AIR QUALITY EXPERT GROUP

Non-methane Volatile Organic Compounds in the UK

Prepared for:

Department for Environment, Food and Rural Affairs;
Scottish Government; Welsh Government; and
Department of Agriculture, Environment and Rural Affairs in Northern Ireland

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This is a report from the Air Quality Expert Group to the Department for Environment, Food and Rural Affairs; Scottish Government; Welsh Government; and Department of Agriculture, Environment and Rural Affairs in Northern Ireland, on non-methane volatile organic compounds in the UK. The information contained within this report represents a review of the understanding and evidence available at the time of writing.

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United Kingdom air quality information received from the automatic monitoring sites and forecasts may be accessed via the following media:

Freephone Air Pollution Information Service 0800556677

Internet http://uk-air.defra.gov.uk

PB 14599

Terms of Reference

The Air Quality Expert Group (AQEG) is an expert committee of the Department for Environment, Food and Rural Affairs (Defra) and considers current knowledge on air pollution and provides advice on such things as the levels, sources and characteristics of air pollutants in the UK. AQEG reports to Defra's Chief Scientific Adviser, Defra Ministers, Scottish Ministers, the Welsh Government and the Department of the Environment in Northern Ireland (the Government and devolved administrations). Members of the Group are drawn from those with a proven track record in the fields of air pollution research and practice.

AQEG's functions are to:

- Provide advice to, and work collaboratively with, officials and key office holders in Defra and the devolved administrations, other delivery partners and public bodies, and EU and international technical expert groups;
- Report to Defra's Chief Scientific Adviser (CSA): Chairs of expert committees will meet annually with the CSA, and will provide an annual summary of the work of the Committee to the Science Advisory Council (SAC) for Defra's Annual Report. In exception, matters can be escalated to Ministers;
- Support the CSA as appropriate during emergencies;
- Contribute to developing the air quality evidence base by analysing, interpreting and synthesising evidence;
- Provide judgements on the quality and relevance of the evidence base;
- Suggest priority areas for future work, and advise on Defra's implementation of the air quality evidence plan (or equivalent);
- Give advice on current and future levels, trends, sources and characteristics of air pollutants in the UK;
- Provide independent advice and operate in line with the Government's Principles for Scientific Advice and the Code of Practice for Scientific Advisory Committees (CoPSAC).

Expert Committee Members are independent appointments made through open competition, in line with the Office of the Commissioner for Public Appointments (OCPA) guidelines on best practice for making public appointments. Members are expected to act in accord with the principles of public life.

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Executive Summary

Volatile organic compounds (VOCs) are a broad class of air pollutants which act as precursors to tropospheric ozone and secondary organic aerosols (a component part of $PM_{2.5}$). The National Atmospheric Inventory (NAEI) indicates that UK emissions of anthropogenic VOCs peaked around 1990 at 2,840 kt yr^{-1} and then declined to ~810 kt yr^{-1} in 2017. Notable has been success in reducing emissions from the tailpipe of gasoline vehicles and other evaporative losses of VOCs from fuels (including natural gas) during their production and distribution. Ambient observations of selected VOCs in the Defra Automated Hydrocarbon Network also show significant declines since the 1990s, including species that are emitted directly from fuel loss, such as alkanes and mono-aromatics, and VOCs that are by-products of incomplete combustion such as alkenes and ethyne. The rates of reduction in ambient concentrations slowed around 2010 and have now plateaued. Benzene and 1,3 butadiene have specific limit and target values in the UK and concentrations of these have been successfully reduced such that the UK has reported no exceedances in recent years. Whilst both emissions and concentrations of VOCs have fallen, further reductions in VOC emissions are anticipated for the UK to meet obligations under the National Emission Ceiling Directive in 2030 and UNECE Convention on Long-Range Transport of Air Pollution.

The relative contribution to UK emissions from solvents is estimated to have increased over the past 20 years, in 2017 representing ~74% of national emissions. Notable has been a post-2000 growth in emissions of oxygenated VOCs, none of which are routinely measured in regulatory networks. Ethanol is now the largest VOC emitted by mass (~136 kt yr^{-1} in 2017 or ~16.8% of total UK emissions) followed by n-butane (52.4 kt yr^{-1}) and methanol (33.2 kt yr^{-1}). Alcohols more generally have grown in significance, representing ~10% of VOC emissions in 1990 rising to ~30% in 2017. The growth in ethanol is due to increased reported emissions from the whisky industries and in estimated domestic use of ethanol as a solvent, for example contained within personal care, car care and household products. For some simple hydrocarbons there have also been notable changes in the major contributing sources. N-butane for example is currently the second most abundant VOC in the UK inventory; in 1990 n-butane was emitted overwhelmingly from gasoline extraction and fugitive distribution losses (139.8 kt yr^{-1}). In 2017 the largest anthropogenic source of n-butane in the inventory was from its use as a domestic aerosol propellant (25.5 kt yr^{-1}), with the gasoline/fugitive losses having been reduced to 23.3 kt yr^{-1}.

Recent changes in the contributing VOC sources to emissions then impacts on the observational strategies to verify emission reduction policies. In 1992 UK national monitoring in the Defra Automated Hydrocarbon Network quantified 19/20 of the most abundant anthropogenic VOCs emitted (all non-methane hydrocarbons), but by 2017 monitoring captured only 13/20 species. To evaluate progress across Europe towards meeting the future VOC emissions targets requires a revision of ambient monitoring strategies. Adding ethanol, methanol, formaldehyde, acetone, 2-butanone and 2-propanol to existing non-methane hydrocarbon measurements would provide full coverage of the 20 most significant VOCs emitted on an annual mass basis in the UK.

1. Introduction and scope of this report.

Non-Methane Volatile Organic Compounds (NMVOCs) are a broad class of organic chemicals that are, in a small number of cases, directly harmful to health, but that more generally act as precursors to the formation of ozone and particulate matter (PM). In the past AQEG has reviewed the available observations and science associated with NMVOCs as part of its assessment of photochemical ozone in the UK. Over the past 20 years it has become clear that the air quality effects of NMVOCs in the atmosphere extend beyond ozone, influencing PM mass, number and chemical composition through the contributions made by organic compounds to primary and secondary organic aerosols (SOA). Organic compounds are also increasingly recognized as occupying a continuum of vapour pressures, ranging from those that reside solely in the gas phase to those split between gas and particulate phase. More recently the total national emission of anthropogenic NMVOCs as a class of pollutants has come into focus as attention turns to meeting UK emissions obligations under the National Emissions Ceiling Directive (NECD) in 2020 and 2030.

Evidence has also emerged that human exposure to NMVOCs is increasingly associated with indoor environments rather than outdoor air. The topic of NMVOCs and air quality is therefore extremely broad and potentially too diverse for one single AQEG report to cover in its totality. A prioritisation of the evidence requirements as they relate to NMVOCs has been made and a staged approach to reviewing current evidence is taken. This report deals with questions associated with evaluation of current sources and emissions, including recent trends and observational approaches. An evaluation of the state of the science of NMVOCs as they relate to ozone chemistry and PM production, and NMVOCs as directly harmful chemicals, may be undertaken in future separate reports.

1.1. Evidence used in this report.

The report uses 107 previously published scientific and technical articles on volatile organic compounds in the atmosphere, of which around 90 are from peer-reviewed academic journals and the remainder from reports prepared by, or for, Defra and other international agencies. Where data on UK trends in atmospheric concentration are shown, these are generated from publicly available datasets available for download from the Defra UK-AIR website[1]. Where analysis of VOC source contributions and trends in emissions are shown these are taken from the National Atmospheric Emissions Inventory[2].

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[1] UK Air Information Resource. https://uk-air.defra.gov.uk/

[2] https://naei.beis.gov.uk/

1.2. Key questions related to NMVOC sources and emissions.

National targets for emissions of anthropogenic NMVOCs are set out in the NECD and also form part of UK obligations to the UNECE Convention on Long-range Transport of Air Pollution (CLRTAP). In overall terms UK NMVOC emissions have reduced substantially from a peak in the early 1990s, however the overall rate of decline has slowed in recent years. Current projections of future emissions suggest that without further actions there is some risk of the UK not meeting its emission ceiling limits in 2030. National objectives to decrease the fraction of the population who are exposed to more than 10 micrograms m^{-3} of $PM_{2.5}$ as an annual mean will likely need further reductions in secondary particles, of which NMVOCs are a contributing precursor source.

Key scientific questions:

- **What have been the recent trends in UK ambient concentrations of NMVOCs and how do these trends compare to National Atmospheric Emissions Inventory estimates of emissions?**

Quick answer: Substantial atmospheric declines have been observed in many non-methane hydrocarbons that are primarily derived from fossil fuel and road transport sources over the last 25 years, from a ~1990 peak, although the rate of decline has now slowed. The decline in many observed hydrocarbons is broadly matched with reductions predicted in emissions for those same species in the National Atmospheric Emissions Inventory (NAEI).

- **Have the key sources of emission of NMVOCs changed over the past two decades?**

Quick answer: Yes. There has been a substantial reduction in emissions of short-chain hydrocarbons related to fossil fuels and combustion and an increase in the relative contributions of VOCs emitted from solvent and product use. Solvents and the use of chemicals in industry and domestic products, and other non-combustion sources, are estimated to account for ~70% of UK emissions in 2017 according to the NAEI. Over the last decade there has been a growth in the estimated national emissions of oxygenated VOCs, including ethanol, methanol, butanone and acetone.

- **What are the current sectors that are emitting most NMVOCs in the UK, including energy, transport, industrial, domestic, and indoor?**

Quick answers: The largest emission sectors in 2018 were solvents and related product use, plus the agricultural and waste sectors. Consumer products are estimated to be the largest single contributing source of VOCs from the solvent and industrial processes sector, implying substantial VOC emissions being released as diffuse emissions from UK homes. This contrasts with 1990 when transport, combustion and fossil fuel extraction / distribution dominated the national emission of VOCs.

- **Has the mixture of different NMVOCs being emitted in the UK changed and are there effects arising from a change in speciation?**

Quick answer: The VOC content of the UK atmosphere is different in 2019 compared to 30 years ago. Research observations indicate that short chain aldehydes and alcohols are now the most abundant VOCs, and that longer-chain VOCs from diesel vehicles and consumer products are also a component of urban VOC emissions. Whilst VOC emissions have shifted away from aliphatic compounds towards alcohols there has not been any significant change in overall ozone production potential per kilotonne of emissions.

- **Does the current monitoring infrastructure provide sufficient information to evaluate the most important VOC sources and determine emission trends?**

Quick answer: No, the existing Defra monitoring only partially reflects current emissions. The species prioritised for measurement in the current automatic hydrocarbon monitoring network are those VOCs that formed a major part of emissions in the 1980s and 1990s, but many of these have declined substantially, and some are frequently below detection limits. Of the 10 most abundant VOCs found in London air (based on short-term research observations), only 4 are included in routine monitoring. Of the 20 most abundant VOCs in the NAEI (which comprise ~70% of national emissions by mass), 9 are not currently monitored.

- **Are there recent examples of NMVOC interventions that have reduced emissions?**

Quick answer: The reductions seen in non-methane hydrocarbons related to road transport and fossil fuel production and distribution have been substantial, and these have had major impacts on the attainment of air quality standards for benzene and 1,3 butadiene as well as leading to large reductions in overall national emissions, a likely contributing factor in the reduction of peak ozone concentrations. VOCs emissions have been successfully reduced through multiple targeted regulatory interventions including Euro vehicle standards, the Solvents Directive and the Paints Directive, which in combination have led to substantial reductions in atmospheric concentrations.

2. Regulatory background

The term ‘volatile organic compound’ or VOC (used interchangeably with the longer abbreviation non-methane [3]volatile organic compound, NMVOCs) is a catch all for any organic compound found as a gas in the atmosphere. In urban air this can encompass many thousands of different organic compounds including non-methane hydrocarbons, oxygenated and halogenated species (Lewis *et al.* 2000). The technical definition of NMVOCs is given in official guidelines issued by the European Monitoring and Evaluation Programme (EMEP)/CLRTAP for inventory reporting of emissions, and the same definition is also used in the EC Directive 1999/13/EC (Solvent Emissions Directive) and National Emissions Ceiling Directive (NECD).

“*NMVOCs comprise all organic compounds except methane which at 293.15 K show a vapour pressure of at least 0.01 kPa (i.e. 10 Pa) or which show a comparable volatility under the given application conditions”*

A different definition of VOCs is given in the 2004/42/EC Paints Directive, which refers to a VOC as “*an organic species with a boiling point less than 250 ºC at a standard pressure of 101.3 kPa*.”

The practical realisation of both of these definitions is that most non-methane hydrocarbons with a molecular weight falling within the carbon number range C_2 to C_{14} are thought of as VOCs. Longer-chain hydrocarbons (>nC_{14}) may fall outside of the definition, as may more highly functionalised organic compounds such as organic acids, alcohols or organic peroxides. The majority of persistent organic pollutants (POPs) have lower vapour pressures than this definition, although notably some two and three ring polycyclic aromatic hydrocarbons such as naphthalene are considered as NMVOCs as well as POPs. Whilst the above EMEP / NECD definition is the most widely accepted European definition of a VOC it is worth noting that the Air Quality Directive 2008/50/EC includes within it a broader definition of a VOC as:

“volatile organic compounds’ (VOC) shall mean organic compounds from anthropogenic and biogenic sources, other than methane, that are capable of producing photochemical oxidants by reactions with nitrogen oxides in the presence of sunlight”

The use of this broader definition captures a wider range of organic compounds as VOCs, essentially treating any reactive organic compound that can sustain itself at least partly as a gaseous vapour as a VOC.

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[3] Methane is excluded in the context of air pollution context it has low reactivity and is not harmful, low reactivity means it has a long lifetime in the atmosphere and therefore is an important greenhouse gas.

2.1. UK Air Quality Objectives for VOCs

The majority of NMVOCs are relatively safe chemicals in air if directly inhaled in trace (part per trillion or low per billion) amounts. Their emissions and concentrations have historically been controlled to help limit the secondary formation of tropospheric ozone. However, a small number of NMVOCs do have direct toxicological impacts on health, either as lung irritants or cancer-causing agents. The Air Quality Strategy for England, Scotland, Wales and Northern Ireland (July 2007) sets out specific UK Air Quality Objectives for two of those, benzene and 1,3-butadiene (Table 1).

Table 1: UK Air quality objectives for benzene and 1,3-butadiene

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

These hydrocarbons are 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 which 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 concentrations 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 concentrations of benzene are modelled or measured to be above the LAT, for example where notably impacted by 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 UK Hydrocarbon network, it is estimated that this is <2% based on a typical calibration regime. The minimum time coverage is 35% (distributed over the year) for urban background and traffic sites and 90% for industrial sites. [The relatively low figure of 35% reflects that tube-based samples are discontinuous in nature and that their individual sampling periods are frequently not overlapping, and indeed can have gaps between measurement.]

Annex X of the Directive (EC, 2008) lists 31 other Volatile Organic Compounds (VOCs) which are ozone precursors and which are recommended to be measured in at least one urban or suburban area to support the understanding of ozone formation. With the exception of formaldehyde and the summation of 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 should have a minimum data capture target of 50%. [Although the original rationale for a 50% target is not available to AQEG, this relatively low % likely reflects the technical complexity of the measurement and that one single measurement must in practice report on many individual variables].

EMEP is a scientifically based and policy driven programme under CLRTAP for international co-operation to solve transboundary air pollution problems. Defra support the programme by funding operation of two UK monitoring sites to Level 2 status, which includes the measurement of ozone precursors. The same VOCs monitoring system deployed for AQD compliance is used for EMEP reporting at two Rural Background locations; Chilbolton Observatory, Hampshire (which replaced the long-running Harwell EMEP site, Oxfordshire, in 2016) and Auchencorth Moss, Midlothian.

2.2. Monitoring networks: background and methods

The UK Hydrocarbon Network is one of several air quality compliance 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, the Heavy Metals and

Polycyclic Aromatic Hydrocarbons Networks, which meet the requirements of the AQD and Fourth Daughter Directive[4].

2.2.1. Non-Automatic Benzene Monitoring

The Non-Automatic Hydrocarbon network started operation in 2001, measuring benzene and 1,3-butadiene. In addition to being measured in the automatic hydrocarbon network, benzene measurements are also made using a dual sample tube flow-controlled pump unit that complies with EN 14662-1:2005, 'Ambient air quality – Standard method for measurement of benzene concentrations', using a method described in Martin *et al*. (2003). This methodology currently produces measurements as nominal fortnightly averages at 34 sites.

The benzene monitoring method involves drawing ambient air at a controlled rate (nominally 10 ml min^{-1}) alternately through two tubes (A and B) containing a carbon-based sorbent (Carbopack X). Each tube samples at 10 ml min^{-1} 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 a laboratory for subsequent analysis of benzene by gas chromatography-mass spectrometry. The sampling period and sample flow rate are important such that enough benzene is captured onto the sorbent to enable fully quantifiable analysis, but not too much that there is breakthrough of the sample.

Until 2007, passive diffusion tubes using the same sorbent were also used to measure 1,3-butadiene in order to assess compliance with the UK Air Quality Strategy Objective (2.25 µg m^{-3} expressed as a running annual mean). The method was validated in Martin *et al*. (2005). This monitoring programme was reviewed in 2007 and it was found that:

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

On this basis Defra took the decision to discontinue routine monitoring of 1,3-butadiene with passive diffusion tubes from 2007.

2.2.2 Automatic Hydrocarbon Monitoring

Automatic hourly measurements of speciated hydrocarbons, made using advanced automated gas chromatography, started in the UK in 1991. By 1995 the monitoring network 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 by 2015 there were only four UK sites in operation to satisfy network requirements. The London Eltham site fulfills requirements of the Air Quality Directive to monitor ozone precursors at an urban

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

background location, Marylebone Road measurements are made to inform research into roadside concentrations of VOCs, and the two rural background sites support EMEP[5]. 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 each of the individual VOCs.

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

Table 3: Species measured by the automatic gas 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 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	C5H8	biogenic	114
ethyne	alkyne	C2H2	SNAP7 (46%)	7
1-Pentene	alkyne	C5H10		95
trans-2-pentene	alkyne	C5H10		111
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	C9H12	SNAP6 (74%)	110
1,3,5-trimethylbenzene	aromatic	C9H12	SNAP6 (71%)	107

There is currently no standard European 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. Within the UK automated network thermal desorption with *in situ* gas chromatography and flame ionisation detection (FID) is used to measure hourly hydrocarbon concentrations. During 2017, hydrocarbons at all sites were measured using automatic Perkin Elmer Ozone Precursor Analysers. A known volume of air (800 mL) is dried and drawn through a cold trap, which contains adsorbent material. The cold trap is held at -30 ^{o}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 ionisation detector (GC-FID). The analyser is calibrated using an on-site 30 component gas mixture in nitrogen balance gas. Thermal desorption and GC-FID require the ambient air sample to be dried to a low dew point in order and this is achieved using a Nafion permeation membrane. This impacts on the range of chemical classes that can be measured, and creates an operational limitation in the current network such that it can only measure non-methane hydrocarbon species.

3. Recent trends in ambient concentrations of VOCs in the UK.

Routine observations of VOCs in the UK have been made as part of Defra activities since around 1995 using both continuous GC systems that differentiate between a range of different small non-methane hydrocarbons and Tenax adsorbent tubes for the quantification of benzene and 1,3 butadiene. As described in section 2.2.2 the network has changed substantially over the last 20 years; at its most extensive it included 13 sites in the UK, however as VOCs have generally declined in concentrations the network has reduced, and in 2018 was limited to four automated sites. The evaluation of long-term trends to the present day is therefore restricted to a relatively small number of geographic locations, Marylebone Road, Eltham, Harwell/Chilbolton, and Auchencorth Moss, however historic data for now closed sites is also informative in showing how different sources and interventions have impacted ambient concentrations.

Since VOCs are a class of chemicals with a range of different sources, each emitting a unique fingerprint of VOCs, no canonical trend for all VOCs would be expected. It can be helpful to group together different compounds into a smaller number of source classes that are indicative of particular emissions, and then in turn examine how the trends for each group have evolved over the past two decades. It is rare however for an individual VOC to be only emitted by one specific source. For example, propane concentrations in the UK atmosphere are affected by leakage from the natural gas network and LPG use, toluene by both solvent consumption and gasoline evaporation. It is also important to note that recent trends in VOCs can only be established for the relatively small subset of VOC for which there is ambient monitoring data. Many VOCs that are significant in terms of NAEI inventory estimates, notably methanol, ethanol and acetone, have never been routinely measured, and this is discussed further in later sections.

Figure 1 shows a simple classification of key sources and the attribution of individual non-methane hydrocarbons in the Automated Hydrocarbon Network to emission classes. The largest font size in each class indicates the VOC that is the most dominant in emissions from that sector, but in many cases there are overlaps with individual VOC being emitted from multiple sources.

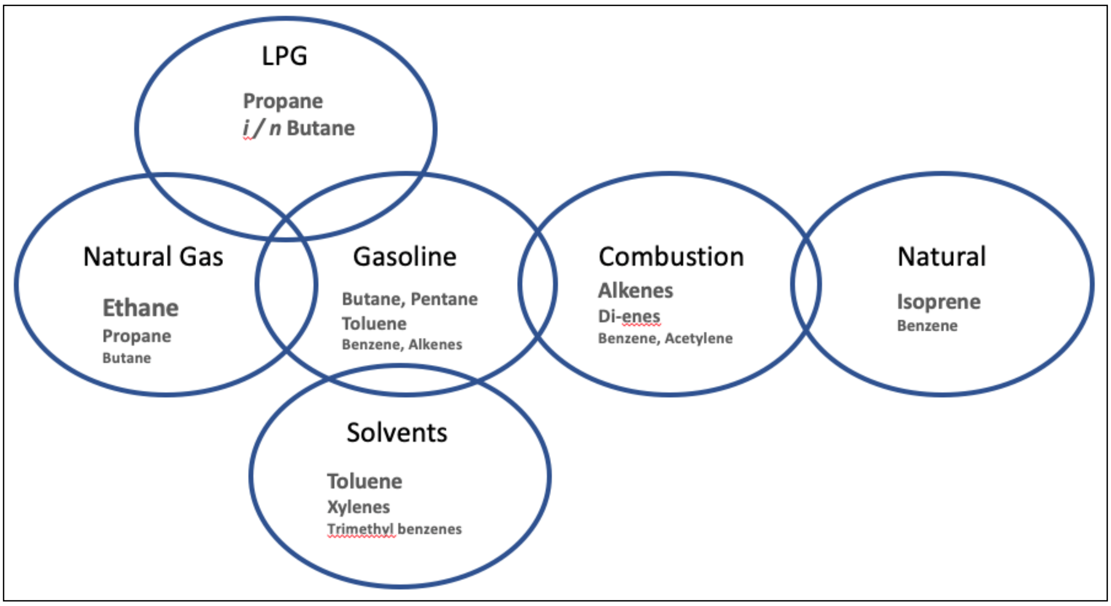

Figure 1. Some major contributing emission sources for those VOCs that are measured in the current Defra automatic network. Overlapping sectors indicates where VOCs that are common to multiple sources exist, and size of text indicates relative magnitude of emission from that source for each VOC.

3.1 Natural gas and ethane.

Analyses of VOC trends typically use the behaviour of atmospheric ethane as a proxy for changes in emissions resulting from anthropogenic consumption of natural gas, including upstream gas extraction industries, processing and leakage from storage and distribution networks. Ethane is one of the more straightforward VOC trends to interpret since natural gas is by far the largest anthropogenic source to the atmosphere. Since ethane is relatively long-lived in the atmosphere (lifetime around 2 months at mid-latitudes) locally measured trends reflect changes in emissions over a range of space scales, including the hemispheric.

At the global scale ethane concentrations declined from the mid-1970s through to around 2010 (e.g. Aydin *et al*., 2011), with similar trends and declines seen throughout the Northern hemisphere background atmosphere. Around 2009-2010 the long-term decline reversed and there has followed a period of increasing ethane in Northern hemisphere background air. Helmig *et al.* (2016) showed that across the Northern hemisphere most background VOC monitoring sites were detecting increasing ethane after 2009, over the range 2.9 - 4.7 % yr^{-1} and attributed this to increases in Northern American gas extraction from unconventional hydrocarbon sources, notably from hydraulic fracturing). Of relevance to the UK, included within this analysis was data from Mace Head, Ireland, which showed ethane growth post-2009 > 50 pmol mol^{-1} yr^{-1}.

