Consumer Products as a Source of Volatile Organic Compound Emissions

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Abstract

The contribution of consumer product volatile emissions to indoor air pollution, and the resulting health and environmental implications, is an area of research that has gained increased interest in the past couple of decades. Being able to characterise, quantify, report, and subsequently predict these emissions is essential if any changes are to be made, either in consumer attitudes, manufacturing processes or government product regulations. This thesis aims to address this by three distinct analyses on consumer products using on-line mass-spectrometry, accompanied by a detailed global literature assessment, structured as four published journal papers.

Selected-Ion Flow-Tube Mass Spectrometry (SIFT-MS) has been utilised for headspace analysis of around 30 common personal care products (PCPs) to identify the most prevalent volatile organic compound (VOC) emissions. Emission rates were then calculated based on the amount of product used. A second experiment measured VOC emissions after the application of products in a shower study using Proton-Transfer-Reaction Mass Spectrometry, identifying discrepancies between expected VOC mass emitted (based on headspace analysis) and what was observed after real-life application. The relationship between product application site (proximity) and inhalation of VOCs from facial moisturisers was subsequently assessed using a novel mannequin-head applicant replica, utilising SIFT-MS in another real-life application scenario coupled with product headspace analysis. Finally, global industry data for the production of aerosolised consumer products was assessed to predict both current and future VOC emissions that arise from their use. This analysis is supported by population and economic classification predictions for 215 nations, some of which are grouped for ease of analysis, up to the year 2050.

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To my yoga instructor Laura for remining me to be kind to, and take time for, myself – Namaste!

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Finally, I thank my family, my brother Travis, and most importantly my parents Jackie and Stuart for all their love and encouragement, and for everything they have done to support me over the years.

Author’s declaration

I declare that this thesis is a presentation of original work and I am the sole author. This work has not previously been presented for an award at this, or any other, University. All sources are acknowledged as References. This thesis encompasses four original peer review publications, of which I was first author, as Chapters 2, 3, 4, and 5, which are detailed below:

Yeoman AM, Shaw M, Carslaw N, Murrells T, Passant N, Lewis AC. Simplified speciation and atmospheric volatile organic compound emission rates from non-aerosol personal care products. *Indoor Air*. 2020;30(3):459–72. https://doi.org/10.1111/ina.12652.

Yeoman AM, Shaw M, Lewis AC. Estimating person-to-person variability in VOC emissions from personal care products used during showering. *Indoor Air*. 2021;31(4):1–11. https://doi.org/10.1111/ina.12811.

A. M. Yeoman, A.C. Heeley-Hill, M. Shaw, S. J. Andrews, A.C. Lewis, *Indoor Air,* 2021;(Early Access). https://doi.org/10.1111/ina.12948.

Yeoman AM, Lewis AC. Global emissions of VOCs from compressed aerosol products. *Elem Sci Anthr*. 2021;9(1):1–15. https://doi.org/10.1525/elementa.2020.20.00177.

Chapter 1 : Consumer products in context - A review of indoor air pollution and its sources

1.1: A short review of volatile organic compounds

Volatile organic compounds (VOCs) are a class of prevalent pollutants present in both outdoor and indoor environments. Loosely classified by various organisations, the European Union (EU) defines a VOC as “any organic compound having at 293.15 K a vapour pressure of 0.01 kPa or more, or having a corresponding volatility under the particular conditions of use”[1]. Emitted from a variety of sources, both biogenic (predominantly vegetation) and anthropogenic, they have the potential to react with hydroxyl (OH) radicals, nitrous oxides (NOx), and other species to form tropospheric ozone and secondary organic aerosols (SOAs), which themselves are reactive pollutants. For this reason, VOCs have been widely regulated, and research into their chemistry and global impact expansive.

1.1.1: Formation of tropospheric ozone

The troposphere is the lowest level of Earth’s atmosphere, the one in which we live, and where anthropogenic pollutants are emitted. There is a small amount of `background ozone` present in the troposphere, due to natural influxes from the stratospheric ozone layer[2]. However, unusually high levels of tropospheric ozone is predominantly a result of photochemical reactions involving anthropogenically emitted VOCs. Promoted by OH radical oxidation, RO_2 radicals are formed and subsequently react with NOx pollution. These reactions are detailed in Equations 1.1-1.7, where R is an alkyl group[3,4].

$$^{\bullet}OH + RH \longrightarrow \overset{\bullet}{R} + H_2O \tag{1.1}$$

$$\overset{\bullet}{R} + O_2 \longrightarrow R\overset{\bullet}{O}_2 \tag{1.2}$$

$$R\overset{\bullet}{O}_2 + NO \longrightarrow NO_2 + R\overset{\bullet}{O} \tag{1.3}$$

$$NO_2 \xrightarrow{hv} NO + O \tag{1.4}$$

$$O + O_2 \longrightarrow O_3 \tag{1.5}$$

$$R\overset{\bullet}{O} + O_2 \longrightarrow H\overset{\bullet}{O}_2 + RO \tag{1.6}$$

$$H\overset{\bullet}{O}_2 + NO \longrightarrow OH + NO_2 \tag{1.7}$$

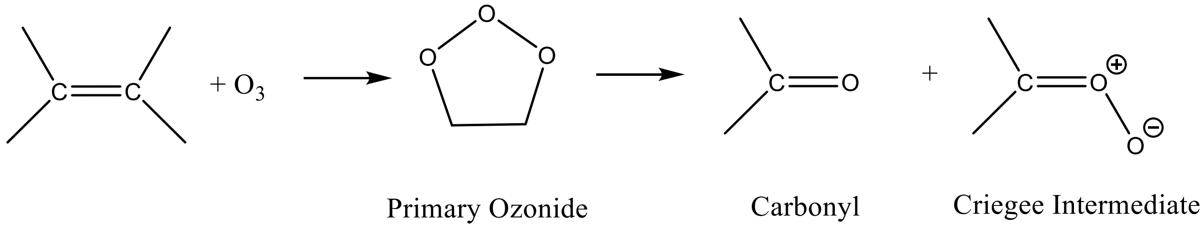
OH radicals are found in both clean and polluted air, including indoor environments, meaning they are widely available to initiate these reactions. Most commonly formed by the photolysis of ozone and nitrous acid (HONO)[5], they are considered the most important chain-initiator oxidising agent in atmospheric chemistry[6]. NOx is a prevalent pollutant found in high concentrations in areas with poor air quality, with its biggest anthropogenic source being the burning of fossil fuels[7].

Tropospheric ozone acts as a greenhouse gas[2], absorbing and re-emitting infrared radiation from the sun back to the Earth's surface[8], therefore contributing to climate change by increasing the global surface temperature. It also has negative health implications, causing respiratory problems such as shortness of breath, inflammation of the airways, and the aggravation of lung conditions like asthma and emphysema[2]. The Maximum Incremental Reactivity (MIR) scale, developed in 1994[9], can be used to quantify the impacts on tropospheric ozone formation by VOC reactions[10]. A higher MIR value indicates more ozone production from a specified weight of a compound under worst case conditions. With values ranging from >0.001 to <15 O_3 per gram of VOC, both the environmental and health impacts of each compound must be considered individually as their ozone formation potentials differ so widely.

1.1.2: Formation of SOAs

SOAs are compounds formed by the oxidation of VOCs over several generations by ozone, OH radicals, nitrate (NO_3) radicals, or by reaction with Cl atoms. In a series of complex chemical reactions, the formation of innumerable SOAs are possible, with reaction mechanisms specific to each compound[11]. Said mechanisms often start with H atom extraction by either OH or NO_3 radicals, or Cl atoms, as seen in Equation 1.1, or by addition to a carbon double bond or aromatic ring. As explained in the previous section, reactions with OH and NO_3 radicals are common as they are prevalent in the atmosphere, whereas Cl atom reactions are more frequent in marine and coastal environments.

Ozone initiated oxidation usually occurs with VOCs possessing carbon double bonds, forming a Criegee Intermediate[12,13]. In a three-step mechanism, a primary ozonide (POZ) is formed from the addition of ozone to the carbon double bond. The POZ quickly decomposes into a carbonyl compound and a "carbonyl oxide" (the Criegee Intermediate), outlined in Scheme 1.1. In the third step, the Criegee Intermediate may add back to the carbonyl compound, rearrange, dimerise, or it may react with NOx, sulfur dioxide (SO_2), or OH radicals in the atmosphere causing the formation of SOAs. Additionally, the decomposition of Criegee Intermediates is an important source of OH radicals, which affects the oxidising capacity of the atmosphere.



Scheme 1.1: Formation of a Criegee Intermediate from the oxidation of a double bond containing VOC by ozone.

SOAs make up a large fraction of particulate matter, and have the ability to scatter and absorb solar and terrestrial radiation, and influence cloud formation. This means they play a significant role in climate change and may also contribute to undesirable health effects[14,15], discussed further in section 1.2.1.

1.2: Understanding indoor air pollution

Outdoor air pollution has been extensively studied for over 6 decades, with the UK introducing its first Clean Air Act in 1956, and establishing the world's first co-ordinated national air pollution monitoring network in 1961[16]. The known environmental and health issues surrounding pollution have been well documented[17,18], but tend to focus on outdoor air, as do the policies set out to reduce pollution worldwide. Notable international agreements include the 2016 Paris Agreement and the 1989 Montreal Protocol, both of which address greenhouse gas emissions and climate change. The equivalent level of interest and concern for indoor pollution has only recently been piqued, with no large-scale international policies specifically intended for tackling IAP.

IAP and indoor air quality (IAQ) go hand in hand, with the former causing a decline in the latter. IAQ relates to the health and comfort of building occupants[19], and is influenced by many factors. As such, the state of IAQ can be very different across the world where things such as cooking, heating, and consumer product habits are dissimilar. Therefore, the review of IAP and IAQ in this thesis refers more specifically to the UK, and other culturally similar nations (in Europe, North America, etc.).

1.2.1: Health implications of poor IAQ

Humans spend on average 90% of their time indoors[20,21], and we inhale more than half of the body's air intake during a lifetime while at home[22]. Unlike controllable health factors, such as diet and exercise, the quality of the air we breathe is not entirely a personal choice that can be made, as we are obliged to inhale whatever is around us. Ensuring our indoor environments do not contain harmful pollutants, at least at dangerous levels, is therefore a necessity. A simple factor that can influence IAQ is ventilation, but in colder climates (the UK included), windows are often closed for a good portion of the year, and air-exchange rates have been reduced in recent decades in response to an increase in energy efficient buildings[23,24]. As such, there is motivation to understand exposure to harmful pollutants from indoor environments.

IAQ, although it would not always have been referred to as such, is not a new concern. Throughout history `bad air` was widely believed to spread disease, even before the discovery of the composition of air and the function of the respiratory system[22]. The theory that miasmas (unpleasant odours) were the cause of diseases was popular and commonly accepted up until the end of the 19th century, and the development of the Germ theory of diseases[25]. Around this time other issues, such as dampness and overcrowding, were being studied as potential causes of health problems related to indoor air[22]. As we now know, the spread of diseases is not caused by the air itself, and scientific interest has moved from the removal of malodour and dampness in indoor spaces to the health conditions caused by chemical pollutants.

In the late 1970s interest grew in a new illness, sick building syndrome (SBS), which relates to a group of symptoms caused by poor IAQ from chemical and biological contaminants, and inadequate ventilation[26]. Sufferers may experience headaches, watery eyes, and lethargy, among other ailments[27]. The condition cannot be fully described, but was recognised by the World Health Organisation (WHO) in 1982. Guidance on SBS was one of the first responses of the UK government to the improvement of IAQ[28]. Since then, other substances and behaviours have been regulated for IAQ purposes. A full ban on the import of all forms of asbestos came in 1999[29], as the links to negative, and sometimes deadly, health effects from its inhalation mounted up[30]. The most recent significant regulation to impact IAQ in the UK was the 2007 smoking ban (Health Act 2006)[31]. Environmental tobacco smoke (second-hand smoke that non-smokers are exposed to) contains carcinogenic particulate matter and VOCs, and has the potential to be a significant contributor to IAP, causing disease, cancer, and premature death[32–34].

There are many more species, from a variety of sources, that contribute to poor IAQ that have yet to be fully acknowledged or regulated, by either the UK government or the WHO, that may lead to negative health effects. There has been growing research in the past decades to identify the full scale of abundant air pollutants in indoor environments. Table 1.1 shows the findings of a selection of studies, displaying a small representation of the wide range of compounds commonly measured and identified when examining the pollutants in indoor environments.

Table 1.1: Review of literature surrounding indoor air pollutants. A mark in the box indicates the compound was identified in the associated study.

