



# UK HYDROCARBONS NETWORK

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# 1. EXECUTIVE SUMMARY

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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 AQD annual mean limit value of  $5 \mu\text{g m}^{-3}$  as well as achieving compliance with Objectives in the UK Air Quality Strategy (Defra, 2007). The provisions of the AQD were transposed by the Air Quality Standards Regulations 2010 in England, the Air Quality Standards (Scotland) Regulations 2010 in Scotland, the Air Quality Standards (Wales) Regulations 2010 in Wales and the Air Quality Standards Regulations (Northern Ireland) 2010. This report details the 2021 data and compares against the UK limit values.

The AQD 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 2021 was 95%. The annual mean concentration across all non-automatic monitoring stations in the UK was  $0.54 \mu\text{g m}^{-3}$ . All 34 monitoring stations used for non-automatic benzene measurements are situated in urban locations.

The AQD 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 as well as the ACTRIS Network. 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 station at Auchencorth Moss reports data to the Global Atmosphere Watch (GAW) programme, operated by the World Meteorological Organisation.

The mean data capture for benzene measured by the automatic hydrocarbon network in 2021 was 72%. The annual mean across all automatic monitoring stations in the UK was  $0.41 \mu\text{g m}^{-3}$ .

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 2021.

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 2021:

- In 2021, none of the automatic or non-automatic monitoring stations in the UK exceeded the  $5 \mu\text{g m}^{-3}$  annual mean Limit Value or the Upper Assessment Threshold of  $3.5 \mu\text{g m}^{-3}$  for benzene set out in the AQD.
- The results confirm no exceedances of EU or UK limit values and objectives at any of the Urban, Traffic and Background monitoring stations during 2021.

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## 2. INTRODUCTION

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This report provides a summary of the site management activities and data produced in 2021 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 (AQD). The provisions of the AQD were transposed by the Air Quality Standards Regulations 2010 in England, the Air Quality Standards (Scotland) Regulations 2010 in Scotland, the Air Quality Standards (Wales) Regulations 2010 in Wales and the Air Quality Standards Regulations (Northern Ireland) 2010. The UK's interpretation of the AQD 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 AQD, 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](#).

### 2.1 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 2020, ordered by their 2020 values. VOC emissions from road vehicles and fuel use predominated emissions until around 2001. However, the predominant source today is solvent use.

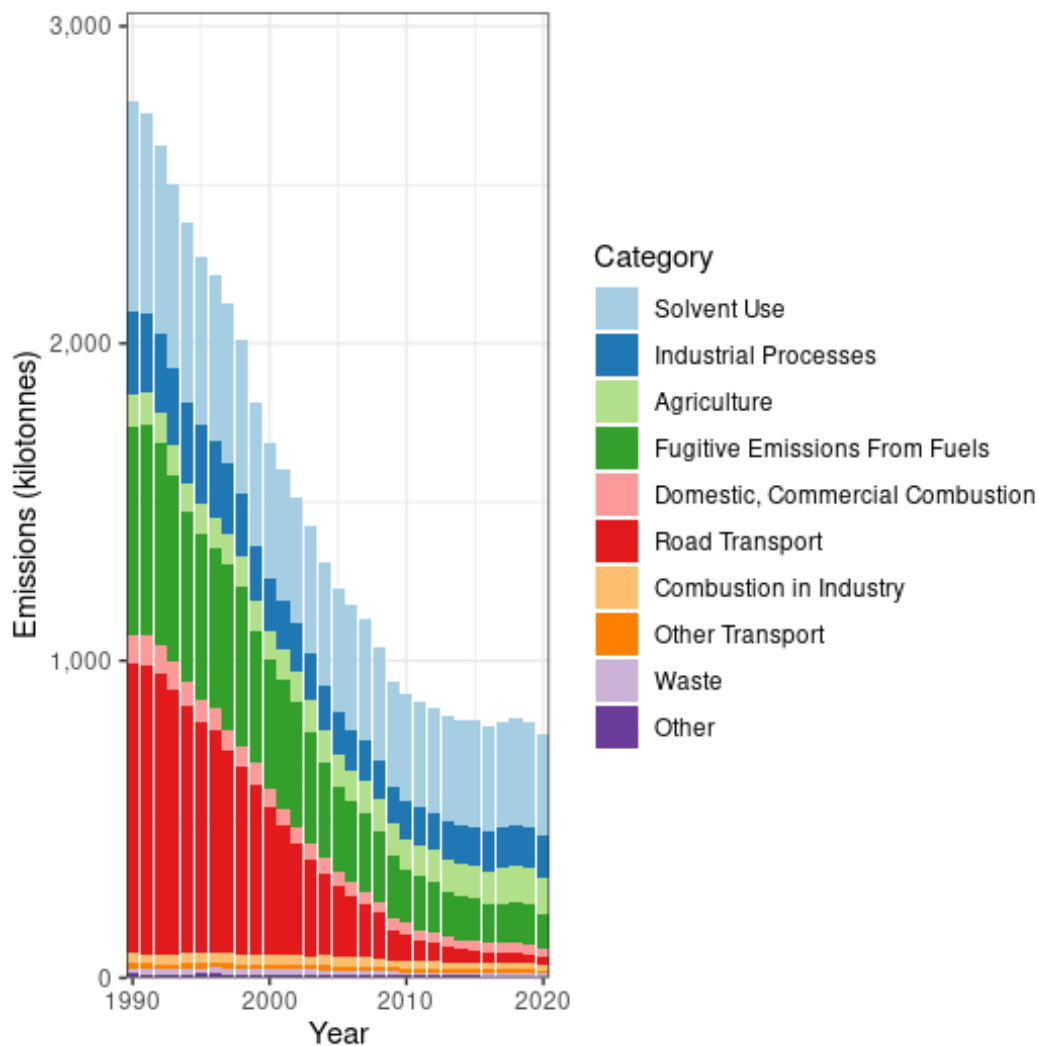


Figure 1: NAEI estimated NMVOCs emission from 1990.

## 2.2 REGULATORY BACKGROUND

### 2.2.1 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. These objectives are tabulated in Table 1.

Table 1: UK Air Quality Objectives

Pollutant	Applicable to	Concentration ( $\mu\text{g m}^{-3}$ )	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

### 2.2.2 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 (AQD). The provisions of the AQD were transposed by the Air Quality Standards Regulations 2010 in England, the Air Quality Standards (Scotland) Regulations 2010 in Scotland, the Air Quality Standards (Wales) Regulations 2010 in Wales and the Air Quality Standards Regulations (Northern Ireland) 2010. The AQD sets a limit value for annual mean benzene concentrations across Member States as well as lower and upper assessment thresholds, tabulated in Table 2.

Table 2: European Benzene Limit Value and Assessment Thresholds.

Threshold	Concentration ( $\mu\text{g m}^{-3}$ )	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  $5 \mu\text{g m}^{-3}$  as a calendar year mean, to be achieved by 1st January 2010. The upper and lower assessment thresholds,  $3.5 \mu\text{g m}^{-3}$  (70% of limit value) and  $2 \mu\text{g m}^{-3}$  (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 Lower Assessment Threshold (LAT) such as for assessment of emissions from industrial sources or from road transport.

The Data Quality Objective for benzene measurement uncertainty is  $\pm 25\%$  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 AQD 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%.

### 2.2.3 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).



## 2.3 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, nitrogen dioxide (NO<sub>2</sub>), carbon monoxide (CO), sulphur dioxide (SO<sub>2</sub>) and ozone (O<sub>3</sub>), 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 Particle 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.

### 2.3.1 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'.

Defra took the decision to discontinue monitoring 1,3-butadiene with passive diffusion tubes in 2007, details can be found in previous annual reports.

### 2.3.2 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. Table 3 lists the 29 species currently measured by the automatic gas chromatographs. 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 <sub>2</sub> H <sub>6</sub>	SNAP5 (65%)	8
propane	alkane	C <sub>3</sub> H <sub>8</sub>	SNAP5 (36%)	14
n-butane	alkane	C <sub>4</sub> H <sub>10</sub>	SNAP6 (44%)	31
isobutane	alkane	C <sub>4</sub> H <sub>10</sub>	SNAP5 (61%)	28
n-pentane	alkane	C <sub>5</sub> H <sub>12</sub>	SNAP5 (42%)	40
isopentane	alkane	C <sub>5</sub> H <sub>12</sub>	SNAP5 (41%)	34
n-hexane	alkane	C <sub>6</sub> H <sub>14</sub>	SNAP6 (42%)	40
2-methylpentane	alkane	C <sub>6</sub> H <sub>14</sub>	SNAP6 (43%)	41
n-heptane	alkane	C <sub>7</sub> H <sub>16</sub>	SNAP5 (43%)	35
n-octane	alkane	C <sub>8</sub> H <sub>18</sub>	SNAP5 (64%)	34
isooctane	alkane	C <sub>8</sub> H <sub>18</sub>	SNAP4 (100%)	25
ethene	alkene	C <sub>2</sub> H <sub>4</sub>	SNAP8 (27%)	100
propene	alkene	C <sub>3</sub> H <sub>6</sub>	SNAP4 (36%)	117
1-butene	alkene	C <sub>4</sub> H <sub>8</sub>	SNAP7 (26%)	104
cis-2-butene	alkene	C <sub>4</sub> H <sub>8</sub>	SNAP5 (87%)	113
trans-2-butene	alkene	C <sub>4</sub> H <sub>8</sub>	SNAP5 (90%)	116
1,3-butadiene	alkene	C <sub>4</sub> H <sub>6</sub>	SNAP8 (57%)	89
isoprene	alkene	C <sub>5</sub> H <sub>8</sub>	biogenic	114
ethyne	alkyne	C <sub>2</sub> H <sub>2</sub>	SNAP7 (46%)	7
1-Pentene	alkyne	C <sub>5</sub> H <sub>10</sub>	NA	95
trans-2-pentene	alkyne	C <sub>5</sub> H <sub>10</sub>	NA	111
benzene	aromatic	C <sub>6</sub> H <sub>6</sub>	SNAP2 (35%)	10
toluene	aromatic	C <sub>7</sub> H <sub>8</sub>	SNAP6 (63%)	44
ethylbenzene	aromatic	C <sub>8</sub> H <sub>10</sub>	SNAP6 (54%)	46
o-xylene	aromatic	C <sub>8</sub> H <sub>10</sub>	SNAP6 (50%)	78
m-xylene	aromatic	C <sub>8</sub> H <sub>10</sub>	SNAP6 (71%)	86
p-xylene	aromatic	C <sub>8</sub> H <sub>10</sub>	SNAP6 (50%)	72
1,2,3-trimethylbenzene	aromatic	C <sub>9</sub> H <sub>12</sub>	SNAP6 (79%)	105
1,2,4-trimethylbenzene	aromatic	C <sub>9</sub> H <sub>13</sub>	SNAP6 (74%)	110
1,3,5-trimethylbenzene	aromatic	C <sub>9</sub> H <sub>14</sub>	SNAP6 (71%)	107

There is no standard reference method for measuring ozone precursor substances in ambient air. Development of such a standard is currently being discussed within Technical Committee 264 under CEN Working Group 13.