Urban trends in ethane are influenced by the large-scale regional and hemispheric emissions trends and the effects of emissions from more localised natural gas leakage. An analysis by von Schneidemesser *et al.* (2010) indicated that there had been a small (relative to some other VOCs) downward trend in ethane between 1998 and 2008, of the order - 4% a year at the roadside Marylebone Road automatic monitor in central London but no significant trend in ethane at the more rural Harwell monitor. Extension of those trends in Figure 2 to 2018 shows that UK rural ethane, as measured at Harwell has slightly increased since 2008 (Figure 2), in line with global trends and emissions, but that there have been further modest declines at the roadside in Marylebone Road and at the more urban influenced London Eltham (not shown). [note: since VOCs typically show strong seasonal cycles in concentrations due to the variable rate of their removal by OH between winter and summer, de-seasonalised trends are used here to provide a clearer guide to behaviour.] This suggests that the UK continues to gradually reduce its domestic ethane emissions from the natural gas network, but there are also trans-boundary trend effects that are superimposed.

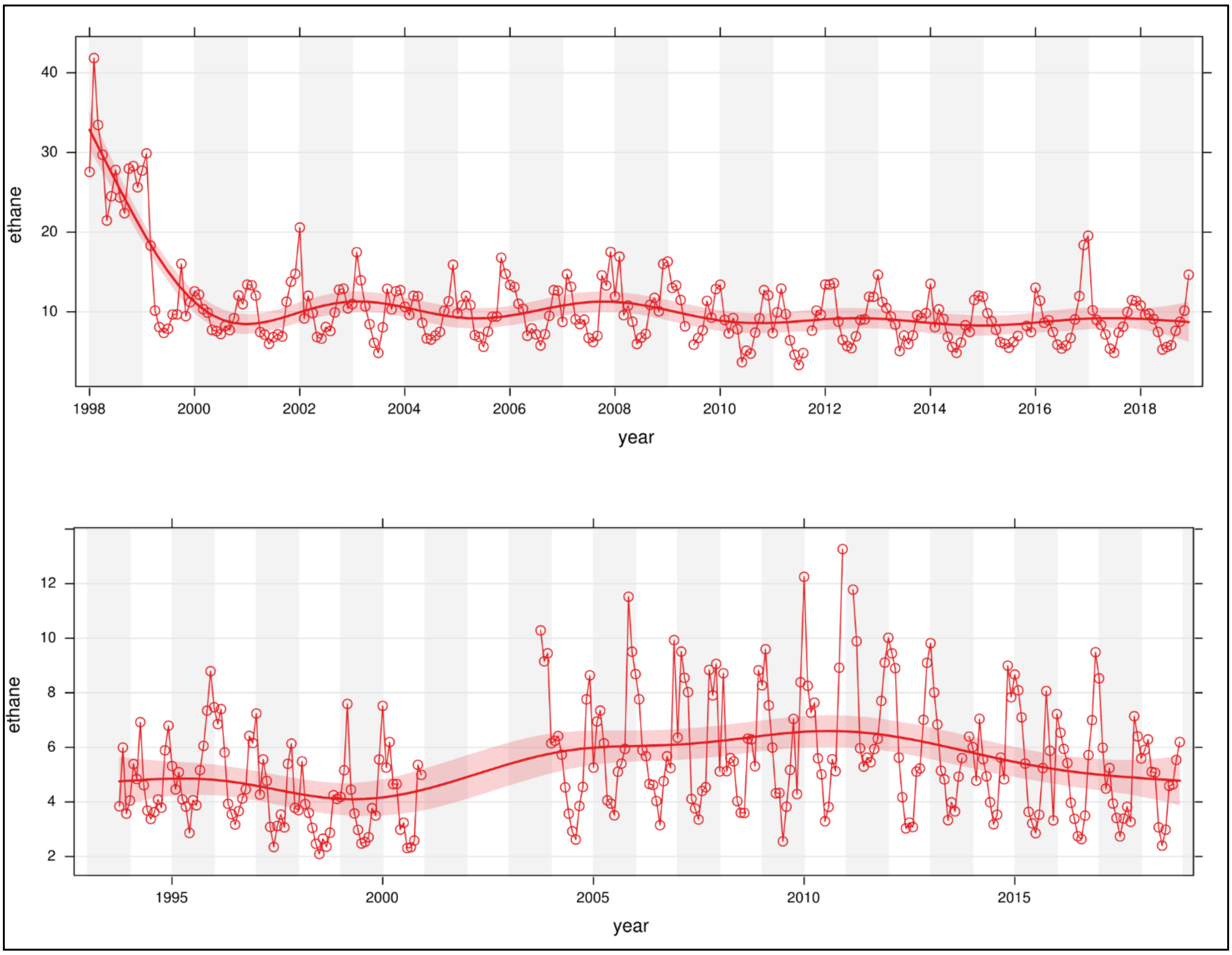

Figure 2. Trends in ethane (µg m^{-3}) at Eltham (bottom) and Marylebone Road (top), data from the Defra Automated Hydrocarbon Network. Solid line is the trend, shaded area 95% confidence interval.

3.2 Fuel-derived alkanes

Gasoline fuel has historically been a major source of VOCs to the atmosphere. The fuel itself is composed primarily of short-chain alkanes such as *i* and *n* butane, *i and n* pentane, hexane, monoaromatics such as benzene, toluene and *m / p* xylenes and a small fraction of unsaturated hydrocarbons. In recent years ethanol has also been added and this now comprises between 5 -10% by volume. The chemical content of gasoline varies by supplier in the UK and by season, with certain aspects of composition subject to EU regulatory controls (e.g. total aromatic content < 30%, di-enes <1%, benzene <1%). VOCs from this source can enter the atmosphere through many routes, from the refining and distribution of the fuel, evaporation from storage in vehicles, from the engine via carburettor and unburnt fuels in exhaust gases. There have been a wide range of technical interventions aimed at reducing VOC emissions from gasoline and associated transport sources, including controls on refineries, recollection of vapours during refuelling at garages, and the elimination of unburnt fuel in the tailpipe via 3-way catalytic convertor and the reduction in use of direct fuel injection engines. In combination these have been successful in reducing emissions and the reductions in ambient concentrations in the UK during early years of emissions control were substantial.

Over the period 1998 to 2008 von Schneidemesser calculated downwards trends in gasoline-related alkanes from UK monitoring stations; kerbside at Marylebone Road trends were: n-butane -17% yr^{-1}, *i* butane -14% yr^{-1}, *n* pentane -12% yr^{-1} and hexane -14% yr^{-1}. A figure from von Schneidemesser is reproduced below, which highlights how the declines in certain gasoline-related alkanes were greater over the 1998-2008 period than reductions seen in ethane, which is from the essentially uncorrelated natural gas source. For many VOCs associated with gasoline close to order-of-magnitude reductions in ambient concentrations were achieved within a decade, and this behaviour was also reproduced in other European cities (e.g. Waked *et al.* 2016).

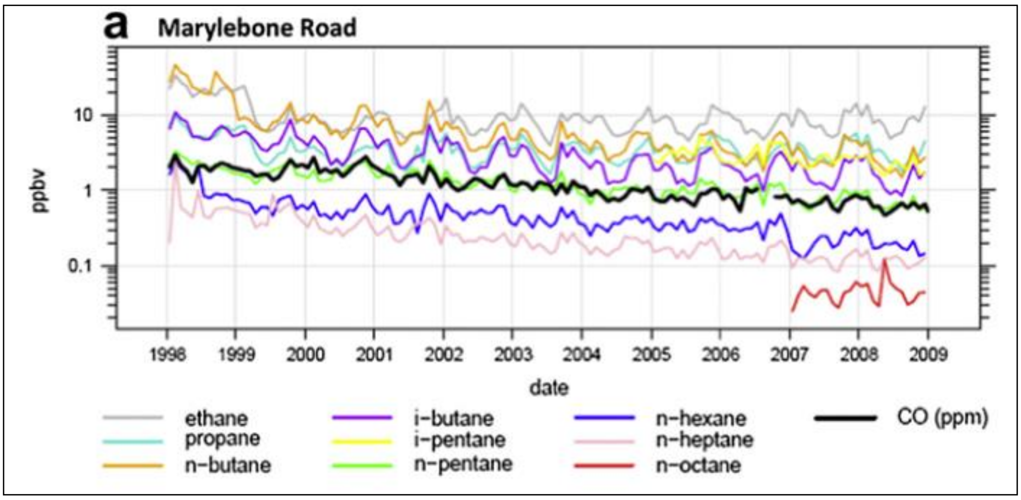

Figure 3. Trends in selected non-methane hydrocarbons indicative of natural gas (ethane and propane) and gasoline sources (all other VOCs) and combustion tracer CO for the period 1996 to 2009 at Marylebone Road. Reproduced from Atmos. Environ. ***44****, 5053-5064, 2010.*

The atmospheric lifetimes of many gasoline-related VOCs are short, (*n*-butane for example has a lifetime with respect to mid-latitude summertime OH of around 1 day), and a consequence is that processing and oxidation of emissions occurs relatively rapidly leading to substantially lower concentrations in the rural environment. Whilst longer-term trends in ethane were seen to reverse around 2009, gasoline related VOC concentrations have continued to decline in the UK atmosphere up to 2018. Figure 4 below shows up to date 2006-2018 (except for Harwell to 2015) trends in *n*-butane and *n*-pentane at Marylebone Road kerbside and Harwell indicative of the rural atmosphere.

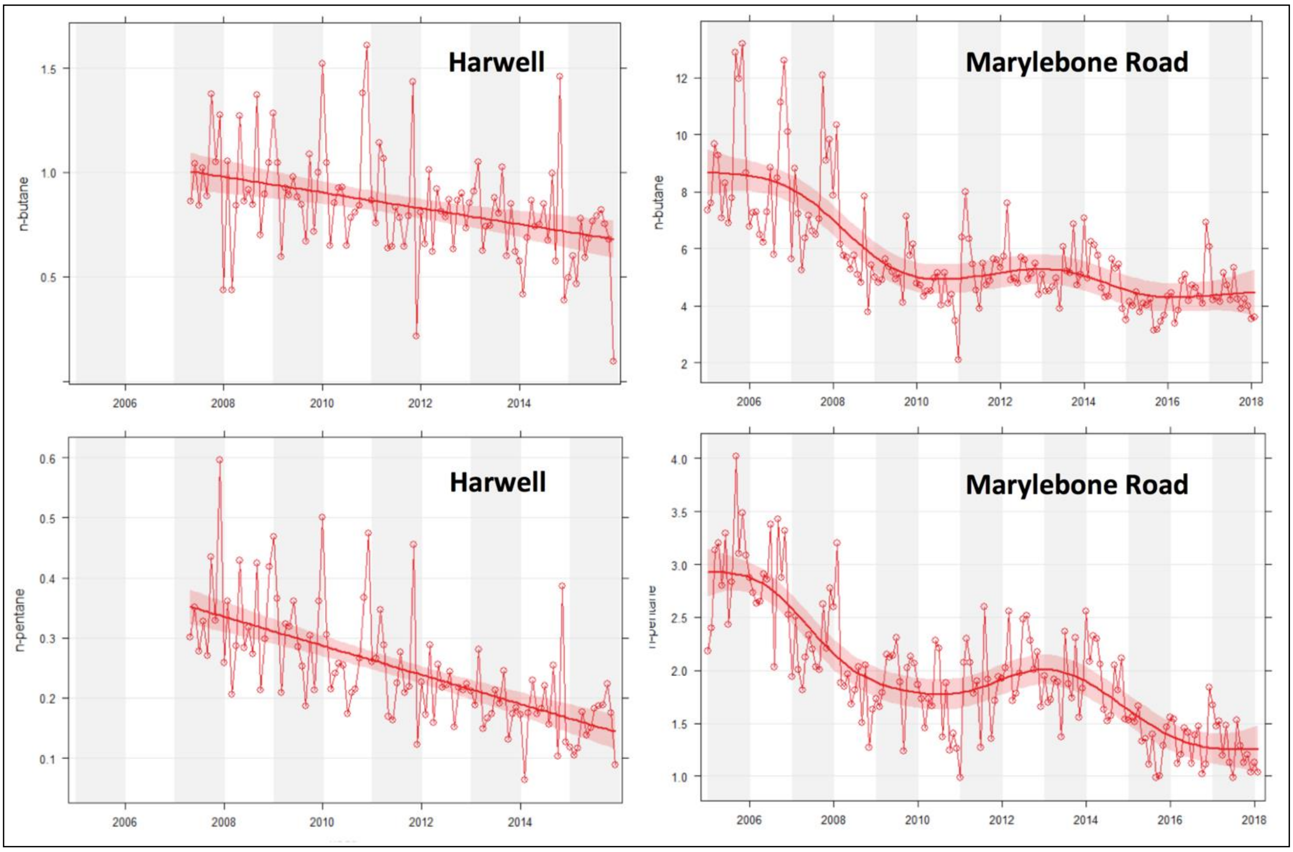

Figure 4. Deseasonalised trends in n-butane and n-pentane (both µg m^{-3}*) over the period 2005-2018 at Marylebone Road and 2005-2015 at Harwell, data from Defra Automatic Hydrocarbon Network. Solid line is the trend, shaded area 95% confidence interval.*

As indicated earlier in this section, emissions of VOCs are never entirely unique to a particular source and sector. Based on emissions inventory estimates the significance of gasoline and road transport as a driver of trends in species such as butane and pentane is declining, and the trends are now affected by other sources including compressed/liquified gas butane consumption in the domestic sector and pentane as a solvent, rather than a fuel. A final note on trends in gasoline-related VOCs is that whilst it is clear that much of the decline seen in atmospheric concentrations is likely due to the implementation of emissions controls, the trends are also affected by fleet changes and the shift away from gasoline to a diesel transport fleet. Light hydrocarbons such as those described here are not found in diesel fuel, but the significance of the fuel change is impossible to establish with monitoring data, since no VOCs indicative of diesel sources are measured in the

Automated Hydrocarbon Network. Dunmore *et al.* 2015 suggested that total fuel-related VOC emissions may not have declined as significantly as might be suggested by monitoring data, rather that there has been a shift in balance from monitored to unmonitored VOCs. This is discussed further in later sections. VOC emissions from road transport are discussed further in Section 4.6.

3.3 Combustion-related VOCs

Incomplete combustion releases a range of different VOCs along with other gaseous pollutants such as CO, NOx and CO_2. The mixture of VOCs produced from combustion is complex, but from within the small suite of VOCs measured in the Automated Hydrocarbon Network it is the unsaturated hydrocarbons and benzene that are most indicative of that source type. 1,3 butadiene and benzene are both carcinogenic hydrocarbons produced from combustion and have been subject to monitoring in both automatic and passive sampling networks in the UK. The introduction of the 3-way catalytic convertor and increasingly stringent controls on VOC emissions from gasoline vehicle exhaust through the introduction of EURO standards has resulted in some steep declines, particularly in 1,3 butadiene for which gasoline combustion has historically been the dominant source. Figure 5 reproduces the trends between 2000 and 2015 for Marylebone Road and Eltham.

The lifetime of 1,3 butadiene is very short-lived during the day, less than 1 hour in summertime, and hence there is limited potential for this pollutant to advect into the rural environment. Based on the Marylebone Road time series there has been an approximate three-fold reduction in ambient concentrations roadside since 2005, and current ambient observations in suburban and rural locations of 0.01 - 0.1 ppb are close to or below the current GC-FID instrumental detection limit.

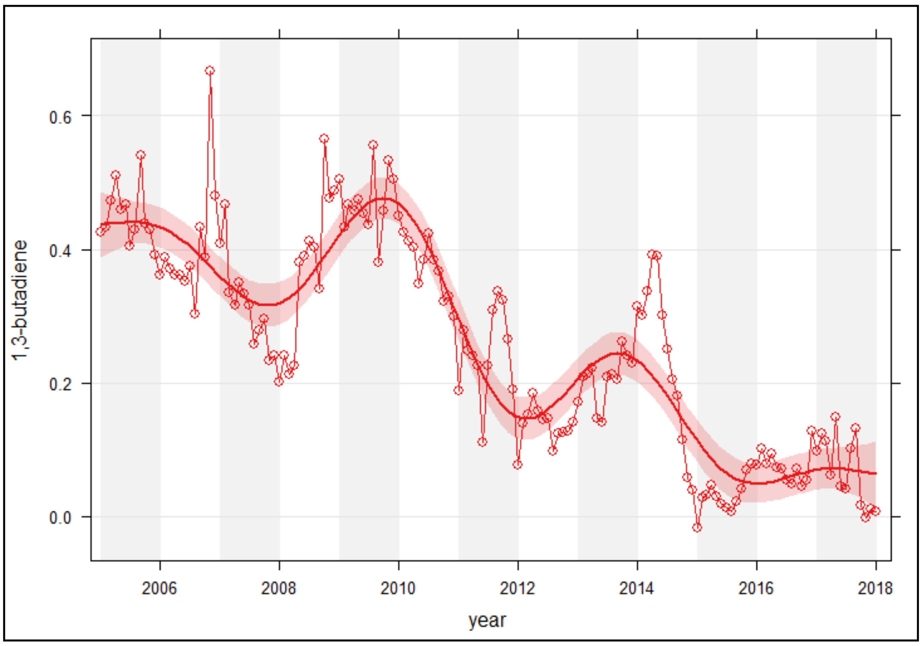

Figure 5. Deseasonalised trends in 1,3 butadiene (µg m^{-3}) 2005-2018 Marylebone Road; data from Defra Automatic Hydrocarbon network. Solid line is the trend, shaded area 95% confidence interval. (Taken from https://uk-air.defra.gov.uk/assets/documents/annualreport/air_pollution_uk_2015_issue_1.pdf)

Combustion of fossil fuels can be a substantial source of atmospheric benzene, including on and off-road transport, aviation, gas heating systems and biomass burning. There is also a semi-natural background in benzene arising from forest fires and other vegetation combustion (Lewis *et al.* 2013). As with many other VOCs, benzene has mixed sources and is also released as either unburnt fuel or fuel evaporation. It was historically used as multipurpose solvent but once its toxicity was fully appreciated it was phased out from industrial processes in the 1980s, a period before monitoring data was routinely available.

The last 20 years of data for benzene show some rapid declines. Von Schneidemesser calculated trends of -26% yr^{-1} between 1998 and 2008 for roadside in London and around -7% yr^{-1} in the rural atmosphere. The initial steep decline in concentration is attributable to the impacts of vehicle exhaust management, reduction in vapour releases during re-fuelling and the final elimination of benzene as a solvent. The time-series in benzene indicates a single step change reduction in 1999 following EU regulations to limit benzene content in gasoline to 1% v/v. In more recent years the reductions in ambient benzene have slowed, but it remains on a downwards trajectory. Figure 6 shows the period 2005-2018 (to 2015 for Harwell); the earlier rapid declines seen at the start reflect a period when road transport combustion emissions of benzene declined due to better tailpipe controls, and the flatter period from 2007 onwards reflecting the residual benzene arising from evaporative losses which is harder to control.

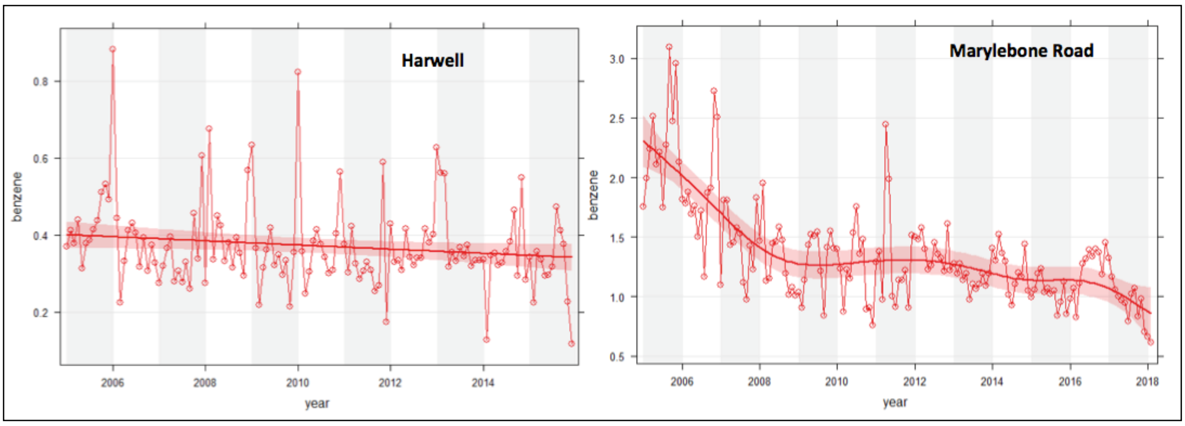

Figure 6. Deseasonalised trends in benzene (µg m^{-3}) at Harwell 2005-2015 (left) and Marylebone Road 2005-2018 (right). Data from Defra Automated Hydrocarbon network. Solid line is the trend, shaded area 95% confidence interval.

Benzene and 1,3 butadiene are the only VOCs for which specific concentration air quality targets exist - benzene has a Directive Limit value of 5 µg m^{-3} as an annual mean and 1,3 butadiene an Air Quality Strategy objective of 2.25 µg m^{-3}, as a maximum running annual mean. For both species reductions over the past two decades have resulted in ambient concentrations that are well below the targets, even in highly traffic-influenced locations and when measured at roadside.

When combining together both automated and non-automated data from the UK monitoring network declines in ambient concentrations have been observed across a range of different site types in the UK. Figure 7 shows the 2002-2017 smoothed trends in non-automatic benzene for roadside, urban background, urban centre and industrial centre.

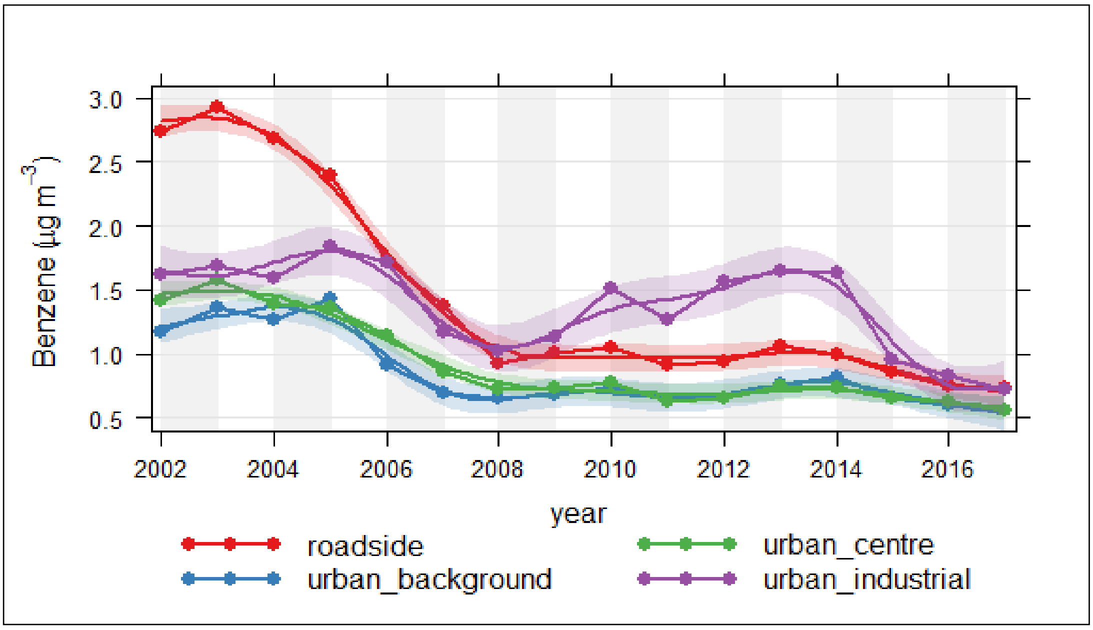

Figure 7 - Smooth trend annual means by UK station type, non-automatic benzene 2002 - 2017

Many other alkenes are released from combustion, of which ethyne, ethene and propene are measured in in the Defra Automated Hydrocarbon Network. In general these all have also showed declines over the past 20 years. Figure 8 shows recent trends for ethyne, ethene and propene roadside at Marylebone Road.

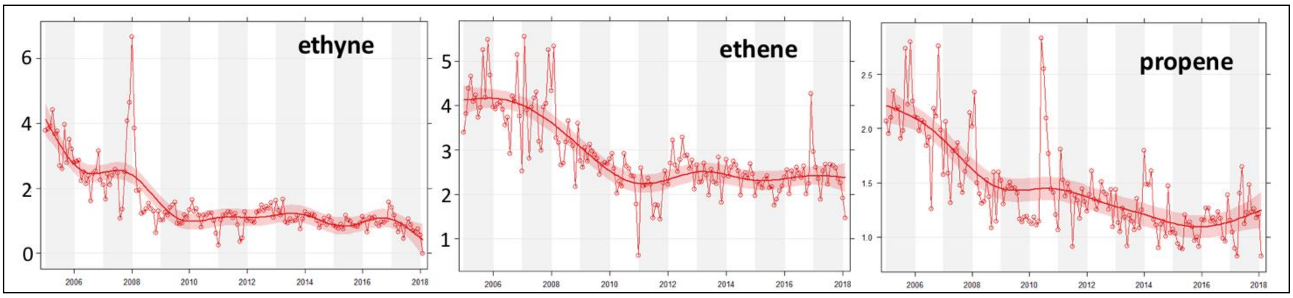

Figure 8. Deseasonalised trends in ethyne, ethene and propene (units µg m^{-3}) at Marylebone Road 2005-2018. Data from Defra Automated Hydrocarbon network. Solid line is the trend, shaded area 95% confidence interval.