	Study						
	Edwards et al. (2001)[35]	Tang et al. (2016)[36]	Jia et al. (2008)[37]	Adgate et al. (2004)[38]	Heeley-Hill et al. (2021)[39]	Villanueva et al. (2015)[40]	Geiss et al. (2011)[41]
Compounds Identified							
Acetaldehyde		x				x	x
Acetic Acid		x					
Acetone		x			x		x
Benzaldehyde	x					x	
Benzene	x	x	x	x	x	x	x
n-Butane					x		
Butylbenzene			x				
cVMS		x					
Dichloromethane			x		x		
Ethane					x		
Ethanol		x			x		
Ethyl Acetate			x				
Ethylbenzene	x		x	x	x	x	x
Formaldehyde						x	x
Formic Acid		x					
Isobutane					x		
Isoprene		x			x		
Methanol		x			x		
Monoterpenes	x	x	x	x	x	x	x
Propanal						x	x
Propane					x		
Styrene	x		x	x		x	x
Toluene	x	x	x	x	x	x	x
Xylenes	x		x	x	x	x	x
Environment Studied	Personal and workplace	University classroom	Home	Home and school	Home	Home	Public buildings, schools, and homes

IAP can be a complex mixture of the compounds outlined in Table 1.1, other VOCs, biological pollutants, O_3, CO, CO_2, NO_x species, and particulate matter in high concentrations[42,43]. The health problems that arise due to the presence of these pollutants in indoor air are numerous and well established, most notably from the inhalation exposure pathway, both directly and indirectly (relating to SOA and tropospheric ozone production)[15,44]. Potential health problems from both short- and long-term exposure are as listed: respiratory diseases, triggering of asthma, headaches, acute respiratory infections, pulmonary diseases, lung and other cancers, allergic reactions, eye and airway irritation, cognitive conditions, and increases in psychological stress[45–48]. Not all VOCs have the same potential to produce harmful products[49], meaning some species are more problematic than others.

There is little data to determine how many people suffer from the effects of poor IAQ. Death and disease statistics are usually reported for air pollution as a whole, including outdoor air pollution. When indoor air is specified, the focus is usually on the impacts of solid fuel burning and PM, just one of many IAP sources (discussed further in section 1.2.3). The WHO report zero deaths or disability-adjusted life years (DALYs) that can be attributed to household pollution, with a cause of death stated as lower respiratory infection, trachea, bronchus, lung cancer, ischaemic heart disease, stroke, or chronic obstructive pulmonary disease, for the year of 2016 across the majority of Europe and the US [50]. However, countries where there are deaths and DALYs reported have a higher reliance on non-clean fuels, meaning the health effects stemming from indoor VOCs from other sources are likely not being recognised, and thus reported. To get an idea of how widespread the full effects of IAP are, we can look at other types of data to help paint a picture. Perceived IAQ studies, although not a precise metric, show the correlation between VOCs and inhabitant complaints, indicating that they are suffering the negative effects of IAP. Kallio et al. (2020)[51] conclude a positive correlation between participant reported stress and poor IAQ, whilst Wolkoff and Nielsen (2001)[52] describe the sensory effects experienced when in the presence of indoor VOCs, including eye and upper airway irritation. The exacerbation of pre-existing or underlying health conditions by exposure to IAP is another indicator of the widespread and unreported suffering of negative health effects. Jie et al. (2011)[47] summarise IAP and its links to asthma morbidity, concluding that home environments must be major sources of pollution putting adult asthma suffers at risk. It can be assumed, therefore, that instances of people suffering negative health impacts due to poor IAQ is more prevalent than currently reported.

Currently, there are no UK IAQ guidelines for specific VOCs, with WHO 2010 IAQ guidelines for selected pollutants[53] being recommended in their place. The guidelines cover nine species: benzene, CO, formaldehyde, naphthalene, NO_2, polycyclic aromatic hydrocarbons, radon, trichloroethylene, and tetrachloroethylene, a fair few short of the numerous VOC species which pollute indoor air. The 2019 Indoor Air Quality Guidelines for selected Volatile Organic Compounds (VOCs) in the UK document[54], therefore, looks to update this by proposing IAQ guidelines for a broader range of VOCs based on recent scientific evidence. The new species included are acetaldehyde, styrene, toluene, xylenes, and monoterpenes α-pinene and D-limonene, mirroring the prevalent species seen in Table 1.1. Both long- and short-term limit values for each species are set based on existing health-based guidelines from other countries and organisations. In terms of policies to provide satisfactory IAQ, that is the sufficient removal of pollutant species, the UK government set out regulations for building ventilation (building regulations 2010 (SI 2010/2214))[55], recently reviewed in 2019[56]. It was determined that current ventilation standards are not sufficient for the removal of VOCs, which were found at levels exceeding guidelines.

1.2.2: Outdoor air quality implications of indoor pollutants

Whilst contained within buildings, potential reactions of IAP species to form SOAs and tropospheric ozone (as discussed in sub-chapter 1.1) have little to no impact on outdoor air quality (OAQ). However, whether by simply opening a window, mechanically ventilating using a fan, or by the use of advanced air circulation systems (often found in operating theatres and other settings requiring a sterile environment), indoor pollutants and their oxidation products will travel from indoors to pollute the outdoor air, causing the same negative health effects as when they are indoors. Whilst there are numerous studies on the indoor-outdoor relationship of air pollutants, the focus tends towards their movement from outdoor sources, most notably vehicles[58,59], to indoor environments[60–62], and the subsequent effects that has on IAQ. Conversely, there is little work outlining the effects of indoor pollution sources on OAQ, although it has been recently determined by both McDonald (2018)[63] and Khare and Gentner (2018)[64] that non-combustion sources, predominantly those from indoors, account for a large portion of urban emissions.

There is also a modest connection between IAQ and climate change, the large-scale, long-term shift in the planet's weather patterns and average temperatures[57], as indoor pollutants and their SOAs may generate either warming or cooling effects in outdoor environments.

1.2.3: Sources of indoor VOCs

Source identification and apportionment of indoor air pollutants is crucial for assessing their associated health and environmental risks, thus determining which of the many source are most relevant and worthwhile addressing. Prominent IAP species benzene and toluene (as seen in Table 1.1), along with other pollutants such as CO, CO_2, and NO_x, can originate from outdoor vehicular emissions[58,65], but outdoor sources only make up 35% of all IAP[36]. The range of contributing indoor sources that make up the other 65% is large, but the major ones have been identified by many studies looking at different indoor environments (home, work, and school, etc.) in countries with lower or no dependence on solid fuels for cooking and heating. Findings from several of said studies are presented in Table 1.2, having used bottom-up research techniques to identify the indoor activities/sources that influence indoor VOCs, with a common aim of promoting the wellbeing of occupants.

Table 1.2: Review of literature surrounding indoor air pollutant sources. A mark in the box indicates a particular source was identified in the associated study.

Identified Sources	Study							
	Guo (2011)[66]	Rivas et al. (2019)[67]	Rösch et al. (2014)[68]	Liu et al. (2019)[69]	Salthammer (2019)[70]	Chin et al. (2014)[71]	Tang et al. (2016)[36]	Kristensen et al. (2019)[72]
Building Materials (incl. paints and textiles)	x	x	x	x	x	x	x	x
Household Cleaning Products	x	x	x	x	x	x	x	x
Personal Care Products	x	x	x	x	x	x	x	x
Smoking (incl. e-cigarettes)		x			x			
Cooking		x		x	x			x
Heating Systems		x						
Candles and Incense					x			x
Human* Processes		x					x	

* Oxidation of skin lipids, respiration, metabolism, etc.

Household cleaning products (HCPs) and personal care products (PCPs), known collectively as consumer products, along with building materials, are identified as VOC sources in all eight studies. The study by Tang et al. (2016)[36] found that 57% of the total mass of VOCs studied were human occupant emissions, classed as any emission that only occurs whilst humans occupy an environment, and do not have outdoor air or fixed sources (building materials, furniture, etc.). Consumer products fall into this classification, and it is clear from their frequent identification that they are a major source of IAP.

1.3: Consumer products

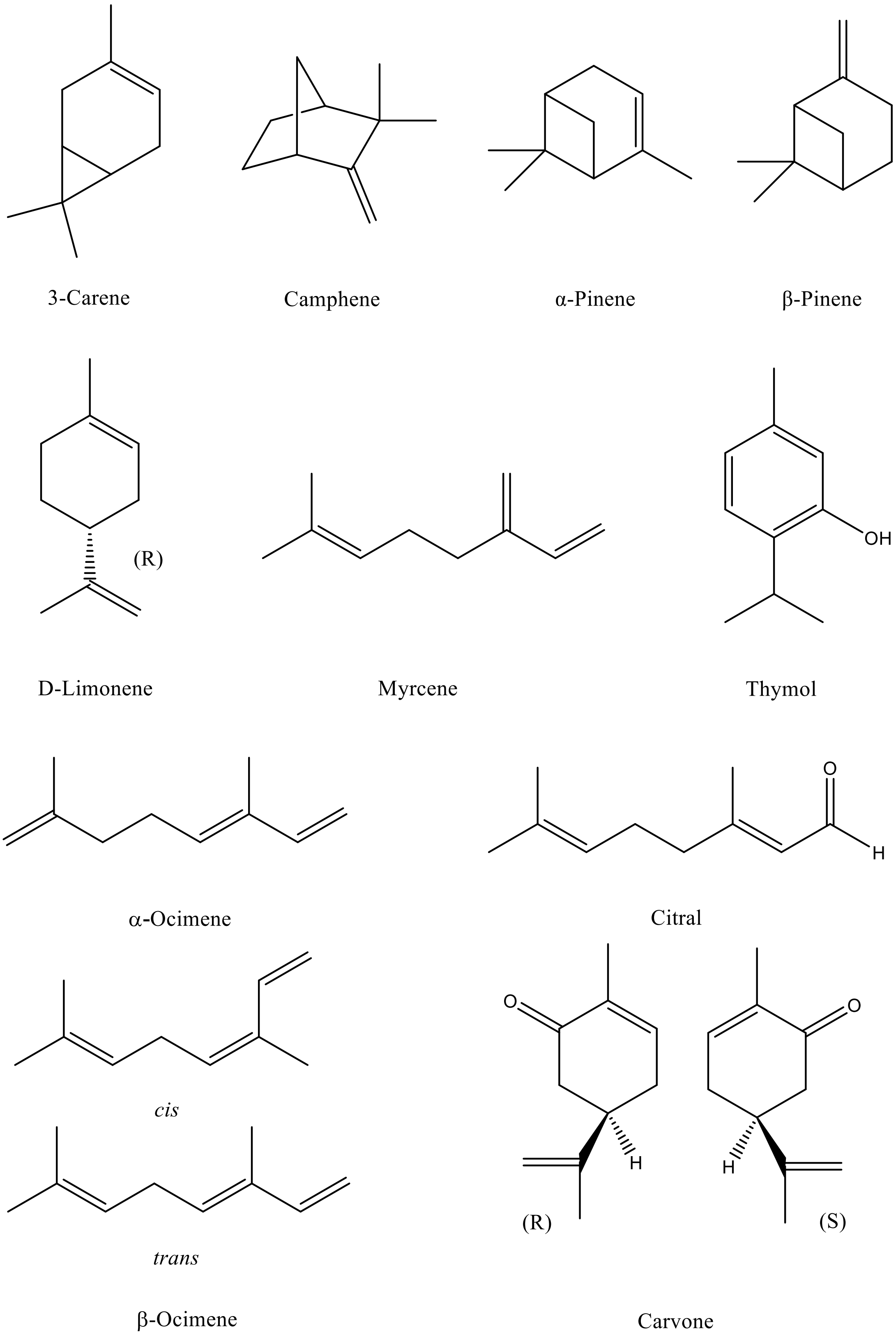
Household cleanliness and personal hygiene have always been important aspects of society. The first known use of a `soap` product has been dated to 1st – 3rd century BC Mesopotamia where animal fats were mixed with wood ash and water[73]. Over the millennia manufacturing techniques gradually evolved, providing people with more sophisticated cleaning and hygiene products. The late 19th and early 20th centuries brought the invention of revolutionary products, including liquid soap, detergents, and antiperspirants[74–76], paving the way for the thousands of cleaning and personal care products we have access to today. These consumer products come in many forms: powder, liquid, aerosol, foams, and solid bars, and constitute a large range of goods, including cosmetics such as self-tanners and moisturisers. Whilst trends in popular products and formulations have changed over the decades, consumer product popularity has only increased, with the global industry’s current annual worth sitting at around £400 billion for beauty and personal care[77], and £130 billion for home and laundry care[78]. They have however, as previously described, been identified as a major source of potentially harmful indoor VOCs.

1.3.1: Current literature

Research into consumer products as an important source of VOCs has attempted to assess prominent species and their SOAs, indoor concentrations, and the potential health risks associated with exposure. The scope for studying this topic is wide, with both top-down and bottom-up techniques being utilised, along with emission inventory assessments, real-life use experiments, chamber studies, and product use surveys.

