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Lewis, Alastair C. orcid.org/0000-0002-4075-3651, Hopkins, Jim R., Carslaw, David C. orcid.org/0000-0003-0991-950X et al. (6 more authors) (2020) An increasing role for solvent emissions and implications for future measurements of volatile organic compounds: Solvent emissions of VOCs. *Philosophical Transactions of the Royal Society of London. Series A, Mathematical and Physical Sciences.* 20190328. ISSN 1471-2962

<https://doi.org/10.1098/rsta.2019.0328>

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MATHEMATICAL, PHYSICAL AND ENGINEERING SCIENCES

An increasing role for solvent emissions and implications for future measurements of Volatile Organic Compounds

| | |
|---|--|
| Journal: | <i>Philosophical Transactions A</i> |
| Manuscript ID | RSTA-2019-0328.R2 |
| Article Type: | Research |
| Date Submitted by the Author: | 01-Jun-2020 |
| Complete List of Authors: | Lewis, Alastair; University of York, National Centre for Atmospheric Science Carslaw, David; University of York, Department of Chemistry Hamilton, Jaqueline; University of York, Department of Chemistry Hopkins, James; University of York, National Centre for Atmospheric Science Nelson, Beth; University of York, Department of Chemistry Stewart, Gareth; University of York, Department of Chemistry Dernie, James; Ricardo Energy and Environment, Gemini Building, Fermi Avenue, Harwell Murrells, Tim; Ricardo Energy and Environment, Gemini Building, Fermi Avenue, Harwell Passant, Neil; Ricardo Energy and Environment, Gemini Building, Fermi Avenue, Harwell |
| Issue Code (this should have already been entered and appear below the blue box, but please contact the Editorial Office if it is not present): | DM1119 |
| Subject: | Analytical Chemistry (5) < CHEMISTRY (1002), Atmospheric Chemistry (11) < CHEMISTRY (1002), Environmental Chemistry (67) < CHEMISTRY (1002), Atmospheric science < EARTH SCIENCES |
| Keywords: | Volatile Organic Compounds (VOCs), air pollution, atmospheric emissions |
| | |

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Yes

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All data in this study is available for free download from public repositories. Data on atmospheric VOC emissions is included in the National Atmospheric Emissions Inventory available at the uk-air.gov.uk website. Ambient monitoring data from the Defra Automatic Hydrocarbon network is also available for download from uk-air. Data on which mean concentrations of VOC in London and Beijing (table 3) is based are available from the Centre for Environment Data and Analysis: www.ceda.ac.uk. Data on VOCs in Delhi is currently subject to embargo but will be available on CEDA in 2021.

Conflict of interest

I/We declare we have no competing interests

Statement (if applicable):

CUST_STATE_CONFLICT :No data available.

Authors' contributions

This paper has multiple authors and our individual contributions were as below

Statement (if applicable):

ACL conceived the research, performed the analysis of VOC emissions trends and subsequent impacts on observations. JRH JFH, GS, BN, JRH and ACL contributed the observations and data for VOCs in London, Delhi and Beijing. DCC provided analysis of atmospheric trends in VOCs from the Defra network. JD, TM and NP undertook the development of the underlying emissions inventory and supported observations made in the Defra Automated Hydrocarbon Network. All authors contributed to the writing of the paper.

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**An increasing role for solvent emissions and implications for
future measurements of VOC-Volatile Organic Compounds measurement
strategies**

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Abstract

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7 Volatile organic compounds (VOCs) are a broad class of air pollutants which act as
8 precursors to tropospheric ozone and secondary organic aerosols. Total UK emissions of
9 anthropogenic VOCs peaked in 1990 at 2,840 kt yr⁻¹ and then declined to ~ 810 kt yr⁻¹ in
10 2017 with large reductions in road transport and fugitive fuel emissions. The atmospheric
11 concentrations of many nonmethane hydrocarbons in the UK have been observed to fall over
12 this period in broadly similar proportions. The relative contribution to emissions from
13 solvents and industrial processes is estimated to have increased from ~35% in 1990 to ~63%
14 in 2017. In 1992, UK national monitoring quantified the 19 of the 20 most abundant
15 individual anthropogenic VOCs emitted (all were non-methane hydrocarbons), but by 2017
16 monitoring captured only 13 out of the top 20 emitted VOCs. Ethanol is now estimated to be
17 the most important VOC emitted by mass (in 2017 ~136 kt yr⁻¹, ~16.8% of total emissions)
18 followed by *n*-butane (52.4 kt yr⁻¹) and methanol (33.2 kt yr⁻¹). Alcohols have grown in
19 significance representing ~ 10% of emissions in 1990 rising to ~30% in 2017. The increased
20 role of solvent emissions should now be reflected in European monitoring strategies to verify
21 total VOC emission reduction obligations in the National Emissions Ceiling Directive.
22 Adding ethanol, methanol, formaldehyde, acetone, 2-butanone and 2-propanol to existing
23 non-methane hydrocarbon measurements would provide full coverage of the 20 most
24 significant VOCs emitted on an annual mass basis.
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Key words: Volatile Organic Compounds (VOCs), air pollution, atmospheric emissions

1. Introduction.

The formation of tropospheric ozone from the reactions of volatile organic compounds (VOCs) and NO_x in the presence of sunlight is very well-established science that dates back to atmospheric chemistry research in the 1950s (e.g. Haagen-Smit and Fox 1954)¹. Sunlight in the near-UV either directly destroys VOCs or initiates reactions that generate free radicals that can lead to the oxidation of VOCs, and the generation of peroxy radicals that can convert NO to NO_2 , and thus create a route to the net photo-chemical production of ozone from NO_2 photolysis. Ozone at the planetary surface has impacts on health that include an exacerbation of asthma² and increased risk of death from respiratory causes³. More recent advances in the atmospheric chemistry of VOCs have included insight that oxidation of certain species⁴ leads to chemical by-products that can create new particles⁵, add mass to existing particulate matter (PM)⁶, or change other properties of PM⁷. There is now a large body of observations confirming the ubiquitous presence of secondary organic aerosol (SOA) in virtually all environments⁸. A consequence is that the environmental motivations for controlling primary anthropogenic VOC emissions now go beyond the established science of ozone formation and form part of $\text{PM}_{2.5}$ reduction strategies⁹.

The term VOC, used frequently and interchangeably with the longer abbreviation non-methane volatile organic compounds (NMVOCs) is a catch-all term for any organic compound found as a gas in the atmosphere. In urban air NMVOCs can encompass many thousands of different organic compounds including non-methane hydrocarbons (NMHCs), oxygenated, nitrated and halogenated species¹⁰. Since the term VOC is so broad, for regulatory and policy purposes more specific definitions are used. One such technical definition is given in official guidelines issued by the European Monitoring and Evaluation Programme (EMEP) and the parallel United Nations Economic Commission for Europe (UNECE) Convention on Long Range Transport of Air Pollution (CLRTAP) for national inventory reporting of emissions. The same definition is also used in the European Commission (EC) Directive 1999/13/EC (Solvent Emissions Directive)¹¹ and EC National Emissions Ceiling Directive (NECD)¹².

“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.

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5 A slightly different definition of VOCs is given within the 2004/42/EC Paints Directive¹³,
6 which refers to a VOC as “*an organic species with a boiling point less than 250 °C at a*
7 *standard pressure of 101.3 kPa.*”
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11 The practical realisation of both definitions is that most simple non-methane hydrocarbons
12 with a carbon number falling within the range C₂ to C₁₄ are thought of as VOCs. Longer-
13 chain hydrocarbons (>nC₁₄) may fall outside of the definition, as may more highly
14 functionalized organic compounds such as organic acids or organic peroxides. The majority
15 of persistent organic pollutants (POPs) have lower vapour pressures than this definition,
16 although some two and three ring polycyclic aromatic hydrocarbons such as naphthalene are
17 considered as VOCs as well as POPs. The EC Air Quality Directive 2008/50/EC¹⁴ includes
18 within it a somewhat broader definition related to an ability to form ozone:
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27 “*volatile organic compounds’ (VOC) shall mean organic compounds from anthropogenic*
28 *and biogenic sources, other than methane, that are capable of producing photochemical*
29 *oxidants by reactions with nitrogen oxides in the presence of sunlight*”
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34 The reporting of emissions as set out in treaties such as NECD and CLRTAP in principle
35 takes into account all species that fall within the relevant technical definition. In the case of
36 the UK this is done through evaluation of hundreds of different sources where statistical data
37 must be collated for the purposes of reporting a single annual VOC emission total. The
38 majority of countries report totals of emissions from various different sectors. The UK is
39 unusual in then mapping the sectoral emissions onto nearly 700 different species.
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46 Pragmatic decisions are obviously needed with respect to those VOCs that might be
47 measured as part of any verification or regulatory activities. Measurements may be needed to
48 inform directly on attainment of specific health-related VOC concentration targets (for
49 example for benzene and 1,3-butadiene), or those VOCs that may act as an independent
50 check that estimated emissions changes are being reflected in the ambient atmosphere.
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56 Since all VOC analytical methods have boundaries on specificity and sensitivity, a very
57 limited range of VOCs are typically monitored in ambient air, compared to those actually
58 emitted. Ideally the species that are routinely monitored in air should reflect those that are
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3 indicative of the most significant emissions, and those that cause the greatest harm to health.
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5 Across Europe routine monitoring of VOCs has followed guidelines in Annex X of the
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7 Directive on Cleaner Air for Europe 2008/50/EC. This recommends the measurement of 31
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9 individual VOCs, all non-methane hydrocarbons, ranging in molecular weight from ethane,
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11 through to 1,3,5-trimethylbenzene. From these recommendations have followed a range of
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13 commercial monitoring instruments based around thermal desorption and the development of
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15 traceable standards for calibration to mole and kilogram¹⁵. The choices around which species
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17 have been measured historically has been a mixture of practically (what can be measured)
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19 informed by which were the most significant VOCs being emitted when routine monitoring
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21 became established in Europe in the 1990s. In the case of the UK, continuous VOC
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23 monitoring began around 1992. It is noteworthy however that unlike virtually all other air
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25 quality parameters covered by the NECD there is no standard European reference method for
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27 measurement, although there have been efforts at standardisation associated with calibration
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29 and reference materials¹⁶. This paper evaluates how VOC emissions have changed over the
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31 last three decades in terms of both absolute amount and VOC speciation, using the UK as a
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33 test case for a high-income country, and the possible implications for future observational
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35 VOC networks used to track progress towards emissions targets in 2030 and beyond.