Automated thermal desorption with in situ gas chromatography and flame ionisation detection (FID) is used to measure hourly hydrocarbon concentrations. During 2021, 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.

### 3. SITE MANAGEMENT

#### 3.1 MONITORING STATIONS DURING 2021

The monitoring stations operating in the UK Hydrocarbon Network during 2021 are shown in Figure 2. Full names of the monitoring stations and their coordinates can be found in Appendix A1. Further details on the sites can be found on [UK-AIR](#).

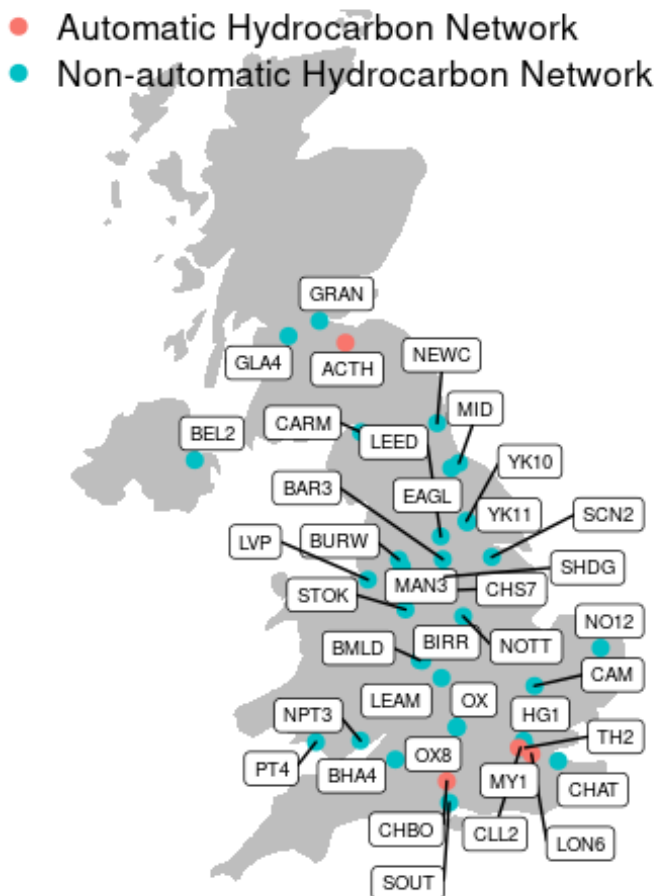


Figure 2: Map of UK Hydrocarbon Monitoring stations in 2021

#### 3.2 EQUIPMENT MAINTENANCE AND AUDITS

All non-automatic benzene monitoring stations were visited by Ricardo field engineers in April and October 2021 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

Routine flow measurements have been used to calculate sample volumes for the 2021 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, Total Organic Carbon (TOC) zero air generator and air compressor is kept by the equipment Support Unit (ESU) such that equipment can be swapped quickly if necessary.

## 4. DATA QUALITY

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### 4.1 ESTIMATION OF UNCERTAINTY

Calculated uncertainty for the Non-Automatic Hydrocarbon sites in 2021 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  $i$

## 4.2 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)
- $\chi$  = 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.

### 4.3 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.

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

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  $\delta v$
- Other (system artefacts)  $\delta_{\chi_{instrument}}$

The overall systematic error is described as:

$$\Delta_{\chi_{sys}^2} = |\Delta_{\chi_{cal}^2} + \Delta_{\delta_{int}^2} + \Delta_{\chi_{vol}^2} + \Delta_{\chi_{instrument}^2}|$$

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.

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

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.

### 4.4 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  $\mu\text{g m}^{-3}$ . Measurements undertaken by the Automatic Hydrocarbon Network are carried out in accordance with this Standard.

The Standard Method for measurement of benzene using an automatic analyser is in the process of review by CEN Working Group 12. Ricardo 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  $\leq 2.0$  %;
- 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.

## 4.5 LIMIT OF DETECTION

The Limit of Detection for the mass of benzene on a desorption tube from the Non-Automatic Hydrocarbon Network is approximately 5 ng. This is equivalent to about 0.05  $\mu\text{g m}^{-3}$  from a 14-day sample period.

The Limit of Detection for each of the 29 species measured by the Perkin Elmer Ozone Precursor Analysers is 10 ppt. These are converted to  $\mu\text{g m}^{-3}$  and shown in Table 4.

*Table 4: Automatic analyser limit of detection*

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



VOC	Limit of detection ( $\mu\text{g m}^{-3}$ )
1,2,3-Trimethylbenzene	0.05

## 5. DATA ANALYSIS

### 5.1 COMPARISON WITH LIMIT VALUES AND OBJECTIVES

The annual mean concentrations of benzene measured using non-automatic samplers over the calendar year 2021 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 A2.

The increased maximum concentrations seen at London Eltham are due to two short episodes where air masses travelling to the station from a southerly direction on 30<sup>th</sup> October and 11<sup>th</sup> December showed an unusually high concentration for 1,3-butadiene. For benzene, the same episode on 11<sup>th</sup> December resulted in the maximum value recorded.

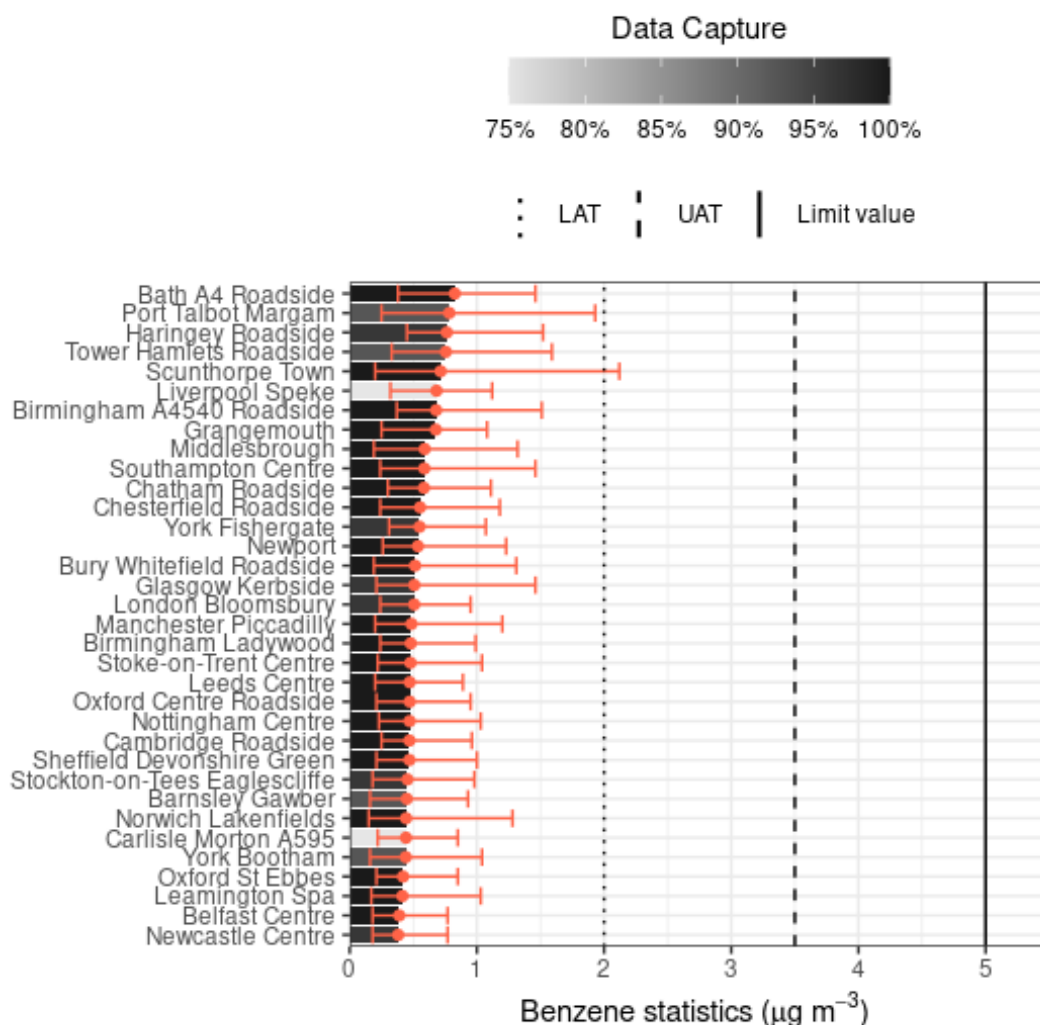


Figure 3: Non-Automatic Benzene annual statistics for 2021. Range shows the annual minimum and maximum nominal fortnightly measurement.