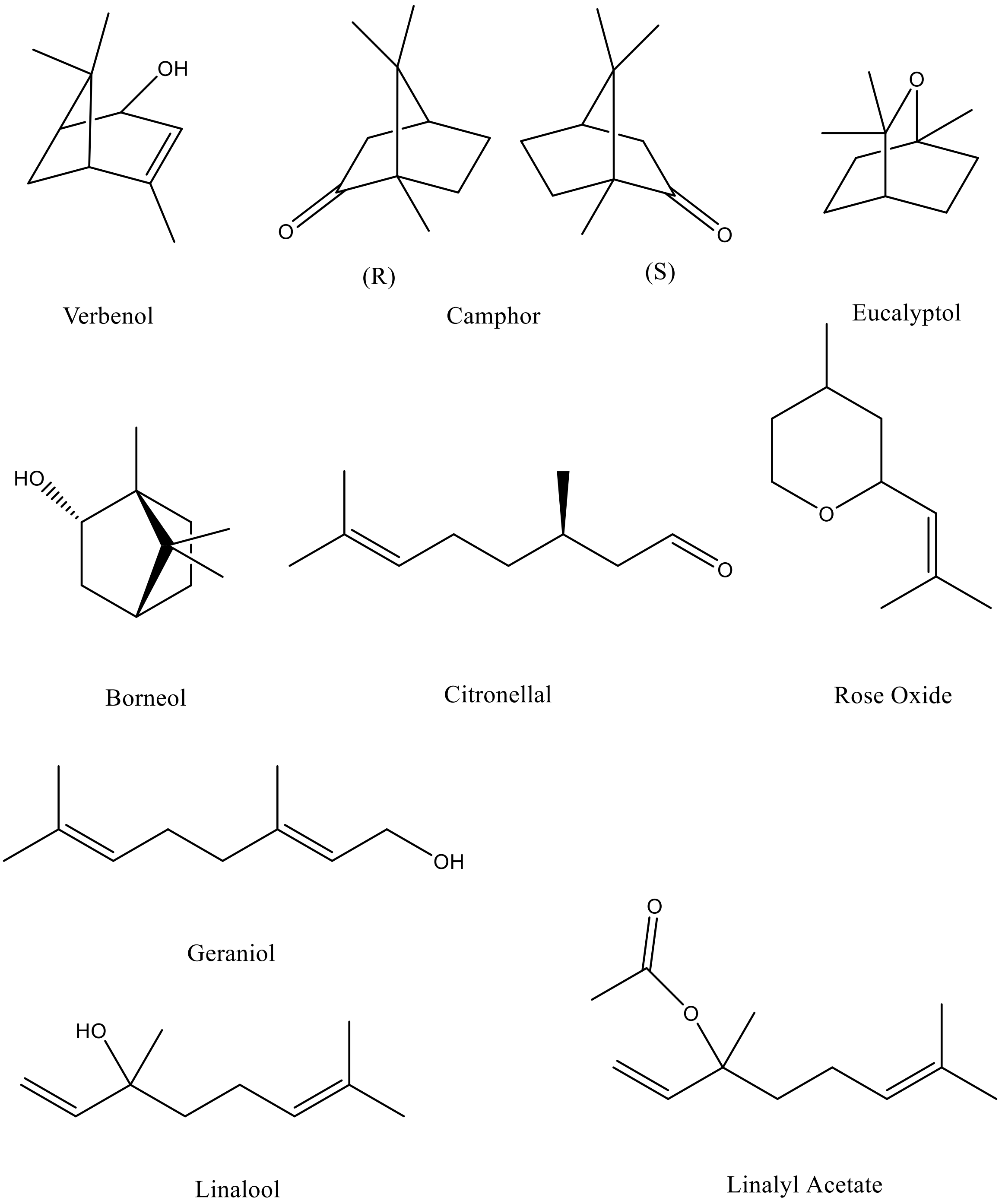
A substantial amount of work has been carried out by Steinemann and her research group on VOC emissions from consumer products, assessing in particular volatile fragrance compounds and their links to labelling and legislation. 98 different VOCs were identified from the screening 6 household products by GC-MS headspace analysis in one study[79], and 133 from 25 products in a subsequent study of both HCPs and PCPs (detergents, dryer sheets, fabric softener, soaps, hand sanitiser, lotions, deodorant, shampoo, household and industrial cleaning supplies, disinfectants, dish detergent, and a range of air fresheners)[79]. In both, several identified species were not disclosed on the ingredients list. This is due to legislation allowing mixtures of fragrance ingredients to be simply labelled as `fragrance` or `parfum`. Additionally, a third study[80] found VOCs classified as toxic or hazardous under US federal laws being emitted from all 37 products tested. Overall, Steinemann’s work summarises the lack of information available to consumers about the compounds contained in their purchases, some of which may be harmful.

The most common chemicals identified in Steinemann's studies were monoterpenes (Figure 1.1), a volatile class of biogenic organic species. Produced by a broad range of vegetation, their characteristic pleasant smells have made them popular for widespread use in consumer products, often being synthetically manufactured for this use. Of this large class of compounds, D-limonene has the highest SOA formation potential compared to other monoterpenes, owing to its two carbon-carbon double bonds[81]. In the atmosphere it is oxidised by O_3 and OH radicals, producing a vast range of products, including many species which are not detailed here. A recent study has shown there to be approximately 530 D-limonene oxidation products formed in a gas-phase model (Carslaw et al, 2012)[82], and its oxidation products have been found to cause upper airway irritation[83] and contribute to perceived poor IAQ[84].



3-Carene
Camphene
α-Pinene
β-Pinene
D-Limonene
Myrcene
Thymol
α-Ocimene
Citral
β-Ocimene
Carvone

Figure 1.1: Structures of a range of monoterpene species



Verbenol

Camphor

Eucalyptol

Borneol

Citronellal

Rose Oxide

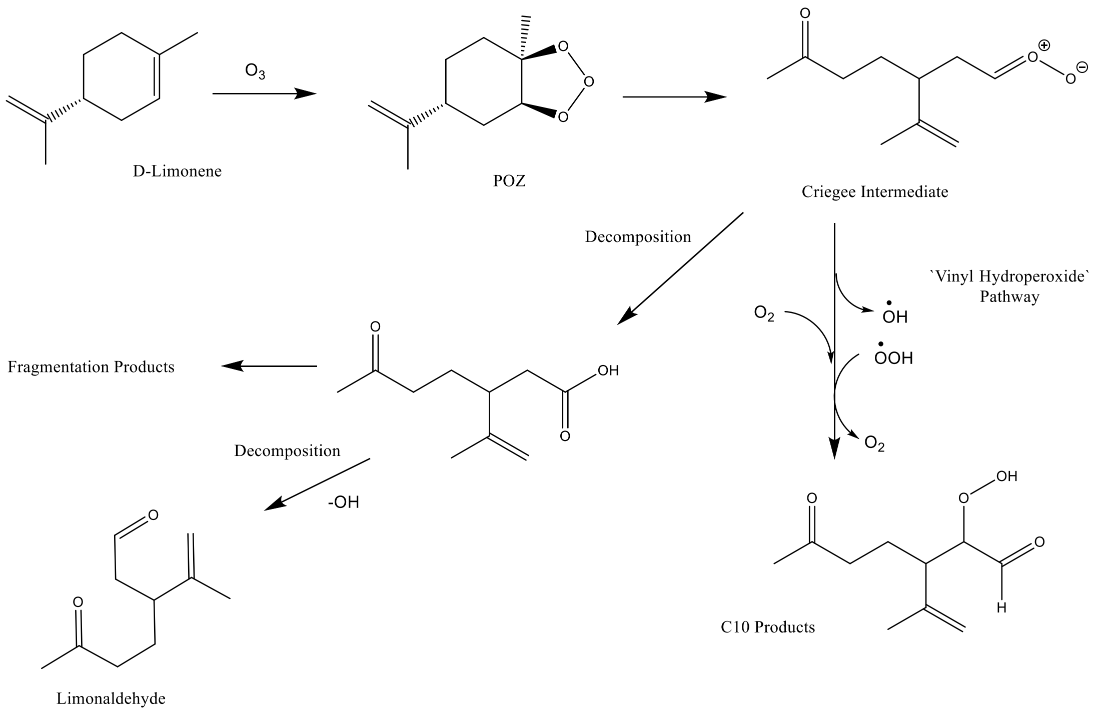
Geraniol

Linalool

Linalyl Acetate

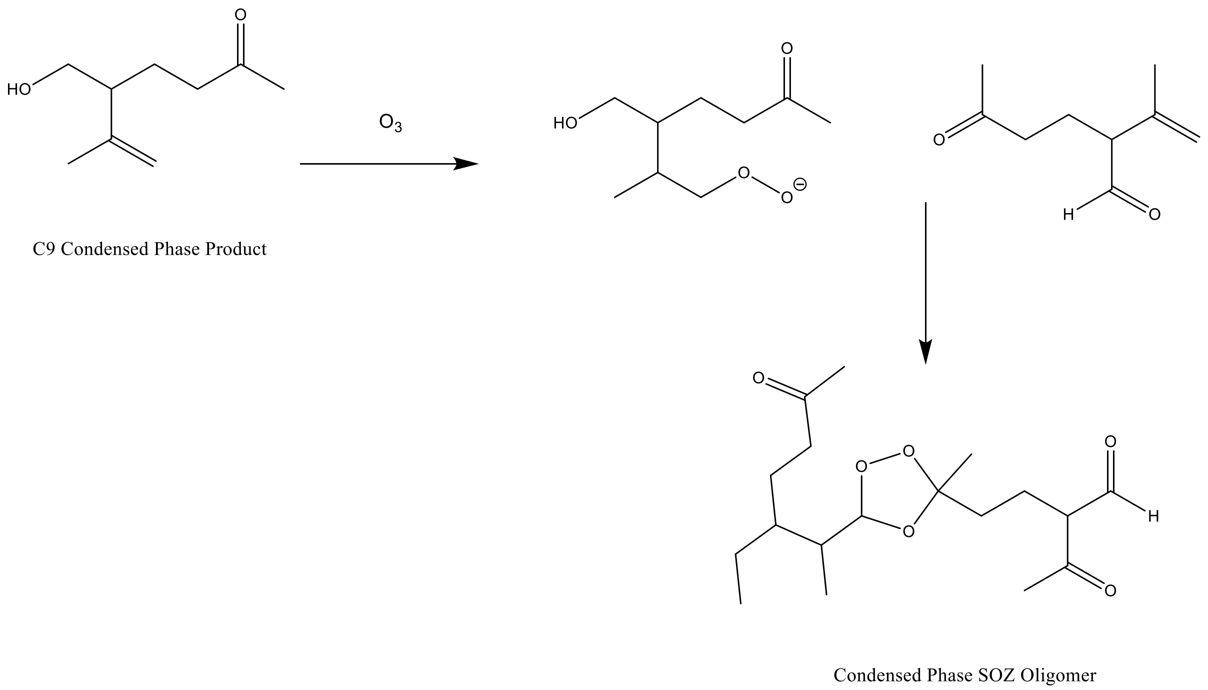
Figure 1.2: Structures of a range of monoterpene species

An initial reaction with O_3 in the gas-phase follows a Criegee Intermediate mechanistic pathway[85]. As shown in Scheme 1.2, endocylic attack is favoured. The resulting primary ozonide (POZ) promptly decomposes to a Criegee Intermediate, which can then follow either of two pathways. Both pathways involve internal rearrangement and organic peroxy-radical chemistry, producing both C9 and C10 products. Further decomposition can result in the formation of limonaldehyde, which can then be oxidised by OH to yield more species.



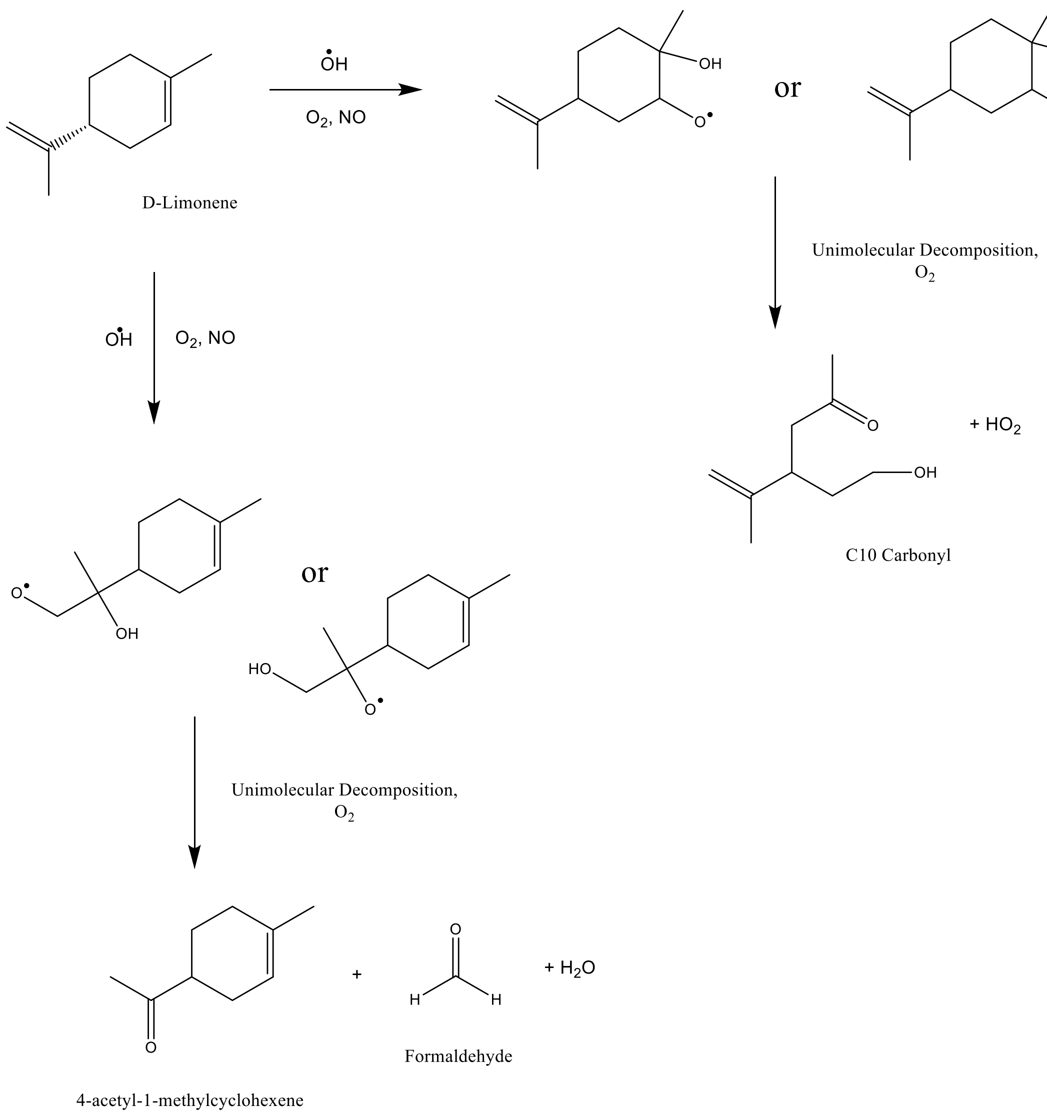
Scheme 1.2: Initial D-limonene oxidation by ozone