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2.1 Evaluating VOC emission changes using inventories

The National Atmospheric Emissions Inventory (NAEI) estimates UK VOC emissions from anthropogenic sources following methods in the EMEP/EEA Emissions Inventory Guidebook¹⁷ for submission under the revised EU Directive 2016/2284/EU on National Emissions Ceilings (NECD) and the reporting framework of CLRTAP¹. Both the NECD and CLRTAP set emissions ceilings with milestone targets for particular dates. For example the NECD sets a ceiling for 2020 that requires a 32% reduction in total UK emissions relative to 2005 levels, excluding agricultural sources. This equates to 724 ktonnes in 2020 based on the latest NAEI estimates for 2005. The NECD then requires a 39% reduction in emissions relative to 2005 levels by 2030, equivalent to 649 ktonnes.

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

¹ 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

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3 included) and the technical definition (see earlier). The Guidebook provides estimation
4 methodologies and default emission factors for each source category, although countries can
5 use country-specific emission factors where these are deemed relevant. Key requirements for
6 inventory reporting are Transparency, Completeness, Consistency, Comparability and
7 Accuracy and in this respect, it is important to provide a national inventory with time-series
8 consistency going back to at least 1990 and forward to 2030.
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14 The NAEI uses a combination of emission factors from the EMEP/EEA Guidebook and
15 emission rates provided by industry and regulators in the UK. The emission factors represent
16 either i) the total mass of all individual VOCs when added together or ii) a metric defined as
17 total hydrocarbons (THCs), a non-speciated mass of VOCs, used for example in the case of
18 tailpipe road transport emissions. The speciation of the total emissions into individual VOCs
19 is undertaken separately. Where THC factors are used, the methane emissions calculated
20 separately are subtracted out.
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27 The NAEI uses three basic approaches for estimating total VOC emissions – top down, point
28 source and industry-reported. In the first case, an emission factor approach (top-down)
29 combined with relevant activity statistics is used for many combustion sources including
30 crude oil refineries, other industrial sites, and in residential buildings. Factors are also used
31 for transport sources, as well as for some processes in the food and drink industry (for
32 example bread baking and whisky production) and for some uses of solvents², including
33 many consumer products.
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39 A point-source approach (bottom-up) can be used where the sum of emissions is
40 estimated/measured and reported by process operators for each emitting site within a sector.
41 The UK estimate is generated simply by summing the emissions reported for all of the sites
42 within a given sector. This approach is used for refinery processes, chemicals industry, oil
43 and gas production and certain types of solvent use in industry such as for printing of flexible
44 packaging, and coating of road vehicles. Key sources for data on point source emissions are
45 the regulators in England, Scotland, Wales and Northern Ireland who maintain inventories for
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54 ². The term ‘solvents’ is rather imprecise and could be possibly interpreted as defining some specific
55 chemical functionality or property, although there is no universally agreed definition. In this paper
56 when we refer to solvents we are referring to those VOCs included in that emissions class for the
57 purposes of international emissions reporting. In a chemistry lab setting the term solvents brings to
58 mind VOCs such as acetone, ethanol, toluene and so on, and they are indeed major species in solvent
59 inventories. For emissions reporting purposes a wider range of VOCs are included under the
60 definition including aerosol propellants such as butane and some long-chain aliphatic compounds.

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3 the processes they regulate, and the BEIS Environmental & Emissions Monitoring System
4 (EEMS) for the offshore oil and gas sector.
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7 In the case of solvent use, the third approach is used for UK emission estimates taking data
8 provided directly by industry. However, this may come with little additional information on
9 emission factors or activity data. Data are often supplied on an *ad hoc* basis and usually
10 cover a limited number of years, thus a time-series may need to be generated by splicing
11 together various data sets, possibly from different data providers. Therefore, there is a risk
12 that a time-series might not be fully consistent and estimates for different years may be
13 subject to different levels of uncertainty. However, industry estimates are essential for the
14 VOC inventory: they provide data for sources where the lack of public domain data means
15 that emission factor or point source approaches cannot be used. Further details of the
16 methods used in the NAEI are provided in the UK's national inventory report submitted
17 annually to the UNECE and NECD. The latest version of the inventory is for years up to
18 2017 (the 2017 NAEI) as submitted in early 2019 (NAEI, 2019).
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28 **2.2 Trends in estimated total VOC emissions in the UK**

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30 Figure 1 shows the trends in anthropogenic VOC emissions from 1990-2017 estimated in the
31 NAEI, grouped into ten major source categories, plus projections for emissions in 2020 and
32 2030. National emissions are estimated to have decreased from a peak of 2,837 ktonnes in
33 1990 to 807 ktonnes in 2017, a fall of 72%, a consequence of major reductions from road
34 transport and fugitive emissions from fuels. The decrease in road transport emissions has
35 been mainly due to the introduction of more stringent vehicle emission standards such that by
36 2017 this sector contributed only ~4% of total UK VOC emissions, compared with 30% in
37 1990.
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44 The largest contribution to VOC emissions in 2017 was from solvents. Overall emissions
45 have decreased for this sector, but by significantly smaller amounts than road transport and
46 fugitive emissions. There have also been relatively smaller reductions in emissions from
47 industrial processes such that this sector contributed 15% of total emissions in 2017; these
48 emissions now mostly come from the food and drink industry which have been increasing
49 since 1990.
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55 The period since around 2000 has seen a substantial re-ordering of the relative contributions
56 from each of the major source sectors. Figure 2 shows six sectoral emissions as an annual
57 percentage contribution made to national VOC emissions. There has been a steep decline in
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3 the road transport contribution and steady growth since circa 2000 in the contribution from
4 solvent use, particularly ethanol. Based on the 2017 version of the inventory, the UK met the
5 2010 NECD emissions target of 1,200 ktonnes VOCs, and then did so for all subsequent
6 years to 2017 (the last year reported here). Whilst a small further reduction in emissions is
7 anticipated to occur up to 2020, emissions then remain fairly constant up to 2030. This
8 situation arises because emissions from large sources important in the past, such as road
9 transport, have already been reduced significantly and there remains little scope for further
10 reductions. For example there are currently no further VOC emission reductions planned
11 beyond the vehicle class of Euro 6/VI. Emissions from sources such as solvent use, food and
12 drink and industrial processes remain fairly flat or increase slightly because emission factors
13 are assumed to remain constant whilst activities are predicted to remain static or increase
14 slightly (often following population change).

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16 Overall, a small exceedance of the 649 ktonne NECD target for 2030 is predicted for the UK
17 unless there are further actions to reduce emissions. The size of additional reduction needed
18 to meet the 2030 target is estimated to be around 30 ktonnes per year by 2030 based on
19 current projections. Meeting those targets is likely to require an increased policy and
20 regulatory focus on those VOCs from the solvent and industrial usage sectors, and so the next
21 section examines which VOC species are significant contributors.

22 23 24 25 26 27 28 29 30 31 32 33 34 35 **2.3 VOC speciation in key emission sectors**

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37 There is no statutory requirement to report national inventories of individual VOC species to
38 the NECD or CLRTAP, but a comprehensive speciated inventory is very valuable for other
39 purposes. Given the different chemical reactivities of each component, a speciated inventory
40 is essential for atmospheric models of ozone and secondary organic aerosol formation. It is
41 also necessary for interpretation of ambient measurements of VOCs and how such
42 information can be used to verify inventory trends.

