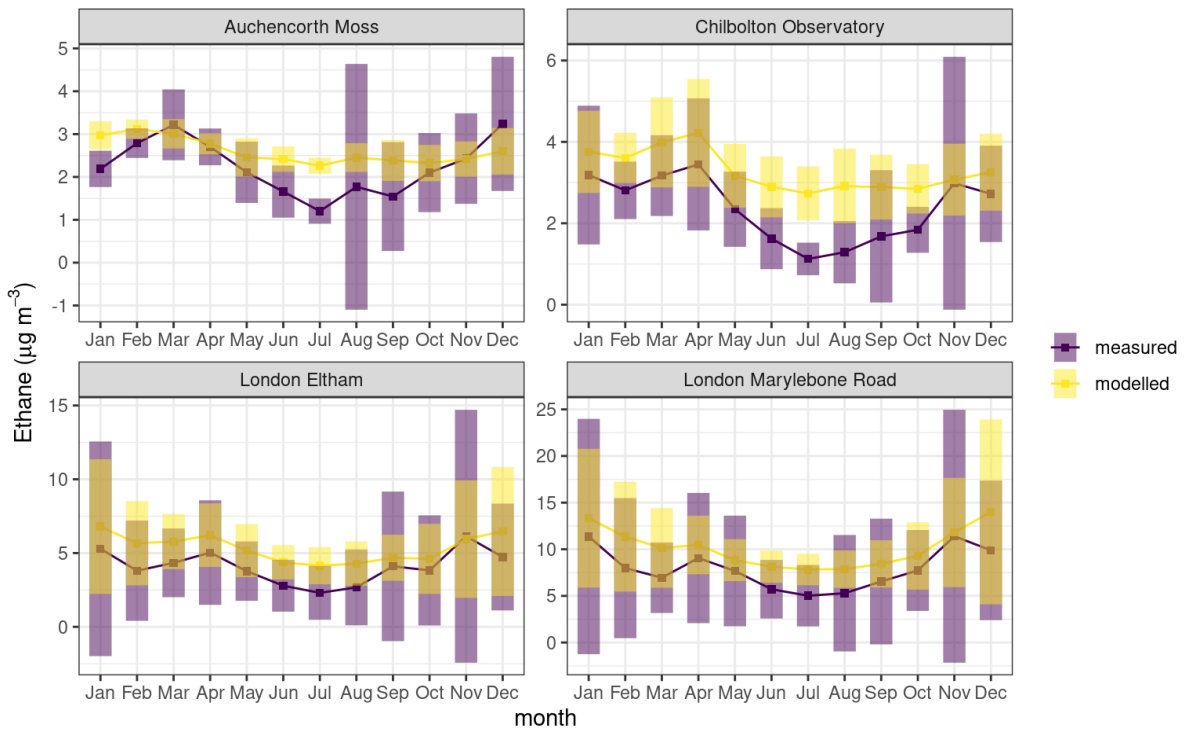
4.5.2.3   NOx
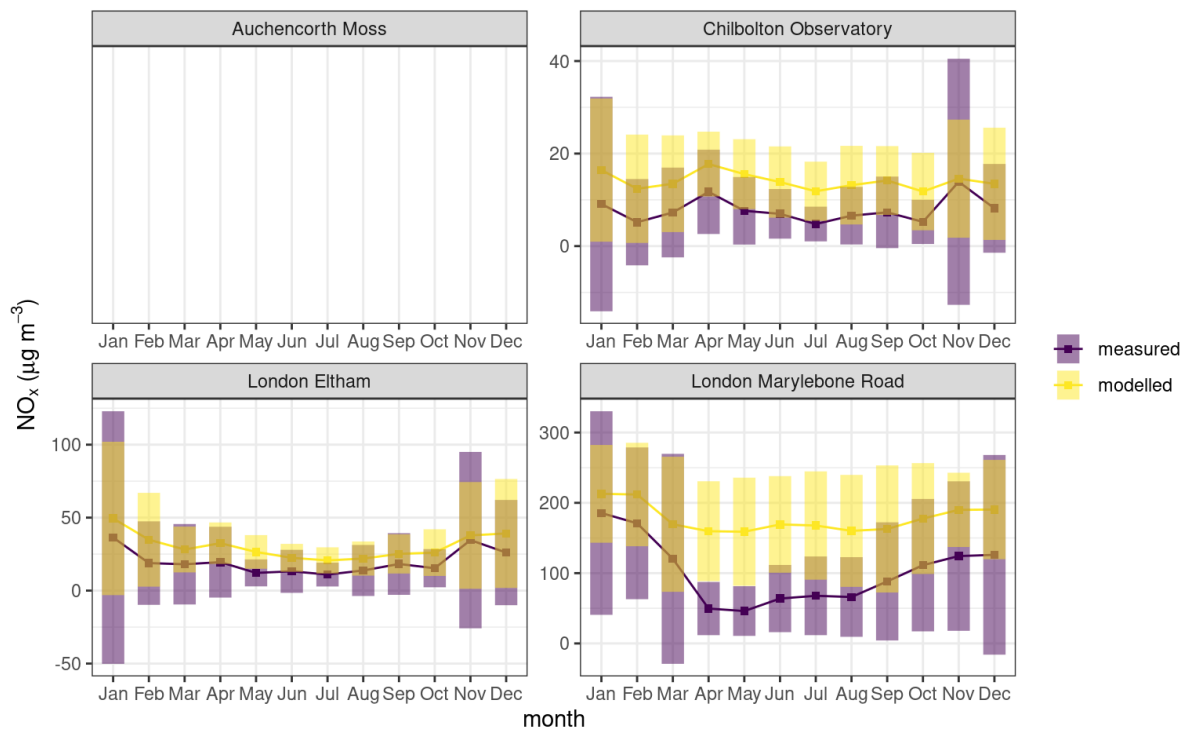
4.5.3   Annual average