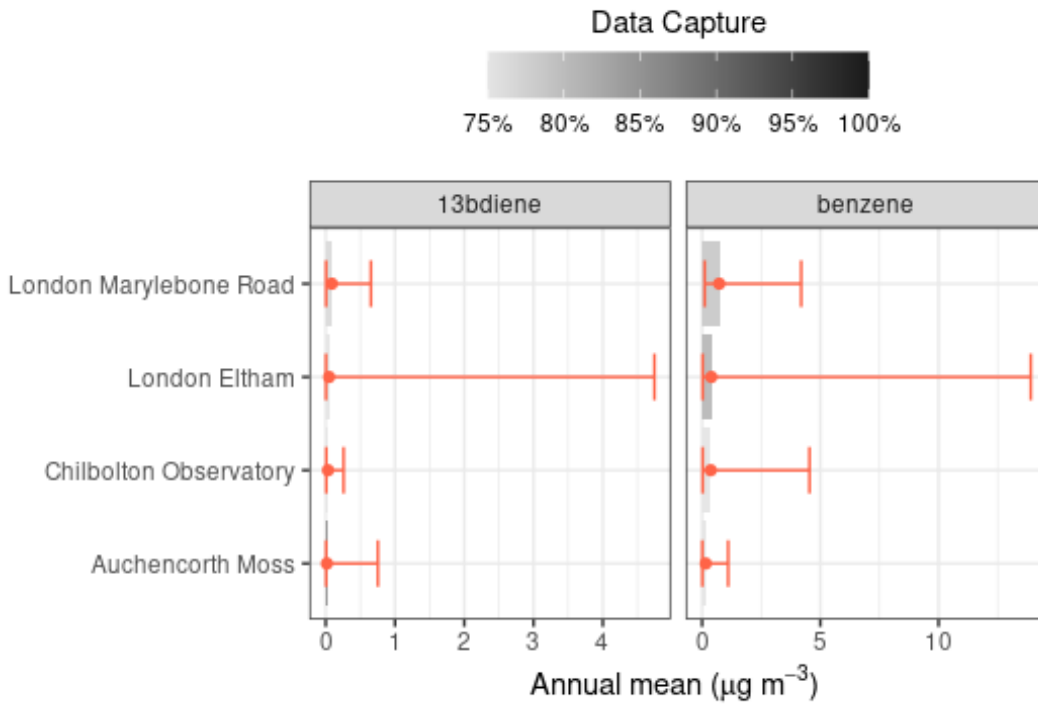


Figure 4: Benzene and 1,3-butadiene annual statistics for 2021. Range shows the annual minimum and maximum hourly measurement.

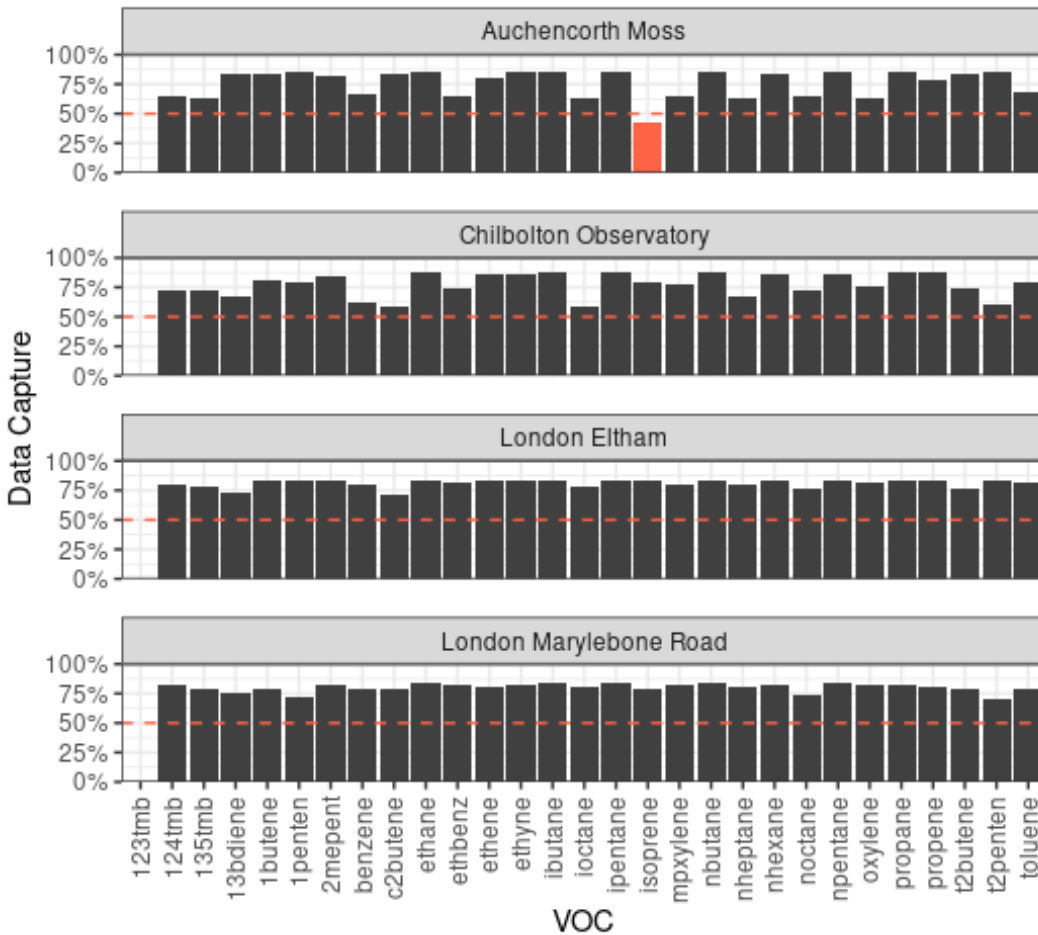


Figure 5: VOCs annual statistics for 2021. The dashed lines show the objective data capture rate; any VOC below the objective are highlighted in red.

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

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

## 5.2 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.

## 5.3 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, so 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 2021, roadside concentrations are on average much closer to background concentrations than they were in the early 2000s.

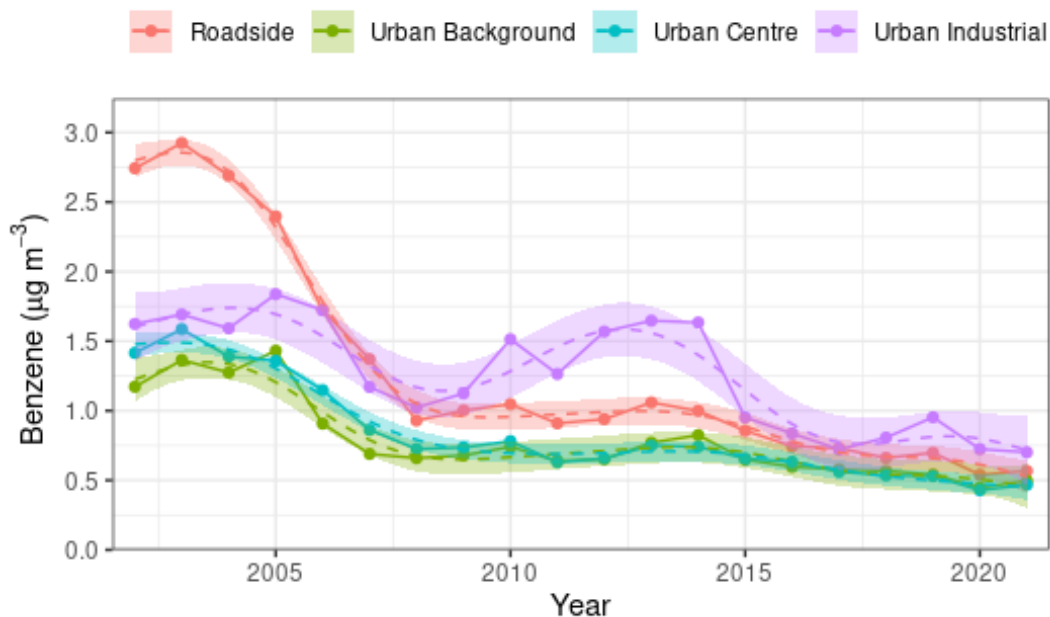


Figure 6: Average Non-Automatic network benzene means by site type from 2002 to 2021.

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 2021. Figure 7 separately considers the trends for these two periods. While the post-2008 trends are significant, the magnitude of their slopes are notably smaller than pre-2008, suggesting more stable benzene concentrations. 2020 and 2021 are likely lower than expected due to Covid lockdown restrictions resulting in reductions in road transport and therefore vehicle emissions in urban areas.