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48 The UK is one of the few countries to have developed a comprehensive speciated inventory
49 for VOC emissions and this is widely used in atmospheric modelling. The speciated
50 inventory was first developed in the mid-1990s but the lack of significant new data sources
51 means that development essentially finished in the early 2000s when the methodology was
52 published¹⁸. The NAEI's VOC inventory is broken down into 664 species with unique VOC
53 profiles for each emission source. These are mostly as chemically unique species although
54 occasionally these are expressed as aggregate groups of VOCs, for example, "C₁₃ aromatics".
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3 The information used in the development of the species profiles came from various sources,
4 for example industry trade associations in the 1990s provided some speciated estimates
5 including the Solvent Industry Association, the British Coatings Federation and British
6 Aerosol Manufacturers Association. The solvent industry also helped with speciation of
7 white spirit and other hydrocarbon mixtures. The Environment Agency's Pollution Inventory
8 and similar inventories compiled by other UK regulators include some details of speciation,
9 although the amount of detail is now much less than was the case in the early 1990s. Some
10 analysis was undertaken of fugitive emissions at petrol stations and species profiles were also
11 provided by the refinery sector. The profiles for vehicle exhaust emissions were taken from
12 the EMEP/EEA Emissions Inventory Guidebook. An important source for other sectors was
13 the US EPA SPECIATE database.
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23 As much of the data used to develop the speciation profiles were gathered during a short
24 period in the late 1990s and early 2000s, and since more recent data are not available, it is
25 assumed that the species emitted by a particular source are the same in all years. While this
26 is likely to be true for sources such as bread baking or gasoline distribution, it is probably not
27 true of technologically evolving sources such as industrial coating processes, chemicals
28 manufacture or the formulation of consumer and household products.
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33 There are ~360 different individual VOC source sectors or processes included within the
34 NAEI and each of these has a representative chemical speciation associated with it, so it is
35 possible to interrogate the NAEI for annual amounts and therefore emission trends of
36 individual VOCs. Although in total the NAEI contains data on nearly 700 VOCs, a much
37 smaller subset of ~40 VOCs represents typically ~70% of the total mass of emissions. The
38 10 most significant individual VOCs in terms of mass emitted represented 45.3% of UK
39 national emissions based on 2017 estimates. Ethanol was the most important VOC
40 comprising 16.8% of all emissions. The recent trends in the ten highest VOCs by mass
41 emission are shown in Figure 3.
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49 Figure 3 highlights a national trend since 1990 of decreasing emissions of simple non-
50 methane hydrocarbons associated with natural gas leakage (ethane), evaporative loss of fuels
51 (e.g. pentane, butane, toluene) and reductions in VOCs from tailpipe emissions (e.g. benzene,
52 ethene). Over the same period there have been increases in emissions of ethanol and
53 methanol. The increase in ethanol in the NAEI is due to increased reported emissions from
54 the whisky industries and in estimated domestic use of ethanol as a solvent, for example
55 contained within personal care, car care and household products. The more recent addition of
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3 bio-ethanol to gasoline is included in the inventory, but due to the relatively low level of
4 contemporary fugitive emissions and exhaust emission, this has not contributed significantly
5 to this upward trend.
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9 Even for simple alkanes there have been some notable changes in the major contributing
10 sources. *n*-butane for example is currently the second most abundant VOC in the UK
11 inventory; in 1990 *n*-butane was emitted overwhelmingly from gasoline extraction and
12 fugitive distribution losses (139.8 kt yr⁻¹). However by 2017 the largest anthropogenic source
13 of *n*-butane in the inventory was from its use as an aerosol propellant (25.5 kt yr⁻¹) with the
14 gasoline / fugitive losses having been reduced to 23.3 kt yr⁻¹.
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19 **2.4 Change to emissions of VOC functional groups**

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21 Figure 3 shows the multi-year trends in the estimated emissions of some of the most
22 significant VOCs from a mass-emitted perspective, but it is possible to look more generally at
23 trends in the types of VOCs being emitted, by categorising the very large number that are
24 individually speciated in the NAEI and then grouping by chemical functional groups. Figure
25 4a shows the estimated emissions trends of 12 VOC functional group types, plus a further
26 'other' category for all other minor functionalised VOCs that do not fall within these 12
27 classes. Figure 4b show the same data but expressed as a group contribution to the annual
28 emissions in percentage terms for each year. The most striking feature is the increased
29 significance of alcohols generally, with significant contributions to 2017 emissions made by
30 1-propanol, 2-propanol and 1-butanol as well from methanol and ethanol highlighted in the
31 previous figure.
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42 Understanding the exact location- and condition-specific impacts of a change in VOC
43 speciation on tropospheric ozone can only be done fully using explicit modelling and is
44 beyond what we report here. It is possible however to evaluate how a change in VOC
45 speciation may impact on the ozone forming potential of national emissions in the
46 atmosphere by considering the Photochemical Ozone Creation Potential (POCP)^{19 20} of the
47 VOC mixture. Using the overall POCP of the ensemble of VOCs emitted it is possible to
48 examine at a bulk level whether the changes in speciation might have led to a change in
49 overall ozone forming potential, per tonne of 'average' UK VOC emissions. Figure 5a shows
50 the trends in total VOC emissions for the UK (by mass) and the normalised POCP for each
51 year derived from the top 40 emitted VOCs in that year using Derwent *et al.* 1998 POCP
52 values. The 40 VOCs for which the calculation is made represent around ~70% of overall
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emissions by mass and assumes that NO_x and all other relevant photochemical parameters are held constant.

Over the 1990-2017 period the normalised POCP of the UK VOC mixture declined slightly, by around 4%. A complex set of changes lie behind this; the largest change in any single VOC is the reduction in ethane emissions (a low POCP compound) and the growth in ethanol (a species of intermediate POCP reactivity). However, there are also concurrent reductions in a range of other high POCP alkenes and aromatic compounds that offset the growth in ethanol. The net change is to an average emissions mixture that is very slightly lower in POCP per unit national emissions in 2017 than the mixture being emitted in 1990, but likely too small a change to materially affect ozone formation rates.

2.5 Changes in ambient concentrations

Continuous measurements have been made of a range of nonmethane hydrocarbons in the UK Automated Hydrocarbon Network since 1992. The shape of the network has changed over the years, although the methodology has always been based around thermal desorption – GC-FID. Further details can be found on the UK-AIR online resource³. Since 2001 there have been four continuous GC-FID systems measuring non-methane hydrocarbons in the UK and of these the monitoring station at Marylebone Road in Central London has the most complete data record. Although Marylebone Road is formally a roadside location it does experience the full range of urban emissions given its central position within the city. Other publications have reported data from the UK up to around 2008, for example von Schneidmesser *et al*²¹. Here we show some of the more recent trends in ambient NMHCs as measured at Marylebone Road and then compare to changes indicated in the NAEI.

Figure 6 shows trends for 25 different species. Each hydrocarbon has a unique behaviour over time, although three distinct trends are observable. For ethane and propane, derived largely from natural gas leakage, there have been only modest reductions in ambient concentrations in central London since 2000. For a range of hydrocarbons derived predominantly from sources such as gasoline evaporation and incomplete combustion, for example xylenes, toluene, 1,3-butadiene there is a broadly log-linear decrease of ~ 2 orders of magnitude with reductions being seen up to the most recent year of observations. For some species like butenes, pentenes and 1,3-butadiene ambient concentrations are now close to instrumental detection limits and there is considerable scatter in the data. There is a third type

³See <https://uk-air.defra.gov.uk/networks/network-info?view=hc> for further details of the UK Automatic Hydrocarbon Network