The annual average benzene concentrations compared to previously are shown below. Benzene concentrations for 2020 are the lowest for the past three years across all sites. It is estimated that the reduction in benzene concentrations caused by the COVID-19 adjusted for the weather conditions is about 20%.
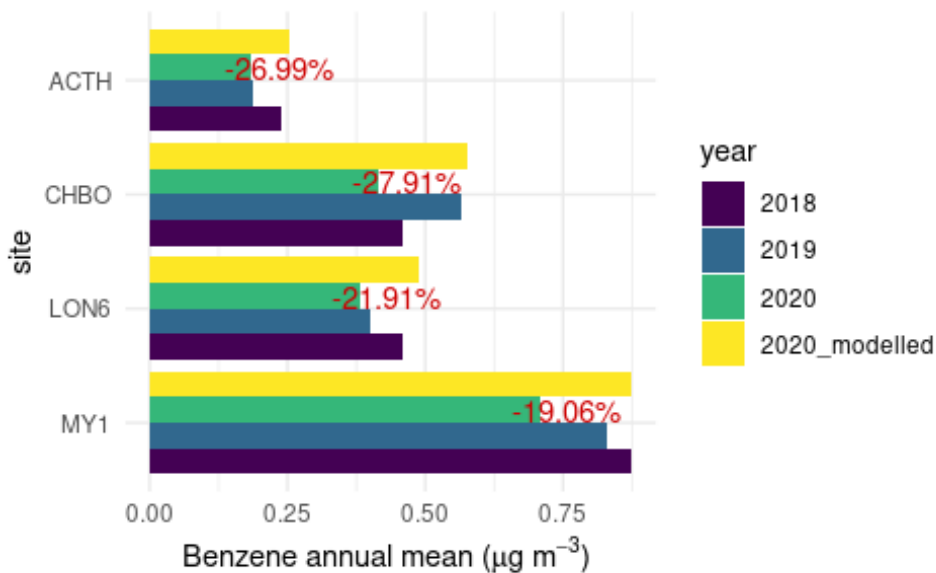
4.6 Automatic Data Time Variations for Benzene

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

4.6.1 Auchencorth Moss
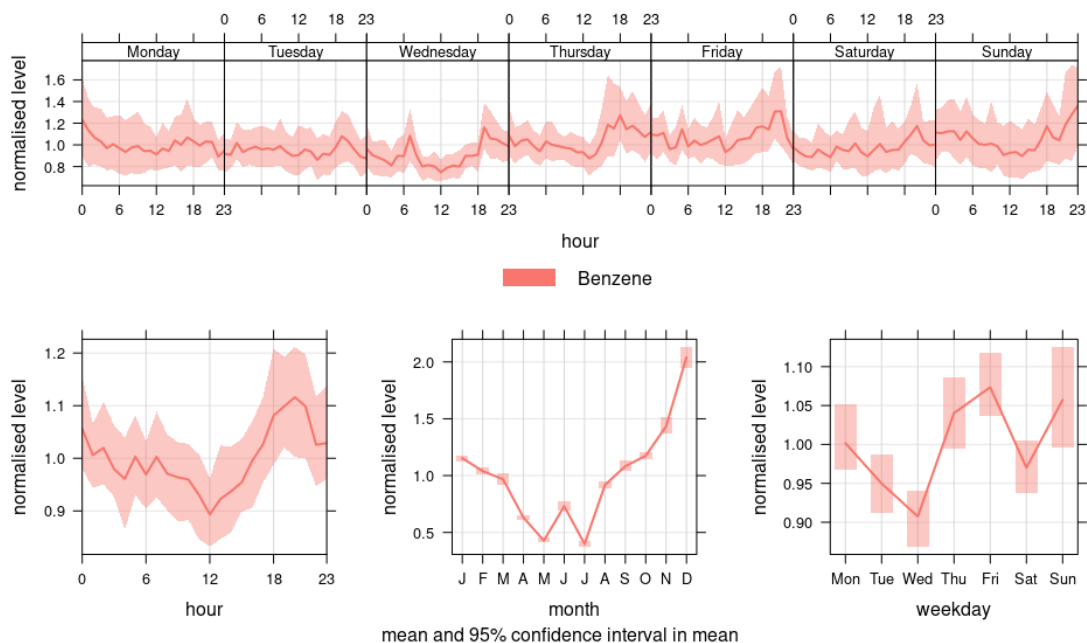
Figure 14: Diurnal, seasonal and week-daily variation of benzene at Auchencorth Moss.