3.4 Solvent-related VOCs

VOCs as solvents are released from many different activities including at the industrial scale (for example in manufacturing, painting and finishing) and domestically from household products (for example personal care, cleaning, glues, ink, paints, sealants, varnishes etc). Many solvents in common usage are not detected in the Defra Automated Hydrocarbon Network, so this is a category of emission that is not particularly well defined in terms of past observed trends. Major solvents such as acetone, methanol, ethanol, isopropyl alcohol, and halogenated solvents such as dichloromethane are not measured routinely in the UK.

Aromatic VOCs such as *m* and *p* xylene, ethyl benzene and *o*-xylene have been observed in the Defra network and these provide some measure of changes to emissions related to VOCs associated with paints and finishing, but these species are also found in fuels and so are not a unique marker for solvent emissions. The introduction of the EC Paints Directive was a specific intervention aimed at reducing VOC emissions, and this in combination with reductions in gasoline emissions has led to some steep declines in atmospheric concentrations of aromatic VOCs.

Over the period 1998 – 2008 von Schneidemesser *et al.* reported declines of -20% yr^{-1} for the sum of *m* and *p* xylenes and -23 % yr^{-1} in *o*-xylene. The decline in xylenes seen since 2008 has been more modest. Concentrations over the 2008-2018 period concentrations at roadside, suburban and the rural environment approximately halved, however since around 2014, there has been little change in the trend in aromatics at the roadside, suggesting that in combination urban gasoline and solvent emission rates have now stabilised.

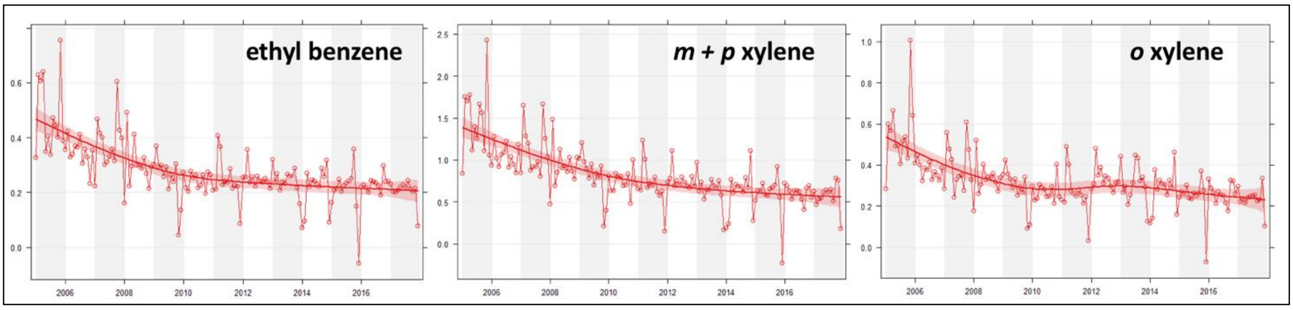

Figure 9. Deseasonalised trends in ethyl benzene, m + p xylene and o xylene (units µg m^{-3}) at Eltham, London 2005-2018. Data from Defra Automated Hydrocarbon network. Solid line is the trend, shaded area 95% confidence interval.

3.5 Other VOCs not routinely measured

Those species measured by the Automated Hydrocarbon Network reflect only a small subset of the true diversity of different VOCs that are present in air. The network was primarily configured for the detection of those VOCs of most relevance ~1990, primarily aromatic solvents from paints and hydrocarbons from natural gas and gasoline / road transport emissions. All three are classes of emissions that have reduced over the past two decades. Other sources of VOC may not however have followed the same trajectory, so it is not possible to say with any certainty what the trends are in ‘total’ amount of VOC in air.

An estimate of the current ratio of ‘measured’ to ‘unmeasured’ VOC in London air can be derived from Dunmore *et al.* (2015). This study used observations of a much wider range of VOCs with several different instrumental techniques to produce a reasonably complete inventory of all the different VOC in urban air. Figure 9 is a reproduction of a figure from that paper that summarises the contribution of different VOC classes to total VOC mixing ratio, mass and ozone formation (as OH reactivity) in summer and winter. In simple terms the existing Defra Automated Hydrocarbon Network measures the VOCs in the classes of *gasoline* and *natural gas*, but does not measure any VOCs in the classes of *OVOCs* or *diesel*. Dunmore *et al*. (2015) indicated that only around 35% of the VOCs of significance to ozone formation are currently measured and that evaporative and unburnt hydrocarbons from diesel fuel, at least in the UK, was underestimated as a source of VOCs to air in the range $>C_n9$.

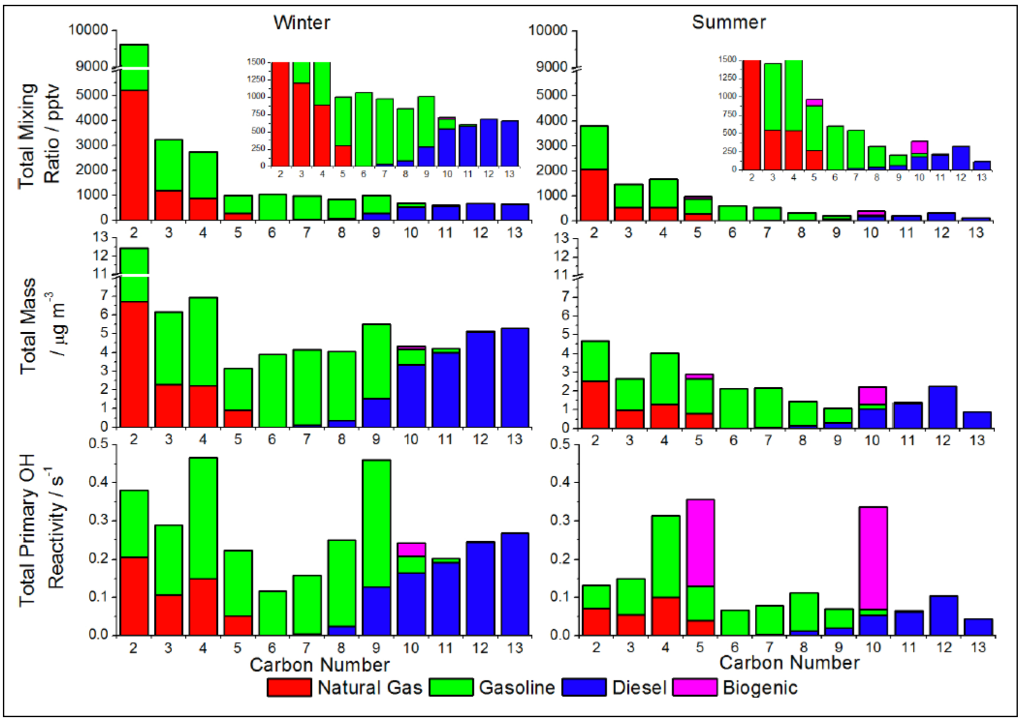

Figure 9. Contribution of different types of VOCs to mixing ratio, mass and OH reactivity in London, North Kensington, based on data from the 2012 Clearflo campaign. VOCs in the Diesel and C10 biogenic groups are not currently measured in the Defra hydrocarbon network, whereas Gasoline, Natural gas and Biogenic are represented by monitoring. Reproduced from Dunmore et al. Atmos. Chem. & Phys ***15****, 9983-9996, 2015.*

3.6 Oxygenated VOCs in UK air

Oxygenated organic compounds are a major class of VOCs for which there is no long-term data to establish trends, but there are some limited datasets collected from research studies to provide a guide to ambient concentrations Whilst many different OVOCs are found in air, the most significant primary emissions are of acetone, methanol, ethanol, *iso*-propanol and butanol, used very widely as solvents, and in the case of ethanol also in fuels and released by food and drink industries. Other oxygenated VOC include formaldehyde and acetaldehyde which are often the most abundant VOCs observed in ambient air, having both primary emissions and being formed as by-products of the oxidation of other VOCs.

The relative significance of OVOCs compared to non-methane hydrocarbons can be seen from data in Table 4. This provides an assessment of the most abundant VOCs measured in 2012 as part of the NERC Clearflo at the North Kensington AURN site. Mean mixing ratios are given for two different types of air masses, those from the South West (generally cleaner) and those from the East (generally more polluted). For further details see Whalley *et al*. 2018.

Table 4. Selected mean summertime VOC mixing ratios measured at North Kensington during the Clearflo project. Adapted from Table 3 in Whalley et al., Atmos. Chem. & Phys. ***18****, 2547-2571, 2018.*

VOC species	**Mean mixing ratio in South Westerly airflow / ppb**	**Mean mixing ratio in Easterly / continental airflow / ppb**
formaldehyde**	6.7	13.8
acetaldehyde**	3.3	6.6
ethane	3.1	6.8
ethanol	2.4	5.7
methanol*	2.4	5.2
acetone*	2.0	3.4
propane	1.2	2.7
butanol	0.6	0.84
propanol	0.3	0.64
iso butane	0.5	1.1
iso pentane	0.5	1.2
toluene	0.36	0.7
1,3 butadiene	0.01	0.02
benzene	0.12	0.2

* Minor contribution *via* secondary production from the oxidation of other VOCs

** Major secondary production from the oxidation of other VOCs

3.7 UK aldehydes study from 2014

In 2011 the AQEG made a recommendation to Defra and the Devolved Administrations that measurements should be established to investigate possible increases in aldehyde concentrations in ambient air. This was linked to concerns resulting from the increasing introduction of bioethanol to conventional petroleum used in road transport[6]. It is expected that low blends ≤5% may increase emission of acetaldehyde from motor vehicle exhaust. For higher strength blends >5%, an increase of formaldehyde may also be seen.

The Renewable Transport Fuel Obligation (RTFO) initially set a target for the proportion of transport fuel supplied as biofuel to be 4.75% by April 2013[7]. In April 2018 these targets were updated to make sure the mix is at least 12.4% biofuel by 2032.

Measuring the impact of biofuel take-up on aldehyde concentrations in air is not straightforward. Acetaldehyde has both primary anthropogenic and biogenic sources and is a common oxidation product generated during the oxidation of many other VOCs. Formaldehyde also has significant photochemical sources from VOC degradation, so significant interference, particularly in summer was expected. Monitoring sites were positioned in locations where the urban roadside and background were closer together and were not located near large areas of well-maintained grass, such as sports fields. The objective was to improve the potential to assess traffic contribution of the compounds and minimise interference from biogenic sources. Locations for aldehyde monitoring are shown in Table 5 and annual mean results for 2014 in Table 6.

Table 5: 2014 Aldehyde Monitoring Sites.

Site	**Lat**	**Long**
Manchester Oxford Road	53.471802°	-2.237572°
Manchester Piccadilly	53.230591°	-1.433563°
Birmingham Tyburn	52.511722°	-1.830583°
Birmingham Tyburn Roadside	52.512194°	-1.830861°
Glazebury	53.460080°	-2.472056°

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[6] AQEG, 2011. Road Transport Biofuels: Impact on UK Air Quality. Advice note prepared for Department for Environment, Food and Rural Affairs; Scottish Government; Welsh Assembly Government; and Department of the Environment in Northern Ireland http://uk-air.defra.gov.uk/reports/aqeg/road-transport-biofuels.pdf

[7] https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/198978/summary-of-responses-and-government-response.pdf

Table 6 – Annual mean results (µg/m^3) of the one-year aldehyde pilot study, 2014

	Birmingham Tyburn Roadside		**Birmingham Tyburn**		**Manchester Oxford Road**		**Manchester Piccadilly**		**Glazebury**	
Site Type	Traffic Urban		Urban Background		Traffic Urban		Urban Background		Rural Background	
Aldehyde	Form	Acet	Form	Acet	Form	Acet	Form	Acet	Form	Acet
Mean	1.42	0.94	1.48	0.83	2.37	1.35	1.70	1.22	0.90	0.83
Max	2.73	2.34	5.47	2.13	5.86	3.32	3.73	3.11	3.12	3.41
Min	0.48	0.33	0.51	0.26	0.21	0.14	0.51	0.25	0.13	0.25

The highest measured concentrations during the UK aldehyde study were seen at the Manchester Oxford Road location - 2.37 µg/m^3 and 1.35 µg/m^3 for formaldehyde and acetaldehyde respectively. The lowest formaldehyde and acetaldehyde measurements of 0.9 µg/m^3 and 0.83 µg/m^3 were seen (as expected) at Glazebury, which is situated approximately 10 miles west of Manchester City Centre.

The results for formaldehyde were inconclusive. In Birmingham concentrations were 0.06 µg/m^3 higher at Birmingham Tyburn than at Birmingham Tyburn Roadside. In Manchester, the site on Oxford Road reported 2.37 µg/m^3 of formaldehyde, compared to 1.7 µg/m^3 seen at the background site, Manchester Piccadilly. In both cities the roadside location recorded a slight, but not significant increase in aldehyde concentrations of just > 0.1 µg/m^3 compared to the urban background, indicating at most the possibility of a relatively small near-road increase resulting from vehicle exhaust emissions.

Whilst it is clear that OVOCs currently represent some of the most abundant VOCs in air, and are at higher urban concentrations than most of the simple hydrocarbons being monitored by the automated hydrocarbon network, their sources are less well characterised and little can be said about past UK atmospheric trends. There are however some noteworthy underlying drivers that *may* have influenced atmospheric trends over the past decade, for example the increased use of ethanol in UK gasoline (Dunmore *et al*. 2016) and general increases in the domestic consumption of solvents, as indicated both by the NAEI and more widely by studies in other countries. These are discussed in more detail in the next sections. Anthropogenic emissions of VOCs based on the UK atmospheric emissions inventory

4. Anthropogenic emissions of VOCs based on the UK atmospheric emissions inventory

4.1 Overview of the inventory approach

The National Atmospheric Emissions Inventory (NAEI) estimates UK emissions from anthropogenic sources following methods in the EMEP/EEA Emissions Inventory Guidebook (EEA, 2016) for submission under the revised EU Directive 2016/2284/EU on National Emissions Ceilings (NECD)[8] and the United Nations Economic Commission for Europe (UNECE) Convention on Long-Range Transboundary Air Pollution (CLRTAP)[9]. Both the NECD and the Gothenburg Protocol to the UNECE CLRTAP set 2010 emissions ceilings for NMVOCs. The Gothenburg Protocol was revised in May 2012 to set more stringent emission reduction obligations from 2020. The revised NECD sets commitments for 2020 (in line with Gothenburg Protocol obligations) and 2030.

The NECD and CLRTAP define those VOC sources to be included and excluded from the national inventory (for example, emissions of NMVOCs from biogenic sources are not included) and the technical definition of NMVOCs (Section 2). They also define how emissions from different sources are categorised. The Guidebook provides estimation methodologies and default emission factors for each source category, although countries can use country-specific emission factors where these are deemed relevant, which may be particularly the case for industrial process emissions, but less so for sources such as road transport. Key requirements for inventory reporting are Transparency, Completeness, Consistency, Comparability and Accuracy and in this respect it is important to provide a

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[8] See https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32016L2284&from=EN for Information on the new NEC Directive (2016/2284/EU).

[9] See http://www.ceip.at/ms/ceip_home1/ceip_home/reporting_instructions/reporting_programme/ for reporting requirements of estimating and reporting emissions data under the CLRTAP

national inventory with time-series consistency going back to at least 1990 and forward to 2030.

The technical definition of NMVOC emissions for inventory reporting as "comprising *all organic compounds except methane which at 273.15 K show a vapour pressure of at least 0.01 kPa or which show a comparable volatility under the given application conditions*" has existed for some time and was probably considered fit for purpose for understanding photochemical production of ozone 20-30 years ago. As stated earlier, it leaves outside this definition longer chain hydrocarbons (>nC_{14}) and more functionalised organic compounds which are now known to play an important role in secondary organic aerosol formation. Moreover, although the Guidebook has this definition, it is not certain that emission factors in the Guidebook itself nor the country-specific factors used in inventories strictly adhere to this definition as the factors for different source sectors come from a variety of sources without always a clear indication of how the emission measurements were made.

The NAEI uses a combination of emission factors from the EMEP/EEA Guidebook and emission rates provided by industry and regulators in the UK. The emission factors represent the total of all NMVOCs or of total hydrocarbons (THCs, in the case of road transport) emitted from a source and not the sum of inventories of individual component VOC species. Methods for speciating the total NMVOC inventory into its component compounds are discussed in Section 4.1.1. Where THC factors are used, the methane emissions calculated separately are subtracted out.

The NAEI uses three basic approaches for estimating NMVOC emissions – top down, point source and industry reported. In the first case, an emission factor approach (top-down) combined with relevant activity statistics is used for many combustion sources including those present at crude oil refineries, other industrial sites, and in residential buildings. Factors are also used for transport sources, as well as for some processes in the food & drink industry (bread baking and whisky production) and for some uses of solvents, including many consumer products.

A point-source approach (bottom-up) can be used where the sum of emissions is estimated/measured and reported by process operators for each emitting site within a sector. The UK estimate is generated simply by summing the emissions reported for all of the sites within a given sector. This approach is used for refinery processes, chemicals industry, oil & gas production and certain types of solvent use in industry such as for printing of flexible packaging, and coating of road vehicles. Key sources for data on point source emissions are the regulators in England, Scotland, Wales and Northern Ireland who maintain inventories for the processes they regulate, and the BEIS Environmental & Emissions Monitoring System (EEMS) for the offshore oil & gas sector[10].

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[10] https://www.gov.uk/guidance/oil-and-gas-eems-database

However, coverage for the significant industrial pollution sources of NMVOCs is limited: there are no data on many food and drink industry processes, or for many industrial uses of solvents. There is also little information which is readily available on the methods used by each operator to quantify emissions which makes it difficult to assess the quality of the data. Time-series consistency is also not guaranteed. Approximately 10% of the UK emission estimates of NMVOCs are derived using data from these datasets.

In the case of solvent use, the third approach is used for UK emission estimates taking data provided directly by industry. However this may come with little additional information on emission factors or activity data. Data are often supplied on an *ad hoc* basis and usually cover a limited number of years only, thus a time-series may need to be generated by splicing together various data sets, possibly from different data providers. Therefore, there is a risk that a time-series might not be fully consistent (for example, in terms of the scope of estimates) and estimates for different years may be subject to different levels of uncertainty. However, industry estimates are essential for the NMVOC inventory: they provide data for sources where the lack of public domain data mean that the emission factor or point source approach cannot be used.

Further details of the method used in the NAEI are provided in the UK's national inventory report submitted annually to the UNECE and NECD. The latest version of the inventory is for years up to 2017 (the 2017 NAEI) as submitted in early 2019 (NAEI, 2019). The following sections of this report show historic and predicted trends in NMVOC emissions and briefly discuss the challenges compiling the inventory and their uncertainties. A further focus is provided on emissions from industrial process and solvent use emissions and road transport sources. The NAEI considers the spatial variability in emissions, generating maps of UK emissions on a 1x1 km grid. These are discussed in Section 4.9. Finally, the chemical speciation of the UK NMVOC inventory into its component parts is discussed in section 4.10.

4.2 Challenges in developing an inventory for NMVOCs

The NAEI currently covers emissions from around 400 individual source categories with a large contribution from a diverse range of industrial processes and solvents, but with very few individually dominant sources. Many of the sources are diffuse and widespread, e.g. domestic solvent use, small Part B processes (e.g. small-scale coating and printing processes), food and drink production and fuel distribution.

There are no suitable Government statistics to provide activity data on many NMVOC sources, which prevents the use of an emission factor approach to generating emission estimates (or the use of an emission factor approach to verify emission estimates generated using other approaches). Industry can sometimes help provide activity or emissions data, but it is not always possible to identify organisations that cover a particular source, e.g. automotive car-care products, and gathering data from industry is very often resource-intensive and difficult to update.

Some emission sources are unregulated in relation to emissions to air, e.g. processes in the food and drink industry such as bread baking and whisky production, use of consumer/household products, and small industrial coating and printing processes. There are therefore no site-specific emissions data for these sites which could otherwise be used in a point-source type approach to generating emission estimates. Even where sites are regulated, many are regulated only at local authority level, so there is no national dataset that covers all these sites and which can be accessed for the purposes of inventory compilation.

For some sectors there is a lack of suitable and up-to-date literature emission factors. This is particularly the case for solvent use in coatings and consumer products: solvents are used in a huge range of products and there is very little information from which to generate emission factors. Emission factors generally can be quite old and these older factors may not be as appropriate for the current day. It can be difficult to track how practices have changed in unregulated and local-authority regulated sites, and how this may have affected emission factors, e.g. due to changes in types of solvents used or abatement of emissions or other process changes.

There are relatively few emissions data available from industry sources for the NAEI's NMVOC inventory compared with the amount of data available for other pollutants such as SO_2, NO_x and CO_2. Overall, these challenges lead to relatively high levels of uncertainty in both the activity data and emission factors that underpin key sectors in the inventory.

4.3 Trends in total NMVOC emissions in the UK

Figure 10 shows the trends in NMVOC emissions from 1990-2017 according to the NAEI, grouped into ten major VOC source categories, plus projections for 2020 and 2030.

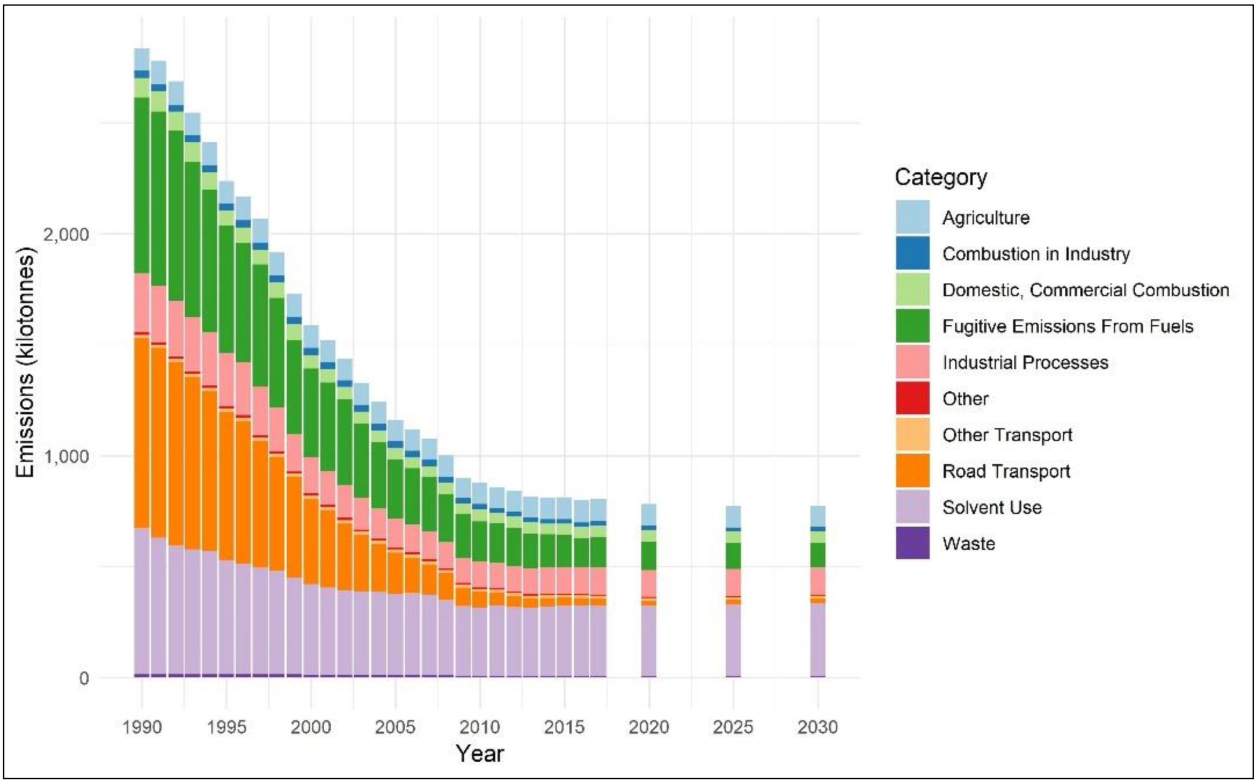


Figure 10: UK NMVOC emissions from anthropogenic sources from 1990-2017 and projected to 2030. Source: 2017 NAEI

National emissions of VOCs have decreased from 2,837 ktonnes in 1990 to 807 ktonnes in 2017, a fall of 72%, mostly driven by reductions in emissions from road transport, and fugitive emissions from fuels. The decrease in road transport emissions has been mainly due to the introduction of more stringent vehicle emission standards such that by 2017 this sector contributes only around 4% of total UK NMVOC emissions compared with 30% in 1990. The decrease in fugitive emissions from fuels mainly reflects the decline in coal mining activity and emission controls in the production of petroleum fuels, although these sources still contributes around 17% of total UK emissions in 2017.