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3 of behaviour for VOCs that showed initial falls in ambient concentrations in the early 2000s
4 but that have plateaued more recently. These include *i* and *n* butane, ethene, benzene, ethyne
5 and propene. This is potentially rationalised as arising from initial falls in concentrations
6 through the reduction of emissions of these species from their road transport source, but that
7 other urban sources also exist that have not declined and that now dominate ambient
8 concentrations.
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14 Ambient concentrations measured at the roadside cannot be expected to directly reflect
15 inventory changes, since roadside monitoring sites of this kind are skewed to detecting
16 changes in the locally dominant road transport source. However, it is still instructive to
17 examine the general scale of reductions seen and the degree of agreement between
18 observation and inventory. Table 1 shows the annual mean concentrations for a range of
19 VOCs and the estimated change in emissions over a similar period. The nature of the
20 Marylebone Road monitoring makes it particularly sensitive to road transport emissions, and
21 for many VOCs the reductions in roadside concentrations have been greater than those
22 estimated as a percentage of overall national emissions, reflecting particular success in
23 reducing emissions from this sector. In the case of natural gas-derived VOCs like ethane and
24 propane, urban concentrations reported through UK-AIR have changed little in recent years
25 whilst national emissions of ethane are estimated to have fallen by 66% between 2000 and
26 2017 for all sources and by 52% for natural gas leakage according to the NAEI. This
27 mismatch between trends in emission estimates and concentrations may in part be
28 rationalised due to the inventory reductions in emissions occurring in remote offshore
29 extraction industries and distribution networks, which are displaced from monitoring sites. It
30 may also be the case that in London gas leakage rates have been higher than the UK average
31 which the NAEI is based on. It is also important to consider that the lifetimes of these
32 species are long and significant hemispheric background concentrations are present.
33 Observations in Europe have shown similar ambient trends to those reported here, with
34 declines across several European roadside locations²².
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51 Making direct like-for-like trend comparisons between observations and inventories is
52 generally not appropriate, given multiple contributing sources that define the ambient
53 concentrations of any given VOC. Urban monitoring stations can be sensitive to a particular
54 subset of sources along with reflecting broader patterns of long lifetime VOCs which are
55 influenced by regional transport. However, 1,3-butadiene is one VOC where some direct
56 comparisons can potentially be made. The lifetime of butadiene during daytime with respect
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3 to hydroxyl radical oxidation is very short, around 30 minutes, and so its measured
4 concentration essentially reflects local sources only. The only major urban source of 1,3-
5 butadiene is thought to be road transport tailpipe emissions. In Figure 7 we show the trend in
6 roadside concentrations of 1,3-butadiene (Marylebone Road) against the inventory estimated
7 emissions of 1,3-butadiene from the road transport sector (i.e. excluding all other sources
8 such as refineries and fossil fuel extraction). There is a remarkable degree of agreement in
9 trends between the estimated emissions and ambient roadside observations, with some
10 evidence that for a period, ambient concentrations reduced faster than reported in the
11 inventory, potentially due to overperformance of emission control technologies in the early
12 and mid 2000s. The trends in 1,3-butadiene can be contrasted with benzene, a much longer-
13 lived VOC, which has significantly greater diversity of emissions sources beyond road
14 transport tailpipe emissions.
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24 **2.6 Impacts of changing speciation on monitoring strategies**

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26 Previous sections have shown how at a national level, current emissions in the UK are now
27 significantly influenced by VOCs released from solvent use, both industrial and domestic. As
28 further reductions in emissions are required across Europe, and most reductions from the
29 fossil fuel and transport sectors have likely already been achieved, reducing solvent
30 emissions appear the most feasible route to meet future NECD objectives. Specific policies
31 and interventions that might achieve these aims are beyond this paper, but there will likely be
32 an overarching requirement for ambient observations to continue to provide some external
33 verification that changes in emissions as determined by inventory reporting processes have
34 occurred. This situation creates a measurement challenge since the solvents sector is heavily
35 influenced by oxygenated compounds, rather than non-methane hydrocarbons which current
36 on-line monitoring infrastructure is generally best configured to detect²³. There are then
37 further questions raised about where geographically representative measurements should be
38 made if transport sources are no longer significant.
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49 The current speciation of VOCs from the class of ‘solvents and related products’ in the NAEI
50 is likely imperfect due to lack of up to date speciation information from manufacturers, but it
51 provides some guide to the key species that are released. Figure 8 shows the fractional
52 contributions for the most abundant 43 VOCs in this solvent emission class in the NAEI for
53 2017, dominated again by ethanol and methanol, but with significant contributions from
54 ketones like acetone and 2-butanone and halocarbons including trichloroethene and
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3 dichloromethane. The figure is annotated by those species that are currently routinely
4 monitored (in green) with those that are not (in red).
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7 An alternative way of visualising the impacts of changing emission speciation on monitoring
8 strategies is to consider the most significant VOCs (either individual species or inventory
9 lumped groups) emitted each year and then whether there is coverage in terms of ambient air
10 measurements. We evaluate this by taking a time slice at 5-year intervals from the VOC
11 speciation in the NAEI and rank order the top 40 VOCs emitted in each year.
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16 VOCs in Table 2 with a white background are currently measured as part of the UK
17 Automated Hydrocarbon Network, and this is mirrored widely in terms of analytical
18 methodology across Europe and elsewhere. Those species shaded are not currently monitored
19 routinely. It is clear that when the UK / EMEP networks for on-line monitoring were first
20 designed there was very good alignment between the major VOCs being emitted and the
21 VOCs being monitored. Of the top 20 unique VOCs emitted in 1990, 19 were captured by the
22 Automated Hydrocarbon Network (this excludes a NAEI lumped group of $>C_{13}$). Over time
23 however the observational coverage has declined, to 2017 when only 13 of the top 20 VOCs
24 were routinely monitored, including omission of two of the top three most significant VOCs
25 emitted by mass.
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34 It is also instructive to note those VOCs which are not as significant as they once were.
35 Ethyne is one of the most challenging VOCs to measure using thermal desorption techniques
36 due to its very low boiling point, and this can be a defining factor for much of the analytical
37 instrumentation for analysis (for example breakthrough volume). By 2017 ethyne had fallen
38 to 82nd when ranked by mass of emissions from a position in 1990 of 21st. An argument can
39 also be made that the various isomers of butenes and pentenes that were once important as
40 contributors to both total mass emissions and to reactivity and ozone creation potential in the
41 1990s have been reduced so significantly that the effort expended on their measurement in
42 networks may not be particularly productive.
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50 **2.7 Global applicability to emissions and monitoring in other locations.**

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52 Since there is no standardised international requirement to report speciated VOCs as part of
53 emissions control treaties it is difficult to make direct comparisons between the UK-specific
54 conclusions we report here and other global locations. We make some attempt to reality-
55 check whether the influence of oxygenated VOCs is as great as suggested by UK inventories
56 by examining the most significant VOCs detected in ambient air in the UK and in other
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3 countries, using data collected from short periods of research observations and process
4 studies. Ambient data is of course not directly comparable to emissions inventories at a
5 national scale, since large point sources may not be detected at a given measurement location
6 and there may be important seasonal factors not captured in short-term measurements that are
7 reflected in annual averages. Many oxygenated VOCs are also produced through
8 atmospheric oxidation, so they may be elevated in ambient air not solely because of direct
9 anthropogenic emission, but also as a by-product of the degradation of other VOCs. This is
10 particularly important for acetaldehyde and formaldehyde which are common degradation
11 products, including also from natural emissions such as isoprene. We exclude those from this
12 analysis. From recent literature we note the work of McDonald *et al.* 2018²⁴ which shows
13 ethanol, iso-propanol and acetone as three of the four most abundant individual VOCs
14 measured in ambient air in Pasadena, USA. From our own observations made using two-
15 column GC-FID in various locations we find a good degree of consistency between the top
16 VOCs ranked by ambient concentrations in different global locations. Table 3 shows
17 examples of the most abundant VOCs in ambient air in London, Beijing (measured during
18 wintertime) and Delhi (during the post-monsoon period), all part of research-intensive
19 observation periods. We use wintertime data since this is a closer reflection of source
20 emission profiles since oxidation losses are lower than in summer. The concentration of
21 VOCs found in each location differs very significantly, with order magnitude differences
22 between London (lowest) and Delhi (highest). However, for all three urban locations ethanol
23 is the most abundant VOC with methanol and acetone also found in the top 10 species in all
24 three locations.

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27 We note that since research observations exist for many oxygenated VOCs, it demonstrates
28 that there are no insurmountable technical obstacles to improving routine measurement
29 coverage²⁵. This paper does not make recommendations for how best a broadened set of
30 VOCs might be measured in automated networks, but there are several proven analytical
31 approaches available - widely reported in literature are GC-FID²⁶, GC-MS²⁷ and online
32 chemical ionisation mass spectrometry²⁸. Indeed, the World Meteorological Organisation
33 Global Atmosphere Watch (GAW) programme has already supported a set of calibration
34 infrastructure and measurement guidelines for some oxygenated VOCs²⁹, although
35 measurements remain sparse at GAW background stations³⁰.

3. Conclusions

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3 Inventory estimates of total VOC emissions in the United Kingdom show significant
4 decreases over the past 30 years from a peak around 1990, which is mirrored in ambient
5 measurements of some non-methane hydrocarbons. The most significant sources in the 1990s
6 were non-methane hydrocarbons related to fossil fuel usage, in particular from natural gas
7 extraction and distribution, gasoline tailpipe emissions and fugitive fuel losses. Policies and
8 regulations across multiple sectors to reduce emissions have been very effective, particularly
9 from road transport, which now contributes only a small amount (~4%) to total UK VOC
10 emissions. There has been little change in overall emissions from industrial and domestic
11 solvent usage, and this has resulted in a growth of this sector as a proportion of national
12 emissions. Along with this change has been a change in both the relative and absolute
13 amounts of individual VOCs emitted. Ethanol is now the most abundant VOC emitted in the
14 UK and overall, short-chain alcohols are the most important functional group, measured by
15 mass. The shift in functional groups has not however had an appreciable impact on overall
16 average POCP (a 4% decline) since the growth in ethanol has been balanced by losses in
17 reactivity in other species, notably alkenes and mono-aromatics.