Subsequent oxidation of the exocyclic double bond may then occur, and can do so in the gas- or condensed-phase, generating unique oxidation products, influencing volatility, and thus SOA formation potentials. Gas-phase reactions are presumed to follow a similar mechanism to Scheme 1.2. Condensed-phase reactions are expected to undergo traditional synthetic ozonolysis chemistry (Scheme 1.3), with the formation of secondary ozonides (SOZ) occurring as Criegee Intermediates and aldehydes already in the aerosol phase are recombined[86].



Scheme 1.3: Subsequent D-limonene condensed-phase oxidation by ozone

D-limonene oxidation by OH radicals also occurs in both the gas- and condensed-phase, producing a variety of SOAs[82]. It has been observed that OH radical induced SOAs are more volatile than those induced by O_3[87]. Scheme 1.4 demonstrates how an OH radical can add to either of D-limonene's unsaturated C-C bonds. Endocylic reaction gives a C10 product and HO_2 radical, which promotes O_3 formation in the same way that the RO_2 radical does (Equations 1.3-1.5). Exocyclic reaction will form 4-acetyl-1-methylcyclohexene and formaldehyde[88]. The production of PAN-type species (Peroxyacetyl Nitrates) can proceed from both the OH and ozone oxidation of limonene via multiple steps, including from the decomposition of C10 carbonyl[82].



Scheme 1.4: Oxidation of D-limonene by OH radicals

All of these SOAs have the potential to contribute to poor air quality, including as components of $PM_{2.5}$. They may also continue to react in the air, forming more harmful pollutants, with schemes 1.2-1.4 showing only the basic outline of the many reactions that may occur to produce hundreds of species. One species of particular concern is the formation of formaldehyde. There is strong evidence to suggest it has carcinogenic effects with long-term exposure, and has been classified as carcinogenic to humans by the IARC (International Agency for Research on Cancer)[89]. Singer et al. (2006)[90] found formaldehyde to be generated from terpene-containing HCPs in a simulated residential room chamber study. A similar study by Rossignol et al. (2013)[91], investigating the SOAs formed by limonene ozonolysis after the real-life use of cleaning products, detected a wide range of other reaction products. Among a total of around 35 gas and particle phase products, 1-butoxy-2-propanol, di-sec-butyl ether 2-propanol, 1-(2-methoxypropoxy) and dipropylene glycol monomethyl ether were observed in high concentrations (up to 1 mg m^{-3} after 30 minutes). Although the reactions and SOA products of limonene have been outlined here, other monoterpenes (Figure 1.1) will undergo similar oxidation reactions with OH radicals and ozone. This means the production of a vast variety of SOAs is possible from monoterpene species alone.

Aside from monoterpenes, Steinemman (2015)[80] also found a range of alcohols and aldehydes were emitted from consumer products. Other studies consolidate these findings, whilst additionally identify cyclic volatile methyl siloxanes (cVMS), glycol ethers, alkanes, and aromatics, although monoterpenes were often the dominant component of emissions[92–95].

Estimating exposure to these potentially harmful emissions is important for assessing public and consumer health risks, something several researchers have attempted. Generally, Monte Carlo simulations are applied to data obtained using a variety of methods. Safford et al. (2015 and 2017)[96,97] provide an aggregate exposure risk assessment based on literature sources on frequency of product use (consumer habits), skin sites of application of the products, amount per use of each product, chemical concentration of fragrance ingredient in the product, retention factor, penetration factor, subject bodyweight and height, and surface area of product application areas/body sites. Similar literature-based methods are employed by Nazaroff and Weschler (2004)[98] to assess exposure to indoor air pollutants from the use of cleaning products and air fresheners, focussing in particular on toxic air contaminants (TACs) and hazardous air pollutants (HAPs). Hall et al. (2007 and 2011)[99,100] apply their Monte Carlo simulations to industry data, whilst Comiskey (2015)[101] use market research data from subjects logging product use habits, including frequency and application site. These exposure assessments may be useful reference materials for policy development on product safety and indoor air quality.

1.3.2: Inventory assessment and government guidelines

The UK National Atmospheric Emissions Inventory (NAEI) is made up of the Greenhouse Gas Inventory (GHGI) and the Air Quality Pollutant Inventory (AQPI), and is funded by government agencies to record and estimate annual pollutant emissions. The inventory is compiled from a wide range of sources, presenting the trend analysis and source-apportionment for over 600 VOC species. These trends and estimates are important for the UK’s commitments to reporting greenhouse gases (GHGs) and air pollutant emissions to various international committees (such as the United Nations Framework Convention on Climate Change), but also tracking national emissions targets.

The inventory is broken down into source categories (sectors) for total emissions, then speciated for individual VOCs[102]. Found under the “industrial processes and other product use” sector are “aerosol and non-aerosol cosmetics and toiletries, and household product” total NMVOC emission estimates (2D3a – domestic solvent use). Industry data was used to report non-aerosol NMVOC values between 1988 and 1994, purchased market data from 2004 to 2019, and the years 1995 to 2003 being estimated by linear extrapolation from the two sets of data. Aerosol values are based on industry supplied consumption statistics[103,104]. The NAEI have noted that this sector has a high level of uncertainty, relying heavily on old and limited data. Additionally, as this sector is specific to solvent compounds, the VOC contributions of monoterpenes and other fragrance compounds are not included, thus meaning full consumer product emissions are not well characterised in the inventory. Good estimated emissions are beneficial for reliably evaluating changes in national emissions, both sources and amounts, which in turn helps track progress in reducing anthropogenic emissions and inform policy. There have been no UK government recommendations or regulations for the use of consumer products specifically in terms of their VOC emissions since the banning of halocarbon aerosol propellants which occurred in the late 1980s. The work presented in this thesis looks to promote updates to emissions inventories, which should in turn encourage policy regarding the formulation and use of consumer products.

1.4: Thesis outline

The broad aim of this thesis is to investigate the role of consumer products in the emission of anthropogenic VOCs, and establish the extent to which they contribute to poor IAQ. It will provide data to the growing research topic surrounding the VOC content of consumer products by first making qualitative assessments of their content. Quantitative analyses will then be produced for use in emissions inventories to better characterise consumer products as a source of pollution, something that is yet to be achieved on a wide and consistent scale.

This thesis is presented as a series of published work. Each paper is its own chapter, with short introductions and any relevant information, such as data workup, supplied as additional sub-chapters. Supplementary information has been integrated into each paper for clarity, and figures, tables, and equations renumbered for formatting and continuity purposes. Besides this, the work is submitted as published, with references supplied separately at the end of each chapter.

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Chapter 2 : Determining the speciation of non-aerosol personal care product volatile emissions

2.1: Introduction to Selected-Ion Flow-Tube Mass Spectrometry

2.1.1: General process

Selected-Ion Flow-Tube Mass Spectrometry (SIFT-MS) is a relatively modern technique, developed for accurate, real-time analysis of VOCs at detection limits of as low as parts-per-trillion. It is most commonly used for rapid air and breath analysis, which historically has been difficult to study and for which it has been largely developed[1]. Compounds in the air and on the breath can be present at very low levels (parts-per-million and lower), which if measured using traditional mass spectrometry techniques, such as gas chromatography (GC), requires pre-concentration of the sample before analysis. Not only is this not required with SIFT-MS, the need for any sample collection is circumvented altogether. Its ability to simultaneously identify and quantify compounds means absolute concentration of trace gases can be more reliably attained, and real-time monitoring of the formation and degradation of species, providing detailed emission profiles, can be achieved.

This soft ionisation technique utilises a Quadrupole Mass Filter (QMF) to select reagent ions individually by their mass-to-charge ratios. The SIFT-MS used for this research employs three reagent ions, H_3O^+, NO^+ and O_2^+, generated from moist air in the laboratory using a microwave plasma. Sample trace gases are injected into a carrier gas, usually helium but in our case high purity nitrogen at a known flow rate where they react with the selected reagent ions in the flow tube. Although there are an indefinite number of reactions that may occur between each reagent ion and species present in the sample gas, the simplest and most common are outlined here.

H_3O^+ ions undergo a basic proton transfer reaction with the sample gases (Equation 2.1), provided they have a proton affinity higher than 166.5 kcal mol^{-1} [2]. If conditions are humid enough, a water cluster product ion may also be observed (Equation 2.2). A multitude of other cluster or water based reactions may also occur, including secondary reactions, of which there are too many to discuss here.

$$H_3O^+ + R \longrightarrow RH^+ + H_2O \qquad (2.1)$$

$$H_3O^+ + R \longrightarrow RH{\bullet}H_2O^+ \qquad (2.2)$$

NO^+ ions may undergo charge transfer (Equation 2.3), hydride ion transfer (Equation 2.4), hydroxide ion transfer (Equation 2.5) or ion-molecule association (Equation 2.6) reactions, but will usually only yield one or two product ions per species. The ion-molecule association reactions are stabilised by the carrier gas atoms.

$$\mathrm{NO^+ + R \longrightarrow R^+ + NO} \tag{2.3}$$

$$\mathrm{NO^+ + RH \longrightarrow R^+ + HNO} \tag{2.4}$$

$$\mathrm{NO^+ + ROH \longrightarrow R^+ + HNO_2} \tag{2.5}$$

$$\mathrm{NO^+ + R \longrightarrow NO^+R} \tag{2.6}$$

The O_2^+ reagent ion tends to yield more fragmented product ions than would be expected from either H_3O^+ or NO^+ as the ionisation energy of O_2 is particularly high. This means most reactions proceed via either non-dissociative or dissociative charge transfer (Equation 2.7), the latter of which can produce multiple fragment ions.

$$\mathrm{O_2^+ + R \longrightarrow R^+ + O_2} \tag{2.7}$$

The rapid cycling through three reagent ions, and the versatility of being able to choose between them, is advantageous as it allows accurate identification of species with the same mass, being that there is limited fragmentation to aid with this.

A downstream QMF and ion detector detect and count the appropriate product ions formed and any unreacted reagent ions[3]. This information is sent to an on-line computer, which immediately identifies the product ions and calculates their concentrations/mixing ratios, the units of which may be selected. A schematic of the SIFT-MS can be found in section 2.2.3, Figure 2.1.

2.1.2: Compound identification and data processing

Compound identification after a full mass scan has been run is made easier by the fact that there is less fragmentation with SIFT-MS than with traditional mass spectrometry. Fewer peaks mean the mass spectra produced are clearer and easier to interpret. Product ions, fragment ions, and the branching ratios of trace gas reactions for all three reagent ions can be used to identify compounds. Branching ratios are particularly useful in distinguishing between compounds of the same product and fragment ion masses. There are, however, cases where group of species cannot be accurately quantified as separate compounds, as seen with monoterpenes (discussed further in sub-chapter 2.2). Cases like these highlight the possible disadvantages of SIFT-MS compared to traditional, hard ionisation mass spectrometry techniques.

Syft™ Technologies provide a large kinetic database of pre-determined rate coefficients, product branching information, and other relevant reaction data in their LabSyft Software Package (library).