The largest contribution to NMVOC emissions in 2017 is from solvents. Emissions have decreased for this sector, but by smaller amounts than road transport and fugitive emissions from fuel handling such that they now contribute 40% of total UK emissions of NMVOCs. There have also been relatively smaller reductions in emissions from industrial processes such that this sector now contributes 15% of total emissions; these emissions now mostly come from the food and drink industry which have been increasing since 1990. Based on the current inventory, the UK has met the NECD emissions target for NMVOCs of 1,200 ktonnes set for 2010 and all subsequent years.

The last twenty years have seen a substantial re-ordering of the relative contributions of the major VOC source sectors. Figure 11 shows the same data but as a percentage contribution made to overall annual national NMVOC emissions, with a steep decline in road transport contribution and steady growth in the contribution from solvent emissions.

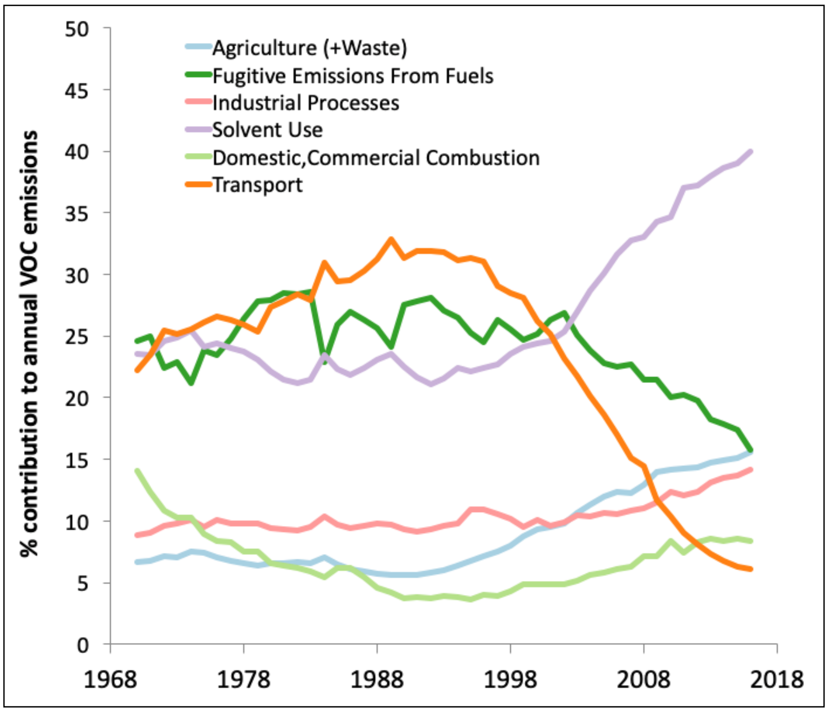


Figure 11. Trends in estimated national emissions of VOCs as a percentage of the overall annual national total, 1970 to 2016, data from uk-air.gov.uk and National Atmospheric Emissions Inventory.

The shift in contributing sources is significant in that that the exact chemical composition of NMVOC in air depends on the dominant emissions source. Historically important sources such as road transport emitted primarily aliphatic non-methane hydrocarbon compounds (reflecting gasoline composition) and many of those hydrocarbon species were prioritised for measurement in the automated hydrocarbon network. The major species emitted under the Solvents categorisation are different (see later sections) and there is evidence of a gap growing between those VOCs that make up the bulk of national emissions and what is currently monitored in ambient air.

4.4 UK Emission Projections for NMVOCs

Figure 10 showed projections of UK NMVOC emissions in 2020, 2025 and 2030. The projections are based on various assumptions on future activities and emission factors. Most assumptions about changes in fuel consumption and industrial activity are based on the ‘Energy & Emissions Projections’ provided by the Department for Business, Energy & Industrial Strategy in February 2019 (BEIS, 2019). Other Government projections, such as those for population, are used to forecast activity for non-combustion sources, e.g. for use of domestic products such as cosmetics and toiletries. For industrial processes where there are only one or a few sites operating that type of process, it is generally assumed that activity remains constant unless information is available indicating either closures of sites or proposals to increase capacity or to construct new sites.

Projections for stationary combustion, solvents and process sources generally assume a ‘worst-case’ scenario where emission factors in future years are the same as in the 2017 base year. This reflects a lack of evidence on which to base projections for emission factors, coupled with the assumption that the potential for further reduction in emissions is likely to be limited at those sites which have already been regulated for many years. The implication of this is that projections for these stationary combustion and process sources are more likely to overestimate than to underestimate emissions, although that overestimation may be slight. Some trade bodies have provided estimates of NMVOC emissions in 2020 and 2030, for example for the use of paints and adhesives.

For road transport, a more detailed set of assumptions are made to predict future emissions using DfT’s latest traffic forecasts and assumptions on new car sales which are used in the NAEI’s fleet turnover model to predict the future fleet composition. This takes into account the fleet penetration of emission standards up to Euro 6d/VI as well as battery and hybrid electric vehicles. The vehicle activity data are projected at a fairly disaggregated level, including by road and area type, and used in conjunction with NMVOC emission factors from the EMEP/EEA Emissions Inventory Guidebook and the COPERT 5 model (Emisia, 2018).

Further details on the UK’s emission projections are provided in the UK’s Inventory Report provided on the NAEI website and projections data submitted to CLRTAP are also available at https://cdr.eionet.europa.eu/gb/un/clrtap/projected/envxio6gq/index_html .

Whilst a small further reduction in emissions is predicted to occur up to 2020, emissions then remain fairly constant up to 2030. This is mainly due to the fact that emissions from certain sources important in the past such as road transport have already been reduced significantly and there remains little headroom for further reductions. There are currently no further regulations for emission reductions beyond Euro 6/VI. In addition to this, emissions from sources which currently make a significant contribution to the UK totals such as solvent use, food and drink and industrial processes remain fairly flat or increase slightly because emission factors are assumed to remain constant whilst activities are predicted to remain static or increase slightly.

Member States are required to report emissions of NMVOCs to the revised NECD from certain agricultural processes (manure management and agricultural soils), but these emissions are not required to be accounted for in the National Total emissions for the purpose of complying with the 2020 and 2030 ceiling targets. The 2020 and 2030 NECD targets for NMVOCs are based on a reduction commitment of 32% and 39%, respectively, relative to 2005 levels excluding these sources. The NAEI’s current projections in the national totals with these agricultural sources included and excluded are shown in Figure 12 and compared with the NECD emission targets for these years. The current NAEI projections predict that the target will be met for 2020, but not for 2030. Based on these latest projections, the UK will need to take further action on reducing NMVOC emissions to meet its commitments for 2030.

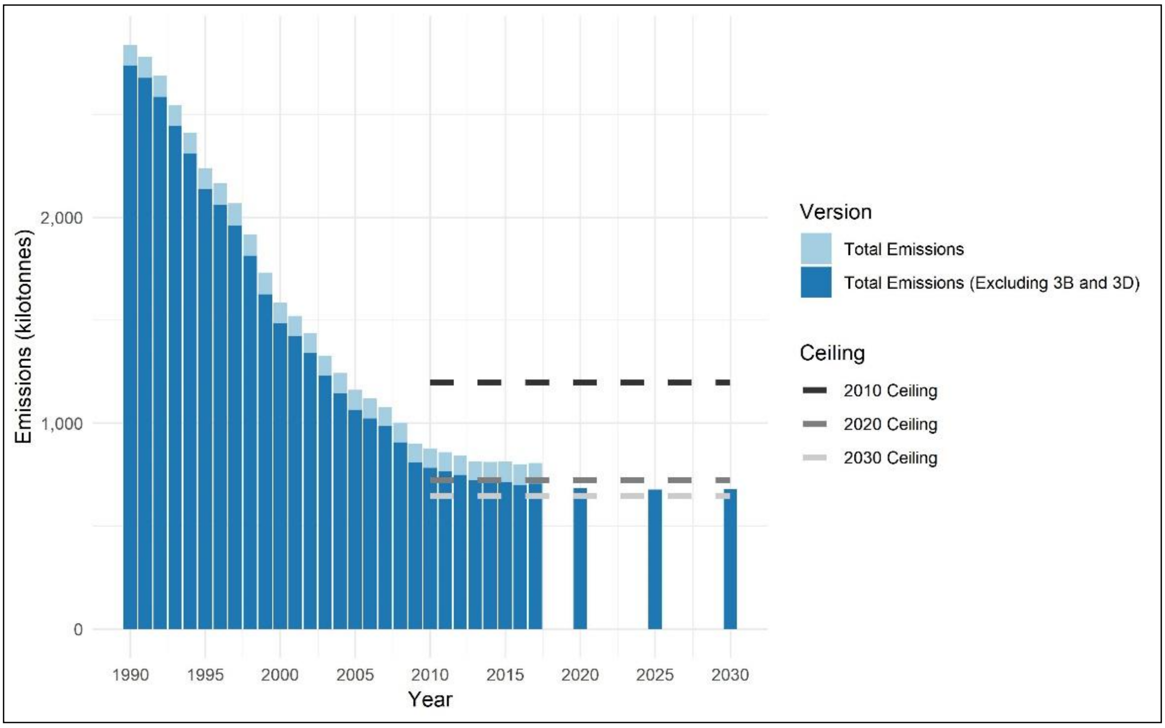


Figure 12: UK NMVOC emissions from anthropogenic sources projected to 2030 with and without agricultural sources (3B and 3D) included for compliance with NECD 2020 and 2030 ceilings. Source: 2017 NAEI

4.5 Solvent and Industrial Process Sectors

Emissions from the use of solvents and other volatile chemicals in industry and in consumer products, fuel production and distribution, food and drink manufacture and other non-combustion industrial processes accounted for 72% (579 ktonnes) of all UK NMVOC emissions in 2017, according to the NAEI. Both the solvent and industrial process sectors cover a diverse range of emission source categories: the NAEI identifies 136 separate categories across the two sectors. In the discussion below, these 136 categories have been grouped into nine sub-sectors and the contributions of the different sub-sectors to overall emissions from solvents and industrial process emissions are shown in Figure 13.

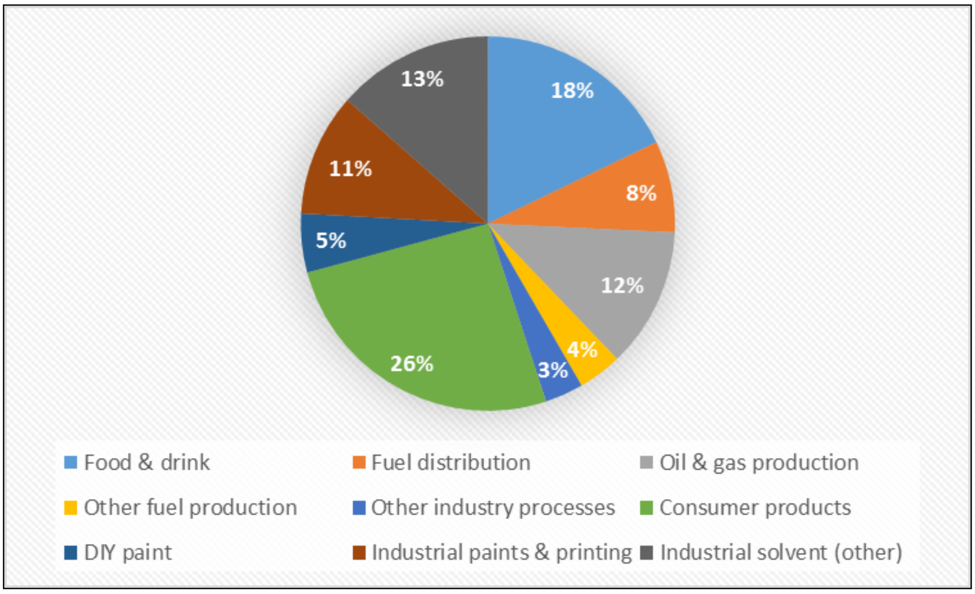


Figure 13 Contribution of different emission sources to the overall solvent and industrial process sector emissions of NMVOCs in 2017.

The largest share within this sector is the consumer products sub-sector which covers aerosol and non-aerosol based personal care, household and car-care products. Emissions occur from a wide range of products but aerosols generally, fragrances, and vehicle screenwash are the largest contributors. The emission estimates are based on data provided by industry for some years with assumptions or extrapolation techniques using available proxy data (e.g. population) to fill gaps for other years. Emissions from industrial use of solvents, for example in paints, adhesives and inks, are similar in magnitude to those from consumer products and are estimated using data provided by industry and regulators. Because of the degree of extrapolation needed to generate emission time-series for the consumer products sub-sector, the estimates are relatively uncertain compared with those for industrial solvent use.

The European Solvents Industry Group (ESIG) has recently reported NMVOC emission inventories for solvent use in individual countries based on industry-wide sales data (Pearson, 2019). This study compared ESIG estimates of solvent emissions with NMVOC emissions reported in national inventories and concluded that national inventories across the EU as a whole are over 30% too high by comparison with ESIG estimates. For the UK, the latest NMVOC figures from the NAEI for the year 2013 are 79% higher than the ESIG figures for solvent. However, there is an important difference in the scope of the two inventories which is acknowledged in the paper by Pearson.

The scope of the ESIG figures is intended to be limited to ‘solvents’ only, whereas the NAEI and other national inventories have to cover all NMVOC emissions, including non-solvents. The ESIG figures do not even include all solvents at present – methanol and ethanol are excluded, as are liquefied propane/butane which are used in aerosols primarily as propellants. The UK inventory does include these NMVOCs and when these are accounted for by subtracting emission estimates for these specific NMVOCs from the NAEI figure, the agreement with ESIG is better, with the UK inventory for the remaining

NMVOCs exceeding the ESIG estimate for 2013 by 21%. It is to be expected that the NAEI figure should still be higher since it will include other non-solvents in addition to those mentioned above, however it is not currently possible to quantify emissions of these other non-solvents.

The use of solvents in many industrial processes has been regulated since the 1990s and, as significant reductions in emissions have already been achieved, further large reductions are thought unlikely to occur. Many industrial users of solvent have installed abatement equipment or use re-formulated products in order to reduce VOC emissions in compliance with EU Industrial Emissions Directive requirements. In most sectors it is likely that there will continue to be modest reductions in emissions over time as business develops improvements in processes or reformulates products to reduce the need for solvents. Industry has provided emission projections for certain types of industrial coatings but for other sectors where there is no information, a conservative approach is adopted: that emission factors will remain constant into the future.

In the case of solvent use in consumer products, emissions can only be reduced by eliminating or reducing the levels of solvent in those products, or by eliminating or reducing the demand for the product itself. In the absence of any regulation specifically to reduce NMVOC emissions from consumer products, it is assumed that there has been no reduction and that instead emissions have grown in line with population, numbers of households or numbers of road vehicles.

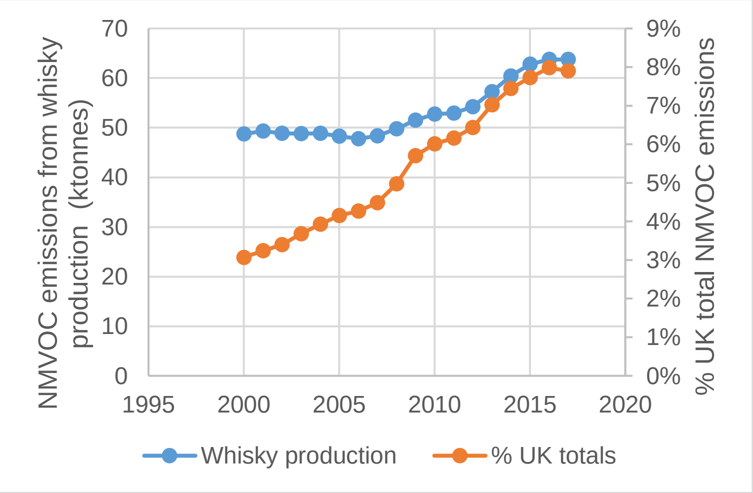
The food and drink industry contributes 18% of all the NMVOC emissions in this solvents and industrial process sector and 13% of total UK NMVOC emissions in 2017. This sector is dominated by emissions from the whisky industry which contributes 62% of the total food and drink industry emissions, but emissions also occur from bread baking (8%), production of cakes, biscuits and cereals, barley malting, processing of meats, fats, oils and animal feeds. Emissions from the production of whisky has been increasing in line with increases in production. Further details are provided in Box 1. NMVOC emissions from these sources are not regulated and so emission factors for 2017 are considered equally appropriate for 2020-2030. Activity projections generally rely on the BEIS projection for industrial output in the food, drink and tobacco sector.

Text Box 1. Emissions of VOCs from Whisky Production in the UK

There are many individual sources that contribute to the total NMVOC emissions inventory in the UK. One of the largest of these is the production of Scotch Whisky which is reported as part of the sector covering emissions from processing in the food and drink industry. Emissions are estimated by the National Atmospheric Emissions Inventory (NAEI) using production activity data sourced from the Scotch Whisky Association. Emission factors are UK-specific and derived from information supplied by industry. The NMVOC emitting processes are either mainly or entirely outside the scope of the Industrial Emissions Directive so remain constant over time. The Figure shows the trends in emissions from whisky production over the period from 2000 to 2017 according to the latest version of the NAEI. Emissions have increased by 31% over this period reflecting the fact that NMVOC emissions from this source have not been regulated, so emission factors remain constant and total emissions increase in line with whisky production. Since NMVOC emissions from other sources have decreased over time, the contribution that whisky production makes to total UK NMVOC emissions has increased from 3.1% in 2000 to 7.9% in 2017.

All the NMVOC emissions from whisky production are in the form of ethanol and it is estimated by the NAEI that whisky production accounts for around 50% of all ethanol emissions in the UK. Emission estimates are considered quite reliable due to close monitoring of production and losses carried out by the industry both because of the value of the product, and the purposes of calculating duty to be paid. The NAEI estimates NMVOC emissions at various stages in the whisky production and storage process including casking, distillation and maturation, but by far the majority of the emissions (>90%) occur during the maturation stage.

Many of the malt whisky distilleries are concentrated in the Speyside area of Scotland and in the Highlands & Islands regions. Large quantities of maturation/storage is carried out at large bonded warehouses and where malt and grain whiskies are blended, not at the distilleries themselves. There are also an increasing number of small micro distilleries in the UK, producing gin, vodka as well as whisky. The NAEI includes emissions from these sources, but these are of a relatively small scale compared with the larger Scotch whisky distilleries and warehouses.



4.6 Emissions from Road Transport.

For the road transport sector, the NAEI reports exhaust emissions of NMVOCs and its emissions from evaporative losses of fuel vapour from petrol vehicles. Emissions from re-fuelling at filling stations are reported separately under the fugitive emissions from fuel distribution sector. The method used for road transport in the NAEI follows the method in the European COPERT 5 model and described in the EMEP/EEA Emissions Inventory Guidebook. The method uses average speed-related emission factors for hot exhaust emissions of total hydrocarbons for detailed vehicle categories (vehicle type, weight and/or engine size) and Euro standards for petrol cars, diesel cars, petrol and diesel light goods vehicles, rigid and articulated HGVs, buses and coaches and mopeds and motorcycles and combines these with detailed traffic and fleet activity data derived from information provided by DfT. Separate estimates are made of methane emissions for each vehicle type and subtracted from the THC emissions to derive the NMVOC emissions.

Details of the method used by the NAEI to calculate UK road transport emissions are provided in the UK Inventory Report and also in the NAEI report by Brown et al (2018). The method is tailored to the road transport activity data for historical years available from DfT. This includes vehicle kilometres travelled each year by vehicle and road type (urban, rural and motorway) according to DfT’s national road traffic statistics and fleet compositional data according to vehicle licensing statistics and on-road information captured by Automatic Number Plate Recognition cameras at approximately 250 sites on different types of roads around the UK from DfT’s roadside surveys. Emission factors are calculated according to average speeds of vehicles on different road types.

A separate methodology from the EMEP/EEA Guidebook based on average trip lengths is used to estimate the excess emissions occurring during cold starts. This was a particularly important source of NMVOC emissions from petrol cars, particularly the early Euro standards because of the time it took for three-way catalyst systems to warm up to their effective operating conditions.

Evaporative emissions from petrol-fueled vehicles are estimated in the NAEI using the Guidebook method for three different processes: diurnal losses, hot soak and running losses. Emissions are dependent on ambient temperature and fuel vapour pressure and different factors are provided for vehicles with and without carbon canisters for evaporative emission controls. All vehicles from Euro 1 onwards are fitted with these devices, so evaporative emissions have been decreasing from the early 1990s with the penetration of these vehicles in the fleet. The method also takes into account the reduction in Reid Vapour Petrol of petrol sold in the UK since 2000, as required for compliance with the EU Fuel Quality Directive 98/70/EC, amended by Directive 2009/30/EC.

The same methodology is used to project future emission projections from road transport, using sources of information from DfT and assumptions described earlier.

Figure 14 shows the trend in NMVOC emissions from road transport in the UK by vehicle type from 1990 to 2017 and projected to 2030. Evaporative emissions are shown separately from exhaust emissions. This figure highlights the dominance of petrol cars and evaporative emissions in the earlier years of the time-series and their rapid decline with the fleet penetration of cars with three-way catalyst and carbon canister evaporative controls from the early 1990s and the successive tightening of further Euro standards for new vehicles. This has been the main driver in reducing overall emissions from the sector, but the gradual switch to lower NMVOC emitting diesel cars in the 2000s has also had an influence. However, this downward trend has been slowing down in more recent years as emission factors for the later Euro standards for petrol cars are so low that further reductions offer little further gains. In 2017, total road transport emissions are estimated to be 29.9 ktonnes (4% of UK total emissions) and whilst petrol cars are still the dominant source of NMVOC emissions from road transport at 66%, the relative contribution of diesel vehicles has increased to 21%.

This slow-down in the rate of emission reductions is expected to continue to 2030, with no further significant reductions in emission factors currently expected and traffic predicted to increase. Emissions for road transport remain fairly static at around 22 ktonnes between 2020 and 2030 and become dominated by evaporative losses.

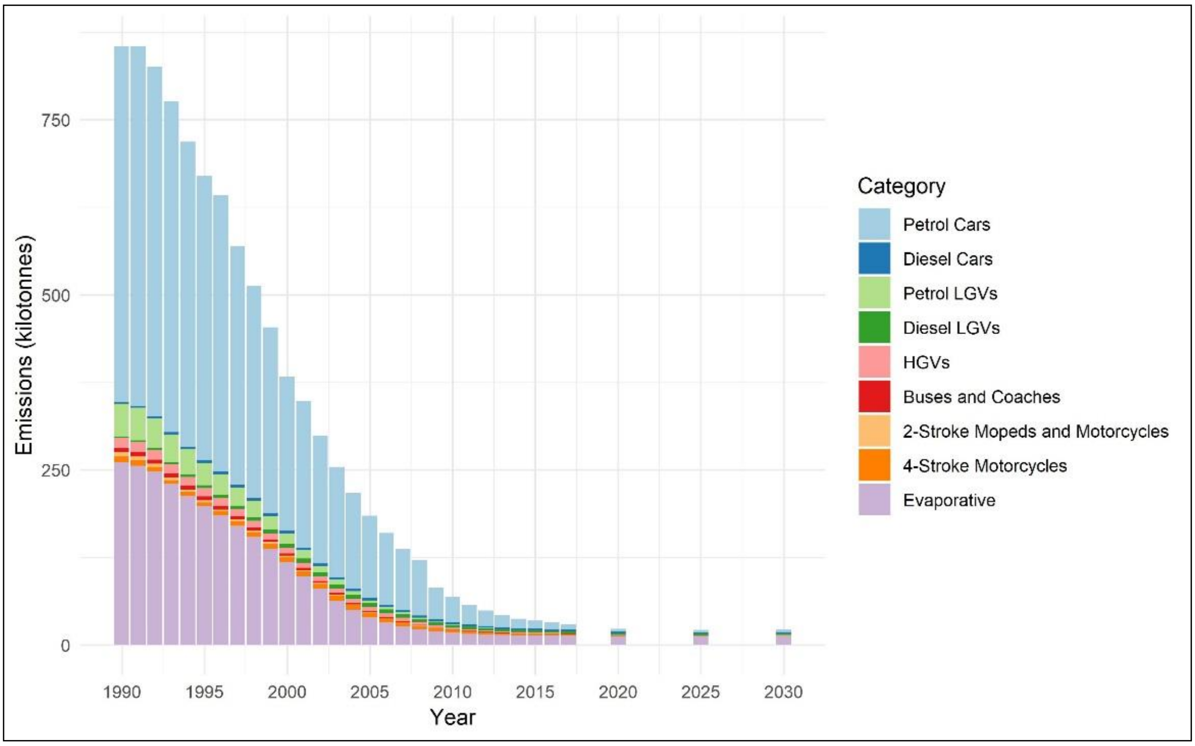


Figure 14. UK NMVOC emissions from road transport by vehicle type from 1990-2017 and projected to 2030. Source: 2017 NAEI

4.7 Emissions from 2-stroke vs 4-stroke petrol vehicles and machinery.

The NAEI takes into account the different emission factors for 2-stroke and 4-stroke mopeds and motorcycles, with much higher emission factors used for 2-stroke vehicles as a consequence of less complete combustion. There are no statistics on the number of 2-stroke and 4-stroke mopeds and motorcycles in the fleet, but according to anecdotal evidence from motorcycle enthusiasts most 2-stroke motorcycles are confined to the smaller <150cc class of vehicles. Moreover, due to the tighter emission regulations on mopeds and motorcycles, fewer vehicles compliant with Euro 3 standards introduced in 2006 will use 2-stroke engines. The NAEI estimates that mopeds and motorcycles contributed 3.8 kt NMVOCs, about 13% to total NMVOC emissions from the road transport sector in 2017, with 0.22 kt NMVOCS, less than 1%, coming from 2-stroke vehicles. As a proportion of total UK emissions these represent 0.5% (all mopeds and motorcycles) and 0.03% (2-stroke) emissions.