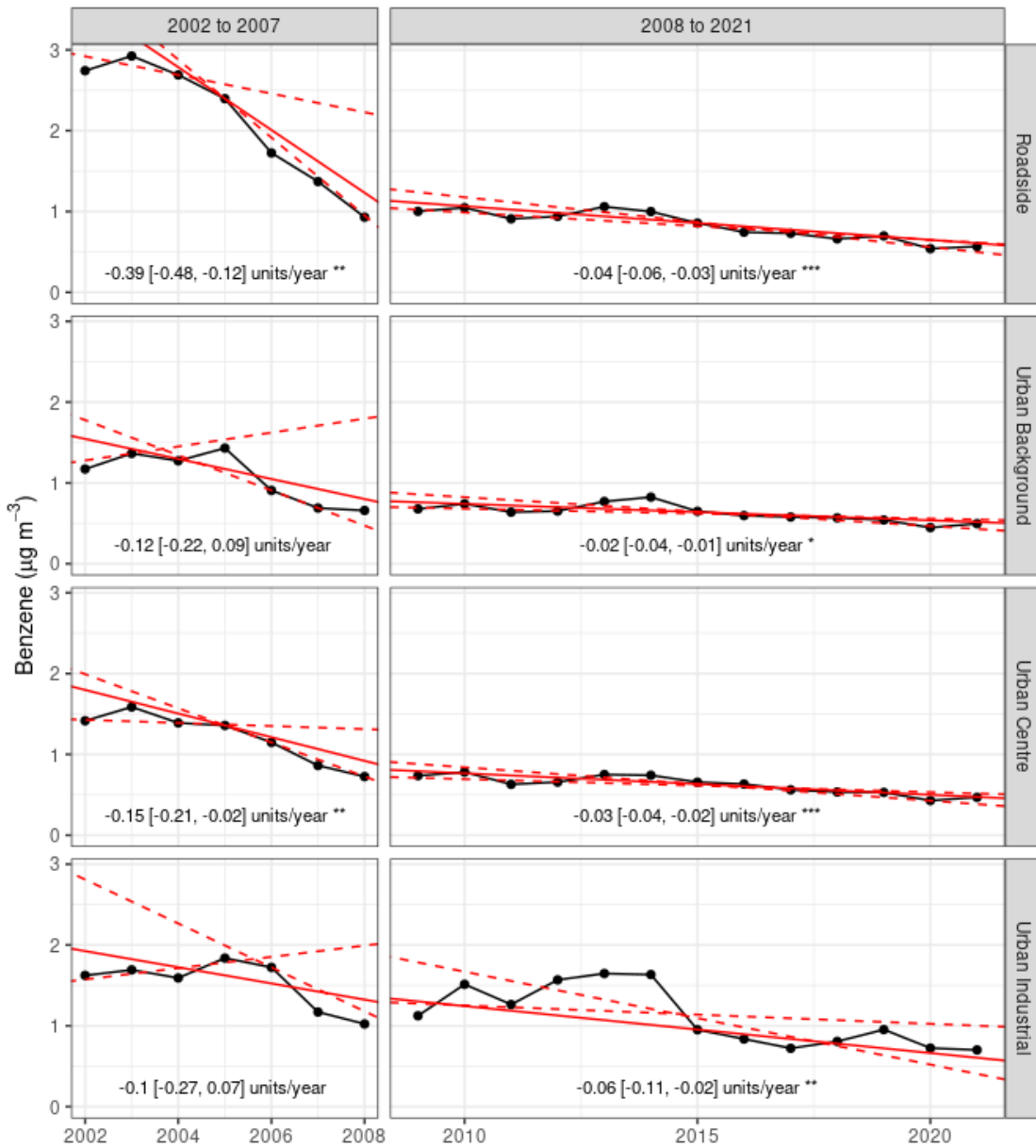


Figure 7: Non-automatic benzene rate of change for 2002-2007 and 2008-2021.

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 2021. 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 2021. 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.

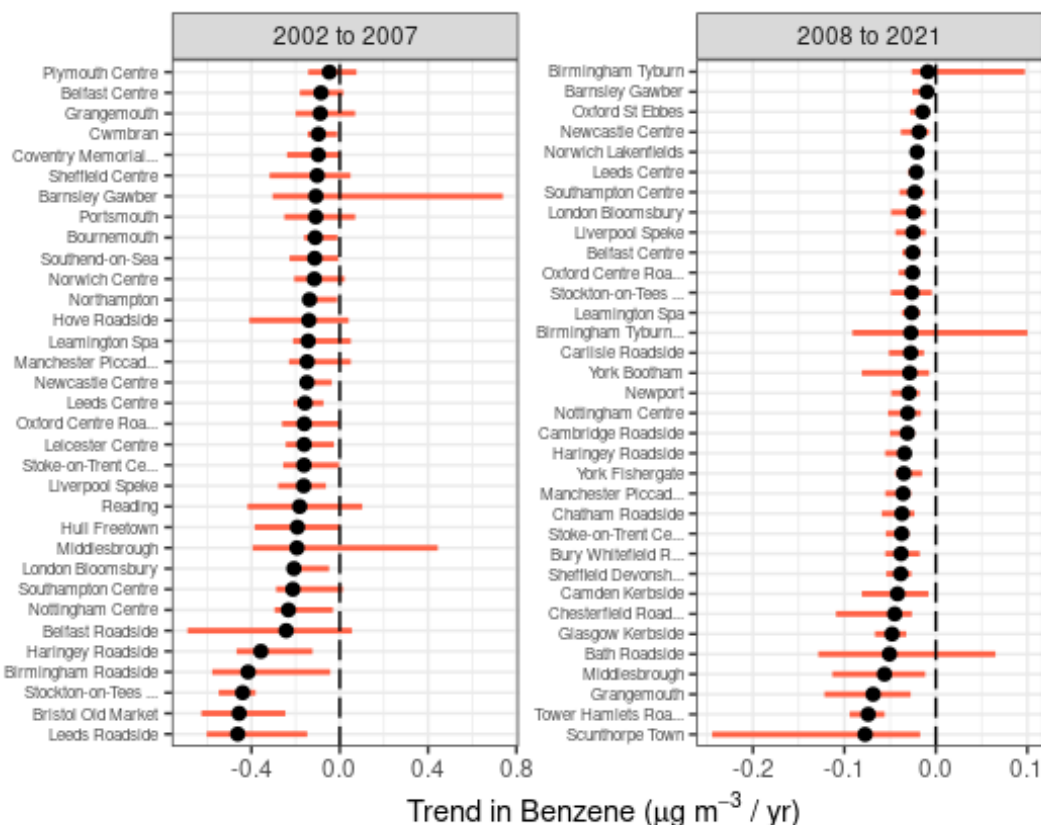


Figure 8: Benzene concentration trend (µg m<sup>-3</sup> / yr) at non-automatic sites from 2002 to 2021.

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. Normalisation involved dividing the annual means by the mean value for the whole time series. Figure 9 shows that 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 2021 is not yet available.



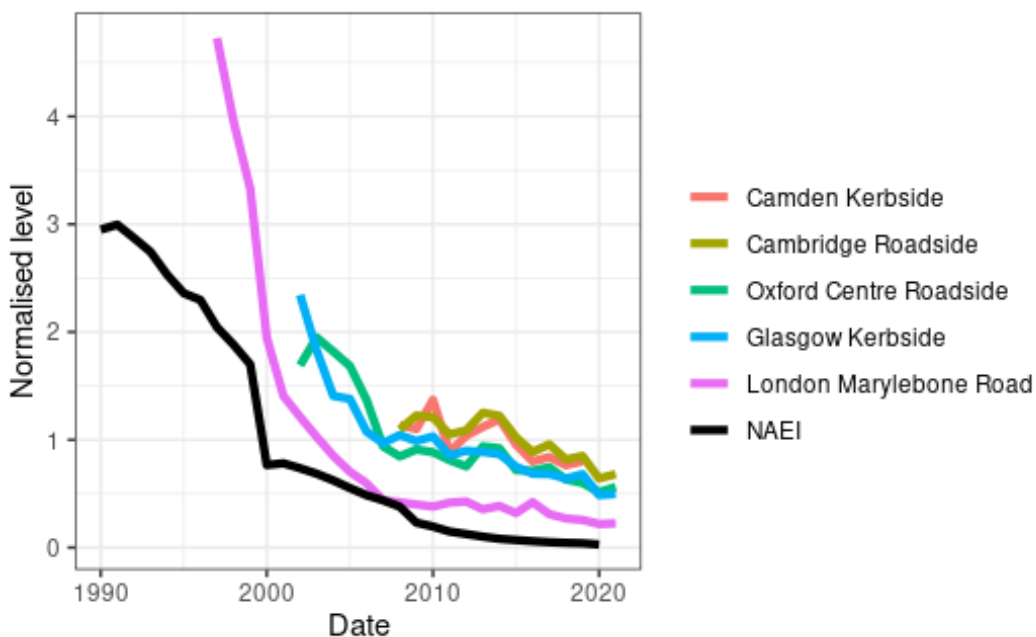


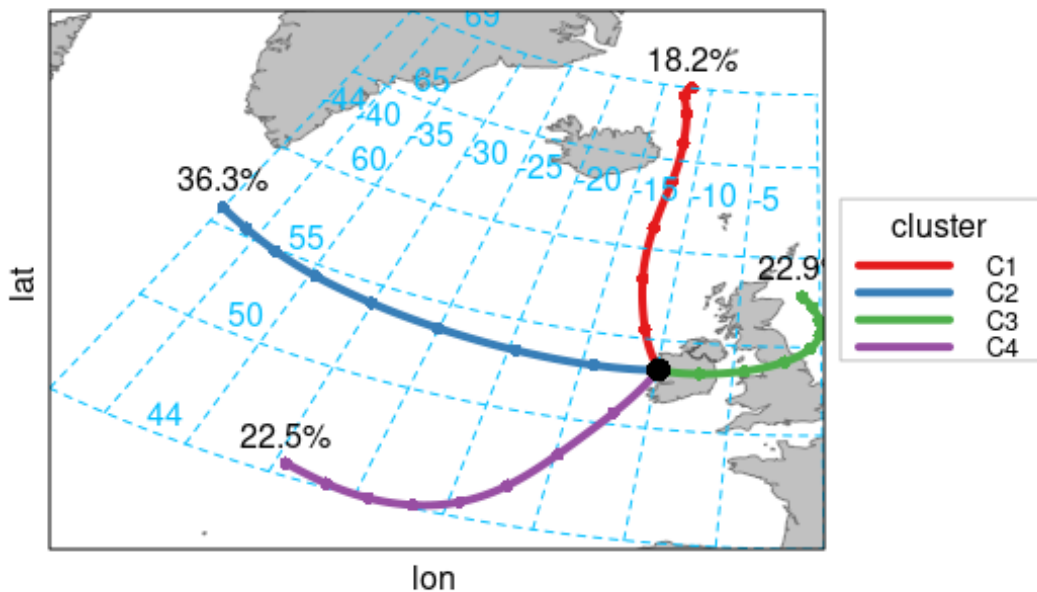
Figure 9: Normalised annual average benzene concentration and NAEI benzene emission estimate (1995 - 2020).

## 5.4 IMPACT OF VOCs ON REGIONAL O<sub>3</sub> FORMATION

### 5.4.1 Regional O<sub>3</sub> increment

The UK measures different species of VOCs due to their ozone creation potential. To understand the contribution of individual VOCs to the O<sub>3</sub> production at the UK (regional) scale, we first need to quantify the O<sub>3</sub> 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<sub>3</sub> production is defined as the O<sub>3</sub> concentration measured at Chilbolton minus the northern hemispheric background O<sub>3</sub> concentration. Chilbolton is a rural monitoring site generally representing the regional background O<sub>3</sub> in southern England. The hemispheric background O<sub>3</sub> 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). These clusters are visualised in Figure 10. The hours corresponding to trajectory clusters from the west and southwest (C2 and C4) are considered to be “clean” air masses, and therefore representing the hemispheric background O<sub>3</sub> concentration.