The concentrations at Auchencorth Moss tend to be relatively stable compared with urban traffic sites, background levels of these compounds tend to fluctuate less. The highest levels of benzene have been observed after 18:00, particularly on Thursday, Friday and Sunday with highest monthly measurements seen in December. Elevated concentrations in early December followed by a loss of data from the 18th December might contribute to some bias that causes the concentrations to appear higher in December compared to previous months. This was not seen at any other station in the UK

4.6.2 Chilbolton Observatory
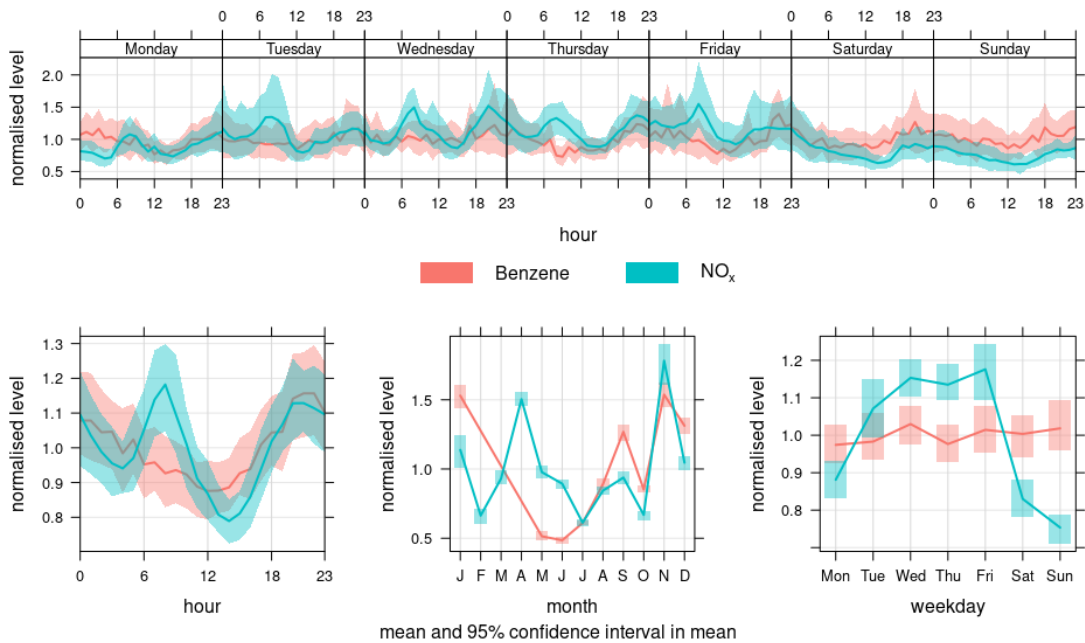
Figure 15: Diurnal, seasonal and week-daily variation of benzene, and NO$_x$ at Chilbolton.

Figure 15 indicates concentrations of benzene tend to peak after 19:00 at Chilbolton Observatory, however concentrations typically remain relatively high until early morning. The highest measurements for benzene have been seen in January and December. During the week, levels remain relatively consistent throughout the week.

4.6.3 Eltham
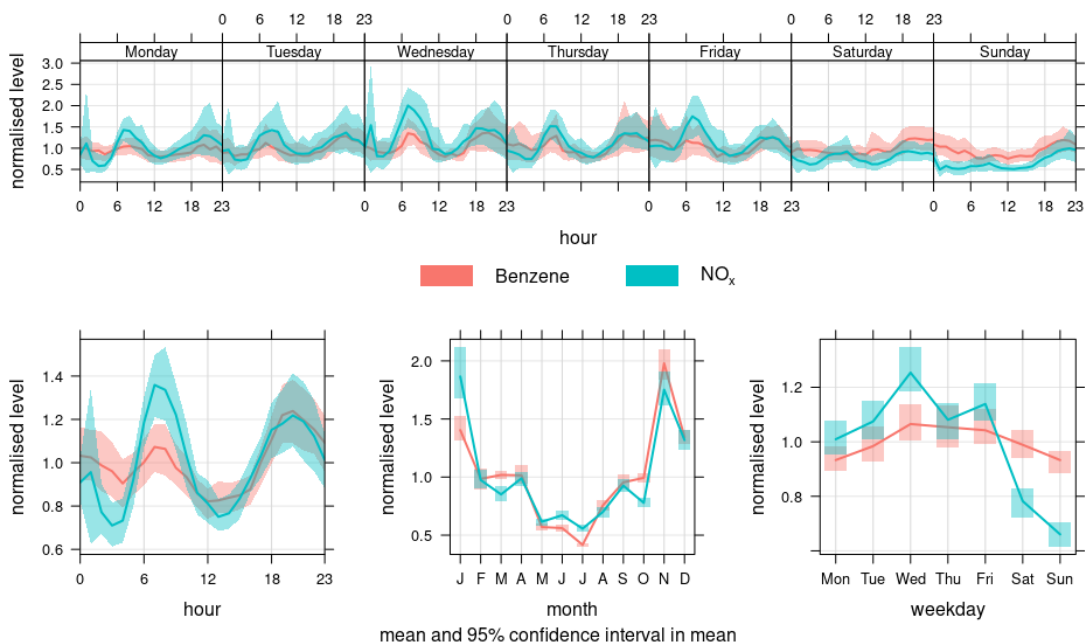
Figure 16: Diurnal, seasonal and week-daily variation of benzene and NO$_x$ at London Eltham.