The NAEI also covers emissions from other transport and non-road mobile machinery running on petrol engines. These include lawn mowers and other forms of handheld garden machinery, small machinery used in industry and forestry and small recreational water craft. Some of these machines will also use 2-stroke engines. The NAEI estimates that altogether these sources contributed 15.4 kt, around 2%, to total UK NMVOC emissions in 2017. The contribution of 2-stroke engines to these emissions is highly uncertain, but are estimated to be 1.4 kt, hence around 0.18% of total UK emissions.

4.8 Spatially resolved inventories of NMVOC emissions.

The NAEI spatially resolves the UK emissions of NMVOCs as maps on a 1x1 km grid. Figure 15 shows a map of NMVOC emissions for 2016.   Details of the methods used for mapping emissions are provided in the NAEI’s annual mapping reports (Tsagatakis *et al*., 2018) and each year a new map of emissions for the most recent inventory year is published. The geographical distribution of emissions across the UK is built up from a number of data sources and methods that are individually tailored to each sector.

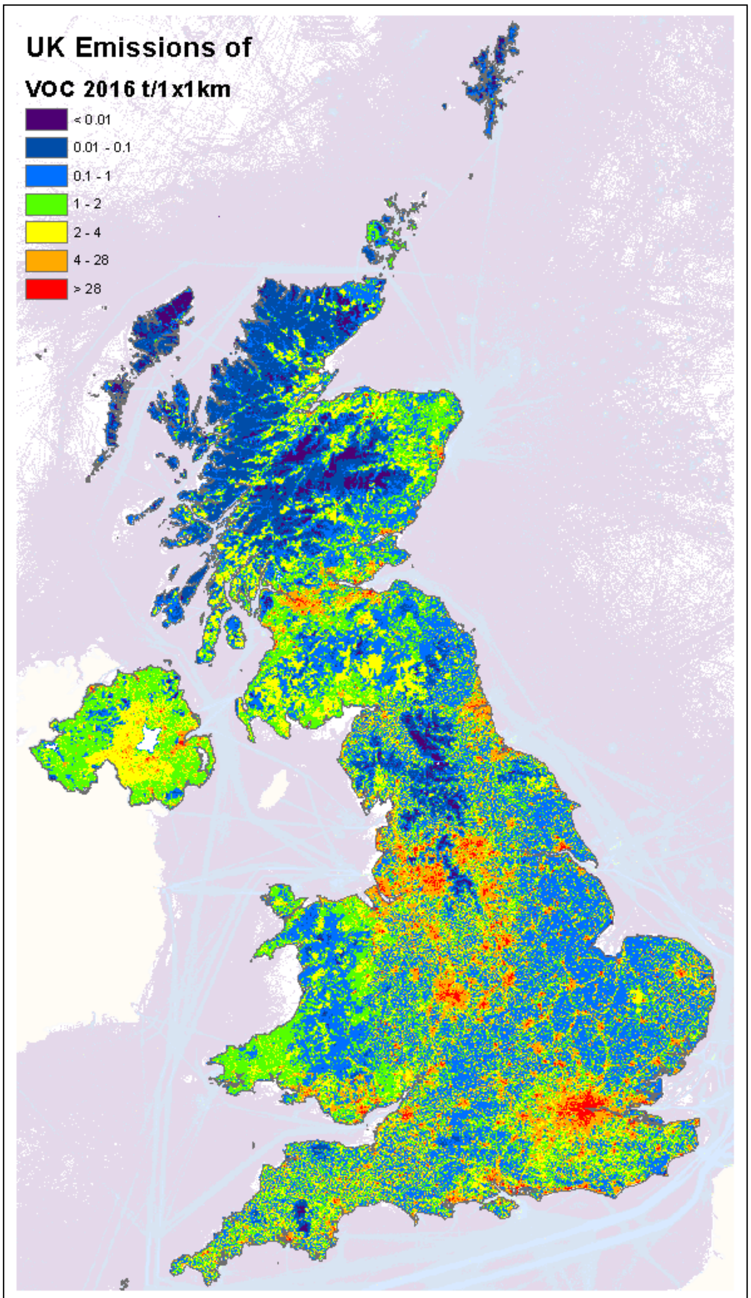


Figure 15 Map of UK emissions of NMVOCs in tonnes per year for 2016 on a 1x1 km grid based on the NAEI.

Point source data for industrial processes received from regulators and operators can be mapped directly using known grid references for the installation. This has been used to map emissions from refineries and chemical industries, for example. Recent point source data for a small number of solvent-using processes are available via the European Pollutant Release and Transfer Register (E-PRTR), but only older data are available for most sites. A significant amount of emissions of NMVOCs come from industrial processes which are not regulated such as bakeries, breweries and the manufacture of malt whisky and other spirits so point source data are not available. The mapping of emissions from these sources, from the use of solvents and other more diffuse sources of NMVOC emissions is therefore much more uncertain and is done using a variety of techniques often with use of a surrogate activity statistic with known geographical coverage to map out national estimates of emissions. For example, in the case of malt whisky distilleries, emissions of VOCs from distillation are distributed using estimates of whisky capacity at each site, except in cases where this is not known and where the number of stills is used as a measure of the scale of operations and therefore emissions. A grid based on census population data is used to map emissions from decorative paint use and other household products.

Emissions from road transport are mapped to the UK road network derived from the Ordnance Survey Open Roads using DfT's traffic count point data allocated to a section of the major road network. Traffic flow data are mapped as annual average daily flows for each type of vehicle and combined with fleet-weighted emission factors calculated for the inventory year for each vehicle type according to average speed of the road link. Different mapping procedures are used for minor roads.

4.9 Uncertainties in emission inventories.

There are uncertainties in the national emission estimates of NMVOCs and in the spatially-resolved inventories. Uncertainties in the national emission estimates are estimated using an approach described in the EMEP/EEA Emissions Inventory Guidebook which investigates the impact of the assumed uncertainty of individual parameters (such as emission factors and activity statistics) upon the uncertainty in the total emission of each pollutant. Details of the approach are given in the UK Inventory Report. The uncertainty in total NMVOC emission estimates for 2017 is ±21% at the 95% confidence interval. The NMVOC inventory is more uncertain than those for SO_2 and NO_x. This reflects:

- the difficulty in maintaining fully up-to-date emission estimates for the many sectors where industry or regulator data are required but can only be obtained periodically (e.g. for solvent use);
- the assumption that NMVOC emissions reported to regulators are generally slightly more uncertain for NMVOC than for NOx or SO_2. NMVOC can be emitted from processes both from stacks and as fugitive leaks, and it is therefore more difficult to monitor than NO_X and SO_2 that tend to be only emitted from stacks. NMVOC emission estimates for processes such as refining and chemicals manufacture are therefore assumed to be relatively uncertain;
- the absence of good activity data for some sources, such as consumer products
- the large contribution to UK emissions of NMVOC of some very uncertain sources such as the agriculture sector.

However, given the broad range of independent sources of NMVOCs, there is a high potential for error compensation and this is responsible for the relatively low level of uncertainty compared with many other pollutants in the NAEI such as metals and persistent organic pollutants.

The spatially-resolved emissions inventory is generally more uncertain than the national totals. This is because it relies on surrogate data of various quality and applicability to map out emissions from certain sources where only national totals can be estimated with any confidence. This is particularly the case for many industrial source categories that are fairly widespread across the UK – sources such as vehicle refinishing or other small coating processes, food manufacture, and dry cleaning. The extent by which an inventory is made up of area sources relative to point sources can be used as a measure of the level of uncertainty in the mapped inventory. A map of a pollutant's emissions which is dominated by point sources (like maps for SO_2) can be considered to have higher quality than a map where emissions are dominated by area sources because the former are based upon reliable data produced for regulatory purposes and the location of emissions is known. Maps of NMVOC emissions fall in the latter category where point sources make up only 17% of emissions in 2016 compared with SO_2 where point sources made up 67% of emissions.

The NAEI also uses a semi-quantitative approach to assess uncertainty in the maps using 'data quality ratings' ranging from 1 (highest quality) to 5 (lowest quality) for the mapping of emissions of each pollutant and source. Details are given in the NAEI's mapping report (Tsagatakis *et al*., 2018) and were also discussed in the AQEG report "*Linking Emission Inventories and Ambient Measurements*" (AQEG, 2013). The rating is based on an assessment of the quality of the emissions data for point sources and area sources and the quality and applicability of the data used to define their geographical distribution. The NAEI mapping report gives the overall quality ranking for maps of different pollutant emissions and shows the quality of NMVOC emissions as being mid-range, i.e. of lower quality than maps of CO_2 and SO_2, but of higher quality than maps of PM_{10} and comparable in quality to maps of NO_x emissions.

4.10 Speciated NMVOC inventory

There is no statutory requirement to report national inventories of individual NMVOC species to the NECD or CLRTAP, but clearly providing a comprehensive speciated inventory is necessary for other purposes[11]. Given the different chemical reactivities of each component, a speciated inventory is essential for atmospheric models of ozone and secondary organic aerosol formation. It is also necessary for interpretation of ambient concentration measurements of organic compounds and how such information can be used to verify NMVOC inventories and identify prominent sources at specific locations. This will ensure that the correct VOC species is tracked to confirm policies aimed at reducing specific sources are effective.

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[11] It should be noted that explicit inventories for benzene and 1,3-butadiene are reported by the NAEI each year so these can be used for modelling ambient concentrations to check for compliance with the UK's Air Quality Strategy for these pollutant

The UK is one of the few countries to have developed a comprehensive speciated inventory for NMVOC emissions and this is widely used in atmospheric modelling in the UK and abroad. The speciated inventory was first added to the NAEI in the mid-1990s but the lack of significant new data sources means that development essentially finished in the early 2000s when details of the methodology were published (Passant, 2002). The NAEI's NMVOC inventory is broken down into 664 chemical species or groups of species using profiles for each detailed emission source sector.

The information that was used in the development of the species profiles came from various sources. Industry trade associations in the 1990s provided some speciated estimates including the Solvent Industry Association, the British Coatings Federation and British Aerosol Manufacturers Association. The solvent industry also helped with speciation of white spirit and other hydrocarbon mixtures. The Environment Agency's Pollution Inventory and similar inventories compiled by other UK regulators include some details of speciation, although the amount of detail is now much less than was the case in the early 1990s. Some local authorities were able to provide data for some solvent users, also in the 1990s. Some analysis was undertaken of fugitive emissions at petrol stations and species profiles were also provided by the refinery sector. The profiles for vehicle exhaust emissions were taken from the EMEP/EEA Emissions Inventory Guidebook. An important source for other sectors was the USEPA SPECIATE database.

Unlike the total NMVOC inventory, the speciated inventory methodology is not currently subject to annual review and improvement, although speciated estimates can still be generated using the existing methodology. This partly reflects an increasing difficulty in obtaining the data which would be needed to improve the speciation, but it also reflects the assumption that many of the existing species profiles are probably as accurate as is possible without committing significant further resources for research.

As much of the data used to develop the speciation profiles were gathered during a short period in the late 1990s and early 2000s, and since more recent data are not available, it has to be assumed that the species emitted by a particular source are the same in all years. While this is going to be essentially true for sources such as bread baking or petrol distribution, it is probably not true of sources such as industrial coating processes, chemicals manufacture or the formulation of consumer and household products. However, even where changes occur, it is likely that they will be gradual and relatively small. For example, the species emitted by the chemical industry will change from year to year because each site will emit a particular mix of NMVOC species but some plants may increase production, or close, or fit abatement technologies, thus changing the contribution of that plant to the overall mix of NMVOCs emitted. Even at the level of individual chemical sites, the speciation may change from year to year: many plant use or produce a variety of volatile chemicals and the contributions of individual NMVOC species will change depending on the consumption/production of that species, as well as being affected by the level of control of emissions. Controls on solvent-using processes have led many process operators to use products that contain less organic solvent, and these products may also contain different organic solvents to those in the products they replace.

Research is needed to identify which profiles may need to change over time, and to assess what impact these changes would be likely to have on overall UK emissions of NMVOC species.

The use and interpretation of the NAEI VOC speciation inventory are covered elsewhere in this report. In spite of the limitations of the speciated inventory, principally because it is based on relatively old information, there are some key themes. For example, the increasing dominance of ethanol and methanol among the emitted species suggests monitoring ambient concentration trends for these compounds may be warranted in order to verify the effectiveness of policies aimed at reducing key sources of NMVOCs. The speciated inventory suggests emissions of light alkanes and alkenes, many of which come from combustion sources, still make a significant contribution, but emissions have decreased from pre-2000 levels following trends in total NMVOCs from these sources, and broadly in line with measurements data from the hydrocarbon monitoring network.

4.11 Impacts of a changing VOC speciation in emissions.

There are around 360 different individual VOC sources included within the NAEI and each of these has some representative chemical speciation associated with it, and so it is possible to interrogate the NAEI for total amounts and trends in individual compounds. Although in total the NAEI contains data on over 700 different VOCs, a much smaller subset of ~ 40 VOCs represents typically between 60 and 70 % of total national emissions by mass. Table 7 shows the top 40 VOC emissions from anthropogenic sources in the UK for five year intervals since 1990 and for the most up to date year, 2017. Those VOCs marked in green are currently included as observations in the automated hydrocarbon network, whilst those marked in red are not routinely measured. Isoprene is excluded from this list, but is measured in the automatic network. In a few cases NAEI classes of VOC are included, where those classes cover complex isomeric groups rather than individual species. The table shows the percentage of VOCs in each time-slice that are measured in the Defra measurement automatic network, for the top 40 and top 20 emissions by mass.

Table 7. Top 40 VOC emissions (by mass) from anthropogenic sources in the UK for selected years 1990 -2017, red = not currently measured, green = measured. Data is taken from the NAEI, and in some cases refers to a sub-class of compound rather than individual VOC.

Rank / Year	**1990**	**1995**	**2000**	**2005**	**2010**	**2015**	**2017**
1	🟩 ethane	🟩 butane	🟩 butane	🟥 ethanol	🟥 ethanol	🟥 ethanol	🟥 ethanol
2	🟩 butane	🟩 ethane	🟥 ethanol	🟩 butane	🟩 butane	🟩 butane	🟩 butane
3	🟥 ethanol	🟥 ethanol	🟩 ethane	🟩 ethane	🟩 ethane	🟩 ethane	🟥 methanol
4	🟩 propane	🟩 toluene	🟩 propane	🟩 propane	🟩 propane	🟥 methanol	🟩 ethane
5	🟩 toluene	🟩 propane	🟩 toluene	🟩 pentane	🟥 methanol	🟩 propane	🟩 propane
6	🟩 pentane	🟩 pentane	🟩 pentane	🟩 toluene	🟩 ethylene	🟩 pentane	🟩 pentane
7	🟩 2-methylbutane	🟩 ethylene	🟩 ethylene	🟩 ethylene	🟩 pentane	🟩 ethylene	🟩 ethylene
8	🟩 ethylene	🟩 2-methylbutane	🟩 2-methylbutane	🟥 methanol	🟩 toluene	🟩 m-xylene	🟩 m-xylene
9	🟩 3-methylpentane	🟩 3-methylpentane	🟩 3-methylpentane	🟩 2-methylbutane	🟩 benzene	🟩 toluene	🟩 toluene
10	🟩 2-methylpropane	🟩 benzene	🟩 hexane	🟩 benzene	🟩 2-methylbutane	🟩 benzene	🟩 benzene
11	🟩 hexane	🟩 2-methylpropane	🟩 benzene	🟩 m-xylene	🟩 m-xylene	🟩 2-methylbutane	🟩 2-methylbutane
12	🟩 benzene	🟩 hexane	🟩 m-xylene	🟩 2-methylpropane	🟩 2-methylpropane	🟥 formaldehyde	🟥 decane
13	🟩 m-xylene	🟩 m-xylene	🟩 2-methylpropane	🟩 hexane	🟩 hexane	🟩 hexane	🟥 formaldehyde
14	🟩 ethylbenzene	🟩 propylene	🟥 methanol	🟥 formaldehyde	🟩 formaldehyde	🟩 2-methylpropane	🟥 acetone
15	🟩 propylene	🟩 ethylbenzene	🟩 ethylbenzene	🟩 heptane	🟥 decane	🟥 decane	🟩 hexane
16	🟩 o-xylene	🟩 2-methylpentane	🟩 propylene	🟩 propylene	🟥 acetone	🟥 acetone	🟩 2-methylpropane
17	🟩 2-methylpentane	🟩 o-xylene	🟩 heptane	🟩 ethylbenzene	🟥 2-butanone	🟥 2-butanone	🟥 2-butanone
18	🟩 heptane	🟥 other, C>13	🟥 formaldehyde	🟥 acetone	🟩 propylene	🟩 ethylbenzene	🟩 1,2,4-tmb
19	🟥 other, C>13	🟩 m & p-xylene	🟩 2-methylpentane	🟥 decane	🟩 heptane	🟩 1,2,4-tmb	🟩 ethylbenzene
20	🟩 m & p-xylene	🟥 methanol	🟥 trichloroethene	🟩 1,2,4-tmb	🟥 2-propanol	🟥 2-propanol	🟥 2-propanol
21	🟩 acetylene	🟩 heptane	🟩 o-xylene	🟩 3-methylpentane	🟩 1,2,4-tmb	🟩 heptane	🟩 heptane
22	🟥 trichloroethene	🟥 formaldehyde	🟩 1,2,4-tmb	🟥 2-butanone	🟩 ethylbenzene	🟩 propylene	🟩 propylene
23	🟥 methanol	🟩 acetylene	🟥 other, C>13	🟩 o-xylene	🟥 3-methylpentane	🟥 ethyl acetate	🟥 ethyl acetate
24	🟩 2-methylpropene	🟥 acetone	🟥 acetone	🟩 2-methylpentane	🟥 2-methylpentane	🟥 C7 alkanes	🟥 undecane
25	🟥 formaldehyde	🟩 2-methylpropene	🟩 m & p-xylene	🟥 trichloroethene	🟥 o-xylene	🟩 3-methylpentane	🟥 nonane
26	🟩 1,2,4-tmb	🟩 1,2,4-tmb	🟩 acetylene	🟥 2-propanol	🟥 nonane	🟥 nonane	🟥 4-me-2-pentanone
27	🟥 acetone	🟥 trichloroethene	🟥 2-butanone	🟥 unspeciated alkanes	🟥 undecane	🟥 undecane	🟥 C7 alkanes
28	🟥 1,1,1-trichloroethane	🟥 methyl acetate	🟥 decane	🟥 other, C>13	🟥 C7 alkanes	🟩 o-xylene	🟩 3-methylpentane
29	🟥 methyl acetate	🟩 C9 aromatic	🟩 2-methylpropene	🟥 m & p-xylene	🟥 ethyl acetate	🟥 4-me-2-pentanone	🟩 o-xylene
30	🟥 C9 aromatic	🟥 2-butanone	🟥 C9 aromatic	🟥 C9 aromatic	🟥 4-me-2-pentanone	🟩 2-methylpentane	🟩 2-methylpentane
31	🟥 2-butanone	🟥 C7 alkanes	🟥 C7 alkanes	🟩 2-methylpropene	🟥 C13+ aromatic	🟥 C8 alkanes	🟥 C8 alkanes
32	🟥 decane	🟥 decane	🟥 2-propanol	🟥 C13+ aromatic	🟥 C8 alkanes	🟥 C13+ aromatic	🟥 1-propanol
33	🟥 C7 alkanes	🟥 C8 alkanes	🟥 unspeciated alkanes	🟥 4-me-2-pentanone	🟩 2-methylpropene	🟥 1-propanol	🟥 trichloroethene
34	🟥 2-propanol	🟥 2-propanol	🟥 methyl acetate	🟥 nonane	🟥 unspeciated alkanes	🟥 trichloroethene	🟥 C13+ aromatic
35	🟥 C8 alkanes	🟥 ethyl acetate	🟥 C8 alkanes	🟩 acetylene	🟥 trichloroethene	🟥 methylethylbenzene	🟥 methylethylbenzene
36	🟥 ethyl acetate	🟥 4-me-2-pentanone	🟥 ethyl acetate	🟥 undecane	🟥 methyl acetate	🟥 2-methylpropene	🟩 2-methylpropene
37	🟥 4-me-2-pentanone	🟥 unspeciated alkanes	🟥 4-me-2-pentanone	🟥 ethyl acetate	🟥 1-propanol	🟥 C10 alkanes	🟥 C10 alkanes
38	🟩 2-butene	🟥 1,1,1-trichloroethane	🟥 C13+ aromatic	🟥 C7 alkanes	🟥 other, C>13	🟩 1,3,5-tmb	🟥 ethyldimethylbenzene
39	🟥 tetrachloroethene	🟩 2-butene	🟥 nonane	🟥 methyl acetate	🟥 C9 aromatic	🟩 1,2,3-tmb	🟩 1,2,3-tmb
40	🟩 1,3-butadiene	🟩 1,3-butadiene	🟥 Alkanes C>13	🟥 Alkanes C>13	🟩 acetylene	🟥 ethyldimethylbenzene	🟩 1,3,5-tmb
% of total NAEI VOC emissions overed by top 40	72	71	70	67	67	67	67
Top 40 Measured: Unmeasured %	57.5	60	52.5	50	42.5	50	52.5
Top 20 Measured : Unmeasured %	90.00	85.00	80.00	75.00	65.00	65.00	65.00

The change in the dominant sources of VOCs that have occurred over the last 30 years has brought with it a change in the speciation of VOCs. This is complex to visualize in detail since the number of individual species within the NAEI is very large. One simple way to observe how the VOC speciation in the UK has changed over time is to examine the trends in mass emissions by VOC functional group type.

Figure 16 shows the absolute (in kilotonnes) and relative (% of annual emissions) contributions made to UK emissions for 13 classes of VOC functional groups. Alkanes, alkenes, aromatics, alcohols, aldehydes and ketones make up the bulk of emissions with small contributions from other classes such as acetates, volatile siloxanes (CVS), halogen-containing VOCs, nitro-VOCs, and vapour phase PAH. A further class of 'other' is used for trace species not falling into these main categories, such as organic acids, anhydrides and di-ols.