*Figure 10: Air mass back trajectories arriving at Mace Head in 2021*

To quantify the regional O<sub>3</sub> increment, 288 month-hourly average O<sub>3</sub> concentrations were calculated at Chilbolton and for the “clean” air masses at Mace Head. The difference between the two is shown in Figure 11 and Figure 12. In general, we would expect higher concentrations for the hemispheric background O<sub>3</sub>, i.e. negative values in Figure 11 and Figure 12. However, elevated regional background O<sub>3</sub> concentrations due to photochemical reactions were evident especially during the summer day hours.

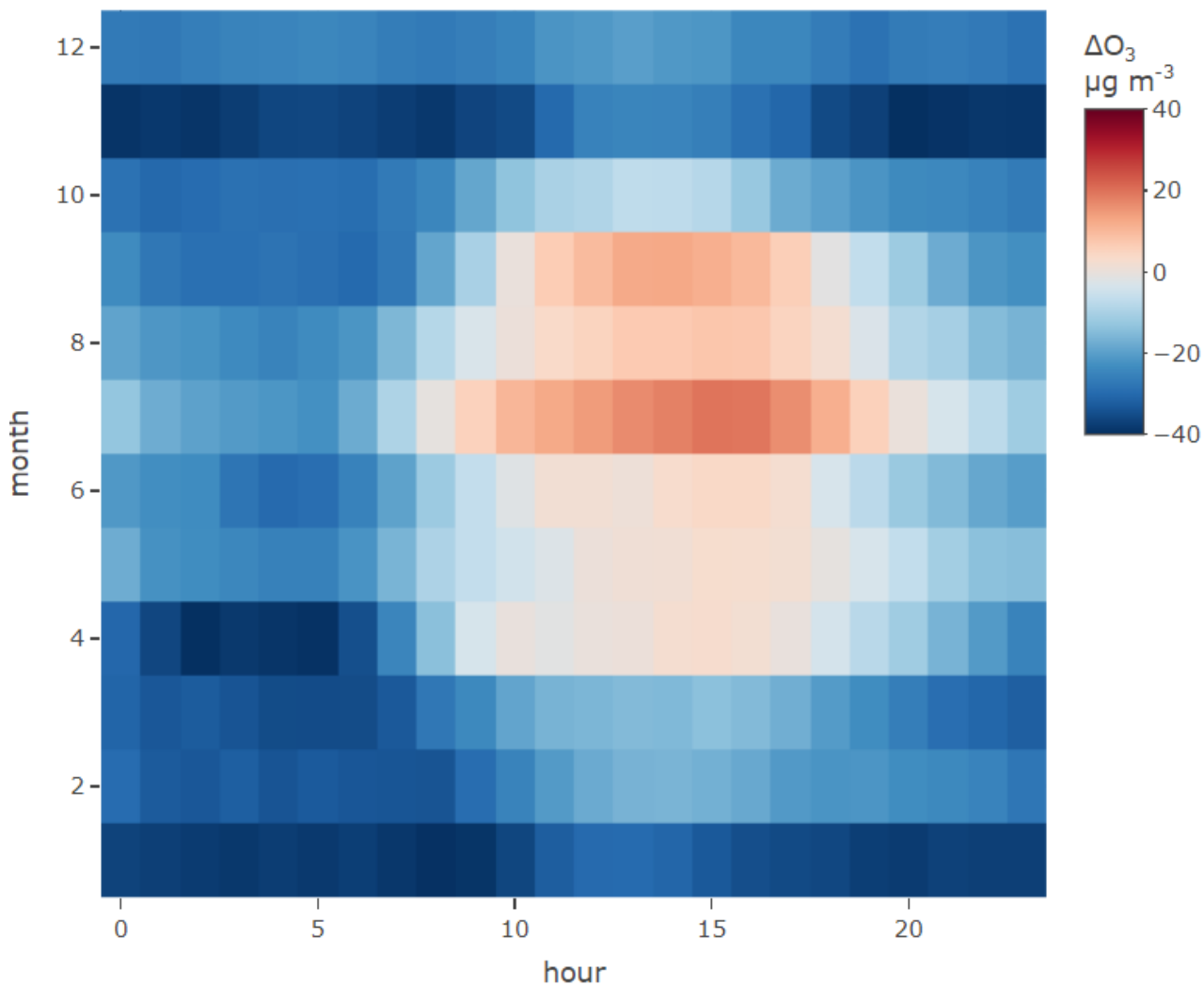


Figure 11: Month–hourly average differences between regional and hemispheric background O<sub>3</sub> for 2021 at Chilbolton.

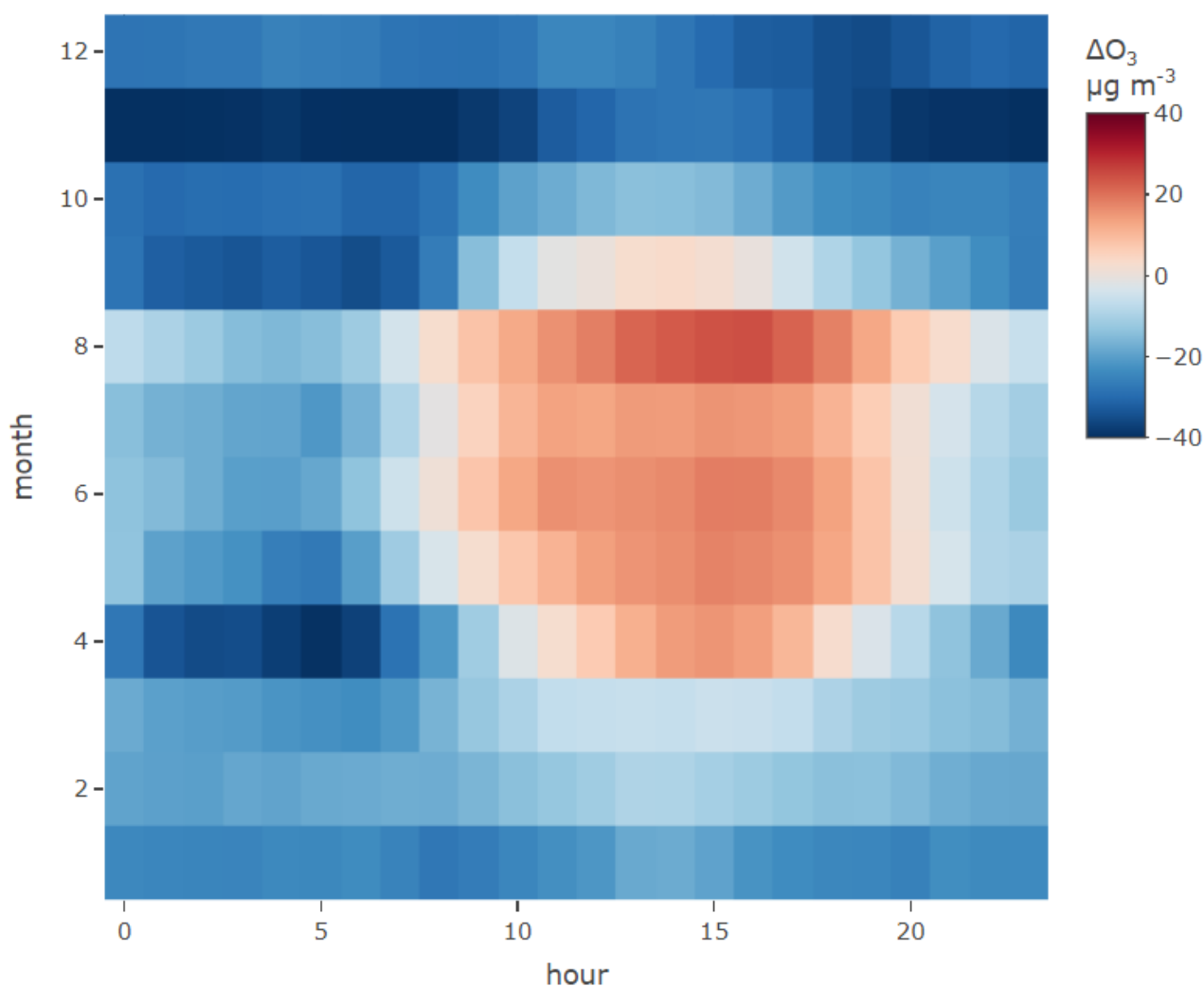


Figure 12: Month-hourly average differences between regional and hemispheric background O<sub>3</sub> for 2020 at Chilbolton.

#### 5.4.2 Photochemical ozone creation potential

Multiple studies have tried to quantify the propensity of each VOC to produce O<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub>. 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<sub>3</sub> 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 (see 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 13. The seasonal pattern of VOC diurnal photochemical depletion matches the seasonal pattern of regional O<sub>3</sub> increment as observed in

Figure 11, i.e. largest VOC diurnal photochemical depletion and regional O<sub>3</sub> 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<sub>3</sub>.