At London Eltham, benzene trends generally follow the trend of NOx, indicating that they are mainly dominated by traffic sources. Elevated levels of benzene and NOx can be seen during the 'rush hours', particularly in the evening for benzene. Levels persist for a period during the late afternoon and evening. The plots also show that benzene levels appear to be more consistent throughout the week. The highest monthly measurements have been observed during January and November.

4.6.4 Marylebone Road
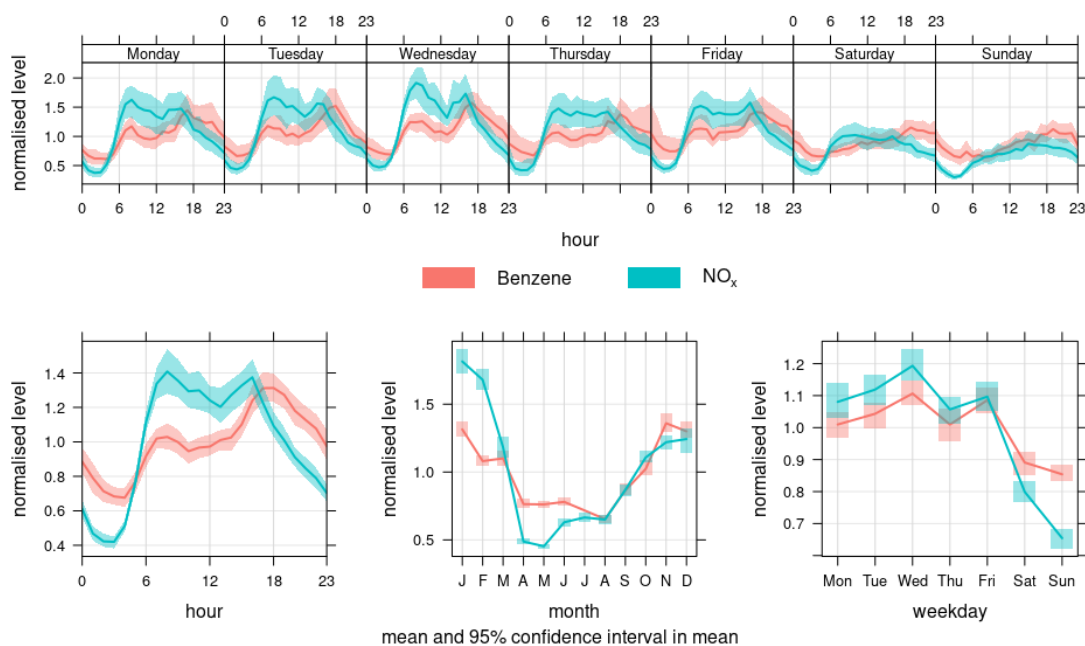
Figure 17: Diurnal, seasonal and week-daily variation of benzene and NOx at Marylebone Road.

The concentration profiles of benzene follow that of NOx more closely at Marylebone Road compared with other sites. There are clearly defined elevated benzene concentrations during the 'rush hours' from Monday to Friday, particularly from 17:00 to 18:00 hours. Highest concentrations have been measured for benzene in November and December. The difference between levels from weekdays to weekends is marked compared with that at London Eltham. Marylebone Road shows a clear drop in both NOx and Benzene in April after the first lockdown restrictions were put in place.

4.7 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 2018, subsequent annual update reports will follow.

There were no exceedances of the 5 µg m^{-3} annual mean LV modelled in 2018. The highest estimated background concentration was 3.2 µg m^{-3} at South Killingholme which is predominantly caused by emissions from combustion in industry.

5 Developments and recommendations

5.1 EN14662-1:2005

European Standard EN14662-3:2005 is currently under revision by CEN Working Group 12. The replacement refers to a sequential benzene sampler as opposed to a simple single tube system. The replacement document is likely to be released in the next two years.

5.2 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.