Using Equation 2.8[4], known as the refined SIFT-MS analysis[5], the concentration of trace gas molecules from the sample is calculated, either during data collection (selected ion monitoring (SIM) scan) or after (full mass scan), providing prompt results. The assumption that the number density of trace gas molecules in the flow tube is proportional to the sum of the signal intensities of all the product ions for a compound is the basis for this analytical method.

$$[M] = \frac{1}{t} \frac{\frac{f_{p1} I_{p1}}{D_{ep1}} + \frac{f_{p2} I_{p2}}{D_{ep2}} + \cdots}{f_{i1} I_{i1} k_1 + \frac{f_{i2} I_2 \left(\frac{k_1 + k_2}{2}\right)}{D_{ei2}} + \cdots} \tag{2.8}$$

M = Trace gas molecules in flow tube

f_{i1} , $f_{i2} \ldots$ = Reagent ion auxiliary coefficients

f_{p1} , $f_{p2} \ldots$ = Product ion auxiliary coefficients

I_{i1} , $I_{i2} \ldots$ = Count rates (ion signals) of reagent ions corrected for mass discrimination and dead time

I_{p1} , $I_{p2} \ldots$ = Count rates (ion signals) of product ions corrected for mass discrimination and dead time

k_1 = Rate coefficient for reactions of reagent ions with each M

k_2 = Rate coefficient for reactions of hydrated reagent ions with each M

D_{ei1} , $D_{ei2} \ldots$ = Reagent ion differential diffusion enhancement correction factors

D_{ep1} , $D_{ep2} \ldots$ = Product ion differential diffusion enhancement correction factors

t = Reaction time

The effects of differential diffusion (D_e) and mass discrimination are taken into consideration, despite usually cancelling each another out, for a more accurate analysis of the sample. Differential diffusion causes enhancement of the currents of the heavier product ions arriving at the downstream QMF, falsely augmenting their count rates, known as diffusion enhancement. This is corrected for in the flow tube. Mass discrimination also affects the heavier ions, but with opposite effects[3]. It is defined as the "differences in overall detection sensitivities for ions of different m/z values in a mass spectrum caused by variations in ionization efficiency, transmission efficiency through the interface between the ion source and the analyser vacuum system, analyser, and detector response"[6], and is corrected for in both the reagent and product count rate terms (*I*). Dead time, the minimum time between two consecutive counts after which they can be recorded as separate events, of the electron multiplier/pulse amplifier/discriminator combination is also corrected for in these terms. Auxiliary coefficients (*f*) are usually 1 for all product ions, except for unusual cases concerning the overlap of isotopomers. For the reagent ions the auxiliary coefficient depends on the D_{ei} term and accounts for the non-linear kinetics involved in H_3O^+ ion conversion into hydrates. All of the terms in Equation 2.8, excluding reaction time and count rates, are recorded in the LabSyft library for hundreds of compounds, and are called upon by the software during data analysis.

2.2: Simplified speciation and atmospheric volatile organic compound emission rates from non-aerosol personal care products

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2.2.1: Abstract

Volatile organic compounds (VOCs) emitted from personal care products (PCPs) can affect indoor air quality and outdoor air quality when ventilated. In this paper, we determine a set of simplified VOC species profiles and emission rates for a range of non-aerosol PCPs. These have been constructed from individual vapour analysis from 36 products available in the UK, using equilibrium headspace analysis with selected-ion flow-tube mass spectrometry (SIFT-MS). A simplified speciation profile is created based on the observations, comprising four alcohols, two cyclic volatile siloxanes, and monoterpenes (grouped as limonene). Estimates are made for individual unit-of-activity VOC emissions for dose-usage of shampoos, shower gel, conditioner, liquid foundation, and moisturiser. We use these values as inputs to the INdoor air Detailed Chemical Model (INDCM) and compare results against real-world case-study experimental data. Activity-based emissions are then scaled based on plausible usage patterns to estimate the potential scale of annual per-person emissions for each product type (eg, 2 g limonene person^{-1} yr^{-1} from shower gels). Annual emissions from non-aerosol PCPs for the UK are then calculated (decamethylcyclopentasiloxane 0.25 ktonne yr^{-1} and limonene 0.15 ktonne yr^{-1}) and these compared with the UK National Atmospheric Emissions Inventory estimates for non-aerosol cosmetics and toiletries.

2.2.2: Introduction

Volatile organic compounds are a diverse class of air pollutants that, in high concentrations, can directly impact human health[7], and have widespread indirect effects through aiding the formation of secondary pollutants such as ozone and secondary organic aerosols (SOA). Both indoors and outdoors, VOCs are readily oxidized by O_3 and radicals such as OH and can produce both tropospheric ozone and SOAs when oxidized over several generations and in the presence of co-pollutants such as NO_x. The ability of SOA to scatter and absorb solar and terrestrial radiation, influence cloud formation, and participate in atmospheric chemical reactions means they play a significant role at scales beyond that of urban and regional air pollution[8]. Additionally, as VOCs are a precursor to ozone and a sub-component of $PM_{2.5}$, they contribute to poor air quality and related health effects such as pulmonary inflammation and respiratory illness[9].

From the 1970s onwards, global regulation and policy has focused primarily on reducing VOC emissions from sources such as the extraction and distribution of fossil fuels, combustion and leakage of fuels from road transport, natural gas networks, landfills, and coal-fired power stations[10]. Recently, as VOC emissions from fossil fuels and the transport sector have declined, the relative importance of other VOCs sources has increased[11]. Historically, aims to regulate indoor VOCs tend to focus on building materials, and with particular attention toward compounds such as formaldehyde, benzene, and toluene. Less thought has been paid to the VOCs emitted from the use of PCPs (personal care products)[12–21] and HCPs (household cleaning products)[22–29] which, along with other domestic emissions of VOCs[30–32] are now known to be a substantial contributor to overall VOC emissions[10]. Within this study, PCPs refer to cosmetic and hygiene products available to the public for personal use. PCPs are often split into two broad classifications for the purposes of VOC emissions reporting, described as non-aerosol and aerosol, and it is non-aerosol products that are reported here. The non-aerosol class is potentially a smaller collective source of VOCs than aerosols, since the product matrix is often aqueous, whereas in the case of aerosol-based PCPs, it is typically a hydrocarbon blend based around butane. Ethanol or oil-based perfumes would be examples of PCPs based on hydrocarbons, although we do not test any of these in this study.

The mixture of VOCs emitted from sources such as gasoline evaporation is highly complex, but the detailed speciation of that source is reasonably constant and has been well-characterized over time (see eg, Europe Environment Agency, emission inventory guidebook 2016[33]). Such mixtures are represented in some emissions inventories by an often complex speciation of VOCs, for example in the UK National Atmospheric Emissions Inventory[34] air pollution models typically have a more simplified speciation, through combining (lumping) different VOCs into a smaller sub-group of surrogate compounds, normally simple hydrocarbons, that are then explicitly treated subsequent oxidation mechanisms (see an overview of the topic in Carter, 2015[35]).

The situation is less well developed for consumer products, since each has a unique, generally proprietary, formulation and a substantial diversity in both speciation and emissions rates exists. To add to the complexity, many of the VOCs used in consumer products are high molecular weight and produce a range of multifunctional species when oxidized, some of which may be more harmful to health than the VOCs contained in the original product[36]. For instance, the Master Chemical Mechanism, which is a near explicit mechanism developed to represent the degradation of VOCs in the atmosphere[37], needs 1244 reactions and 712 species to represent all of the reactions needed to go from limonene to the final oxidation products of water and carbon dioxide. This complexity means that representing their chemistry in models for indoor air chemistry is extremely challenging.

The ability to predict VOC emissions (both in terms of speciation and in absolute amounts) is needed however for management of indoor air quality, and to quantify the effects that domestic releases of VOCs have on outside air once ventilated. Nearly 90% of human exposure to VOCs is now believed to come from this kind of diffuse and largely unregulated set of sources that are within individual or household control, which includes consumer products[13], as well as other domestic sources such as glues, paints, sealants and other building products and materials. Other VOC sources in the home include natural gas leakage, pesticides, cooking, and combustion of wood, coal, and candles[38,39].

To understand our overall exposure to air pollution, it is vital to quantify the different sources of pollution both outdoors and indoors. In developed countries, we spend 80%-90% of our time indoors and so our exposure to air pollutants, whether generated indoors or outdoors, will happen in the indoor environment. The use of PCPs is likely to represent a fraction of our overall exposure to pollution, but to date there has been little information available on how the use of an individual product could contribute to the emissions of VOCs, or the secondary products that can then be formed through subsequent chemical reactions. This knowledge requires detailed emissions measurements with sufficient speciation of the often complex formulations to understand the ongoing chemistry.

The estimation of VOC emissions rates from non-aerosol PCPs is potentially a lengthy and time-consuming process. Quantifying VOC content and emissions from PCPs using traditional methods such as headspace GC-MS relies on the ability to predict the liquid-gas partitioning of any given VOC, something that is virtually impossible to do given unknown formulations. Establishing whether an equilibrium has been reached between sample and the atmosphere above, it is difficult to achieve under realistic conditions with GC-MS since the measurement frequency is rather slow, perhaps one measurement every 30 minutes. In a complex matrix where Henry's Law conditions likely do not apply, and where surface tension effects may be significant, a static headspace established over minutes to hours may not necessarily reflect VOC outgassing under more realistic non-saturated dynamic conditions. The availability of fast responding on-line mass spectrometry methods makes this a more tractable task in terms of tracking equilibration and VOC exchange, albeit with a penalty of less capability to speciate isomers and generally greater uncertainties in quantitative determinations. With on-line methods such as proton-transfer reaction mass spectrometry (PTR-MS) and selected-ion flow-tube mass spectrometry (SIFT-MS), the emission rate from a PCP sample can be tracked over minutes to hours using a dynamic flow of diluent gas over the sample and the temporal profile of concentrations then used to estimate the likely VOC emission rate and general VOC. The major advantage of using this method is that it has sufficient sensitivity for a direct analysis of a diluted dynamic headspace, avoiding the need for a pre-concentration/thermal desorption step, and an equilibrium headspace concentration is typically determined in a few minutes. A limitation however of the method is that, like all online and direct inlet mass spectrometry methods, there is a more limited ability to differentiate between isobaric compounds, a notable issue if resolution between specific isomers (eg, monoterpenes or monoaromatics) is important. There are some advantages in terms of calibration using online MS, in that some reasonable first order estimate can be made of the concentrations of unknown VOCs in an unknown mixture, and without a primary standard available. But on-line methods are inevitably less accurate than GC-MS, if primary calibration mixtures for individual VOCs are available.

In this paper, the aim is to produce simplified emission profiles with a grouped speciation that are suitable for chemical models of indoor air and that can provide a guide to the scale of potential personal emissions of VOCs from this class of products. In turn, these values are then scaled upwards to place national emissions of VOCs from PCPs in context to other sources.

2.2.3: Experimental

Voice200 ultra SIFT-MS

A Voice200 SIFT-MS, by Syft Technologies, Christchurch, New Zealand, was used to identify and quantify VOCs emitted from a range of PCPs. The SIFT-MS was operated with a flow tube temperature of 120°C, pressure of 460 mTorr, a voltage of 25 V, a sample flowrate of 25 sccm, and a Nitrogen (Research grade, BOC) carrier gas flow of 100 sccm which was maintained throughout the measurement period. The microwave ion source current was operated at 40 mW at 440 mTorr pressure.

A schematic outline of the Voice200 SIFT-MS instrument is shown in Figure 2.1. The novel ion source region is where the reagent ions are generated in a microwave discharge, which acts on an air/water mix at a pressure of approximately 440 mTorr to generate the three reagent ions H_3O^+, NO^+, and O_2^+. These ions are extracted into the upstream chamber maintained at a pressure of approx. 5×10^{-4} Torr. The reagent ions pass through an array of electrostatic lenses and the upstream quadrupole mass filter, and those not rejected by the mass filter are passed into the flow tube where they are carried along in a stream of nitrogen. The upstream quadrupole mass filter can rapidly (<1 ms) switch between the available reagent ions allowing a single measurement to use all available reagent ions essentially simultaneously.