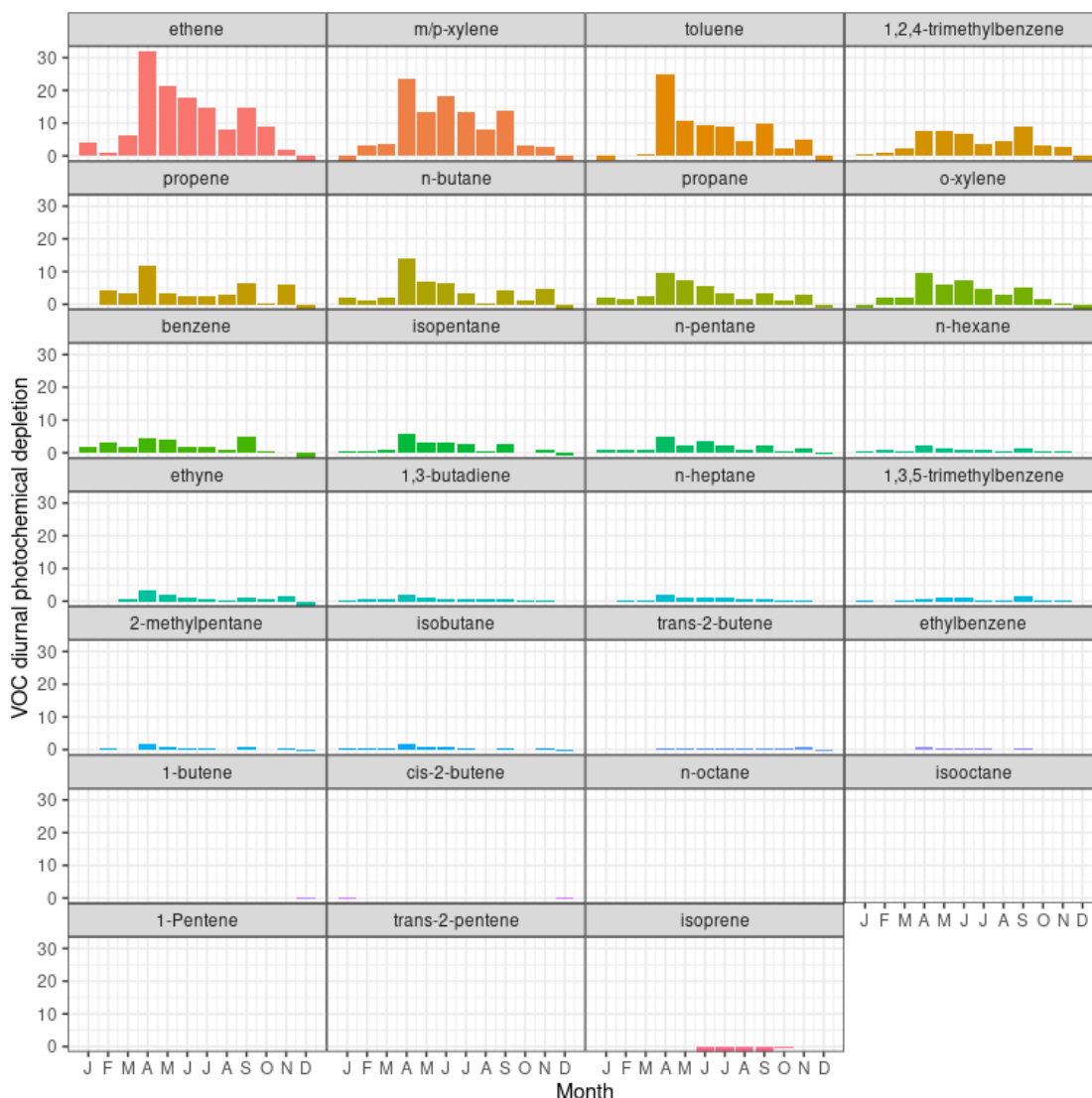


Figure 13: Median of the diurnal VOC photochemical depletion at Chilbolton for each month in 2021. VOCs are ordered by their average diurnal photochemical depletion.

To compare the relative contribution of each VOC to the regional O<sub>3</sub> increment, Figure 14 shows the median VOC diurnal photochemical depletion values in descending order for the months when regional O<sub>3</sub> increment was observed. Ethene consistently showed the largest contribution to regional O<sub>3</sub> increment during these months. M-xylene, p-xylene, toluene, 1,2,4-trimethylbenzene, o-xylene, propane, n-butane, and propene also had a notable contribution to regional O<sub>3</sub> creation and were comparatively larger than other VOC species. The result might suggest that, of the measured VOCs, reduction in emission of Ethene, m-xylene, p-xylene, toluene, 1,2,4-trimethylbenzene, o-xylene, propane, n-butane, and propene emissions would be most effective in reducing regional O<sub>3</sub> increment.

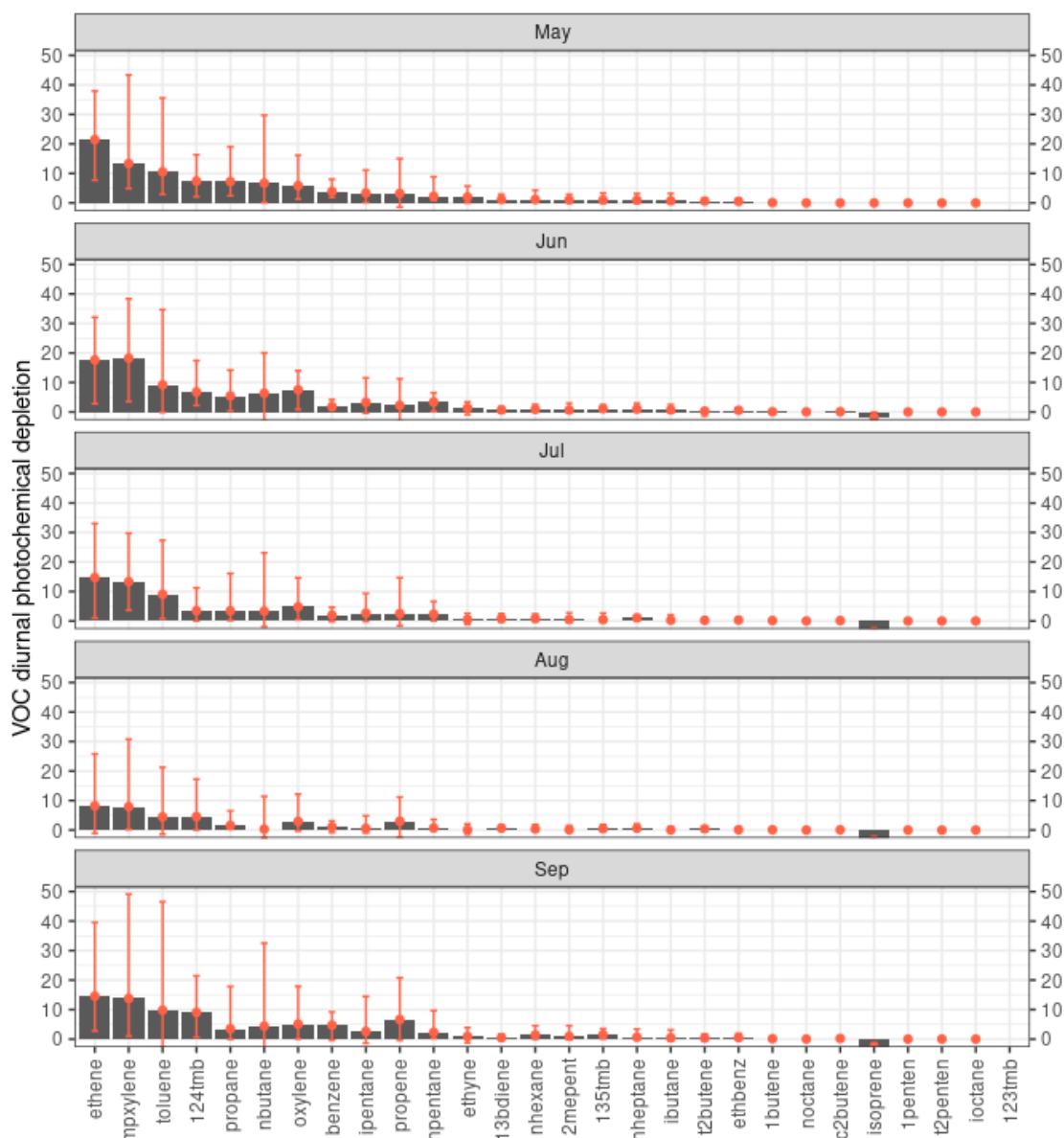


Figure 14: Median of the VOC diurnal photochemical depletion at Chilbolton between May and September in 2021. Error bar indicates the 25 and 75% percentile of the VOC diurnal photochemical depletion for a that VOC in the relevant month.

### 5.5 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.



### 5.5.1 Auchencorth Moss

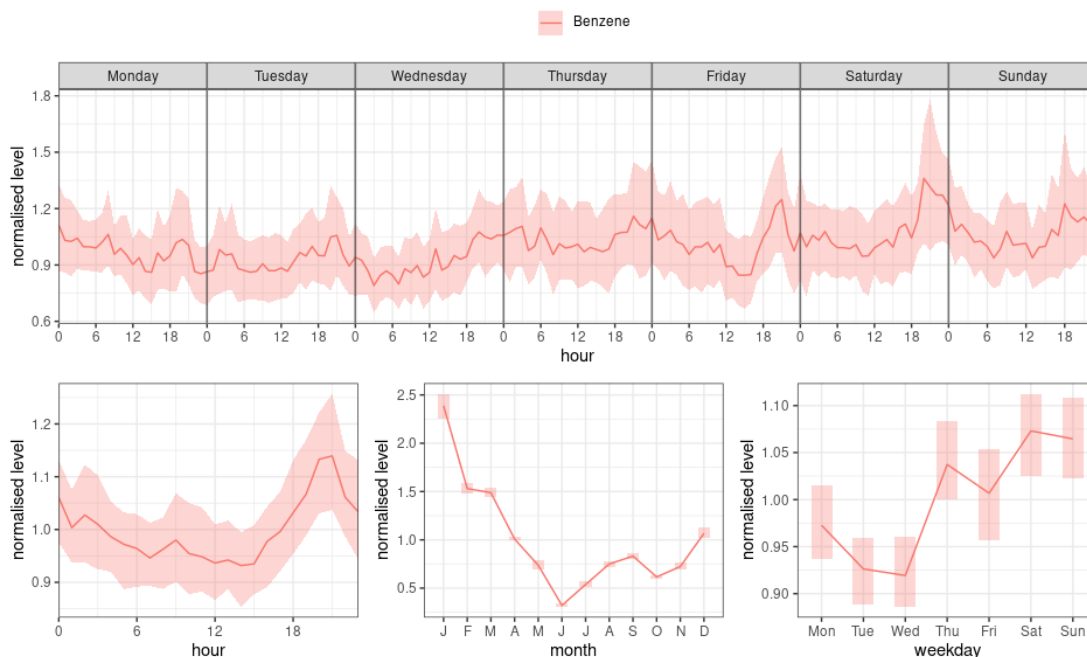


Figure 15: Diurnal, seasonal and week-daily variation of benzene at Auchencorth Moss.

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 Friday and Saturday with highest monthly measurements seen in January.