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If future changes in emissions are to be independently tested against external atmospheric
monitoring, then a revised analytical strategy is needed, both in terms of species quantified
and locations of the measurement themselves. The current online VOC networks used across
Europe predominantly focus on the measurement of non-methane hydrocarbons, with only
rather limited coverage of certain functionalised VOCs using off-line methods, for example
to measure aldehydes. This results in many of the major oxygenated VOCs emissions going
undetected, and skewed in geography towards VOCs emitted from transport sources. Without
some change to this position it will not be possible to evaluate how successful future policies
and technical interventions have been in reducing solvent emissions, noting that reductions in
VOCs are needed in many countries to meet NECD and CLRTAP obligations for 2030. The
addition of ethanol, methanol, formaldehyde, acetone, 2-butanone and 2-propanol to the
existing suite of non-methane hydrocarbon measurements would provide for full
observational coverage of the 20 most significant VOCs emitted on an annual mass basis. It
may be possible for a change in future observational strategy to be brought closer to cost-
neutral in operational terms by ceasing observations of certain analytically challenging
nonmethane hydrocarbons, such as acetylene, butenes and pentenes which have seen their
emissions fall very significantly and that are now often close to or below instrumental
detection limits in UK ambient air.

Acknowledgements.

The authors thank the members of the Defra Air Quality Expert Group (AQEG) for their contributions to the recent analysis of VOCs in the UK, work which has greatly informed the conclusions of this paper. ACL and JRH acknowledge funding from NERC NC LTSS and from NERC grant numbers NE/R011532/1 and NE/T001917/1. This paper draws on data from the version of the National Atmospheric Emissions Inventory programme published in 2019 (the 2017 NAEI) and prepared by Ricardo Energy & Environment under contract to the Department for Business, Energy and Industrial Strategy.

Trends in ambient non-methane hydrocarbons measured at Marylebone Road are drawn from the UK-AIR website operated by Ricardo Energy & Environment under contract to the Department for Environment Food and Rural Affairs.

The Delhi measurements were taken as part of the DELHI-FLUX project, grant reference NE/P016502/1. We acknowledge the logistic support of Ranu Gadi and Shivani (Indira Gandhi Delhi Technical University for Women), Eiko Nemitz and Neil Mulligan (Centre for Ecology and Hydrology) and Tuhin Mandal (CSIR-National Physical Laboratory).

Data Accessibility Statement

All data in this study is available for free download from public repositories. Data on atmospheric VOC emissions is included in the National Atmospheric Emissions Inventory available at the uk-air.gov.uk website. Ambient monitoring data from the Defra Automatic Hydrocarbon network is also available for download from uk-air. Data on which mean concentrations of VOC in London and Beijing (Table 3) is based are available from the Centre for Environment Data and Analysis: www.ceda.ac.uk. Data on VOCs in Delhi is currently subject to embargo but will be available on CEDA in 2021.

Author Contributions

ACL conceived the research, performed the analysis of VOC emissions trends and subsequent impacts on observations. JRH JFH, GS, BN, JRH and ACL contributed the

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3 observations and data for VOCs in London, Delhi and Beijing. DCC provided analysis of
4 atmospheric trends in VOCs from the Defra network. JD, TM and NP undertook the
5 development of the underlying emissions inventory and supported observations made in the
6 Defra Automated Hydrocarbon Network. All authors contributed to the writing of the paper.
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Table 1. Selected comparison of emission reductions for individual Volatile Organic Compounds (VOCs) estimated in the NAEI-National Atmospheric Emissions Inventory (2000-2017) and the change in concentrations observed in central London at the Marylebone Road monitoring station.

| VOC | 2000 annual mean /mg m ⁻³ | 2018 annual mean /mg m ⁻³ | Roadside Change % | 2000 emission /ktonnes | 2017 emission /ktonnes | NAEI Change % |
|---------------------|--------------------------------------|--------------------------------------|-------------------|------------------------|------------------------|---------------|
| ethane | 11.5 | 8.3 | -27.6 | 96.0 | 33.1 | -65.5 |
| propane | 6.2 | 5.2 | -16.4 | 67.1 | 28.1 | -58.1 |
| <i>i</i> -butane | 10.6 | 2.4 | -77.9 | 27.8 | 8.4 | -70.0 |
| <i>n</i> -butane | 22.1 | 2.9 | -86.9 | 112.8 | 52.4 | -58.5 |
| <i>i</i> -pentane | 24.8 | 2.5 | -90.1 | 43.7 | 21.1 | -51.7 |
| benzene | 8.1 | 0.7 | -91.9 | 56.6 | 13.2 | -76.7 |
| toluene | 28.0 | 2.5 | -90.1 | 56.1 | 13.1 | -76.6 |
| ethyl benzene | 5.1 | 0.5 | -90.0 | 22.6 | 6.3 | -72.1 |
| ethene | 14.4 | 2.4 | -83.5 | 43.7 | 21.1 | -51.7 |
| propene | 7.0 | 1.5 | -78.5 | 22.2 | 5.4 | -75.7 |
| 1,3 butadiene | 1.7 | 0.3 | -93.3 | 10.5 | 2.0 | -81.4 |
| <i>t</i> -2 pentene | 1.6 | 0.1 | -93.4 | 2.9 | 0.8 | -72.4 |
| ethyne | 7.0 | 1.9 | -72.0 | 13.0 | 1.7 | -86.9 |

Table 2. Top 40 anthropogenic ~~VOC~~ Volatile Organic Compounds species emitted by mass in the United Kingdom in different time periods 1990-2017. Shaded species are not routinely measured by existing automated ~~nonrotating~~ monitoring networks.

| Rank | 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-me butane | ethylene | ethylene | ethylene | pentane | ethylene | ethylene |
| 8 | ethylene | 2-me butane | 2-me butane | methanol | toluene | m-xylene | m-xylene |
| 9 | 3-me pentane | 3-me pentane | 3-me pentane | 2-me butane | benzene | toluene | benzene |
| 10 | 2-me propane | benzene | hexane | benzene | 2-me butane | benzene | toluene |
| 11 | hexane | 2-me propane | benzene | m-xylene | m-xylene | 2-me butane | formaldehyde |
| 12 | benzene | hexane | m-xylene | 2-me propane | 2-me propane | formaldehyde | 2-me butane |
| 13 | m-xylene | m-xylene | 2-me propane | hexane | hexane | hexane | hexane |
| 14 | ethylbenzene | propylene | methanol | formaldehyde | formaldehyde | 2-me propane | decane |
| 15 | propylene | ethylbenzene | ethylbenzene | heptane | decane | decane | acetone |
| 16 | o-xylene | 3-me pentane | propylene | propylene | acetone | acetone | 2-me propane |
| 17 | 3-me pentane | 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-me pentane | decane | heptane | 1,2,4-tmb | ethylbenzene |
| 20 | m & p-xylene | methanol | TCE | 1,2,4-tmb | 2-propanol | 2-propanol | 2-propanol |
| 21 | acetylene | heptane | o-xylene | 3-me-pentane | 1,2,4-tmb | heptane | C7 alkanes |
| 22 | TCE | formaldehyde | octane | 2-butanone | ethylbenzene | propylene | propylene |
| 23 | methanol | acetylene | 1,2,4-tmb | octane | 3-me pentane | ethyl acetate | heptane |
| 24 | octane | acetone | other, C>13 | o-xylene | octane | C7 alkanes | C8 alkanes |
| 25 | 2-me propene | 2-me propene | acetone | 2-me pentane | 2-me pentane | 3-me pentane | ethyl acetate |
| 26 | formaldehyde | 1,2,4-tmb | m & p-xylene | TCE | o-xylene | nonane | 3-me pentane |
| 27 | 1,2,4-tmb | TCE | acetylene | 2-propanol | nonane | undecane | undecane |
| 28 | acetone | octane | 2-butanone | unspeciated | undecane | o-xylene | nonane |
| 29 | DCM | methyl acetate | decane | other, C>13 | C7 alkanes | me-pentanone | me-pentanone |
| 30 | 111-TCethane | C9 aromatics | 2-me propene | m & p-xylene | ethyl acetate | octane | 2-me pentane |
| 31 | methyl acetate | 2-butanone | C13+ aromatic | C13+ aromatic | me-pentanone | 2-me-pentane | o-xylene |
| 32 | C13+ aromatic | C7 alkanes | C7 alkanes | 2-me propene | C13+ aromatic | C8 alkanes | octane |
| 33 | 2-butanone | decane | 2-propanol | C8 alkanes | C8 alkanes | p-xylene | p-xylene |
| 34 | decane | C8 alkanes | unspeciated | me-pentanone | butyl acetate | butyl acetate | butyl acetate |
| 35 | C7 alkanes | 2-propanol | methyl acetate | nonane | DCM | 1-butanol | DCM |
| 36 | 2-propanol | ethyl acetate | C8 alkanes | acetylene | 2-me propene | DCM | 1-butanol |
| 37 | C8 alkanes | DCM | DCM | DCM | p-xylene | C13+ aromatic | 1-propanol |
| 38 | ethyl acetate | me-pentanone | ethyl acetate | undecane | unspeciated | 1-propanol | C13+ aromatic |
| 39 | me-pentanone | unspeciated | me-pentanone | butyl acetate | TCE | TCE | TCE |
| 40 | 1-butanol | 111-TCethane | butyl acetate | ethyl acetate | 1-butanol | C3-benzene | C3-benzene |