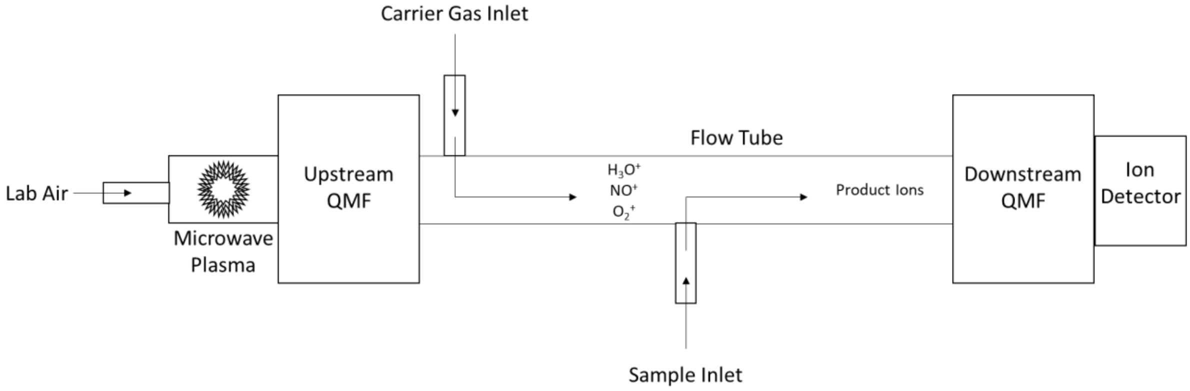

Figure 2.1: Schematic of the Selected Ion Flow Tube-Mass Spectrometer instrument. QMF – Quadrupole Mass Filter

VOC Sampling

A total of 36 individual commercially available PCP samples were acquired from a UK supermarket. The objective was to sample a representative variety of products within each sub-product class, covering a range of brands and formulations. The sample set used here comprised 7 shampoos, 9 shower gels, 12 moisturisers, 3 liquid foundations, and 5 conditioners. A small sub-sample (500 mg) from each product was weighed and placed onto a small open vial, and spread to ensure a high surface area to depth ratio. The sub-sample was then placed into a 10^{-} mL volume stainless steel gas-tight sample vessel. The sample vessel comprised a stainless steel screw-down lid and Viton O-ring seal and two 1/16 in stainless steel Swagelok bulkhead connectors to provide an inlet and outlet for the diluent/sample gas. The stainless steel sample vessel containing the sample of PCP was thermostatted at 25°C for the first hour of the experiment (representative of ambient conditions) and 40°C for the second (to test whether VOCs could be completely driven off within a plausible user temperature envelope).

The samples were drawn into the SIFT-MS at atmospheric pressure from the dynamic headspace of the stainless steel vessel at a flow rate of 25 mL min^{-1}, with the inlet to the vessel connected to a VOC-free supply of N_2 gas. Before and after each PCP sample, an experimental nitrogen blank was carried out which was subsequently subtracted from each sample, although these VOC concentrations were typically very much smaller than the measured amounts, typically < 5%). For all the samples tested here, an equilibrium concentration of VOCs was established in the exiting gas, proportional to the amount of material under test and the VOC content. Over the temperatures and timescales of the testing, which are similar in nature to products in use, each sample acts as an approximately constant emission source of VOCs, and that emission rate is not appreciably changed through VOC depletion in the raw product. Over much longer timescales (hours to days) and/or higher test temperatures, then it is possible to drive off VOCs such that the emission rate declines until ultimately the VOCs are exhausted and emissions fall close to zero. For PCP use, we assume that VOC content in the mixture is not a limiting factor since both time and temperature fall within bounds of a few minutes and no more than 40°C. With that assumption, the amount of VOC released is then proportional to the amount of product used and the time that it is in use when VOC may evaporate. The assumptions we make here are tested against real-world in-use experiments.

Data on the VOC speciation and exact chemical makeup were acquired over a mass range of m/z 18-400 using H_3O^+, NO^+, and O_2^+ reagent ions separately. The suite of selected masses was measured with a dwell time of 0.1 seconds per m/z which resulted in a total measurement cycle of 38.3 seconds. Data acquisition lasted for 120 minutes per sample which provided ~60 mass spectra for each reagent ion for sample averaging. Data acquisition and processing was carried out using the instrument Labsyft software.

Data Analysis

Measured product ions were normalised (for both blank and samples) by dividing the identified product ion intensities by the sum of their reagent and their respective water cluster ion intensities. These were H_3O^+: (m/z 19), $H_3O^{\cdot}\ H_2O^+$ (m/z 37), $H_3O^{\cdot}\ H_2O^{+2}$ (m/z 55), and $H_3O^{\cdot}\ H_2O^{+3}$ (m/z 73), NO^+: (m/z 30), and $NO^{\cdot}H_2O^+$ (m/z 48), O_2^+: (m/z 32), and $O_2^{\cdot}\ H_2O^+$ (m/z 50). To simplify the data analysis, only the most intense 30 ion signals from each reagent ion reaction were then selected for further data processing. It should be appreciated that the most highly emitted compounds on a mass basis may not hold the most significance in terms of their relative health implications and reactivity; however, for the purpose of reporting a simplified speciation profile for personal exposure the data has been selected in this way. It is worth noting that for the purposes of reporting emissions of VOCs under transboundary treaties, a mass-based metric is still used, rather than on VOC reactivity or downstream impact.

To allow for a simple visualization of the key VOC emissions from all PCP samples, tile plots were constructed. These give an overview of the most abundant product ions found in each sample with product ion intensity, displayed as the colour scale. Some known fragmentation and product ions of monoterpenes have been removed to simplify data visualization, leaving m/z 137 and 151 to represent the H_3O^+ product ions, m/z 136 and 154 for NO^+, and 93 for O_2^+. All monoterpenes considered are represented by at least one of these ions. There is confidence that none of the removed ions represent parent compounds other than monoterpenes. All product and fragment ions were identified using the Labsyft software. Further details of the methodology for monoterpene fragmentation and product ion identification are given in Table 2.1. On a small number of occasions where samples contained major VOC ions in the SIFT-MS that could not be directly identified or attributed to a given VOC class, like monoterpenes, we used a confirmatory GC-MS (Agilent 6890-5973) analysis to provide us with further information in toward an identification.

Table 2.1: Monoterpene ions removed from Figures 2.2-2.4

Monoterpene	**Molar Mass**	**Removed Ions (*m/z*)**		
		H_3O^+	NO^+	O_2^+
3-Carene	136	81	92, 93, 135	80, 92, 94, 107, 121, 136
Camphene	136	81	92, 93, 94, 121, 166	80, 92, 107, 108, 121, 136
α-Pinene	136	81	92, 93	80, 92, 107, 121, 136
β-Pinene	136	81	92, 93	69, 80, 92, 107, 121, 136
Limonene	136	51, 69, 77	88	94, 107, 121, 136. 137
Myrcene	136	69, 81, 95	92, 93	69, 80, 92, 94, 121, 136
α/β-Ocimene	136	57, 69, 81, 95	92, 93	68, 80, 92, 94, 107, 121, 136
Carvone	150		150	81, 106, 108, 150
Thymol	150		150	135, 150
Citral	152	95	94, 151, 152, 182	
Verbenol	152	81, 135, 139	93, 94, 134, 150, 152, 182	59, 94, 109, 152
Camphor	152		151, 152, 182	80, 81, 95, 108, 110, 152
Eucalyptol	154	155	184	108, 111, 154
Borneol	154		153	95, 110, 154
Citronellal	154	59, 81, 95, 155	111, 112, 125	43, 84, 110, 111, 112, 121, 136, 139, 154
Geraniol	154	155	137	69, 123, 136
Rose Oxide	154	99	153	139
Linalool	154	81, 95	92, 96, 111	80, 83, 96, 121, 137
Linalyl Acetate	196	59, 81	80, 88	43, 59, 80

Atmospheric Model

The model used in this paper is the INdoor air Detailed Chemical Model (INDCM) described in detail by Carslaw[40] and Carslaw et al[41]. Briefly, the model uses the Master Chemical Mechanism (MCM), v3.2.31[42–44], which treats the degradation of VOC near-explicitly from the initial oxidation step by the hydroxyl radical, the nitrate radical, ozone, or photolysis as relevant and then follows the products of these reactions until carbon dioxide and water are formed as the final oxidation products. The chemical mechanism is then coupled with terms that deal with exchange of pollutants between indoors and outdoors, deposition to internal surfaces, internal emissions, and photolysis (both from attenuated outdoor light and from artificial lighting indoors). The model can be parameterized to be any indoor space (eg, office, bathroom, classroom) and in any geographical location. External pollutant concentrations can then be set as appropriate. The model assumes the internal environment is well-mixed.

For the purposes of this study, the model was set to simulate an en suite bathroom in order to simulate the use of PCPs during a shower. The bathroom was assumed to have dimensions of $1.55 \times 1.8 \times 2.1$ m giving a volume of 5.5 m^3. In order to calculate the overall area to volume ratio for the bathroom, we calculated the area of the floor (2.55 m^2) and the walls (13.65 m^2) and then weighted each according to their typical area/volume ratios as defined in Kruza et al.[45] This gave an overall area to volume ratio of 0.01 cm^2/cm^3. We used a ventilation rate for bathrooms of 50 $m^3\ h^{-1}$ based on a range of values in European residences (Dimitroulopoulou[46]), which provides 9 air changes per hour (ACH). We have also assumed a relative humidity of 70% (based on Laverge et al[47]) and temperature of 293 K.

External pollutant concentrations were typical for a polluted European city such that outdoor ozone, nitric oxide, and nitrogen dioxide mixing ratios were ~24, 20, and 23 ppb, respectively, during the period we show in the Results section (07:00-08:30 h). These external concentrations produced internal mixing ratios for these three pollutants of ~11, 8, and 31 ppb, respectively, for the same period in the absence of any showering activities. External VOCs were as described by Kruza et al[45] and were used to drive the indoor chemistry in the absence of indoor activities.

Out of the seven common VOCs identified in the samples in the previous section, methanol, ethanol, 2-propanol, benzyl alcohol, and limonene are already represented in the chemical mechanism (the MCM) within the INDCM. The D4 and D5 siloxanes are not included. Based on the literature, the fate of the siloxanes outdoors is to react with the OH radical and deposition is relatively unimportant[48]. Indoors, there is a relatively large surface area available and lower OH concentrations, so the relative importance is likely to be different. Therefore, reactions of D4 and D5 with OH were added to the model mechanism, with rate coefficients of 1.01×10^{-12} and 1.55×10^{-12} cm^3 molecule s^{-1}, respectively[49]. These reactions were assumed to form silanols[48,50]. Whelan et al[51] suggested that the cVMS (cyclic Volatile Methyl Siloxane) species had a dry deposition velocity of 0.3 cm s^{-1} outdoors and also that the silanols were more likely to undergo deposition than the parent siloxanes. Based on the method described by Carslaw et al[41], the outdoor deposition velocity was divided by 20 to provide an indoor equivalent of 0.015 cm s^{-1} for the cVMS species. We then doubled this value (0.03 cm s^{-1}) to estimate a deposition velocity for the thiols.

The limonene measured in this study represents the sum of all monoterpenes. For the purposes of modelling, we treat this mechanistically as limonene, but denote it our results as limonene* in recognition that our model is not predicting for limonene exclusively. Although there are differences in chemistry between different monoterpenes in terms of rate coefficients for reaction with OH, O_3 and NO_3 and also yields of radical production, it is the most ubiquitous and abundant monoterpene measured indoors[52] and so this simplification seems reasonable for the purpose of this study.

2.2.4: Results and Discussion

Estimation of Emission Rates

The SIFT-MS is used to measure the time-dependant concentrations of VOCs in the dynamically flowing headspace passing over the sample. By following this concentration over a period of two hours to a continuous equilibrium value, it is implied in all cases that there is no limitation on available VOC for evaporation for the duration of the test (and at test temperature). By knowing the sample flow rate (typically ~10 mL min^{-1}), an estimate was then made for individual VOC emission rates from each PCP. Since no information exists a priori for the speciation of the VOCs in each sample, the calibration and quantification of each VOC relies on the internal instrument/software estimation of concentration made via H_3O^+, NO^+, and O_2^+ reaction kinetic parameters in the MS ionization source. Where it has not been possible to directly calibrate individually for specific compounds, we assume an absolute uncertainty of 20%-25%, based on our own laboratory measurements and as reported in other publications using this instrument[53,54]. For some species, we are able to directly calibrate the SIFT in the laboratory based on gas standards and so have a good understanding of instrument response factors, for example for ethanol, aromatic hydrocarbons, and limonene. For other VOCs, we do not have a primary gravimetric standard but can estimate factors such as relative transmission efficiency and fragmentation patterns, for example for siloxanes, based on stable working mixtures that can be blended over different concentrations ranges and instrument operating conditions. Concentration data for each product is available in Table 2.2. Experiences of using first-principles calibration with other types of PTR-MS instruments suggest the uncertainty could be larger than this, although set in context with the potential uncertainties in the usage scenarios, if a wider uncertainty calibration range is used it does not materially change any conclusions reported here.