### 5.5.2 Chilbolton Observatory

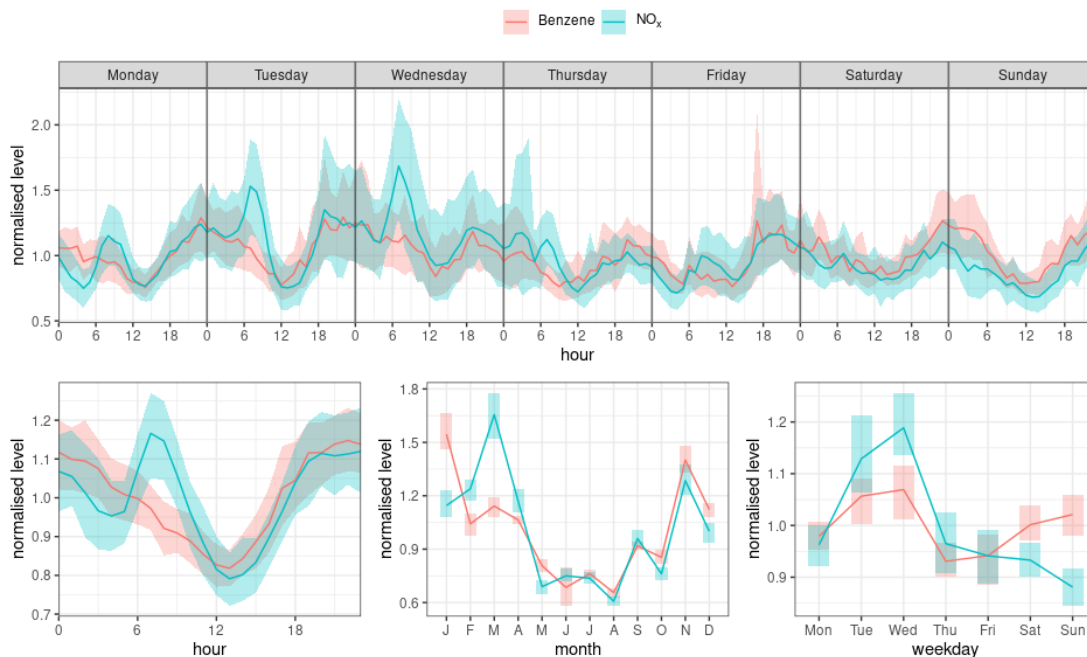
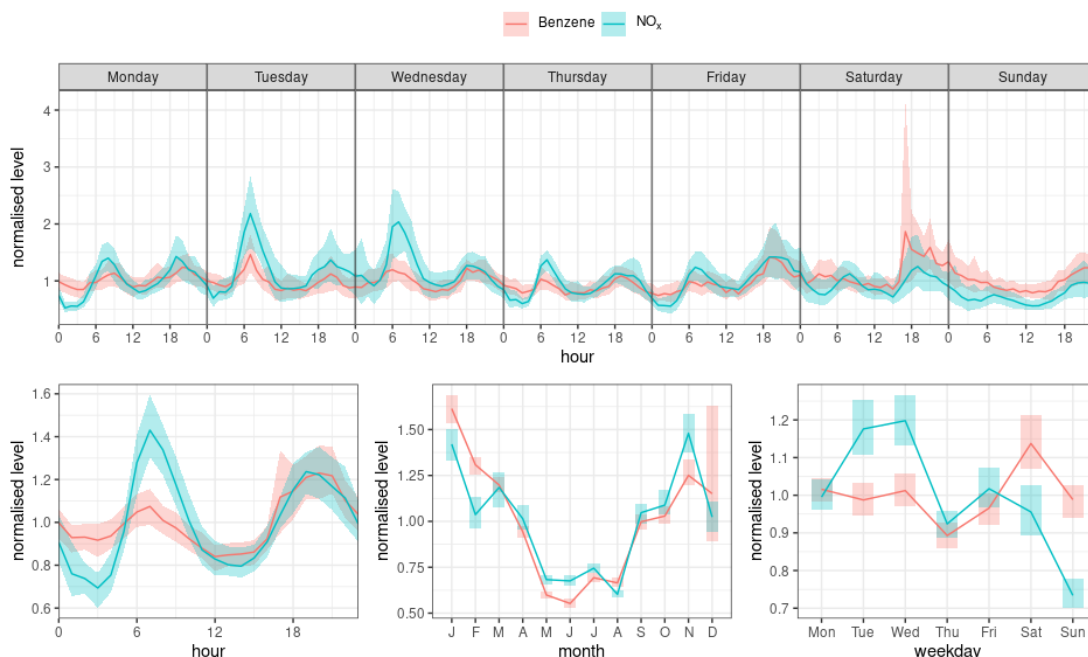


Figure 16: Diurnal, seasonal and week-daily variation of benzene, and NO<sub>x</sub> at Chilbolton.

Figure 16 indicates concentrations of benzene tend to peak after 19:00 at Chilbolton Observatory, with concentrations typically remaining relatively high until early morning. The highest measurements for benzene

have been seen in January, November and December. During the week, levels appear highest on Tuesday, Wednesday and Sunday.

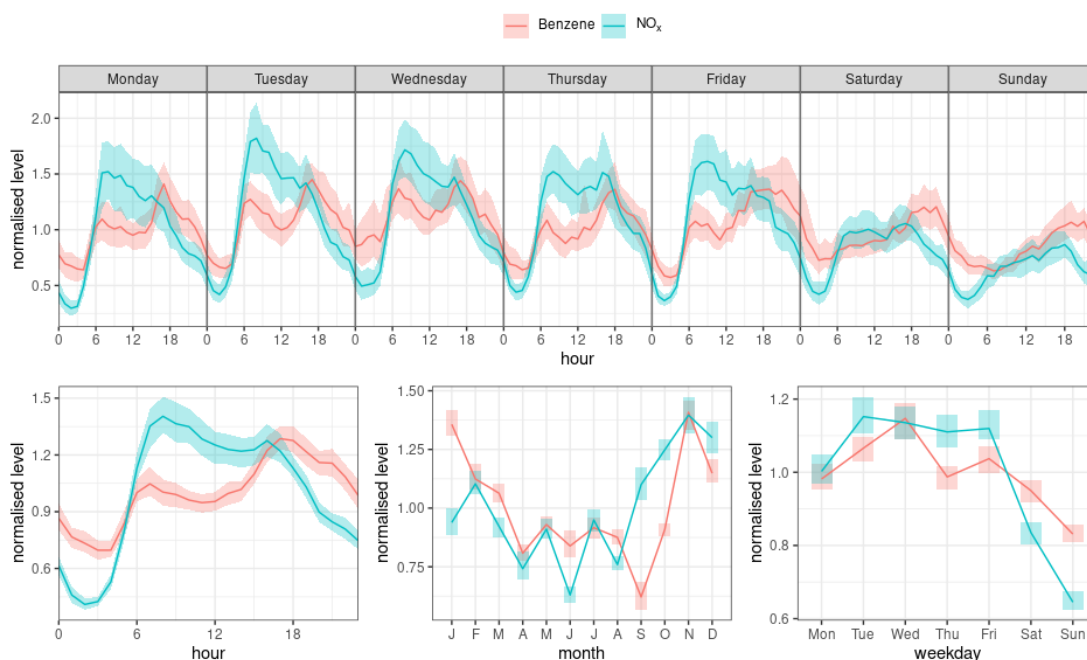
### 5.5.3 Eltham



**Figure 17: Diurnal, seasonal and week-daily variation of benzene and NO<sub>x</sub> at London Eltham.**

At London Eltham, benzene trends generally follow the trend of NO<sub>x</sub>, indicating that they are mainly dominated by traffic sources. Elevated levels of benzene and NO<sub>x</sub> 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 greatest on Saturdays. The highest monthly measurements have been observed during January, February, November and December.

### 5.5.4 Marylebone Road



**Figure 18: Diurnal, seasonal and week-daily variation of benzene and NO<sub>x</sub> at Marylebone Road.**

The concentration profiles of benzene follow that of NO<sub>x</sub> 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 January, November and December. The difference between levels from weekdays to weekends is marked compared with that at London Eltham.

## 5.6 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 under the AQD.

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<sup>-3</sup> annual mean limit value modelled in 2020. The highest estimated background concentration was 2.45 µg m<sup>-3</sup> at South Killingholme which is predominantly caused by emissions from combustion in industry.

# 6. DEVELOPMENTS AND RECOMMENDATIONS

## 6.1 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 2023. The existing samplers on the non-automatic hydrocarbons network would need to be replaced with new samplers once manufacturers have been able to design, test and manufacture new instrumentation to meet the requirements of the new standard method.

## 6.2 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 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.

## 6.3 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 were  $3.4 \mu\text{g m}^{-3}$  in 2017,  $3.2 \mu\text{g m}^{-3}$  in 2018,  $3.25 \mu\text{g m}^{-3}$  in 2019 and  $2.45 \mu\text{g m}^{-3}$  in 2020. 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, therefore no repeat campaign would be necessary.

## 7. CONCLUSIONS

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The annual mean concentration across all non-automatic monitoring stations in the UK for 2021 was  $0.54 \mu\text{g m}^{-3}$ . 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 2021 was 95%.

The annual mean across all automatic monitoring stations in the UK was  $0.41 \mu\text{g m}^{-3}$ , 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 2021 was 72%.

In 2021, none of the automatic or non-automatic monitoring stations in the UK exceeded the  $5 \mu\text{g m}^{-3}$  annual mean Limit Value or the Upper Assessment Threshold of  $3.5 \mu\text{g m}^{-3}$  for benzene set out in the AQD. The results confirm no exceedances of EU or UK limit values and objectives at any of the Urban, Traffic and Background monitoring stations during 2021. The highest concentrations observed during 2021 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  $1 \mu\text{g m}^{-3}$  have been observed at rural background, urban background and urban traffic locations. Bath A4 Roadside, an urban traffic site, recorded the highest time weighted annual mean of  $0.82 \mu\text{g m}^{-3}$ . Newcastle Centre, an urban background site, recorded the lowest annual mean of  $0.39 \mu\text{g m}^{-3}$ .

All sites showed a decrease in benzene concentration over the period 2002 to 2021. 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 2021. Benzene emissions data provided by the National Atmospheric Emissions Inventory shows a steady decline in benzene emissions from 2010 to 2021, 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, m-xylene, p-xylene, toluene, 1,2,4-trimethylbenzene, o-xylene, propane, n-butane, and propene showed the largest contribution to regional O<sub>3</sub> increment during the daylight hours in summer.