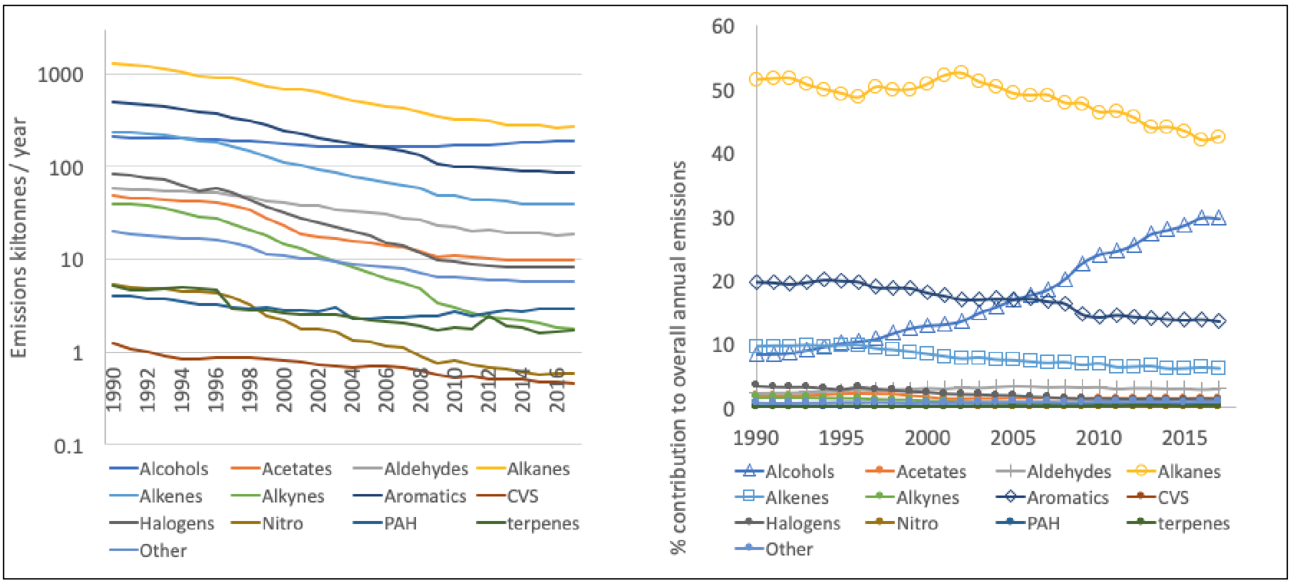


Figure 16. Left: Trends in estimated national emissions of functional group-type classes of VOCs. Right: Contribution of each functional group class to the overall annual national total, 1970 to 2017, expressed as percentage. Data from uk-air.gov.uk and National Atmospheric Emissions Inventory.

The stand out feature from Figure 16 is the growth in the significance of alcohols as a contributing component of the VOC mixture emitted in the UK. The increase arises due to increased emissions of ethanol from the whisky industries and from increases in domestic use of ethanol as a solvent, for example in personal care and household products. The change in emissions for the top 10 individual VOCs by mass between 1990 and 2017 is shown in Figure 17. At the start of the 1990s ethane was the most abundant emission, arising predominantly from leakage during natural gas extraction and the distribution network. Over the three decade period ethane, and the other hydrocarbons decline, whilst methanol remains broadly constant and ethanol emissions initially decrease then increase from around 2005 onwards.

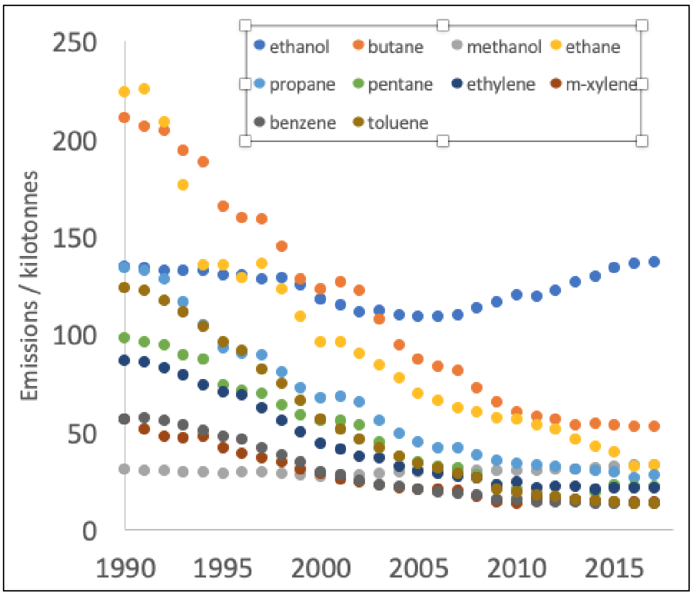


Figure 17. Estimated trends 1990-2017 in the UK emissions of the 10 most abundant VOCs within the UK NAEI.

The sources of ethanol within the inventory have changed over time, and help illustrate how the VOCs in the UK are no longer dominated by historical fossil fuel and combustion sources, and now come from other sectors such as food and drink production and domestic use of solvents. In 2017 the two most abundant VOCs with the NAEI are estimated to be ethanol and butane. Both have undergone very substantial change in terms of their sources of emissions, and this is shown in Figure 18.

For ethanol the past three decades have seen a decline in emissions relating to road transport and industrial usage, but an increase of ~20 kilotonnes / year at the end of the period from the whisky industry. Text Box 1 provided some further commentary on this source. There has also been growth in domestic emissions of ethanol, arising from increases in a range of different sources including cosmetics, toiletries, household products, aerosols and wood combustion and several others.

Examining the second most emitted VOC, *n*-butane, also helps illustrate how the major contributing sectors to VOC emissions are changing. In 1990 the overwhelming source of *n*-butane was related to fossil fuel extraction, refining and gasoline distribution. By 2017 this source of emissions had reduced by over 80%, leaving the domestic use of aerosol canisters as the largest estimated source of *n*-butane to UK air.

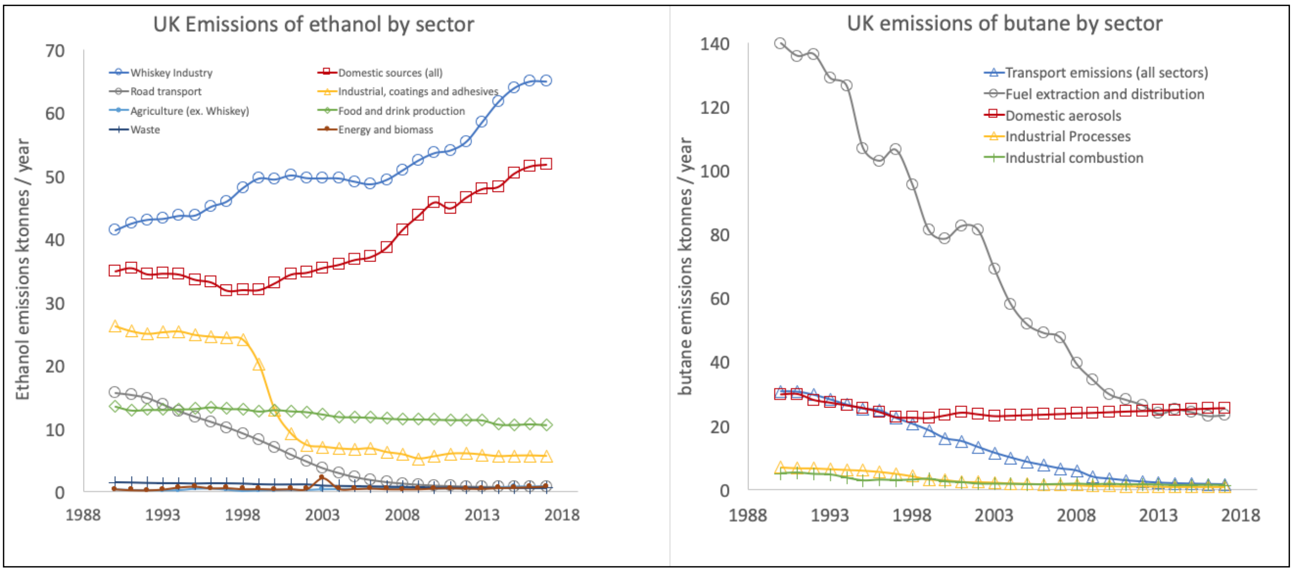


Figure 18. Estimated contributions from different sectors to the 1990-2017 trends in emissions of ethanol and butane. In both cases growth in non-fossil emissions overtake historic sources such as fuel evaporative losses and road transport emissions.

The continued growth in the significance of domestic solvent VOC emissions is particularly challenging since this is a highly diffuse type of emission and is dominated by VOC species that are not currently measured in the automatic network. In many cases the composition of VOCs in products is not well characterised and reporting in the inventory is highly uncertain. Overall estimated emission rates depend not only on information on the composition of products themselves but also on suitable activity figures, for example estimation of the fraction of a product that becomes airborne as a vapour (vs entering waste water systems for example), frequency of use and numbers of users.

Within the solvents classification of the NAEI, emissions are dominated by ethanol, methanol and butane, but many other VOCs are also released. Of the top 10 species emitted in the solvent class only three are currently monitored in the hydrocarbon network. Figure 19 shows the most abundant 43 VOCs emitted from the Solvents class of emission in the NAEI, coloured by whether they are unmeasured / measured within the automated hydrocarbon network.

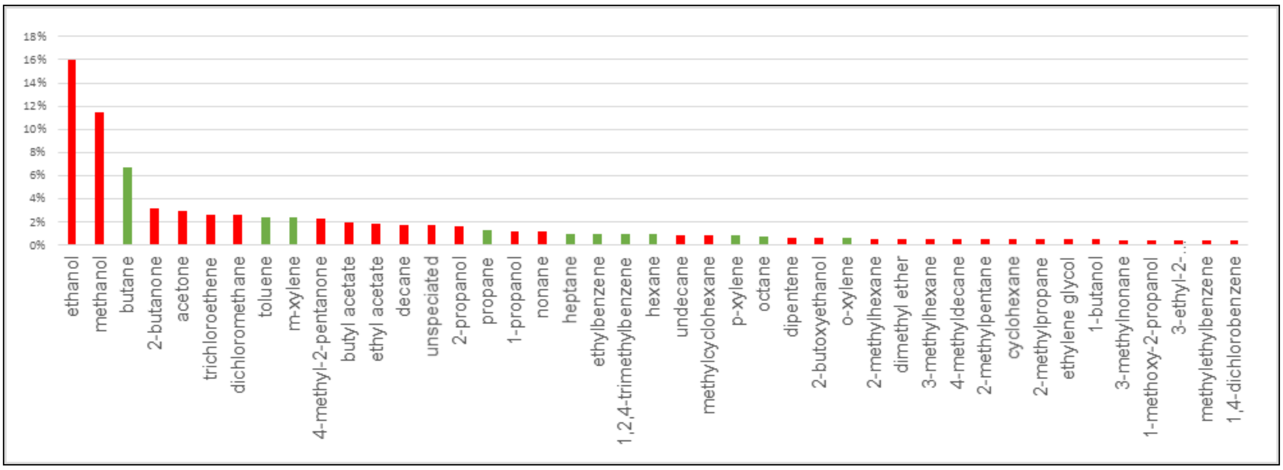
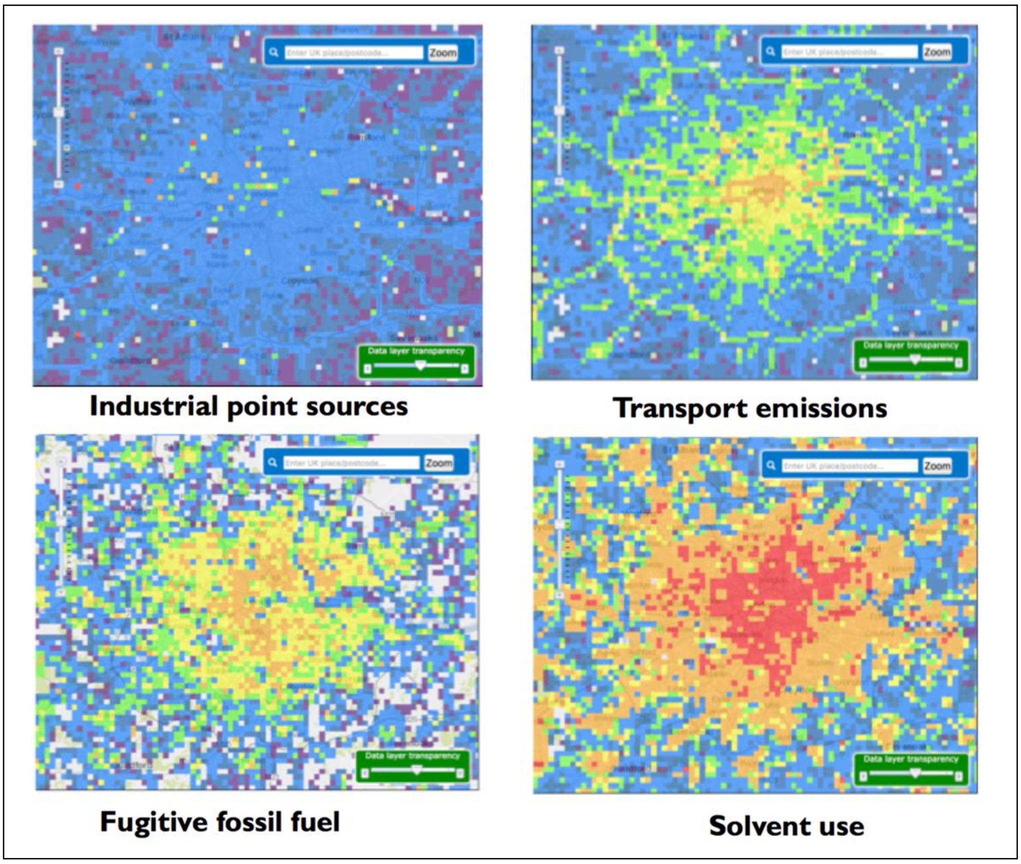


Figure 19. Percentage contribution to the overall emission of VOCs from the 'solvents and related products' class of emissions in the NAEI. Red species are not measured as present, orange species are included in the automated hydrocarbon network.

Trends in emissions for different VOCs can be extracted from the NAEI for past years; in the many cases for simple non-methane hydrocarbons these trends broadly follow the same patterns seen in ambient monitoring. Figure 17 shows the trends in estimated emissions for major VOCs in the UK (all anthropogenic sources). The rate of decline observed in air for n-pentane and toluene, which are both sufficiently short-lived to be considered unaffected by hemispheric changes in emissions, are consistent with changes in the NAEI. For example n-pentane has shown an approximate 8-fold decrease in ambient air since 1990, and 7.5 fold decrease in emissions in the NAEI.

The relative distribution of emissions between the different VOC emissions sectors can be usefully visualised using the different source classifications mapped on a geographic grid. Figure 20 shows the annual estimated emissions for the London region for four different VOC emission sectors, all referenced to the same colour intensity scale. There are a number of point sources recorded, plus clear line source emissions associated with the road transport sector. However by far the largest urban source of emissions by mass is the solvents sector, following essentially London urban population density.



Industrial point sources

Transport emissions

Fugitive fossil fuel

Solvent use

Figure 20. Spatial distribution of VOC emissions over London for four different source categories. Industrial Point Sources, Transport Emissions, Fossil Fuel and Solvent Use.

4.12 Validating estimated changes in emissions using observations.

The growth in the significance of domestic emissions of VOCs has also been observed in other studies. MacDonald *et al.* (2018) for example reported the relative contributions from various VOC sources to the observed outdoor profile in VOCs seen in Pasadena, USA. A substantial domestic sector emission factor was needed to reconcile observations against models when a wide range of VOCs were considered, and the paper highlighted how transport sector emissions had declined to such an extent that previously minor sources such as domestic solvent use now formed the largest single emissions source. Within UK homes VOCs from consumer products often dominant the overall speciation. In a 2017 study of indoor air quality (Wang *et al.* 2017), limonene and alpha-pinene (found in cleaning and personal care products) were always the most abundant VOCs indoors, significantly higher than more traditional solvents such as toluene or xylene.

Whilst the NAEI provides some evidence of significant changes in emissions sources and speciation, it remains challenging to assess the quality of inventories through independent means. Chemistry and transport models (CTMs) are sometimes used to assess whether measured concentrations of a pollutant are consistent with its emission inventory, although this approach relies on the CTM to be fit for purpose. For VOCs, CTMs usually lump VOC compounds of similar chemical properties together to reduce the number compounds treated, and thus cannot predict concentrations of individual species separately. Consequently, there do not appear to be any model/measurement comparisons for the UK.

Instead, there have been a few studies in which fluxes of a range of VOCs were measured directly either from fixed towers at the city scale or from aircraft at the landscape scale (Langford *et al.*, 2009, 2010; Valach *et al.*, 2015; Vaughan *et al.*, 2017). These measurements provide independent top-down assessments of the emission inventories, but are limited in time and space and the species covered. Airborne measurements in the London area (Vaughan *et al.,* 2017) suggested that the NAEI overestimates emissions of toluene outside London, but underestimates emissions within London by a factor of 2, which is consistent with inner-London rooftop tower measurements of Valach *et al*. (2015), with a somewhat smaller difference found by Langford *et al.* (2010), also in London and fairly good agreement found in Manchester (Langford *et al*., 2009). The situation was similar for C_2-benzenes, whilst for benzene predicted and measured emissions agreed within the error across all these studies. Measured fluxes exceeded emission estimates for oxygenated compounds such as acetone and acetaldehyde by factors ranging from 1.4 to 8. For methanol, good agreement was found in the more recent study of Valach *et al*. (2015), whilst in the older studies measurements were twice as high as emission predictions. It is unclear whether emissions changed or whether the NAEI was revised in the interim. Fluxes of isoprene and acetonitrile were detected, but not included in the anthropogenic NAEI.

5 Biogenic emissions of volatile organic compounds

Volatile organic compounds are not only emitted from manmade sources, but also from plants and soils. Whilst these so-called biogenic emissions do not need to be reported or controlled under current national and international legislation, emissions from managed land (i.e. agriculture and forestry) change with selection of plant species. Anthropogenic emissions are typically estimated using fixed emission factors that are independent of meteorological conditions. By contrast, biogenic emissions are highly dependent on light levels and temperature and they are therefore usually calculated in numerical models as a function of meteorology. As a result, estimates of the emission from plants change between years and also between different models even if the same plant species distribution is assumed.

In general terms, biogenic emissions are at their highest in the warmer summer months, declining to close to zero in the winter, and they are controlled on a day to day basis by prevailing ambient temperature and solar insolation. They therefore differ markedly from anthropogenic VOC emissions, which can be thought of as broadly year-round emission sources. It is also worth noting that the majority of biogenic VOC emissions are geographically dislocated from the major urban source of NOx, and this is particularly pronounced for monoterpenes species that are released predominately from rural Scotland. VOCs that are emitted in low NOx environments may be oxidized through to CO_2 and water with only limited impact on incremental additional formation of ozone. In contrast, anthropogenic VOCs are typically co-located with NOx emissions, maximizing the potential for photochemical ozone creation. Because of this difference it is important to view the relative impacts of biogenic vs anthropogenic VOC emissions not simply on a per tonne released basis, but rather on their relative potential for secondary pollution formation, which requires the wider chemical environmental to be considered in addition.

Most work has focused on estimating the emissions of isoprene and monoterpenes, both of which have the potential to react to form secondary pollutants ozone and SOA in the atmosphere (cf Section 6). In the UK, isoprene emissions tend to be dependent on both light and temperature, whilst monoterpene emissions mainly increase with temperature. Globally, the emission of isoprene alone (500 to 750 Tg a^{-1} (Guenther et al., 2006)) is thought to dwarf the emissions of all (considered) compounds from anthropogenic sources (127 Tg a^{-1}), dominated by large emissions in the tropics. This picture is different at the European scale, where reported anthropogenic emissions (6.7 Tg a^{-1} EMEP- CEIP[12]) are three times the sum of biogenic isoprene (1.17 Tg a^{-1}; Keenan et al., 2009) and monoterpene emissions (1.10 Tg a^{-1}; ibid).

In Europe, isoprene emissions are dominated by deciduous oaks, whilst the main contributors to monoterpene emissions are evergreen oaks, Scots pine, common beech,

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[12] https://www.ceip.at/webdab_emepdatabase/reported_emissiondata

and common spruce (Keenan et al., 2009). Compared with large parts of Europe tree cover in the UK is fairly small and this combined with low light levels and temperatures means that the contribution of biogenic emissions is estimated to be smaller than at the European scale. As Table 8 demonstrates, estimates vary widely, accounting for between 8 and 34% of the estimated UK emissions of anthropogenic VOCs of 835 kt a^{-1} (2018 NAEI for 2015). Isoprene emissions in the UK are thought to be dominated by oaks and beech in S England, whilst the spatial pattern of monoterpene emissions follows the distribution of Sitka spruce in the UK (Figure 21). There have been a few new UK-specific BVOC emission studies, the results of which have not yet fed into the emission modelling, covering, e.g., Sitka spruce (Hayward *et al*., 2004), oak (Langford *et al*., 2017), biofuel crops (Copeland *et al*., 2012; Morrison *et al*., 2016) and peatland (Langford *et al.,* 2017).

Whilst BVOC emissions may be relatively small compared with anthropogenic VOC emissions at the annual average, biogenic emissions have a very different spatial pattern to anthropogenic emissions and are very unevenly distributed over the year and their impact on air quality can be very important during warm spells. For example, some studies have linked high O_3 concentrations during heatwaves to elevated emissions of BVOCs (Lee *et al*., 2006; Churkina *et al*., 2017), although alternative causes such as a switch-off of O_3 deposition have also been proposed *(Vieno et al.,* 2010).

Table 8. Summary of various model estimates of BVOC emissions [kt a^{-1}] (from Hayman et al., 2017; modified)

Estimate	Isoprene	Mono-terpenes	Others	Total	Year
Anastasi et al. (1991)	115			211	
Hewitt and Street (1992)				50-100	
Simpson et al. (1995)	22.7		29.4		
Simpson et al. (1999)	58	30	90	177	
Winiwater et al. (2001) [PELCOM]				67	
Stewart et al. (2003)	8	83			1998
Karl et al. (2009)				219	2005
Steinbrecher et al. (2009)				281	2003
Hayman et al. (2010): forests only	7	52	37	96	2003
EMEP/CORINAIR (2002, 2016)	53	39	27	119	

NAEI (up to 2002)	58	31	89	178	-2002
NAEI (from 2003)	8	83		91	2003-present
Hayman et al. (2017)					2001-2013
EMEP4UK	33-44*	110-125*			
JULES	21-38*	45-71*			
CHESS	26-32*	88-104*			

* Dependent on the year, due to changing meteorology.

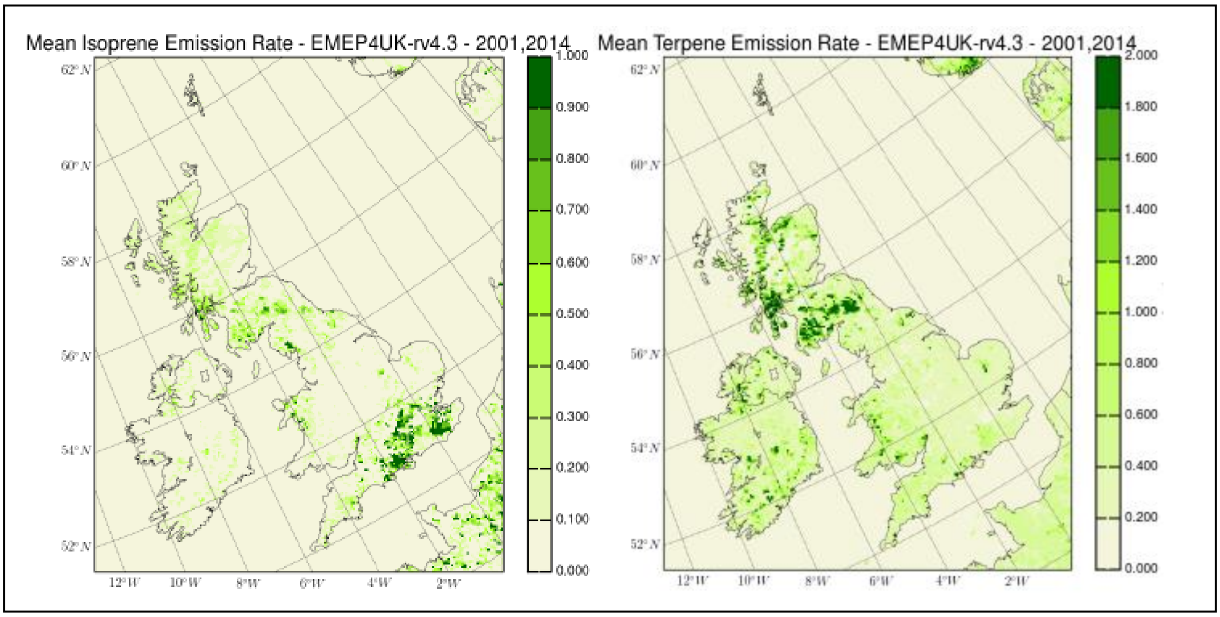

Figure 21. Emission of (a) isoprene and (b) monoterpenes as predicted by the EMEP4UK modelling system, averaged over the period 2001-2014.