5.3 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 had been requested in order to start a five-year process for development of such a standard. A mandate for this has now been issued, however the funding requested was costed for the preparation of a single standard method, the EC issued a mandate for six standard methods to be developed. These include:

- automatic pumped sampling, pre-concentration and on-line gas chromatography with flame ionisation detector (FID) and/or mass spectrometer detector (MSD);
- manual or automatic canister sampling followed by off-line gas chromatography with FID and/or MSD;
- manual or automatic pumped sampling followed by off-line thermal desorption and gas chromatography with FID and/or MSD;
- diffusive sampling followed by thermal desorption by off-line gas chromatography with FID and/or MSD;
- manual or automatic pumped sampling of formaldehyde on dinitrophenylhydrazine (DNPH) followed by off-line high performance liquid chromatography (HPLC)/ ultraviolet (UV) detection;
- diffusive sampling of formaldehyde on DNPH followed by off-line HPLC/UV detection.

A first draft work programme has been provided to the EC in August 2019. Working Group 13 has been resumed in order to cover most parts of this, with Working Group 11 covering the diffusive methodologies. Ricardo maintain one member within working group 13.

5.4 Requirement for network changes

From 2017, modelled benzene data (from Defra's Pollution Climate Mapping model) suggests the highest background concentrations of benzene are in South Killingholme, North Lincolnshire. Modelled concentrations of benzene at 3.4 µg m-3 in 2017 and 3.2 µg m-3 in 2018. The model has predicted higher levels in this area previously as a result of the emissions inventory. However, measurements made in the area in 2008 (Butterfield et al., 2009) confirmed no exceedances of the limit value.

Concentrations in the Swansea urban area were modelled at 1.9 µg m-3 and 2.7 µg m-3 for 2017 and 2018 respectively, however measurements have since been introduced in the area.

5.5 Network changes at Port Talbot Margam

From 2014 and 2016, modelled benzene data (from Defra's Pollution Climate Mapping model) suggested the highest background concentrations of benzene were in the Swansea urban area. PCM estimates for this zone were below the annual limit value of 5 µg m^{-3} but in excess of the upper assessment threshold of 3.5 µg m^{-3}. The predominant source is local industry in Port Talbot. There were no benzene measurements made anywhere in the Swansea Urban area during this period. Since the City of London had three samplers in operation at urban traffic stations, with Haringey Roadside and Camden Kerbside offering essentially the same data set, the sampler at Camden Kerbside was relocated to the Port Talbot Margam AURN monitoring station in January 2020. The most recent modelled value in the Swansea Urban area was estimated to be 2.17 µg m^{-3} in 2019, above the lower assessment threshold. The measurements confirm no exceedances of the limit value or assessment thresholds in 2020 (Figure 18).
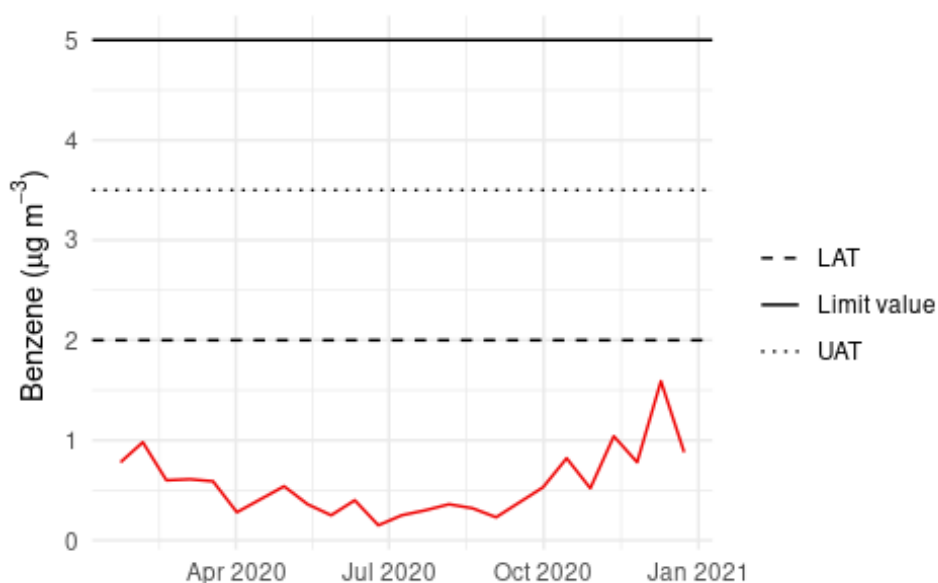

Figure 18: Port Talbot Margam 2020 benzene concentration.

6 Conclusions

The annual mean concentration across all non-automatic monitoring stations in the UK for 2020 was 0.55 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 2020 was 93%.

The annual mean across all automatic monitoring stations in the UK was 0.42 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 2020 was 72%.

In 2020, none of the automatic or non-automatic monitoring stations 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 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 2020. The highest concentrations observed during 2020 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 rural background, urban background and urban traffic locations. Scunthorpe Town, an industrial location, recorded the highest time weighted annual mean of 0.87 µg m^{-3}. Camden Kerbside was relocated to the Port Talbot Margam station. Measurements of benzene at the station show concentrations of benzene are below the Lower Assessment Threshold during 2020.