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# APPENDICES

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## Appendix 1 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 2021.*

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	52.47615	- 1.874978	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
CARM	Carlisle Morton A595	urban traffic	North West & Merseyside	54.88582	- 2.964955	non-automatic
CHAT	Chatham Roadside	urban traffic	South East	51.37426	0.547970	non-automatic
CHS7	Chesterfield Roadside	urban traffic	East Midlands	53.23175	- 1.456928	non-automatic
GLA4	Glasgow Kerbside	urban traffic	Central Scotland	55.85894	- 4.259122	non-automatic
GRAN	Grangemouth	urban industrial	Central Scotland	56.01032	- 3.704399	non-automatic
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

Site code	Site name	Site type	Region	Latitude	Longitude	Network type
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	52.61482	1.302686	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	50.90817	- 1.395757	non-automatic
EAGL	Stockton-on-Tees Eaglescliffe	urban traffic	North East	54.51667	- 1.358547	non-automatic
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

Site code	Site name	Site type	Region	Latitude	Longitude	Network type
MY1	London Marylebone Road	urban traffic	Greater London	51.52253	- 0.154611	automatic

## Appendix 2 Automatic Hydrocarbon Statistics for all VOC species

Table 6: Summary statistics for all VOCs measured at the automatic monitoring sites 2021.

Site	VOC	Annual data capture	Annual maximum	Annual mean	Annual minimum
Auchencorth Moss	123tmb	0.00	NA	NA	NA
Auchencorth Moss	124tmb	0.65	0.38	0.03	0.01
Auchencorth Moss	135tmb	0.63	0.23	0.02	0.01
Auchencorth Moss	13bdiene	0.84	0.75	0.02	0.01
Auchencorth Moss	1butene	0.84	0.43	0.02	0.01
Auchencorth Moss	1penten	0.85	0.19	0.02	0.01
Auchencorth Moss	2mepent	0.82	3.31	0.03	0.00
Auchencorth Moss	benzene	0.67	1.10	0.16	0.01
Auchencorth Moss	c2butene	0.84	0.25	0.01	0.01
Auchencorth Moss	ethane	0.85	15.19	2.47	0.89
Auchencorth Moss	ethbenz	0.64	0.28	0.03	0.01
Auchencorth Moss	ethene	0.81	3.48	0.29	0.01
Auchencorth Moss	ethyne	0.85	1.36	0.23	0.03
Auchencorth Moss	ibutane	0.86	22.56	0.30	0.02
Auchencorth Moss	ioctane	0.63	0.29	0.03	0.01
Auchencorth Moss	ipentane	0.86	16.69	0.18	0.01
Auchencorth Moss	isoprene	0.42	8.64	0.10	0.01
Auchencorth Moss	mpxylene	0.64	0.90	0.03	0.01
Auchencorth Moss	nbutane	0.86	48.56	0.55	0.02
Auchencorth Moss	nheptane	0.62	1.07	0.03	0.01
Auchencorth Moss	nhexane	0.84	4.56	0.04	0.01
Auchencorth Moss	noctane	0.64	0.20	0.02	0.01
Auchencorth Moss	npentane	0.86	16.45	0.15	0.01
Auchencorth Moss	oxylene	0.63	0.40	0.03	0.01
Auchencorth Moss	propane	0.86	56.99	1.13	0.08
Auchencorth Moss	propene	0.79	3.33	0.07	0.01
Auchencorth Moss	t2butene	0.84	0.33	0.02	0.01
Auchencorth Moss	t2penten	0.86	0.15	0.01	0.01
Auchencorth Moss	toluene	0.69	2.79	0.08	0.01
Chilbolton Observatory	123tmb	0.00	NA	NA	NA
Chilbolton Observatory	124tmb	0.72	1.38	0.11	0.02
Chilbolton Observatory	135tmb	0.72	0.52	0.04	0.01
Chilbolton Observatory	13bdiene	0.68	0.26	0.03	0.01

Site	VOC	Annual data capture	Annual maximum	Annual mean	Annual minimum
Chilbolton Observatory	1butene	0.82	0.87	0.09	0.01
Chilbolton Observatory	1penten	0.79	0.27	0.02	0.01
Chilbolton Observatory	2mepent	0.85	2.36	0.12	0.01
Chilbolton Observatory	benzene	0.61	4.54	0.37	0.03
Chilbolton Observatory	c2butene	0.59	0.30	0.06	0.01
Chilbolton Observatory	ethane	0.88	14.54	2.52	0.76
Chilbolton Observatory	ethbenz	0.74	1.29	0.11	0.01
Chilbolton Observatory	ethene	0.86	7.44	0.52	0.02
Chilbolton Observatory	ethyne	0.85	2.29	0.29	0.03
Chilbolton Observatory	ibutane	0.87	19.35	0.57	0.05
Chilbolton Observatory	ioctane	0.59	0.79	0.07	0.00
Chilbolton Observatory	ipentane	0.87	10.17	0.44	0.02
Chilbolton Observatory	isoprene	0.79	3.08	0.07	0.00
Chilbolton Observatory	mpxylene	0.77	4.02	0.27	0.02
Chilbolton Observatory	nbutane	0.88	21.13	0.87	0.03
Chilbolton Observatory	nheptane	0.68	1.42	0.09	0.00
Chilbolton Observatory	nhexane	0.86	2.42	0.11	0.01
Chilbolton Observatory	noctane	0.73	0.92	0.07	0.01
Chilbolton Observatory	npentane	0.86	4.51	0.27	0.01
Chilbolton Observatory	oxylene	0.76	1.34	0.12	0.01
Chilbolton Observatory	propane	0.87	74.13	1.87	0.10
Chilbolton Observatory	propene	0.87	4.19	0.29	0.01

Site	VOC	Annual data capture	Annual maximum	Annual mean	Annual minimum
Chilbolton Observatory	t2butene	0.73	0.23	0.05	0.01
Chilbolton Observatory	t2penten	0.60	0.52	0.02	0.01
Chilbolton Observatory	toluene	0.79	4.70	0.47	0.06
London Eltham	123tmb	0.00	NA	NA	NA
London Eltham	124tmb	0.81	2.23	0.17	0.01
London Eltham	135tmb	0.79	0.74	0.07	0.01
London Eltham	13bdiene	0.73	4.75	0.05	0.00
London Eltham	1butene	0.83	9.60	0.08	0.00
London Eltham	1penten	0.83	1.50	0.03	0.00
London Eltham	2mepent	0.84	15.08	0.30	0.02
London Eltham	benzene	0.80	13.90	0.39	0.03
London Eltham	c2butene	0.71	2.96	0.04	0.01
London Eltham	ethane	0.84	56.33	4.70	1.01
London Eltham	ethbenz	0.81	27.17	0.21	0.01
London Eltham	ethene	0.83	52.64	0.73	0.03
London Eltham	ethyne	0.84	15.61	0.37	0.05
London Eltham	ibutane	0.84	23.99	1.41	0.10
London Eltham	ioctane	0.79	1.95	0.16	0.01
London Eltham	ipentane	0.84	31.06	1.10	0.06
London Eltham	isoprene	0.84	7.70	0.23	0.01
London Eltham	mpxylene	0.80	18.77	0.52	0.02
London Eltham	nbutane	0.84	38.30	2.56	0.16
London Eltham	nheptane	0.81	1.59	0.15	0.01
London Eltham	nhexane	0.84	60.62	0.25	0.02
London Eltham	noctane	0.77	1.00	0.07	0.01
London Eltham	npentane	0.84	11.42	0.51	0.03
London Eltham	oxylene	0.81	6.57	0.23	0.01
London Eltham	propane	0.84	40.86	2.57	0.25
London Eltham	propene	0.83	29.56	0.33	0.00
London Eltham	t2butene	0.76	3.83	0.05	0.01
London Eltham	t2penten	0.83	1.57	0.04	0.01
London Eltham	toluene	0.81	141.91	0.79	0.05
London Marylebone Road	123tmb	0.00	NA	NA	NA
London Marylebone Road	124tmb	0.83	6.30	0.63	0.02
London Marylebone Road	135tmb	0.78	2.91	0.21	0.01

Site	VOC	Annual data capture	Annual maximum	Annual mean	Annual minimum
London Marylebone Road	13bdiene	0.76	0.65	0.09	0.01
London Marylebone Road	1butene	0.79	2.04	0.27	0.07
London Marylebone Road	1penten	0.72	0.72	0.07	0.01
London Marylebone Road	2mepent	0.83	7.34	0.44	0.03
London Marylebone Road	benzene	0.78	4.19	0.73	0.11
London Marylebone Road	c2butene	0.79	0.90	0.10	0.02
London Marylebone Road	ethane	0.83	80.19	7.45	1.47
London Marylebone Road	ethbenz	0.83	4.85	0.44	0.01
London Marylebone Road	ethene	0.81	28.24	1.89	0.12
London Marylebone Road	ethyne	0.83	43.26	1.19	0.04
London Marylebone Road	ibutane	0.83	156.77	2.16	0.23
London Marylebone Road	ioctane	0.80	3.44	0.37	0.00
London Marylebone Road	ipentane	0.83	36.92	1.81	0.13
London Marylebone Road	isoprene	0.79	2.20	0.13	0.01
London Marylebone Road	mpxylene	0.83	16.79	1.55	0.02
London Marylebone Road	nbutane	0.83	550.06	3.89	0.32
London Marylebone Road	nheptane	0.81	101.14	0.41	0.02
London Marylebone Road	nhexane	0.83	3.86	0.28	0.02
London Marylebone Road	noctane	0.74	2.44	0.18	0.01
London Marylebone Road	npentane	0.83	24.66	0.79	0.08
London Marylebone Road	oxylene	0.83	5.59	0.60	0.01
London Marylebone Road	propane	0.83	417.75	4.75	0.63



Site	VOC	Annual data capture	Annual maximum	Annual mean	Annual minimum
London Marylebone Road	propene	0.81	10.49	0.87	0.23
London Marylebone Road	t2butene	0.79	1.45	0.14	0.03
London Marylebone Road	t2penten	0.70	1.61	0.09	0.01
London Marylebone Road	toluene	0.80	28.57	2.04	0.09

## Appendix 3 Title

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