Abbreviations used: me – methyl; tmb – trimethylbenzene; TCE – Trichloroethylene; DCM – Dichloromethane;

Table 3. Most abundant **VOCs-Volatile Organic Compounds** ranked by concentrations based on recent research of wintertime city centre observations in London³¹, Beijing³², Delhi all based on a common two-channel **gas chromatography – flame ionisation detection GC-FID** method.

| Rank Order | London Monthly Mean ($\mu\text{g m}^{-3}$) | Beijing Monthly Mean ($\mu\text{g m}^{-3}$) | Delhi Monthly Mean ($\mu\text{g m}^{-3}$) |
|------------|---|--|--|
| Year | 2012 | 2016 | 2018 |
| Period | Jan | Nov-Dec | Oct-Nov |
| 1 | ethanol (10.7) | ethanol (23.7) | ethanol (72.4) |
| 2 | ethane (8.3) | acetone* (19.6) | n-butane (60.8) |
| 3 | acetone* (8.1) | m+p xylene (17.7) | methanol* (53.7) |
| 4 | methanol* (6.8) | methanol* (13.2) | propane (48.5) |
| 5 | n-butane (5.2) | propane (13.1) | iso-butane (32.3) |
| 6 | propane (4.9) | ethane (11.8) | toluene (30.4) |
| 7 | iso butane (2.6) | ethene (9.4) | iso-pentane (28.8) |
| 8 | iso pentane (3.5) | toluene (7.8) | acetone* (25.3) |
| 9 | toluene (2.6) | n-butane (7.0) | ethane (23.1) |
| 10 | butanol (2.5) | i-pentane (6.5) | m+p-xylene (15.1) |

* Minor contribution to ambient concentrations possible from the oxidation of other VOCs

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3 Figure 1: United Kingdom VOC emissions of Volatile Organic Compounds from
4 anthropogenic sources 1990-2017 and projections for 2020 and 2030. The solid black
5 marker lines represent the NECD-National Emissions Ceiling Directive ceiling for that
6 time period. The 2020-2029 NECS ceiling is applicable to all the sectors included in the
7 series minus emissions from Agriculture (light blue bar)'. The dotted lines indicate the 2020-
8 2029 UNECE-CLRTAP ceiling of the revised Gothenburg Protocol and is applicable to all
9 sectors, including Agriculture.
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17 Figure 2. Trends in sectoral contributions to national emissions of Volatile Organic
18 CompoundsVOCs as a percentage of the overall annual national total, 1970 to 2017, data
19 from uk-air.gov.uk and National Atmospheric Emissions Inventory.
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24 Figure 3. Estimated trends (1990-2017) in the UK emissions of (by rank order in 2017) 1.
25 ethanol, 2. n-butane, 3. methanol, 4. ethane, 5. propane, 6. n-pentane, 7. eEthylene, 8. m-
26 xylene, 9. bBenzene and 10. tToluene.
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30 Figure 4. Upper: Trends in estimated national emissions of functional group classes of
31 Volatile Organic CompoundsVOCs. 4a (left) Contribution of each functional group class to
32 the overall annual national total, 1970 to 2017. Lower: b) Contribution of each functional
33 group class expressed as percentage of annual emissions. Legend common to both plots.
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38 Figure 5. Normalised POCP-Photochemical Ozone Creation Potential per average UK unit of
39 Volatile Organic CompoundsVOC emissions-emitted 1990-2017 (left hand y-axis) and total
40 mass of Volatile Organic CompoundsVOC emissions-emitted (right hand y-axis).
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45 Figure 6. Trends in selected ambient non-methane hydrocarbons measured at the Marylebone
46 Road automated hydrocarbon network station in the centre of London.
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49 Figure 7. Comparison of trends in roadside 1,3-butadiene and benzene concentrations at
50 Marylebone Road in central London with the National Atmospheric Emissions Inventory
51 estimate of total 1,3-butadiene emissions from the road transport sector (solid black line).
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56 Figure 8. Percentage contribution to the overall emission of Volatile Organic
57 CompoundsVOCs from the '*solvents and related products*' class of emissions in the NAEI
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3 | National Atmospheric Emissions Inventory (2017 edition). Red species are not routinely
4 measured, green species are included in the UK Defra automated hydrocarbon network.
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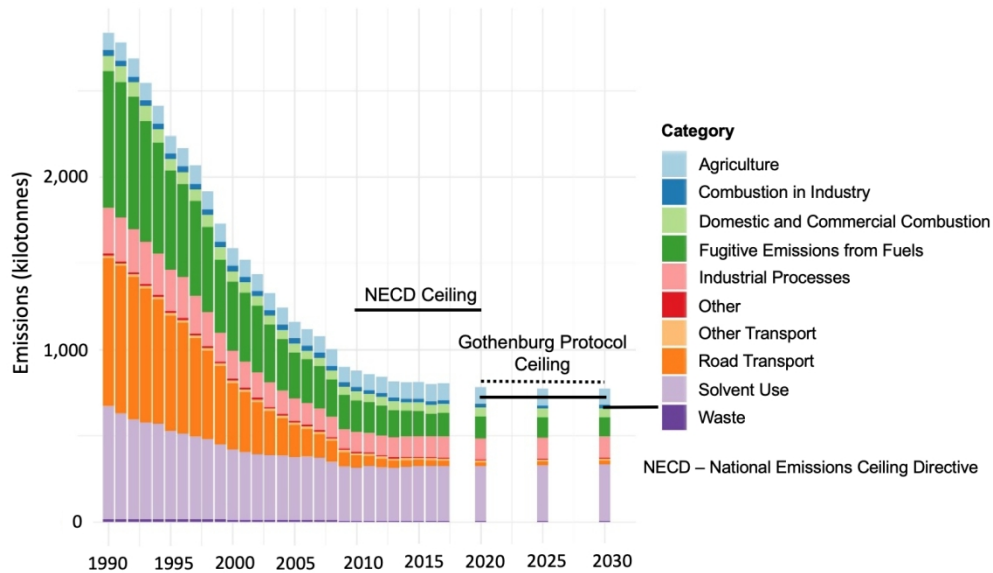


Figure 1: United Kingdom emissions of Volatile Organic Compounds from anthropogenic sources 1990-2017 and projections for 2020 and 2030. The solid black marker lines represent the National Emissions Ceiling Directive ceiling for that time period. The 2020-2029 ceiling is applicable to all the sectors included in the series minus emissions from Agriculture (light blue bar)'. The dotted lines indicate the 2020-2029 ceiling of the revised Gothenburg Protocol and is applicable to all sectors, including Agriculture.

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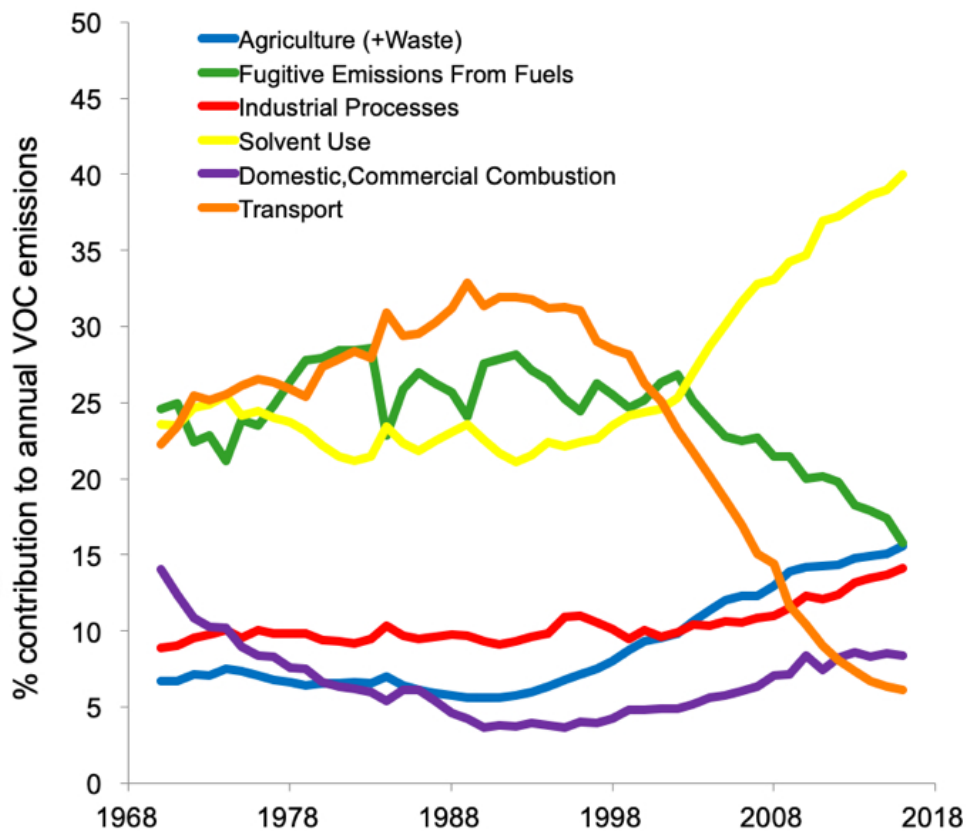


Figure 2. Trends in sectoral contributions to national emissions of Volatile Organic Compounds as a percentage of the overall annual national total, 1970 to 2017, data from uk-air.gov.uk and National Atmospheric Emissions Inventory.