All sites showed a decrease in benzene concentration over the period 2002 to 2020. 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 2020. Benzene emissions data provided by the National Atmospheric Emissions Inventory shows a steady decline in benzene emissions from 2010 to 2019, conversely, the stability seen in benzene monitoring data could be due to alternative sources of benzene, such as from increased use of wood-burning appliances used for domestic and commercial space and water heating.

Data measured at Chilbolton Observatory indicates that, of the VOCs measured, ethene, Meta + Para-Xylene, toluene, 1,2,4-trimethylbenzene and nbutane showed the largest contribution to regional O$_3$ increment during the daylight hours in summer.

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Appendices

Appendix I Details of the monitoring sites in automatic and non-automatic hydrocarbon networks

Table 5: Information of the monitoring stations in the automatic and non-automatic hydrocarbon network in 2020.

Site code	Site name	Site type	Region	Latitude	Longitude	Network type
BAR3	Barnsley Gawber	urban background	Yorkshire & Humberside	53.56292	- 1.510436	non-automatic
BHA4	Bath A4 Roadside	urban traffic	South West	51.39092	- 2.355030	non-automatic
BEL2	Belfast Centre	urban background	Northern Ireland	54.59965	- 5.928833	non-automatic
BIRR	Birmingham A4540 Roadside	urban traffic	West Midlands	52.47609	- 1.875024	non-automatic
BMLD	Birmingham Ladywood	urban background	West Midlands	52.48135	- 1.918235	non-automatic
BURW	Bury Whitefield Roadside	urban traffic	North West & Merseyside	53.55903	- 2.293772	non-automatic
CAM	Cambridge Roadside	urban traffic	Eastern	52.20237	0.124456	non-automatic
CA1	Camden Kerbside	urban traffic	Greater London	51.54421	- 0.175269	non-automatic
CARM	Carlisle Morton A595	urban traffic	North West & Merseyside	54.88582	- 2.964955	non-automatic
CARL	Carlisle Roadside	urban traffic	North West & Merseyside	54.89483	- 2.945307	non-automatic
CHAT	Chatham Roadside	urban traffic	South East	51.37426	0.547970	non-automatic
CHS7	Chesterfield Roadside	urban traffic	East Midlands	53.23172	- 1.456944	non-automatic
GLA4	Glasgow Kerbside	urban traffic	Central Scotland	55.85917	- 4.258889	non-automatic
GRAN	Grangemouth	urban industrial	Central Scotland	56.01032	- 3.704399	non-automatic

Site code	Site name	Site type	Region	Latitude	Longitude	Network type
HG1	Haringey Roadside	urban traffic	Greater London	51.59930	-0.068218	non-automatic
LEAM	Leamington Spa	urban background	West Midlands	52.28881	-1.533119	non-automatic
LEED	Leeds Centre	urban background	Yorkshire & Humberside	53.80378	-1.546472	non-automatic
LVP	Liverpool Speke	urban industrial	North West & Merseyside	53.34633	-2.844333	non-automatic
CLL2	London Bloomsbury	urban background	Greater London	51.52229	-0.125889	non-automatic
MAN3	Manchester Piccadilly	urban background	North West & Merseyside	53.48152	-2.237881	non-automatic
MID	Middlesbrough	urban industrial	North East	54.56930	-1.220874	non-automatic
NEWC	Newcastle Centre	urban background	North East	54.97825	-1.610528	non-automatic
NPT3	Newport	urban background	South Wales	51.60120	-2.977281	non-automatic
NO12	Norwich Lakenfields	urban background	Eastern	52.61419	1.301976	non-automatic
NOTT	Nottingham Centre	urban background	East Midlands	52.95473	-1.146447	non-automatic
OX	Oxford Centre Roadside	urban traffic	South East	51.75174	-1.257463	non-automatic
OX8	Oxford St Ebbes	urban background	South East	51.74481	-1.260278	non-automatic
PT4	Port Talbot Margam	urban industrial	South Wales	51.58395	-3.770822	non-automatic
SCN2	Scunthorpe Town	urban industrial	Yorkshire & Humberside	53.58634	-0.636811	non-automatic
SHDG	Sheffield Devonshire Green	urban background	Yorkshire & Humberside	53.37862	-1.478096	non-automatic
SOUT	Southampton Centre	urban background	South East	50.90814	-1.395778	non-automatic
EAGL	Stockton-on-Tees Eaglescliffe	urban traffic	North East	54.51667	-1.358547	non-automatic