Table 2.2: Average concentrations of VOCs emitted for each non-aerosol PCP product during headspace analysis over a period of two hours (mg L^{-1}). These values were used to calculate the emission factors in Table 2.3

		2-Propanol	Benzyl Alcohol	D4	D5	Ethanol	Limonene	Methanol
Shampoo	1	8.07 x10^{-4}	1.55X10^{-4}	1.96 x10^{-3}	1.99 X10^{-4}	5.74 x10^{-5}	4.47 x10^{-2}	7.22 x10^{-5}
	2	2.84 x10^{-4}	9.48 x10^{-4}	3.08 x10^{-3}	3.20 x10^{-4}	2.71 x10^{-4}	6.88 x10^{-3}	3.29 x10^{-4}
	3	1.02 x10^{-4}	1.98 x10^{-4}	1.38 x10^{-3}	1.95 x10^{-4}	9.13 x10^{-5}	1.84 x10^{-2}	1.56 x10^{-4}
	4	5.36 x10^{-5}	6.38 x10^{-5}	1.62 x10^{-3}	2.07 x10^{-4}	1.91 x10^{-4}	1.81 x10^{-2}	4.72 x10^{-4}
	5	8.53 x10^{-4}	4.09 x10^{-2}	1.50 x10^{-3}	3.26 x10^{-4}	1.28 x10^{-4}	1.12 x10^{-3}	8.99 x10^{-4}
	6	4.55 x10^{-5}	3.12 x10^{-2}	1.22 x10^{-3}	2.69 x10^{-4}	5.75 x10^{-5}	5.42 x10^{-3}	1.39 x10^{-3}
	7	1.04 x10^{-4}	7.23 x10^{-4}	1.53 x10^{-3}	3.35 x10^{-4}	3.57 x10^{-4}	5.33 x10^{-2}	1.38 x10^{-4}
Shower Gel	1	8.73 x10^{-5}	1.37 x10^{-2}	-	-	1.88 x10^{-4}	3.32 x10^{-3}	1.28 x10^{-3}
	2	2.45 x10^{-3}	5.18 x10^{-4}	-	-	4.53 x10^{-4}	9.30 x10^{-2}	7.73 x10^{-3}
	3	5.32 x10^{-5}	5.12 x10^{-5}	-	-	7.60 x10^{-3}	1.10 x10^{-2}	5.83 x10^{-5}
	4	3.70 x10^{-5}	5.07 x10^{-4}	-	-	1.22 x10^{-4}	4.87 x10^{-3}	2.06 x10^{-4}
	5	6.46 x10^{-5}	1.99 x10^{-4}	-	-	6.03 x10^{-5}	1.10 x10^{-3}	6.72 x10^{-5}
	6	4.37 x10^{-5}	2.91 x10^{-5}	-	-	6.97 x10^{-5}	3.10 x10^{-2}	1.41 x10^{-4}
Moisturiser	1	2.31 x10^{-3}	3.72 x10^{-5}	-	1.48 x10^{-2}	4.92 x10^{-4}	1.01 x10^{-3}	3.05 x10^{-4}
	2	1.97 x10^{-5}	3.19 x10^{-6}	-	9.94 x10^{-3}	8.02 x10^{-5}	4.05 x10^{-5}	6.46 x10^{-5}
	3	2.23 x10^{-4}	1.94 x10^{-5}	-	1.11 x10^{-2}	6.47 x10^{-3}	2.11 x10^{-3}	1.89 x10^{-4}
	4	1.61 x10^{-5}	2.06 x10^{-5}	-	1.53 x10^{-2}	2.30 x10^{-4}	2.39 x10^{-4}	3.67 x10^{-5}
	5	6.30 x10^{-5}	7.64 x10^{-4}	-	1.27 x10^{-1}	2.34 x10^{-3}	1.75 x10^{-3}	1.60 x10^{-4}
	6	3.06 x10^{-5}	8.78 x10^{-5}	-	1.06 x10^{-2}	4.56 x10^{-5}	5.72 x10^{-4}	6.61 x10^{-5}
	7	5.41 x10^{-5}	7.75 x10^{-5}	-	3.50 x10^{-2}	2.39 x10^{-3}	2.19 x10^{-5}	8.73 x10^{-4}
	8	3.02 x10^{-4}	9.07 x10^{-4}	-	1.61 x10^{-2}	7.52 x10^{-5}	3.98 x10^{-3}	6.06 x10^{-5}
	9	7.66 x10^{-4}	1.44 x10^{-2}	-	2.84 x10^{-2}	8.49 x10^{-5}	8.51 x10^{-5}	1.71 x10^{-4}
	10	4.83 x10^{-4}	4.93 x10^{-3}	-	2.79 x10^{-2}	2.59 x10^{-4}	1.15 x10^{-4}	1.31 x10^{-4}

		2-Propanol	Benzyl Alcohol	D4	D5	Ethanol	Limonene	Methanol
Liquid Foundation	1	-	-	-	1.97 x10^{-4}	4.65 x10^{-4}	1.18 x10^{-5}	-
	2	-	-	-	4.69 x10^{-1}	5.38 x10^{-4}	2.08 x10^{-4}	-
	3	-	-	-	4.79 x10^{-1}	2.93 x10^{-5}	1.28 x10^{-5}	-
Conditioner	1	4.62 x10^{-4}	1.03 x10^{-2}	3.96 x10^{-4}	1.27 x10^{-2}	3.58 x10^{-5}	3.60 x10^{-4}	1.47 x10^{-5}
	2	5.78 x10^{-2}	2.74 x10^{-3}	1.09 x10^{-3}	4.32 x10^{-4}	4.00 x10^{-5}	2.39 x10^{-3}	1.56 x10^{-3}
	3	2.77 x10^{-2}	7.48 x10^{-5}	1.00 x10^{-3}	4.29 x10^{-4}	3.27 x10^{-5}	1.15 x10^{-3}	6.73 x10^{-4}
	4	2.05 x10^{-3}	4.64 x10^{-4}	5.50 x10^{-4}	3.30 x10^{-4}	5.30 x10^{-5}	5.60 x10^{-3}	4.68 x10^{-4}
	5	4.24 x10^{-5}	7.90 x10^{-5}	7.52 x10^{-4}	2.57 x10^{-4}	1.87 x10^{-3}	1.11 x10^{-3}	5.12 x10^{-4}

Figure 2.2 shows the relative VOC emissions rates by product ion for the H_3O^+ reagent for each of the different PCPs. The product ion intensities for each PCP dataset are normalised to the highest product ion. While it is clear that each sample is unique in terms of its VOC speciation, common “bands” of species do emerge across the sample types. The tile plots generated from the NO^+ and O_2^+ ions are shown in the Figures 2.3 and 2.4), but they indicate a similar speciation to that from H_3O^+, albeit with different individual ion intensities reflecting differing ion chemistries.

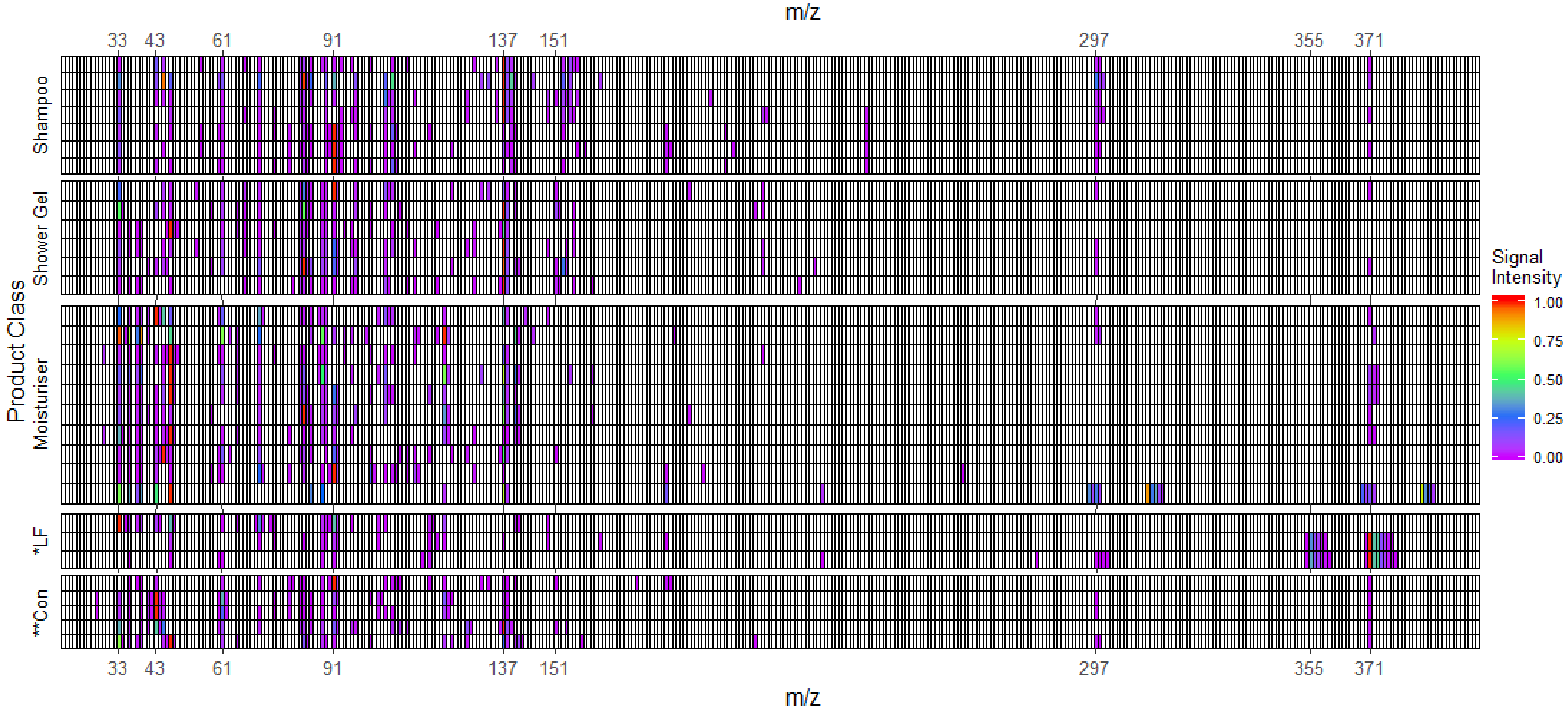

Figure 2.2: Visualisation of VOC emissions from 36 different PCPs based on H_3O^+ ionisation. Data from each PCP sample is normalised to the maximum product ion intensity in that sample. Fragment ions are removed. *LF- Liquid Foundation, **Con-Conditioner

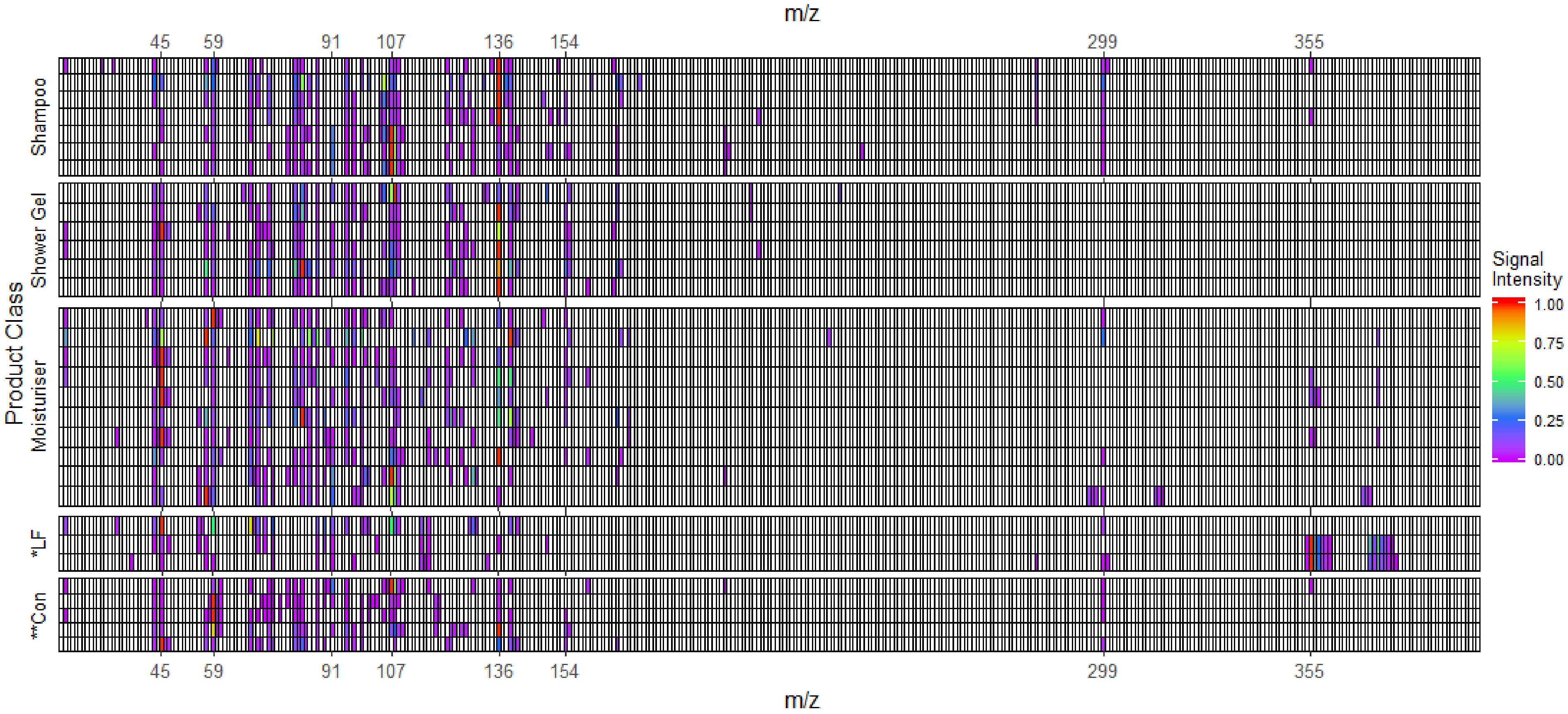

Figure 2.3: Visualisation of VOC emissions from PCPs based on NO^+ ionisation. Data from each PCP sample is normalised to the maximum product ion intensity in that sample. Fragment ions are removed. *LF- Liquid Foundation, **Con-Conditioner