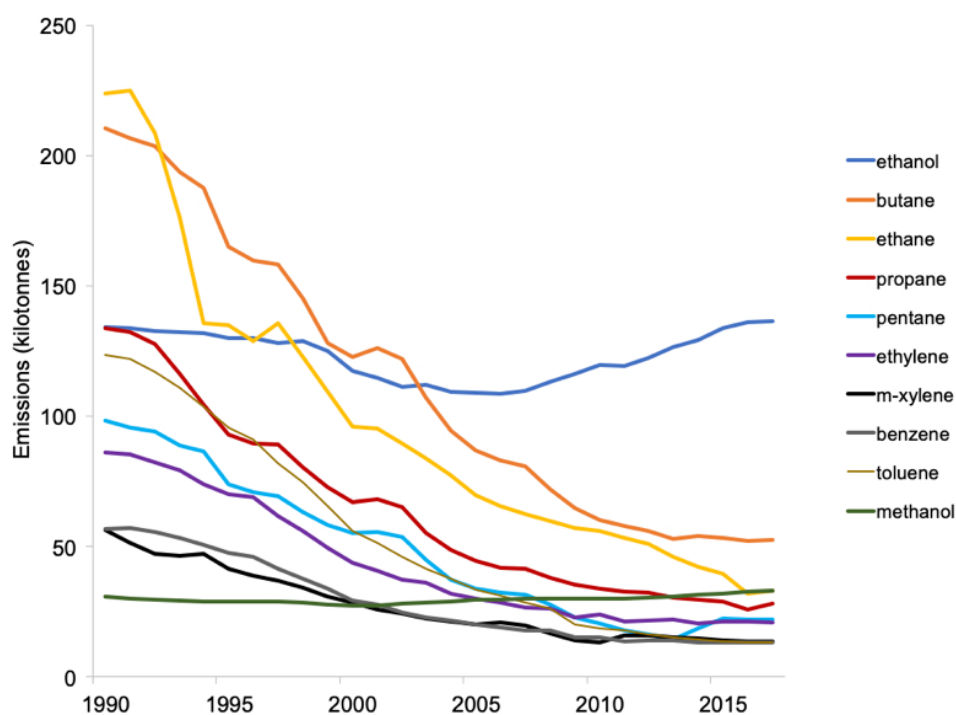


Figure 3. Estimated trends (1990-2017) in the UK emissions of (by rank order in 2017) 1. ethanol, 2. n-butane, 3. methanol, 4. ethane, 5. propane, 6, n-pentane, 7. ethylene, 8. m-xylene, 9. benzene and 10. toluene.

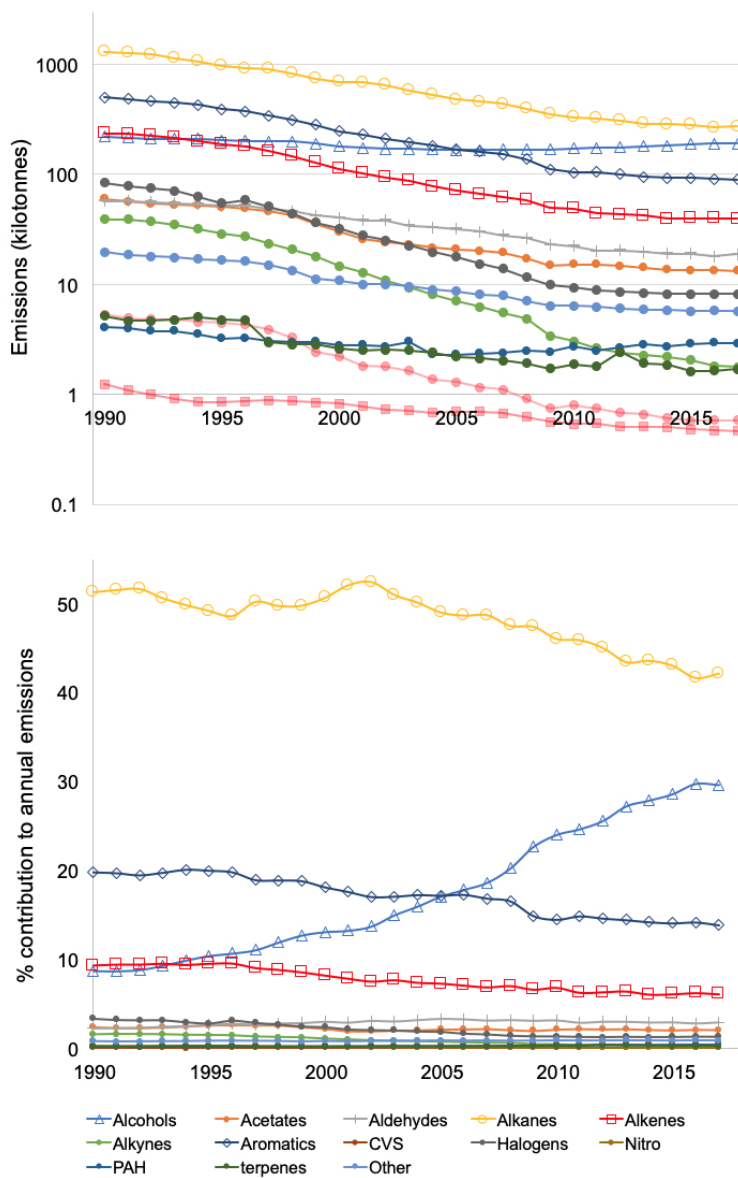


Figure 4. Upper: Trends in estimated national emissions of functional group classes of Volatile Organic Compounds. 4a (left) Contribution of each functional group class to the overall annual national total, 1970 to 2017. Lower: b) Contribution of each functional group class expressed as percentage of annual emissions. Legend common to both plots.