Site code	Site name	Site type	Region	Latitude	Longitude	Network type
STOK	Stoke-on-Trent Centre	urban background	West Midlands	53.02821	-2.175133	non-automatic
TH2	Tower Hamlets Roadside	urban traffic	Greater London	51.52253	-0.042155	non-automatic
YK10	York Bootham	urban background	Yorkshire & Humberside	53.96751	-1.086514	non-automatic
YK11	York Fishergate	urban traffic	Yorkshire & Humberside	53.95189	-1.075861	non-automatic
ACTH	Auchencorth Moss	rural background	Central Scotland	55.79216	-3.242900	automatic
CHBO	Chilbolton Observatory	rural background	South East	51.14962	-1.438228	automatic
LON6	London Eltham	urban background	Greater London	51.45258	0.070766	automatic
MY1	London Marylebone Road	urban traffic	Greater London	51.52253	-0.154611	automatic
MH	Mace Head	urban traffic	West Ireland	53.32644	-9.903917	automatic

Appendix II Automatic Hydrocarbon Statistics for all VOC species

Table 6: Summary statistics for all VOCs measured at the automatic monitoring sites 2020.

Site	VOC	Annual data capture	Annual maximum	Annual mean	Annual minimum
Auchencorth Moss	123tmb	0.00	0.15	0.04	0.02
Auchencorth Moss	124tmb	0.03	0.29	0.09	0.02
Auchencorth Moss	135tmb	0.02	0.12	0.05	0.02
Auchencorth Moss	13bdiene	0.42	0.28	0.03	0.01
Auchencorth Moss	1butene	0.47	0.30	0.02	0.01
Auchencorth Moss	1penten	0.42	0.09	0.01	0.01
Auchencorth Moss	2mepent	0.73	1.69	0.03	0.01
Auchencorth Moss	benzene	0.69	1.26	0.19	0.02
Auchencorth Moss	c2butene	0.44	0.11	0.02	0.01
Auchencorth Moss	ethane	0.81	44.66	2.30	0.79
Auchencorth Moss	ethbenz	0.09	0.62	0.08	0.02
Auchencorth Moss	ethene	0.75	8.84	0.30	0.02
Auchencorth Moss	ethyne	0.80	3.27	0.54	0.07

Site	VOC	Annual data capture	Annual maximum	Annual mean	Annual minimum
Auchencorth Moss	ibutane	0.80	15.88	0.34	0.02
Auchencorth Moss	ioctane	0.34	0.74	0.03	0.02
Auchencorth Moss	ipentane	0.80	13.61	0.23	0.02
Auchencorth Moss	isoprene	0.76	2.18	0.04	0.01
Auchencorth Moss	mpxylene	0.10	2.26	0.19	0.02
Auchencorth Moss	nbutane	0.81	36.03	0.62	0.01
Auchencorth Moss	nheptane	0.36	1.29	0.04	0.02
Auchencorth Moss	nhexane	0.78	3.23	0.05	0.01
Auchencorth Moss	noctane	0.04	0.36	0.05	0.02
Auchencorth Moss	npentane	0.80	15.47	0.20	0.01
Auchencorth Moss	oxylene	0.08	0.74	0.08	0.02
Auchencorth Moss	propane	0.81	39.41	1.27	0.10
Auchencorth Moss	propene	0.46	1.55	0.05	0.01
Auchencorth Moss	t2butene	0.44	0.14	0.02	0.01
Auchencorth Moss	t2penten	0.42	0.06	0.01	0.01
Auchencorth Moss	toluene	0.33	4.81	0.18	0.01
Chilbolton Observatory	123tmb	0.00	NA	NA	NA
Chilbolton Observatory	124tmb	0.77	1.89	0.12	0.02
Chilbolton Observatory	135tmb	0.52	0.70	0.06	0.02
Chilbolton Observatory	13bdiene	0.83	0.79	0.06	0.01
Chilbolton Observatory	1butene	0.89	1.47	0.11	0.02
Chilbolton Observatory	1penten	0.90	0.15	0.02	0.01
Chilbolton Observatory	2mepent	0.88	1.36	0.08	0.00
Chilbolton Observatory	benzene	0.56	3.09	0.42	0.04
Chilbolton Observatory	c2butene	0.77	1.10	0.04	0.00
Chilbolton Observatory	ethane	0.90	20.46	2.31	0.52
Chilbolton Observatory	ethbenz	0.90	2.21	0.10	0.01

Site	VOC	Annual data capture	Annual maximum	Annual mean	Annual minimum
Chilbolton Observatory	ethene	0.88	10.22	0.44	0.02
Chilbolton Observatory	ethyne	0.90	6.07	0.58	0.06
Chilbolton Observatory	ibutane	0.90	19.27	0.51	0.03
Chilbolton Observatory	ioctane	0.89	0.65	0.05	0.00
Chilbolton Observatory	ipentane	0.90	9.44	0.42	0.01
Chilbolton Observatory	isoprene	0.90	4.47	0.07	0.00
Chilbolton Observatory	mpxylene	0.86	6.36	0.25	0.02
Chilbolton Observatory	nbutane	0.90	41.19	0.85	0.04
Chilbolton Observatory	nheptane	0.90	0.62	0.07	0.00
Chilbolton Observatory	nhexane	0.89	1.27	0.09	0.00
Chilbolton Observatory	noctane	0.90	0.71	0.05	0.02
Chilbolton Observatory	npentane	0.90	3.43	0.25	0.01
Chilbolton Observatory	oxylene	0.90	2.43	0.10	0.01
Chilbolton Observatory	propane	0.90	91.76	1.68	0.07
Chilbolton Observatory	propene	0.87	11.27	0.27	0.02
Chilbolton Observatory	t2butene	0.74	0.82	0.04	0.00
Chilbolton Observatory	t2penten	0.90	0.18	0.02	0.01
Chilbolton Observatory	toluene	0.91	4.56	0.47	0.08
London Eltham	123tmb	0.00	NA	NA	NA
London Eltham	124tmb	0.85	5.67	0.15	0.02
London Eltham	135tmb	0.84	1.79	0.06	0.02