The relative importance of BVOC emissions has increased over the past 30 years as anthropogenic emissions have been reduced and this trend is likely to continue should anthropogenic VOCs decline further. The evolution in the absolute emissions, however, is less certain: a warmer atmosphere and increased occurrence of heatwaves, coupled with more biomass, may increase emissions, but some studies suggest that a further increase in ambient CO_2 will have a mitigating effect and emissions also change with changing plant species composition. The climate effect can be isolated by assuming a static description of land cover. Most estimates of BVOC emissions under future climate scenarios, however, have been calculated with so-called dynamic vegetation models, in which vegetation adapts to changing conditions both in terms of species composition and in terms of biomass. Whilst this may be appropriate for predicting global emission changes dominated by unmanaged vegetation (tropical and Boreal forests; savannah), this approach is not appropriate for predicting emission changes in the UK, where changes will depend more on how land management responds to climate change. Even at the global scale land-use and land-use change are major drivers of BVOC emissions (Rosenkranz *et al*., 2015; Szogs *et al*., 2017).

Changes in plant species selection for agriculture, but in particular for forestry in response to climate change pressures and pests arriving in the UK as well as economic and policy drivers could alter emissions significantly, but the sign of this change is in the hands of land managers. Fast growing tree species used for biomass production such as poplar and willow, for example, are characterised by large isoprene emission potentials. Substantial conversion of agricultural land to support such production could therefore increase BVOC emissions significantly. Similarly, some tree species adapted to warmer and drier conditions, such as eucalyptus, are also large isoprene emitters. City councils are increasingly looking into green urban infrastructure as a means of removing a fraction of urban pollutants such as NOx and PM, although it should be noted that the evidence is that the scope for this seems limited (AQEG, 2018). Unless the emission potential for BVOCs is considered when selecting such tree species, increases in emissions could offset much of the intended benefit through the emission of precursors for O_3 and PM.

In summary, emissions from vegetation are not considered in the anthropogenic emissions inventory or for current legislation and emission reduction targets. Because most land in the UK is managed, they are nevertheless under the control of human intervention. Unless BVOC emission potentials are taken into consideration when making changes to species selection for agriculture and forestry, the air quality benefits achieved by cuts in anthropogenic emissions could potentially be reduced or even cancelled by increases in BVOC emissions (Donovan *et al*., 2005; Rosenkranz *et al*., 2015). Conversely, through smart species selection BVOC emissions can be reduced, although research is needed to balance this against economic drivers. Whilst such BVOC emission reductions do not count towards current emission reduction goals, they would nevertheless be beneficial for air quality. Schemes for urban tree planting and green infrastructure should factor in potential changes in BVOC emissions, since any increase in BVOC emissions in an urban setting has the potential to lead to additional secondary pollution formation. The previous AQEG report on the impacts of vegetation on air quality provides further details on the relative emissions rates of VOCs from various common tree types.

It should be noted that O_3 and PM that derives from the oxidation of BVOCs is not typically considered to be of biogenic origin, because the oxidants required for this process usually derive from anthropogenic activities. Thus, emission reduction in NO_x for example, will also reduce the impact of BVOC emissions.

6 The role of VOCs in the production of photochemical ozone pollution.

The formation of tropospheric ozone from the reactions of VOCs and NO in the presence of sunlight is very well-established science that dates back to research of Haagen-Smit in the 1950's (e.g. Haagen-Smit *et al.* 1954). Sunlight in the near-UV initiates reactions that generate free radicals that can promote the oxidation of VOCs, and the generation of hydroxyl and peroxy radicals that can convert NO to NO_2, and thus create a route to the net photochemical production of ozone from NO_2 photolysis.

The science of VOCs and photochemical ozone is sufficiently well described in many textbooks that it does not require substantial recounting here. The last scientific review of VOCs and air pollution was in the Fourth Report of the Photochemical Oxidant Review Group 1997, and the basics of VOC chemistry reported then still hold true for gas phase atmospheric chemistry in 2019. The 1997 review is however now clearly outdated in that it makes no direct links between VOC emissions, chemistry and particulate matter, and this science is updated in section 6.1 to follow.

Nonetheless it is worth considering that most existing policy and regulation associated with VOC emissions controls has been formulated with tropospheric ozone formation in mind, and not the formation of other pollutants like organic aerosols. The wide range of different chemical reactivity found within the broad mixture of VOCs in air leads to differential impacts of each species on ozone (and other pollutants). Not all VOCs are equal in their capacity to generate ozone and concepts such as Photochemical Ozone Creation Potential (POCP) have aimed to provide a simple weighting of the relative ozone formation from a given VOC when passed along a common atmospheric trajectory and chemical field (Derwent and Jenkin, 1991). In general terms alkenes, aromatics and aldeyhydes have higher POCPs and ozone forming potential, per molecule, than alkanes, alkynes, alcohols or chlorinated compounds (Andersson_Skold *et al.* 1992).

Although the concepts of POCP and related measures of ozone potential based on gas phase reactivity and mechanisms are well established, they do not play any formal role in guiding the controls on emissions of VOCs, which continue to be regulated and managed solely in terms of overall mass of national emissions. This AQEG report will not report in detail on the current state of the science relating to gas phase ozone formation, but it is valuable to re-state here that detailed modeling tools do already exist to support the study of differential impacts of different VOC mixtures and emissions, should that become a policy consideration in the future (Lewis, 2018).

The UK maintains a highlighted detailed explicit mechanism of tropospheric chemistry and VOC degradation, the Master Chemical Mechanism[13]. The MCM was initially developed at University of Leeds in the 1990s, supported by Defra (then Department for the

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[13] www.ncas.ac.uk/mcm

Environment), and has been continually updated as new kinetic and mechanistic information has become available. At this time there are no UK or EU proposals to move away from a mass-based measure of VOC emissions control or regulation, but from a scientific perspective, alternative methods for evaluating impacts of controlling individual VOCs based on ozone outcomes are available.

6.1 Modeling the effects of VOCs on ozone production.

VOCs are unusual in how they are typically treated within predictive models of air quality based on chemical transport (CTM) approaches. The need to retain model simplicity means that all CTMs make very substantial simplifications of VOCs, reducing drastically the number of VOCs that are included, and then simplifying substantially the oxidation mechanisms, for example using common reactive intermediates. Widely used regional air quality models such as CMAQ, WRF-Chem, and GEOS-Chem attempt to carry the correct overall mass of reactive carbon, and do this by scaling the mass of a small number of individual VOC species upwards such that in total it captures the overall amount of VOC in the underlying inventory, and with the correct reactivity.

Models vary in how they implement this, but typically ethane, propane and lumped C4 and C5 species are treated explicitly along with isoprene, and occasionally toluene. The considerable simplification of VOCs that routinely occurs in regional air quality models means that the more subtle effects of changing speciation may well not be captured and it becomes difficult to compare model performance against observations of individual VOCs. As with observations, there are some clear gaps in the explicit treatment of VOCs such as ethanol and methanol.

Understanding the impacts of individual VOCs and how a change in the speciation of those VOCs may impact on ozone can only be done using the explicit modeling of the kind described earlier with the MCM. It is possible to evaluate how a shift in VOC speciation may impact on the ozone forming potential of national emissions in the atmosphere by considering the POCP of each species emitted and the relative amount of that emission. The anthropogenic emissions inventory has shown particularly steep reductions in emissions of hydrocarbons associated with road transport and combustion, for example short-chain alkenes and mono-aromatics. These types of VOCs have some of the highest POCP values. The NAEI indicates a shift towards solvent-related emissions, and the relative growth in emission of VOCs such as ethanol and methanol. Ethanol is a species of intermediate POCP, broadly similar to *n*-butane, but lower than some unsaturated hydrocarbons. Considering the balance of species is possible through interrogation of the NAEI.

Using the overall POCP as a measure of ozone forming potential from an ensemble of VOCs emitted, it is possible to examine at a bulk level whether the changes in speciation seen over the last two decades have led to any change in ozone forming potential, as a function of mass emitted. The concept of this calculation is shown in Figure 22, which illustrates the trends in total VOC emissions for the UK and the total POCP derived from the top 40 emitted VOCs, which represent around ~70% of overall emissions. The absolute mass of emissions and the absolute ozone forming potential (arb. Units) of UK emission, as would be expected, declined substantially over the period 1990 – 2017.

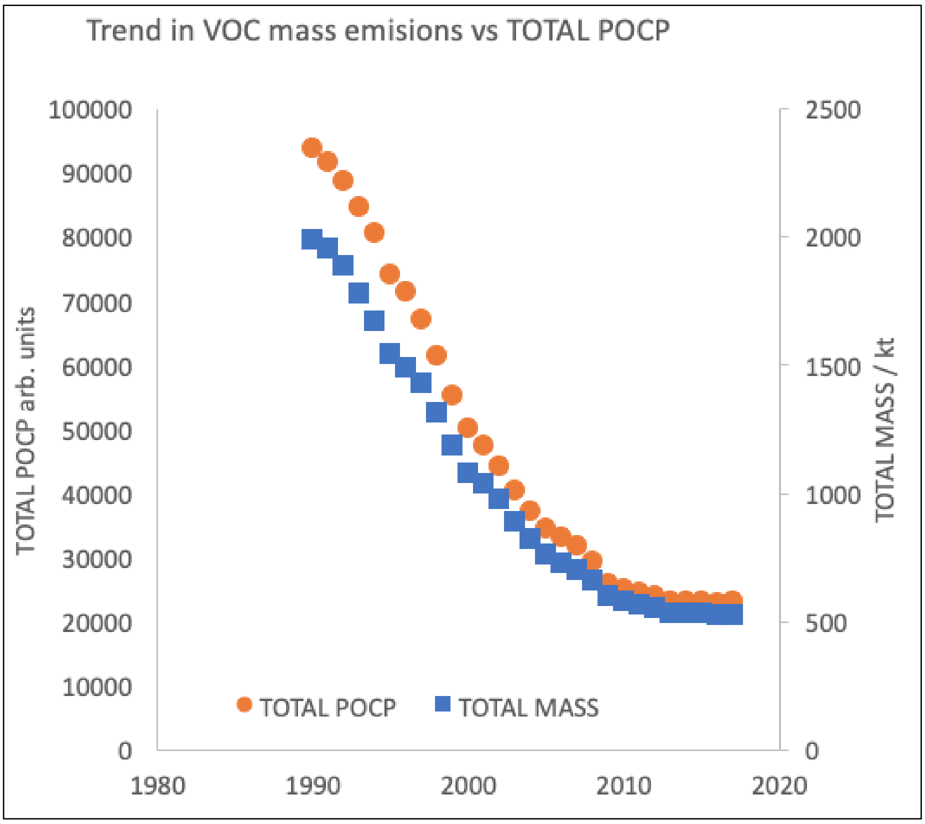

Figure 22. Estimated change in UK national emissions of VOC by total mass and by accumulated total photochemical ozone creation potential. (POCP), 1990-2017.

It is possible to calculate the POCP of an average mixture of VOC emitted at any point on the 1900 – 2017 time series (calculated here for the top 40 inventory species, using Derwent *et al.* 1998 POCP values. Over the 1990-2017 period the POCP of the VOC mixture declines slightly, by around 4%, shown in Figure 23. A complex set of changes drive this change. The largest change in any single species is the decline in ethane (a low POCP compound) and the growth in ethanol (an intermediate reactivity species). However there are also declines in a range of different alkenes and aromatic compounds that more than offset the growth in ethanol. The net change is to a mixture that is slightly lower in POCP per unit mass in 2017 than the mixture being emitted in 1990. Considering POCP in terms of contributions from different functional groups show alcohols growing to become the largest single POCP contributing class of VOC (Figure 23). The impacts of this change in speciation are not straightforward to quantify, and would require a more detailed modeling study. For example, to assess whether the shift to greater amounts of ethanol changes ozone production and peroxy acetyl nitrate (PAN) cycles, since it readily oxidizes to form acetaldehyde in a way that other VOCs that have diminished in emissions over time do not.

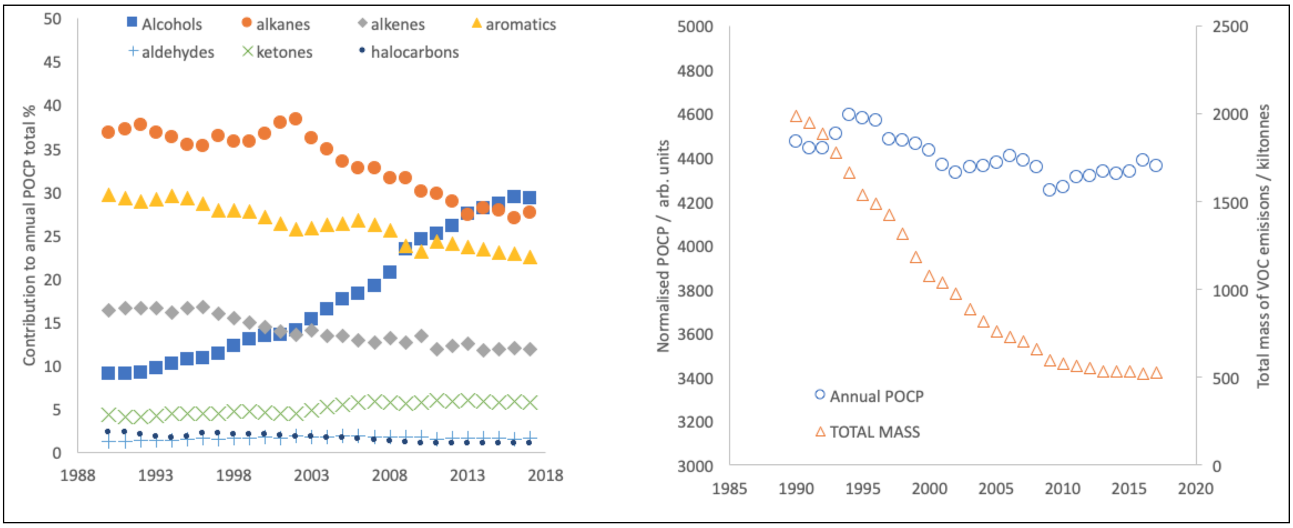

Figure 23. Left: Estimated contributions to overall annual POCP by functional group type for top 40 VOCs in the NAEI. Right: Total mass of VOC emissions and normalised POCP per unit mass for each year in the NAEI time series.

6.2 Volatile organic compounds as precursors of particulate matter

One of the most significant recent scientific advances related to the atmospheric chemistry of VOCs has been the insight that atmospheric oxidation of some VOCs leads to chemical products that can create new particles, add mass to particulate matter (PM), or change the chemical nature of PM. There is now a large body of observations confirming the ubiquitous presence of secondary organic aerosol (SOA) in virtually all environments. Over the last two decades it has become clear that VOCs can impact the composition of urban and rural PM and the amount of PM found in air. A consequence is that the motivations for controlling VOC emissions now go beyond the well-established science of ozone formation, although the evidence on this has not yet been formally reviewed or summarised by AQEG. A full review of the chemistry of VOCs and PM would be a substantial task, but a summary of some of the key reactions and processes is given here.

6.2.1 Chemical makeup of secondary organic aerosol (SOA).

Secondary organic aerosol has a very diverse composition, depending upon the precursor from which it is formed, and the degree of chemical processing. The chemical and physical environment in which formation occurs will also influence the ultimate composition. Hence SOA production rates and composition can depend upon the oxides of nitrogen present, and aqueous phase formation may lead to different products than gas phase reactions of the same molecules. Since SOA is formed through oxidative processes, the main functional groups in first generation products are hydroxyl, carbonyl, hydroxycarbonyl, nitrate, hydroperoxide and peroxynitrate (Hallquist *et al.*, 2009). Carboxylic acids are subsequently formed, and Russell e*t al*. (2011) show how the ratios of alkane, carboxylic acid, hydroxyl and carbonyl groups are characteristic of different SOA sources. Reaction products are highly diverse, and Forstner *et al*. (1997) list 77 compounds identified in the condensed phase oxidation products of simple aromatic precursors such as methyl and ethyl derivatives of benzene. Oxidation rates and SOA yields (ΔSOA:Δprecursor) vary according to the NO_x content of the reaction chamber and the presence of ammonium sulphate seed aerosol *(Ng* et al., 2007). Reaction products can also react with one another to form larger oligomeric molecules (Kalberer *et al*., 2004; Gao *et al*., 2004) with molecular weight from 200 to in excess of 1000 (Hallquist *et al*., 2009). Because of huge variability in composition, SOA varies in volatility, the lower molecular weight and less oxidised species tend to be semi-volatile and partition actively between vapour and the condensed phase, while the more oxidised higher molecular weight species reside almost entirely in the condensed phase. While the complete characterisation of SOA at the molecular level is generally impracticable (Nozière *et al*., 2015), the Aerosol Mass Spectrometer is able to distinguish the major groupings on the basis of molecular composition as revealed by the particle mass spectra and numerical factorisation. While not generally giving molecular identification, this is of use when budgeting SOA mass based on generalised functionality (Jimenez *et al*., 2009).

There are currently very few chemical tracer molecules which when measured within SOA allow the SOA to be associated with specific chemical precursors. Rather, a rough estimate of the contribution of individual VOCs to SOA mass can be made by using the results of chamber studies which relate initial VOC concentrations to mass yields of SOA (Odum *et al*., 1996). However, such yields depend upon the extent of VOC processing, and due to non-linearities, predictions of the effects of VOC emissions reductions upon SOA concentrations are very uncertain.

6.2.2 Anthropogenic secondary organic aerosol (aSOA)

Atmospheric oxidation of VOCs typically leads to the formation of less volatile reaction products which may partition into the condensed phase to form SOA, which is a major component of $PM_{2.5}$ in continental environments (Crippa *et al.*, 2014; Jimenez *et al.*, 2009). While some of the more abundant anthropogenic VOCs such as toluene make a significant contribution to SOA (e.g. Ng *et al*., 2007), in recent years it has become apparent that a major fraction of anthropogenic SOA originates from precursors that could be classed as intermediate-volatility or semi-volatile organic compounds (IVOCs and SVOCs) (Robinson *et al*., 2007).

These are much larger molecules (typically C13 and higher) and are emitted in large quantities from the transport sector, especially diesel vehicles, but the instrumentation to study these directly has only become available relatively recently (Gentner *et al*., 2012; Alam *et al*., 2018). Due to their high SOA yields, their contribution to the anthropogenic SOA budget is thought to be highly significant if not dominant, and this is likely to be especially true of the UK due to the relative proportion of diesel in the emissions fleet (Dunmore *et al*., 2015). However, the scientific understanding of this is currently relatively poor (Gentner *et al*., 2017), owing to several factors, including:

- The great diversity of specific molecules that comprise the IVOCs and SVOCs and the resulting complexities in the atmospheric chemistry
- Uncertainties in the emissions, as these have not traditionally been targeted in emissions studies
- Limitations of the instrumentation and laboratory facilities used to study these
- Reversible partitioning between the gas and particle phases

6.2.3 Biogenic secondary organic aerosol (bSOA)

It is well established that biogenic VOCs, specifically isoprene, monoterpenes and sesquiterpenes, are a major source of secondary organic aerosols in the atmosphere (Hallquist *et al.*, 2009; Hoffmann *et al*., 1997; Zhang *et al.*, 2018). Because these molecules are unsaturated, they can be subject to initial oxidation through ozone and nitrate radicals, in addition to OH radicals. Most of these VOCs need to undergo multiple reactions before they produce products involatile enough to result in particulate matter (Kroll *et al*., 2011). Each reaction stage can also potentially produce multiple products that may or may not ultimately form aerosols, so accounting for the explicit chemistry associated with an individual precursor molecule can quickly become extremely complex (Valorso *et al*., 2011).

Most biogenic VOCs are emitted from plants such as trees (cf Section 5) and these form a natural background that must be considered when modelling atmospheric chemistry. Furthermore, there are direct anthropogenic sources of these VOCs; the transport sector is known to release isoprene (Park *et al*., 2011) and terpenes are often used as fragrances. A notable example of this is limonene, which is used extensively in cleaning products and is known to produce SOA with a high yield *(Zhang et al.*, 2006).

The state of the science regarding biogenic VOC emission is fairly mature, with models taking into account things like the species of plant present, season and temperature (Guenther *et al.*, 1995). Likewise, SOA production has also been heavily studied through a combination of laboratory and chamber studies (Hallquist et al., 2009). Some specific species, in particular α-pinene and isoprene, have received particular attention because of their abundances in the atmosphere. SOA yields have been shown to be variable and depend on various factors, such as temperature, humidity, interactions with anthropogenic pollutants and the properties of any pre-existing aerosol (Czoschke *et al*., 2003; Saathoff *et al*., 2009; Richards-Henderson *et al*., 2016; Hoyle *et al.*, 2011).

Of particular note is isoprene, whose SOA formation potential is strongly dependent on the amount of NO_x and SO_x present, thus its contribution to PM can be modulated by anthropogenic emissions (Carlton *et al*., 2018). The detailed study of these VOCs has revealed that they can be subject to complex and unconventional mechanisms such as auto-oxidation, multiphase reactions and oligomerisation that can be challenging to constrain (Ehn *et al.*, 2014; Shrivastava et al., 2017). However, the current level of scientific understanding and thus predictive capability for the biogenic SOA budget is still generally regarded as more advanced than our understanding of anthropogenic SOA; this is mainly thanks to our ability to isolate and study individual precursor molecules and intermediate reaction products (Hunter *et al*., 2017).

6.2.4 Modelling SOA formation from precursor VOCs.

In spite of much effort to develop the field, predictive capabilities for SOA remain somewhat limited in comparison to ozone. Where precursor VOC molecules have been identified, explicit or semi-explicit SOA models have been developed, coupling a gas phase chemistry model (such as the MCM) to a phase partitioning model to simulate the condensation of the products (Valorso *et al*., 2011; Johnson *et al*., 2006; Aumont *et al*., 2012). Models can also include multiphase processes, which in the last two decades have become established as atmospherically important (Knote *et al*., 2014; Budisulistiorini et al., 2017). Because the very detailed models are computationally expensive, the application of these is generally limited to 0D (‘box’) or Lagrangian models.

While every effort is made to incorporate as much scientific knowledge as possible, models based solely on well-characterized molecules and processes are recognized to significantly underpredict the SOA budget (Volkamer *et al*., 2006). This may be in part due to molecules that have yet to be isolated and studied in detail (which is particularly true for IVOCs) but there is always the potential that yet-to-be-identified chemical processes are having a significant effect (e.g. McFiggans *et al*., 2019; Paulot *et al*., 2009). Furthermore, for their application in the Eulerian models needed for air quality modelling, chemical models often have to be simplified to reduce computational cost, to the detriment of accuracy (Santiago *et al*., 2012).

To get around these problems and deliver more quantitatively realistic concentrations, a number of models use schemes for a few specific and well-studied precursors and scale the outputs, for example taking laboratory data for α-pinene and assuming that this is representative of all terpene SOA (Spracklen *et al*., 2011; Zhang *et al.*, 2012). An alternative is to adopt an agglomerated approach such as the volatility basis set (VBS), where VOCs are grouped together and their mass summed according to properties such as volatility and oxygen content. Once grouped, their oxidation chemistry and SOA formation are treated as a whole (Jathar *et al*., 2014; Ots *et al*., 2016; Donahue et al., 2011). This is particularly useful for IVOCs and SVOCs, where fully resolved molecular data is not available. However, as neither approach can claim to be chemically explicit, even if they can claim to realistically reproduce current observations when simulating SOA concentrations, any predicted changes in SOA concentrations based on future emission scenarios must be treated with caution.

6.2.5 Estimates of SOA concentrations in the UK and responses to VOC changes.

The secondary organic aerosol component is not routinely quantified in isolation in the UK's air quality monitoring networks. It has been quantified during intensive field studies either from the application of multi-component analyses to organic mass spectra obtained by aerosol mass spectrometry (AMS), from measurements of total water soluble organic carbon (WSOC), or from chemical mass balance model applied to measurements of organic marker compounds. During 2012, AMS instruments were operated for an entire year at two sites in London (N Kensington and Marylebone Road) (Young *et al*., 2015), and since 2013 an Aerosol Chemical Speciation Monitor has been operated continuously in London (2013-2019 at North Kensington, 2019-present at Honor Oak), now providing a continuous estimate of the SOA concentration (Reyes-Villegas *et al*., 2016). SOA concentrations in PM_1 were found to be 1.5 µg m^{-3} in 2012 and 0.4 µg m^{-3} in 2013, with the concentrations during the top 10% of PM_1 concentrations being 4.0 and 3.0 µg m^{-3} respectively.