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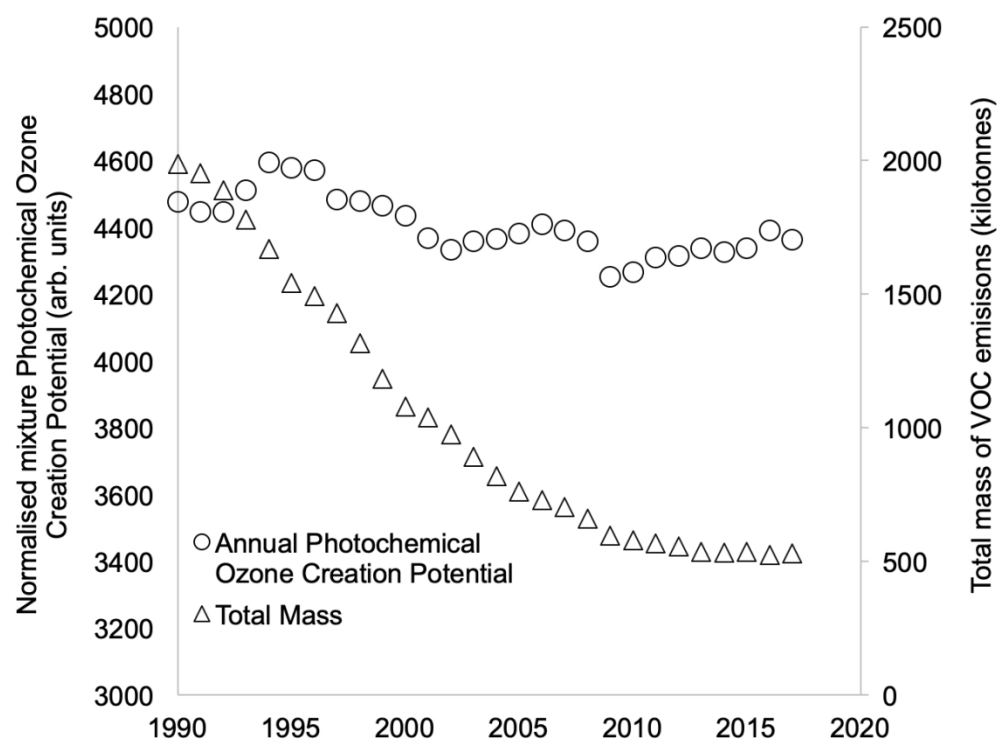
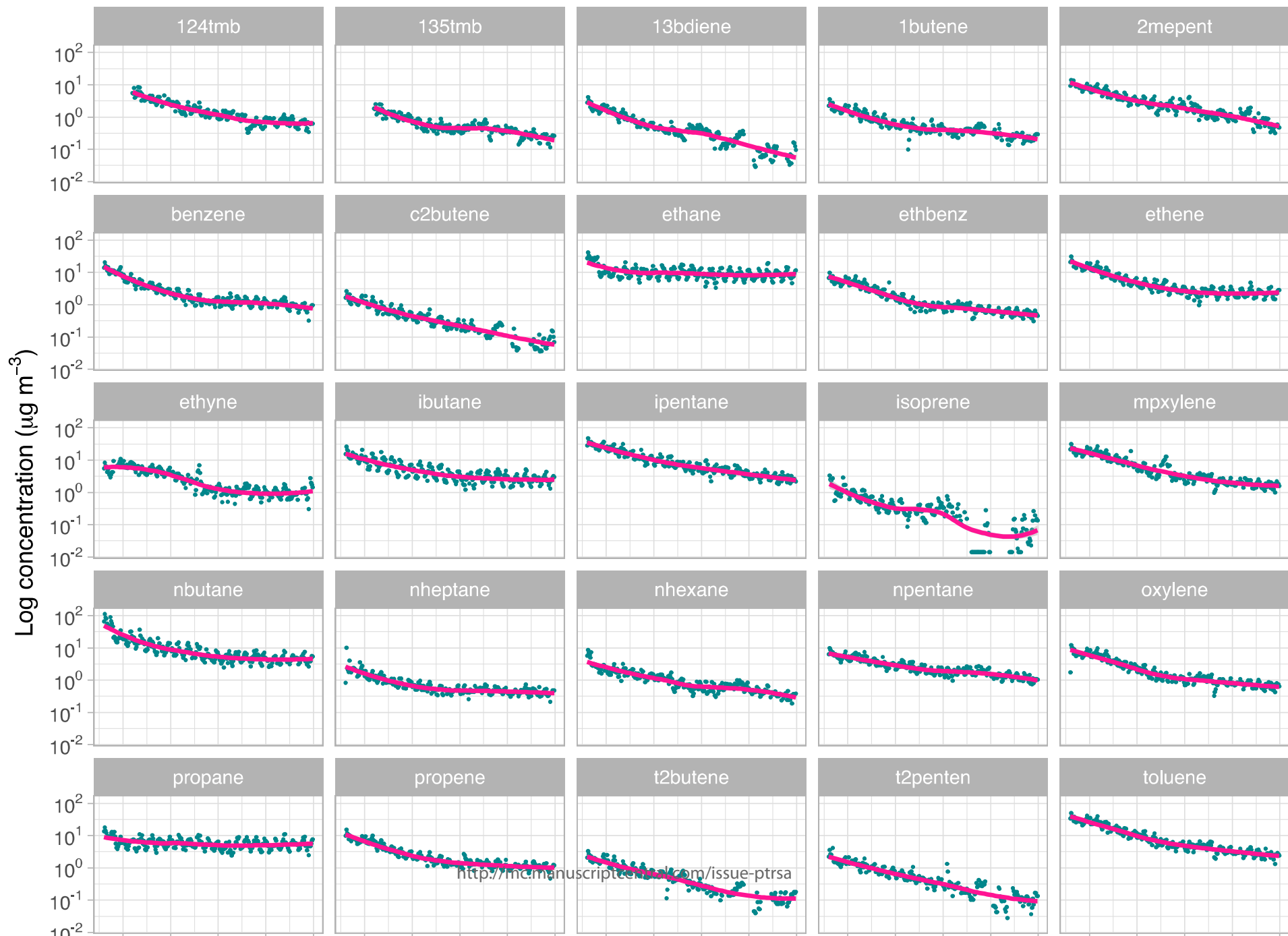


Figure 5. Normalised Photochemical Ozone Creation Potential per average UK unit of Volatile Organic Compounds emitted 1990-2017 (left hand y-axis) and total mass of Volatile Organic Compounds emitted (right hand y-axis).

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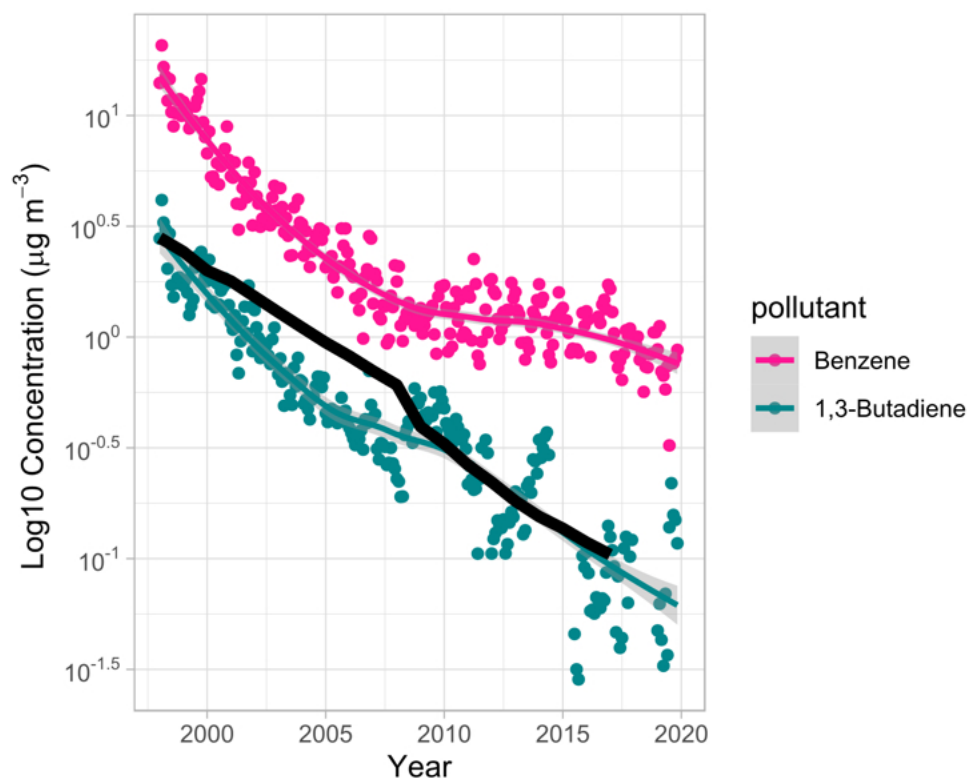


Figure 7. Comparison of trends in roadside 1,3-butadiene and benzene concentrations at Marylebone Road in central London with the National Atmospheric Emissions Inventory estimate of total 1,3-butadiene emissions from the road transport sector (solid black line).

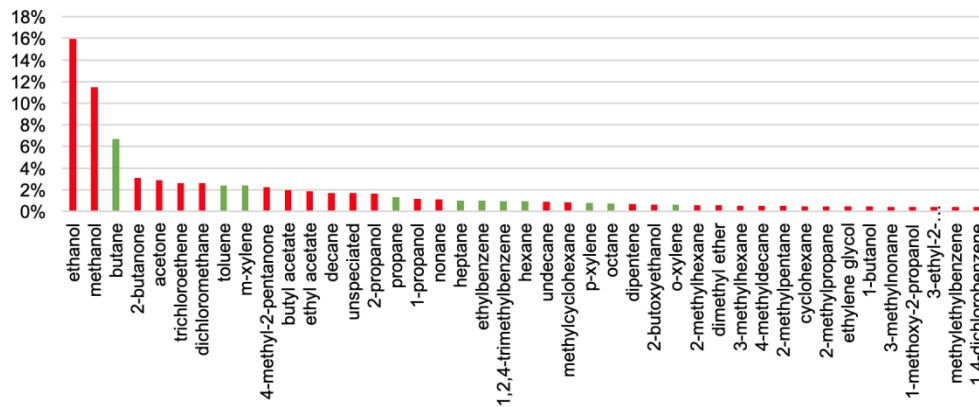


Figure 8. Percentage contribution to the overall emission of Volatile Organic Compounds from the 'solvents and related products' class of emissions in the National Atmospheric Emissions Inventory (2017 edition). Red species are not routinely measured, green species are included in the UK Defra automated hydrocarbon network.

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