Site	VOC	Annual data capture	Annual maximum	Annual mean	Annual minimum
London Eltham	13bdiene	0.84	0.98	0.06	0.01
London Eltham	1butene	0.86	2.76	0.10	0.01
London Eltham	1penten	0.83	0.73	0.04	0.01
London Eltham	2mepent	0.85	7.71	0.28	0.02
London Eltham	benzene	0.83	5.63	0.38	0.04
London Eltham	c2butene	0.85	1.05	0.05	0.01
London Eltham	ethane	0.86	59.41	4.16	0.90
London Eltham	ethbenz	0.78	3.63	0.18	0.01
London Eltham	ethene	0.85	11.83	0.75	0.01
London Eltham	ethyne	0.86	6.41	0.39	0.07
London Eltham	ibutane	0.86	39.45	1.29	0.12
London Eltham	ioctane	0.85	6.78	0.10	0.02
London Eltham	ipentane	0.86	70.70	1.08	0.08
London Eltham	isoprene	0.84	12.19	0.25	0.01
London Eltham	mpxylene	0.83	12.33	0.47	0.02
London Eltham	nbutane	0.86	65.81	2.46	0.23
London Eltham	nheptane	0.57	2.29	0.17	0.02
London Eltham	nhexane	0.85	11.33	0.22	0.02
London Eltham	noctane	0.81	0.90	0.06	0.02
London Eltham	npentane	0.86	33.88	0.51	0.05
London Eltham	oxylene	0.86	4.81	0.19	0.01
London Eltham	propane	0.86	35.77	2.44	0.21
London Eltham	propene	0.84	15.72	0.43	0.01
London Eltham	t2butene	0.85	1.31	0.05	0.01
London Eltham	t2penten	0.84	1.59	0.05	0.01
London Eltham	toluene	0.86	18.96	0.69	0.05
London Marylebone Road	123tmb	0.00	NA	NA	NA
London Marylebone Road	124tmb	0.63	9.13	0.55	0.02
London Marylebone Road	135tmb	0.53	1.96	0.18	0.02
London Marylebone Road	13bdiene	0.00	NA	NA	NA
London Marylebone Road	1butene	0.84	1.89	0.22	0.04

Site	VOC	Annual data capture	Annual maximum	Annual mean	Annual minimum
London Marylebone Road	1penten	0.73	1.15	0.07	0.01
London Marylebone Road	2mepent	0.84	13.26	0.46	0.02
London Marylebone Road	benzene	0.79	6.07	0.71	0.13
London Marylebone Road	c2butene	0.81	0.76	0.08	0.01
London Marylebone Road	ethane	0.84	60.71	7.94	1.31
London Marylebone Road	ethbenz	0.76	4.27	0.41	0.02
London Marylebone Road	ethene	0.84	12.39	1.59	0.12
London Marylebone Road	ethyne	0.84	23.47	0.81	0.09
London Marylebone Road	ibutane	0.84	19.82	2.00	0.08
London Marylebone Road	ioctane	0.74	7.81	0.30	0.02
London Marylebone Road	ipentane	0.84	44.33	1.89	0.12
London Marylebone Road	isoprene	0.70	1.71	0.11	0.01
London Marylebone Road	mpxylene	0.77	13.97	1.36	0.02
London Marylebone Road	nbutane	0.84	34.98	3.48	0.21
London Marylebone Road	nheptane	0.74	6.07	0.27	0.02
London Marylebone Road	nhexane	0.84	4.53	0.29	0.02
London Marylebone Road	noctane	0.70	0.90	0.15	0.02
London Marylebone Road	npentane	0.84	12.02	0.81	0.07
London Marylebone Road	oxylene	0.77	4.97	0.54	0.02
London Marylebone Road	propane	0.84	36.52	4.61	0.49

Site	VOC	Annual data capture	Annual maximum	Annual mean	Annual minimum
London Marylebone Road	propene	0.84	11.83	0.96	0.26
London Marylebone Road	t2butene	0.84	1.02	0.11	0.02
London Marylebone Road	t2penten	0.73	2.47	0.08	0.01
London Marylebone Road	toluene	0.78	25.80	1.90	0.13