Additional estimates of the SOA come from Chemistry and Transport Models (CTMs). However, because the representation of processes of SOA formation is complex, SOA tends to be the least certain of the aerosol components predicted by these models and tend to underestimate SOA concentrations, which was also demonstrated during a recent European model intercomparison exercise (Bessagnet et al., 2014). Model estimates of the (population weighted) contribution of SOA to total $PM_{2.5}$ are in the range of 14 and 17% (1.6 and 1.8 µg m^{-3}), based on the PCM model for 2010 (AQEG, 2012) and the CMB model for 2007/08 (Yin *et al*., 2010), respectively. The majority of this derives from UK VOC emissions, rather than emissions outside the UK. The models suggest that the absolute SOA concentration decreases moderately from the SE to the NW of the country, but the relative contribution to $PM_{2.5}$ increases (with some local exceptions), because primary components decrease more strongly.

Some of the models are able to distinguish between aSOA and bSOA, but estimates vary significantly, reflecting the state of the science. Redington and Derwent (2013) estimated that in the UK between 76 and 90% of the SOA derives from biogenic VOCs, similar to measurements by Heal *et al*. (2011) in Birmingham of 78%. Simpson *et al*. (2007) estimated an even larger relative contribution from bSOA of >90%.

Using the EMEP CTM, Vieno *et al*. (2016) estimated that a 30% reduction of UK anthropogenic VOC emissions would result in a maximum UK average reduction of 0.08 µg m^{-3} $PM_{2.5}$ and a maximum reduction of 0.15 µg m^{-3} (1.5%) in central and northern England and central Scotland. A European study (Fountoukis et al., 2014) assessed $PM_{2.5}$ responses to a 50% a VOC emission reduction using the PMCAMx model, and found similar modest decreases over Western Europe (up to 0.2 µg m^{-3} or 1.1%). The relative weak response of $PM_{2.5}$ to VOC emission reduction has been explained by the large contribution of bSOA as well as non-linear chemistry: in NO_x-limited areas the decrease in aVOC emissions results in an increase of oxidant levels, which accelerate the oxidation of bVOCs as well as NOx and SO_2, offsetting some of the reduction. The authors however highlight a particularly strong impact of VOC reductions on $PM_{2.5}$ predicted in the southern UK (and N France) in summer. This may be linked to the high NOx shipping emissions in the English Channel resulting in a strongly VOC limited regime, where a reduction in VOC emissions decreases oxidant levels and thus aerosol formation. The understanding of SOA formation is constantly progressing, however. Recent investigations of the potential contribution of IVOC emissions from diesel vehicles to aSOA formation, a compound class which is not explicitly treated in most models, suggest that this route alone could be the precursor of 30% of the annual SOA in and around London (Ots e*t al*., 2016). If substantiated, this additional process would imply a stronger sensitivity of SOA to aVOC emission changes at least in urban areas.

Because of the large contribution of bSOA to total SOA, bVOC emission changes associated with choices in land-use and plant / tree species (Section 5) are likely to have a significant impact on SOA concentrations, but this has not been explored in detail.

7 Methods for future measurement.

Previous sections of this report have highlighted that VOCs are a complex class of compounds and that measurements in ambient air often only represent a small sub-group of VOCs that are actually present in emissions or ambient air. The species recommended for measurement in the EC Directive on Air Quality were set at a time when evaporation of fuels and direct tailpipe emissions of VOCs from combustion were the dominant sources to European air. Many species within this list are now found in air at vanishingly small concentrations, often at or below the detection limit of the instruments used for monitoring.

The UK automated hydrocarbon network includes measurements of three isomers of butene, two isomers of pentene and 1,3 butadiene, however in rural locations these species are now frequently undetectable. Considerable observational effort and resource is still placed on extracting trace level data for these species, but it is unclear whether that is the best prioritisation. The network does not measure any of the most abundant OVOCs (e.g ethanol, methanol, formaldehyde, acetaldehyde etc) in the UK atmosphere, and it would seem timely to consider a reshaping of the speciation of VOC monitoring that would yield more insight into current emissions and trends. There is however no single analytical method that can determine all VOCs that are present in the atmosphere, so a range of different methods could be considered, each with strengths and weaknesses.

7.1 Methods based around gas chromatography

There is typically a trade-off made between instrument complexity, time resolution and speciation, and the most challenging VOC species often sit at the extremes of vapour pressure and polarity. The most commonly employed method for VOC measurement remains thermal desorption – gas chromatography (GC), since this provides a reasonably robust method for the measurement of very volatile (e.g. ethane, ethene, ethyne) and volatile organic compounds (up to nC_{10} typically).

GC methods are constrained by a number of important factors i) can a particular VOC pass successfully through an inlet to the instrument, including avoiding effects associated with a change to gas-particle partitioning? ii) is the VOC unaffected by any methods used to remove water from the sample? iii) can the VOC be pre-concentrated and then re-released in thermal desorption? iv) can the species be separated and isolated by a GC column without re-arrangement or molecular changes and v) can it be detected and quantified (e.g. by FID or MS)?

The research literature can be used to provide current state of the possible in terms of VOC speciation and automated measurements. There are a number of long-term observation stations within the World Meteorological Organisation's Global Atmosphere Watch Programme (WMO-GAW) for background VOCs that take a similar approach to measurement as the current Defra network, but extend the species range to include some oxygenated compounds by using two different GC columns and two detectors. Many research methodologies in the literature are based on methods originally reported by Hopkins *et al*., (2003). The figure below shows an urban measurement of VOCs, using a standard Al_2O_3 PLOT column with FID to detect simple NMHCs (similar to the current Defra / EA hydrocarbon network), and second column (Agilent, LOWOX) and FID detecting a small range of the more abundant oxygenated VOCs.

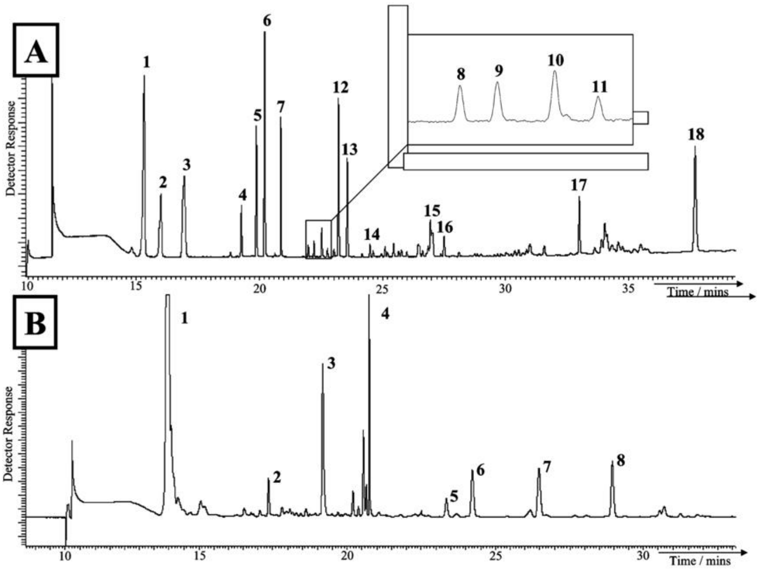

Fig. 3 Sample chromatograms produced from A; Al_2O_3 PLOT column where 1; ethane, 2; ethene, 3; propane, 4; propene, 5; iso-butane, 6; n-butane, 7; acetylene, 8; but-1-ene, 9; *trans*-but-2-ene, 10; iso-butene, 11; *cis*-but-2-ene, 12; iso-pentane, 13; n-pentane, 14; buta-1,3-diene, 15; 2+3-methylpentane, 16; n-hexane, 17; benzene, 18; toluene. And B; LOWOX column where 1; Aliphatic NMHCs, 2; benzene, 3; toluene, 4; acetaldehyde, 5; methanol, 6; acetone, 7; ethanol, 8; propanol.

Figure 24. Reproduction of chromatograms generated using a water condensation method coupled to thermal desorption and two-column GC-FID.

Thermal desorption-gas chromatography and FID detection of simple OVOCs is reasonably straightforward, with high specificity high polarity columns providing a means to isolate this class of VOCs from the complex hydrocarbon background. The major experimental obstacles are related to the management and removal of water vapour and long-term calibration. In the existing Defra automated hydrocarbon network water vapour is removed from the air stream using a permeation Nafion drier, however this also strips out any polar compounds from the sample stream. Research instruments typically now use a low temperature freeze out of water vapour (at -30 C or colder), either in a cold trap that requires replacement or through a regenerating trap. Various combinations have been reported in the research literature and some commercial instruments also exist.

Calibration of oxygenated VOCs remains challenging. Whilst simple low ppb-level gas standards for non-methane hydrocarbons exist, at present provided by NPL, no equivalent standards exist for ethanol and methanol. Instead part per million gas standards must be blended in humid air to lower more relevant ambient concentrations, and the process of calibration is onerous and can introduce uncertainty. Alternative methods of calibration such as gas permeation of VOCs through a Teflon membrane, with subsequent weight loss assessment of emission rate are also difficult to implement in the field, and require frequent hands-on high precision weighting.

Whilst many VOC instruments have used FID as a detector, alternatives with mass spectrometry also exist. MS as a detector offers many advantages, not least that the detector itself offers an additional dimension of analytical resolution. If a GC-MS is used in ‘full scan’ or a time-of-flight (TOF) detector is used then to some degree the instrument provides an untargeted analysis, that is it can provide insight into species that emerge during periods of measurement, rather than being preselected as part of the operating method. The mass response of mass spectrometry is however far less stable than FID and so typically on-line monitoring of VOCs with GC-MS requires very high frequency calibration. In the case of the AGAGE network[14] used for global halocarbon measurements, every VOC measurement is bracketed before and after by a working standard measurement. This creates a very substantial experimental overhead, both on-site where personnel are needed and in a central calibration laboratory producing working standards.

A variant of thermal desorption – gas chromatography is the use of GCxGC where two columns of differing polarities are used to increase the degree of speciation that can be achieved. Whilst first reported by Lewis *et al.* 2000 the use of the technique remains limited to research intensive observations, primarily due to the high workload and complexity of data interrogation which can generate information of 100’s to 1000’s of different VOCs in a single analysis.

7.2 Methods based around on-line mass spectrometry.

The major alternative method for the measurement of atmospheric VOCs is the use of a variant of on-line mass spectrometry, sometimes referred to as direct-inlet mass spectrometry or chemical ionisation mass spectrometry. Some of the most impactful breakthroughs in online MS for atmospheric measurement were made around 20 years ago, e.g. Lindinger *et al.* 1998. The most commonly used technique uses proton-transfer reactions with H_3O+ ions to soft ionize atmospheric VOCs with mass spectrometry detection of the resulting product ions. The proton-transfer chemistry occurs in a drift-tube reactor, which aims to enhance the ion kinetic energy and limits cluster ion formation with the abundant water molecules in ambient air.

The technique is generically referred to at PTR-MS (proton transfer reaction mass spectrometry). Within the research community there has been a widespread adoption of these techniques since they provide fast response, e.g. 1 Hz measurements with ppb or better sensitivity. They have been widely used to quantify fluxes of emissions of VOCs and on mobile platforms such as aircraft. A comprehensive review of PTR-MS is available from Yuan *et al.* (2017). Whilst early PTR-MS instrument used quadrupole MS detection with

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[14] https://agage.mit.edu

unit mass resolution, in recent years these have been superseded by time-of-flight detection, often at high mass resolution.

PTR-MS and other chemical ionisation methods aim to produce a molecular ion from the original VOCs, with that ion product becoming available for detection. The mass/charge (m/z) ratio of a product ion carries information on the original VOC from which it was generated, however it is rare for a particular m/z to be produced by only a single VOC in the atmosphere. In this regard PTR-MS data often produces information on the abundance and behaviour associated with groups of isomeric species, rather than molecular-specific measurements which are produced from slower GC methods. For example ethyl benzene, as well as *m, p* and *o* xylene are all reported as a single species, as are different monoterpenes. PTR-MS methods have been shown to be capable of measuring hundreds of different species simultaneously, but they do not have the capacity to accurately quantify some of the major smaller hydrocarbon species such as ethane, ethene, acetylene, propane, or speciate key compounds such as *n*-butane from *i*-butane.

In practice most research observations of VOCs deploy both GC and PTR-MS methods in parallel and combine the strengths associated with the good time resolution of online MS with the accurate and complete speciation by GC. As with GC methods, calibration of instruments is a crucial factor, and whilst some first approximation quantification can be made based on ion kinetics, these types of instruments also need active calibration, and this is often where much of the research effort in the field is expended. On-line MS also requires an extensive set of zero and blank measurements, since the continuous nature of the instrument means assessment of zero levels is less straight forward than the assessment of peaks on a chromatogram. Zero air is typically generated *in situ* with the instrument and frequently supplied to the instrument as part of the calibration cycle.

More recently instruments using other reagent ions (eg I^-, NO^+, O_2^+, O^- etc) have become commercially available (for example from Aerodyne Corp, Syft Technologies), with each reagent ion offering some additional degree of specificity for the measurement of particular types of VOCs or inorganic compounds in air, and the ability to target additional compounds.

Although the research literature on PTR-MS and related online methods is very extensive, it is worth noting that these methods are rarely used for long-term (multi-year) routine monitoring in regulatory or compliance networks. This is likely a result of high capital and maintenance costs, more complex data and calibration requirements and that many simple hydrocarbons recommended by EC Directives cannot be detected with the method.

Table 9 summarises some of the key features strength and weaknesses of various methods used currently in research for speciated VOC measurements.

7.3 Bulk or total VOC detection.

Several analytical methods exist that provide a bulk or total (*i.e.* not speciated) measurement of VOCs in ambient air. These are used most commonly for emissions control, sample screening and fence-line detection rather than for more mainstream ambient air measurements. Bulk measurements of VOC typically aim to provide overall NMVOC amount express as mg C m^{-3}, and have most use in identifying general qualitative short-term VOC trends. There are standardised quantitative measurements of total atmospheric VOCs reported using a variant of gas chromatography, where a simple packed column is used to separate methane from all other VOCs (US EPA 1999). The methane is eluted from the column and then the remaining VOC back-flushed in reverse as a single peak onto a FID detector. The method has some advantages in that it provides a single simple VOC mass metric value, the FID has well understood response characteristics (essentially a carbon-counter) and it is relatively stable in response over time. It is also possible to calibrate the method with traditional binary gas standards, but the method offers no insight into what VOCs are actually present, only how much VOC in total. It is difficult to integrate data of this kind into modelling given the lack of speciation.

A number of lower-cost sensor methods exist for bulk VOC detection, with instruments primarily targeted at occupational health and short-term hazard detection. These are typically used to provide alarm systems for very high concentrations of VOCs, for example in paint spraying facilities, petrol stations and so on. Very simple sensors based on metal oxide (MO) semiconductors generate a bulk response to VOCs in air, but they show considerable dependence on ambient humidity and temperature (Smith *et al.* 2017), such that even with suitable data correction methods their utility is for sensing total concentrations in the ppm rather than ppb range.

More sophisticated photoionsiation detectors also exist that give a bulk measurement of VOCs based on UV ionisation, and detection of the resulting ion current. The response of different VOCs in the detector depends on the ionisation potential of the compounds and the wavelength of the lamp. Aromatic compounds for example give a very strong response, alkanes a much weaker one (Lewis *et al.* 2010). Since the response to different VOCs is highly variable, changes in speciation create major problems when attempting to interpret time series data. As with other sensor-based methods the sensitivity to water vapour is high, and although the intrinsic sensitivity of PIDs is low ppb, in practice detecting meaningful changes in ambient VOCs is difficult. The relative short lifetime of the PID lamps makes the method inappropriate for continuous monitoring. Both MO and PID sensor methods suffer from a lack of traceability to primary VOC gas standards which have N_2 as the balance gas.

7.4 Quantification of VOCs using Earth Observation.

The number and type of VOCs that can be measured at the surface from space is relatively limited and in the main are formaldehyde (HCHO) and glyoxal (Gonzalez Abad *et al.*, 2019; Martin, 2008). Satellite VOC measurements are often complemented by similar measurements of carbon monoxide (Kopacz *et al*., 2010). Figure 25 shows a regional assessment of HCHO taken from TROPOMI, the current state for the art sensor (in terms of spatial and temporal resolution, sensitivity and accuracy) for satellite measurements of HCHO.

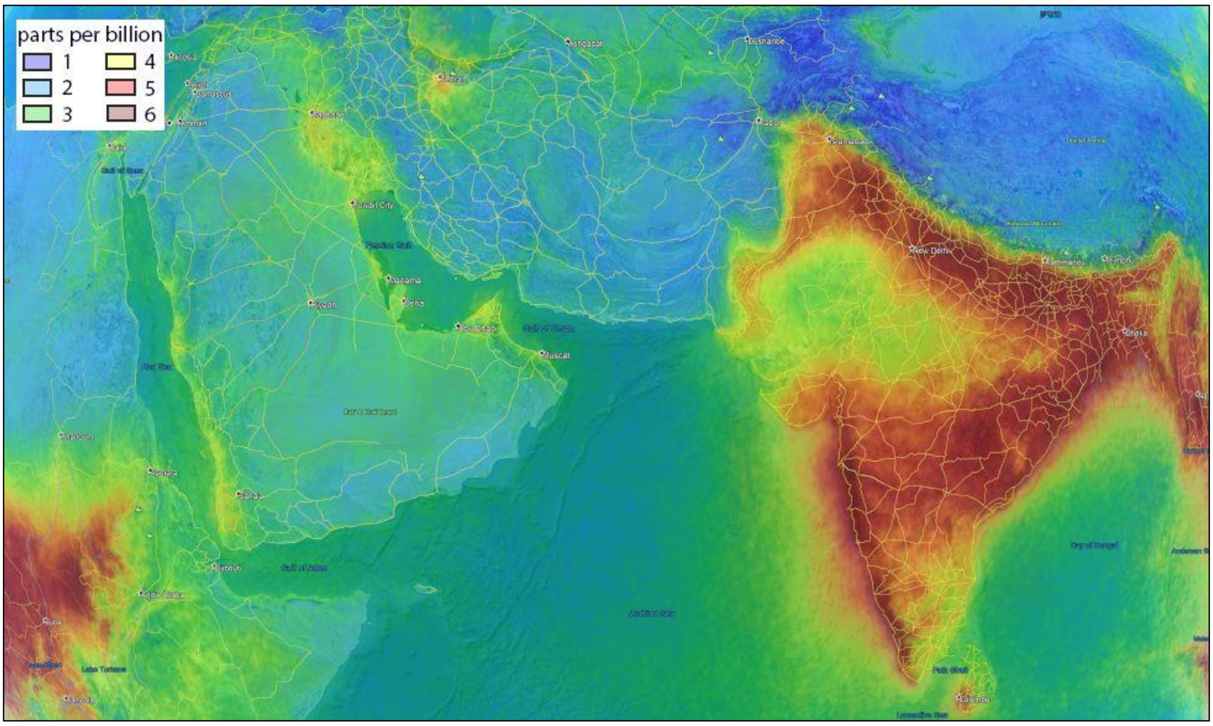

Figure 25 - Formaldehyde as measured by S5P-Tropomi: The map contains four months of observations up to April 2018 (Copernicus Sentinel data 2018/BIRA-IASB/DLR)

Earth Observation (EO) measurements have wide and varied potential applications in air quality. For example, satellite and aircraft measurements have been used in combination to directly assess exposure risks (Zhu *et al*., 2017) for HCHO. Given the lifetime of HCHO (typically a few hours) and that it is a by-product of the oxidation of many other VOCs, it has been extensively utilised as a satellite-derived proxy for primary VOCs emissions (Palmer et al., 2003; Millet et al., 2006). EO data has provided unique top-down constraints on bottom-up biomass burning and biogenic VOC emissions inventories used in for example chemical transport models *(*Kaiser *et al.,* 2018*;* Millet *et al*., 2006). Combinations of satellite and ground based measurements have been widely used to verify VOC emission inventories (Li *et al*., 2019; Cao *et al.*, 2018). Since the speciation that can currently be achieved with EO is limited, and measurements sensitivities in the boundary layer are limited, the technique is most suited at this time for providing a top down external check on overall emissions, and can provide insight into the transboundary transport of the by-products of VOC, in the form of secondary species such as formaldehyde.

Table 9. Summary of potential methods for speciated VOC measurements in ambient air.

	Existing Defra automated hydrocarbon network	**WMO-GAW two-column TD-GC-FID method**	**AGAGE type TD-GC-MS**	**PTR-MS or similar**
Measurement of recommended C_2-C_8 NMHC 30 compound suite	Yes	Yes	No, ~20-25 species, generally no C_2	~ 10 species yes, some others grouped as isomers, C_2 and C_3 not detected
Key OVOCs? methanol, ethanol, acetone, acetaldehyde	No	Yes	Yes	Yes
Untargeted analysis	No	No	Yes, if TOF-MS	Yes, if TOF-MS
Detection limit	~50 ppt	~10 ppt	~10 ppt	~20 ppt (better for hourly)
Time resolution	1 sample / hour	1 sample / hour	1 sample / hour	Up to 10 Hz
Cost per unit (£)	~50K	~80K	~£120K	~300K
Operational complexity inc. infrastructure	Medium	Medium	Medium/High	High

Annual running costs, including data work-up	Currently under a commercial contract	£40K per instrument per year.	£50K per instrument per year, plus central calibration lab needed for working standards	£60K instrument per year
Calibration	Monthly NPL 30 NMHC mixture cylinder	Weekly NPL 30 NMHC mixture cylinder, OVOC cylinders blended / diluted	Multiple times / day with real-air working standards, plus transfer and gold standards	Daily NPL 30 NMHC mixture cylinder, OVOC cylinders blended / diluted
Strengths	Simple, proven for NMHCs	Modest evolution of existing methods, proven for long-term observations, adds key OVOCs	Proven for long-term observations, flexible, sensitive, adds OVOCs.	Fast response, flexible, very sensitive to some OVOCs
Weaknesses	Speciation is not reflective of current VOCs in UK air	Difficult to calibrate for OVOCs, more limited speciation vs other methods.	Not compatible with all existing 30 NMHCs, substantial effort to calibrate.	Isobaric responses, Not compatible with all existing 30 NMHCs, rarely used long-term, expensive capital.

8 Recommendations

1. VOCs remain central to the formation of both ozone and particulate matter in ambient air. The non-linear nature of the atmospheric chemistry interactions that form these secondary pollutants means that further reductions in emissions of VOCs will continue to bring air quality benefits. Anticipated future reductions in NOx in the UK will require that VOCs are also reduced in concert if optimal ozone controls are to be achieved.

2. The modelling of the conversion of gas phase VOCs to secondary aerosols is currently uncertain and more evidence is needed to better quantify how further VOC emission reductions will impact on ambient $PM_{2.5}$. The role of biogenic VOC emissions as contributors to UK $PM_{2.5}$ is also uncertain, and should be considered in any assessment of VOC effects on $PM_{2.5}$.

3. VOCs such as benzene and 1,3 butadiene are now at ambient concentrations that are below the EU Directive limit and UK Air Quality Strategy target values for each. The Defra Automated Hydrocarbon network continues to provide however a critical data resource that gives some independent verification of the trends in emissions estimated by the NAEI and this network should be continued as a very high priority.

4. Recent changes in the major sources of VOC emissions in the UK require that revisions are now made to the analytical methods used for monitoring VOCs long-term. Adding ethanol, methanol, formaldehyde, acetone, 2-butanone and 2-propanol to the existing Defra non-methane hydrocarbon measurements would provide full observational coverage of the 20-most significant VOCs emitted on an annual mass basis in the UK.

5. The National Atmospheric Emissions Inventory is probably the most detailed speciated inventory of its kind anywhere in the world. However there has been little investment in the past decade in updating emission factors for either industrial or domestic solvent releases of VOCs, in terms of absolute amount, emission factors, activity data or chemical speciation. Policies and interventions to further reduce VOC emissions to meet NECD targets would be greatly informed by an updating of the VOC emission information in the NAEI to reflect current conditions.

6. The impact of domestic emissions of VOCs on indoor air quality is not covered in this report however there are clear co-benefits in linking management and standards for

the built environment with strategies for reducing overall national VOC emissions, since some fraction of VOCs that are released indoors are ventilated outside and contribute negatively to outdoor air quality.

7. VOCs form an integral part of thousands of everyday products as well as being key ingredients and by-products in a huge range of industrial, medical and food production processes. Awareness of VOC emissions from solvent sources, and their impacts, is relatively poor however and the VOC content and emissions from individual products is difficult to evaluate, something that could be potentially improved through public awareness and labelling.

8. Transformation in the UK towards Net Zero Carbon in 2050 will not necessarily lead to further reductions in VOCs, since emissions are increasingly de-coupled from energy and gasoline consumption and are now predominately driven by industrial and domestic use of manufactured volatile chemical products. Meeting future NECD targets for emissions, particularly in 2030, will need additional VOC-specific reduction strategies that are not reliant solely on further reductions from fuel distribution or road transport.

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