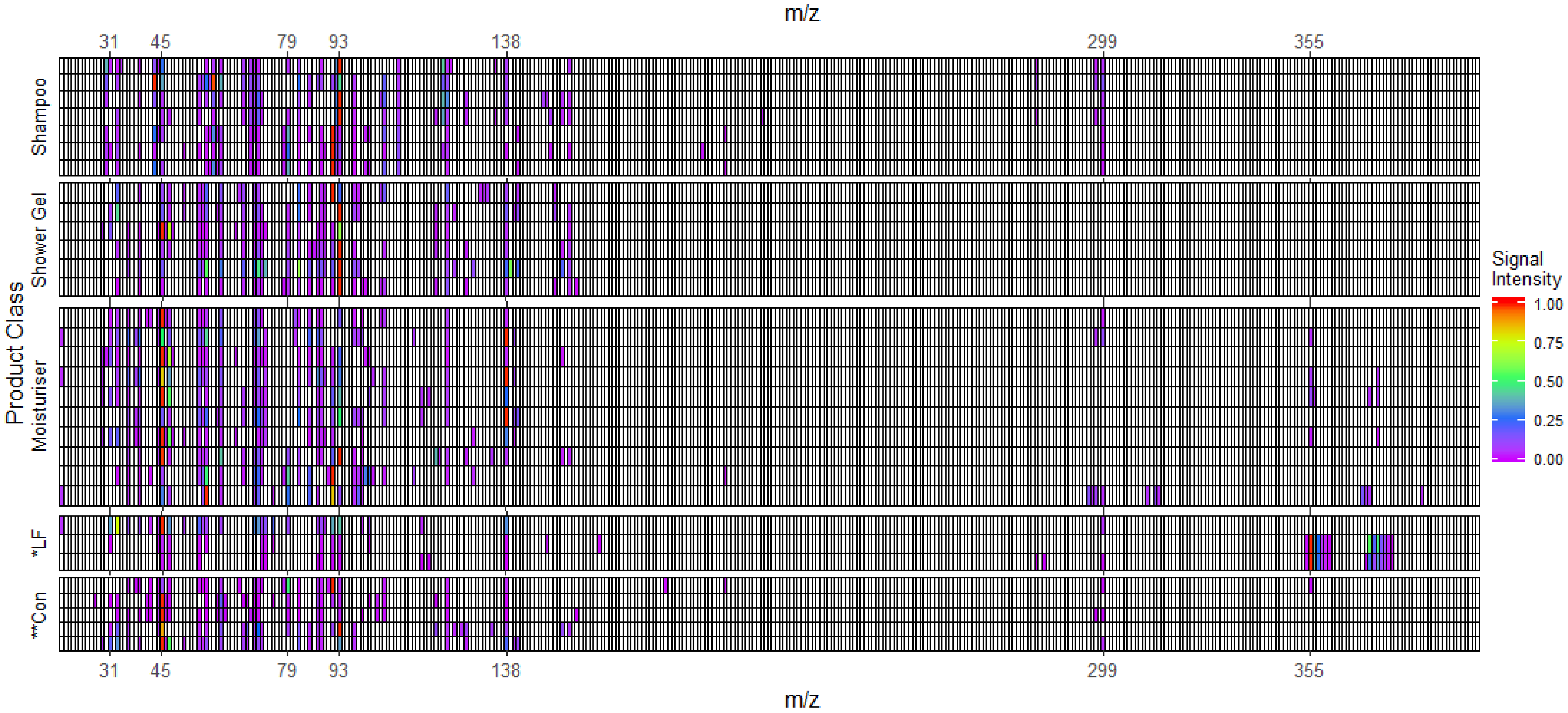

Figure 2.4: Visualisation of VOC emissions from PCPs based on $O2^+$ ionisation. Data from each PCP sample is normalised to the maximum product ion intensity in that sample. Fragment ions are removed. *LF- Liquid Foundation, **Con-Conditioner

From this analysis, a simplified emission profile based on seven most common and abundant individual VOCs is proposed, lumping in cases where isobaric overlaps exist, and/or where the data does not allow for speciation, for example among different monoterpenes. The simplified PCP VOC speciation comprises methanol, ethanol, 2-propanol, benzyl alcohol, limonene (representing the sum of monoterpenes), D4 (Octamethylcyclotetrasiloxane), and D5 (Decamethylcyclopentasiloxane).

A simplified overview of total VOC emission from each product can be gained from examining the relative differences in total ion count (when normalised for reagent ion amounts) for each sample. This provides a basic indication of how variable VOC emissions rates are both between and within PCP product classes. The 30 largest product ion signals from each of the three different reagent ions, including all fragmentation and product ions, were summed (eg, giving 90 ions in total), to provide a total VOC product ion count, taken as a proxy for overall VOC emission rate by mass. It should be stressed that this is essentially an arbitrary unit and cannot be directly transferred as an absolute mass of carbon emissions, but it is helpful in understanding how variable emissions rates are between products. This is shown for the various sample classes in Figure 2.5 as total peak intensity for each PCP under test along with the median value for each class of PCP.

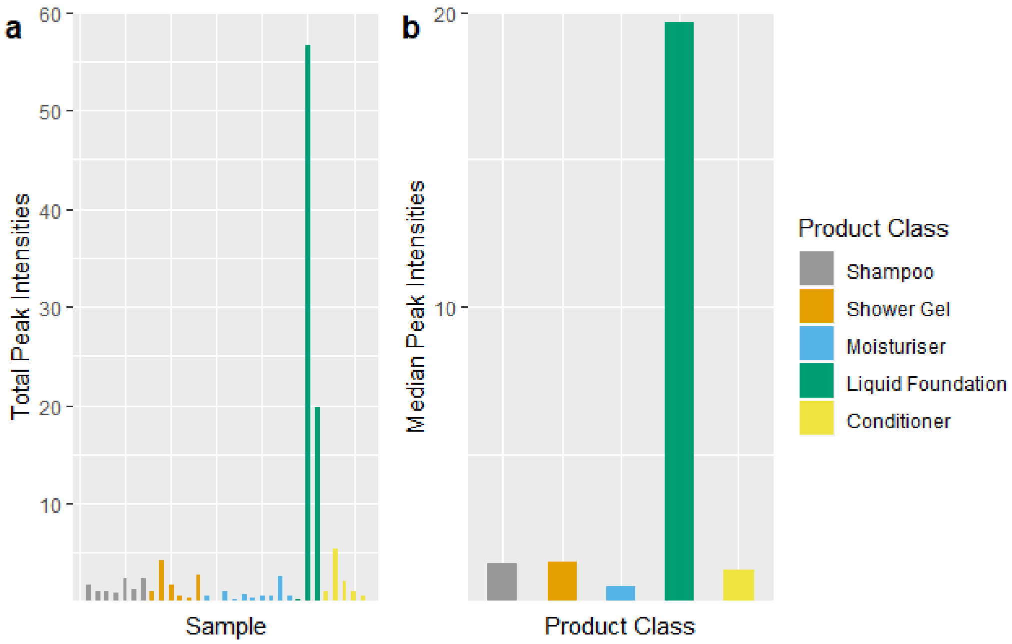

Figure 2.5: a) Summation of total VOC product ion peak intensities for each PCP tested and b) median emission intensity for each product class.

Highest total VOC emissions were associated with liquid foundation, predominantly due to very high emission rates of cVMS D4 and D5. Within the individual product classes, total VOC emission rates varied considerably, often by more than an order of magnitude, suggesting that a very specific level of VOC content is not a fundamental pre-requisite in the formulation of these products.

The emission of VOCs from non-aerosol PCPs is potentially complex, since it is likely that only a fraction of the overall VOC content in each sample is released in the room where the product is used. Our approach is to estimate the emission rate as a function of amount of product and time in use. For wash-off products, some fraction of the VOC content of the product is not released, but instead remains in the aqueous phase in dilute amounts, washed away. The fate of this fraction of the VOC is essentially unknown. Within our calculations, we assume the only VOC emissions are those which occur during the direct product use in-room. It is possible that VOCs also escape to the air at some later stage, for example from waste-water, but we do not attempt to account for this in the scale-up calculations. For leave-on products such as moisturisers and liquid foundation (which remain on the skin, not washed off) more time is potentially available for VOCs to evaporate to air compared to wash-off products. Here, longer "in-use" scenarios are probably appropriate, but these must have some upper bound since the amount of VOC in the product is finite. We chose to express the individual VOC emissions as a mass released per unit time per gram of product and then, in a later section, apply an in-use period to each product. For example, one scenario is that a shower gel unit of activity may comprise a 4 g PCP sample in use for 30 seconds. Such an approach has to assume that as for the laboratory equilibrium determinations, over the actual periods of PCP activity/usage, the VOC liquid phase concentrations are not a limiting factor for VOC transfer to the gas phase, but rather the limitation is the mass transfer of VOC out of the product as a vapour. Table 2.3 shows the calculated emission factors from the simplified emission profiles as a function of time and mass of product at 25 °C.

Table 2.3: Estimated product emission factors at 25 °C for each non-aerosol PCP type using a simplified VOC emission profile.

		PCP in-use Emission Factors (µg s^{-1} g$_{[product]}$$^{-1}$)						
		2-Propanol	Benzyl Alcohol	D4	D5	Ethanol	Limonene	Methanol
Shampoo	1	1.1	2.1 x10^{-1}	2.6	2.6 x10^{-1}	7.6 x10^{-2}	5.9 x10^{1}	9.6 x10^{-2}
	2	3.7 x10^{-1}	1.2	4.0	4.2 x10^{-1}	3.5 x10^{-1}	9.0	4.3 x10^{-1}
	3	1.4 x10^{-1}	2.8 x10^{-1}	1.9	2.7 x10^{-1}	1.3 x10^{-1}	2.6 x10^{1}	2.2 x10^{-1}
	4	7.3 x10^{-2}	8.7 x10^{-2}	2.2	2.8 x10^{-1}	2.6 x10^{-1}	2.5 x10^{1}	6.4 x10^{-1}
	5	1.2	5.8 x10^{-1}	2.1	4.6 x10^{-1}	1.8 x10^{-1}	1.6	1.3
	6	6.0 x10^{-2}	4.1 x10^{1}	1.6	3.5 x10^{-1}	7.5 x10^{-2}	7.1	1.8
	7	1.4 x10^{-1}	9.5 x10^{-1}	2.0	4.4 x10^{-1}	4.7 x10^{-1}	7.0 x10^{1}	1.8 x10^{-1}
	Median	1.4 x10^{-1}	9.5 x10^{-1}	2.1	3.5 x10^{-1}	1.8 x10^{-1}	2.5 x10^{1}	4.3 x10^{-1}
Shower Gel	1	1.2 x10^{-1}	1.8 x10^{1}	-	-	2.5 x10^{-1}	4.4	1.7
	2	3.3	6.9 x10^{-1}	-	-	6.0 x10^{-1}	1.2 x10^{2}	1.0 x10^{1}
	3	7.2 x10^{-2}	6.9 x10^{-2}	-	-	1.0 x10^{1}	1.5 x10^{1}	7.9 x10^{-2}
	4	4.7 x10^{-2}	6.5 x10^{-1}	-	-	1.6 x10^{-1}	6.2	2.6 x10^{-1}
	5	8.0 x10^{-2}	2.5 x10^{-1}	-	-	7.4 x10^{-2}	1.4	8.3 x10^{-2}
	6	5.9 x10^{-2}	3.9 x10^{-2}	-	-	9.4 x10^{-2}	4.2 x10^{1}	1.9 x10^{-1}
	Median	7.6 x10^{-2}	4.5 x10^{-1}	-	-	2.4 x10^{-1}	1.1 x10^{1}	2.3 x10^{-1}
Moisturiser	1	3.2	5.2 x10^{-2}	-	3.1 x10^{-1}	6.8 x10^{-1}	1.4	4.2 x10^{-1}
	2	2.5 x10^{-2}	2.2 x10^{-2}	-	2.1 x10^{-1}	1.0 x10^{-1}	5.2 x10^{-2}	1.3 x10^{-1}
	3	2.9 x10^{-1}	2.5 x10^{-2}	-	2.2 x10^{-1}	8.5	2.8	2.5 x10^{-1}
	4	2.1 x10^{-2}	2.7 x10^{-2}	-	3.0 x10^{-1}	3.0 x10^{-1}	3.1 x10^{-1}	4.8 x10^{-2}
	5	8.7 x10^{-2}	1.1	-	2.6	3.2	2.4	2.2 x10^{-1}
	6	4.0 x10^{-2}	1.2 x10^{-1}	-	2.1 x10^{-1}	6.0 x10^{-2}	7.6 x10^{-1}	8.7 x10^{-2}
	7	7.2 x10^{-2}	1.0 x10^{-1}	-	7.1 x10^{-1}	3.2	2.9 x10^{-2}	1.2
	8	4.4 x10^{-1}	1.3	-	3.5 x10^{-1}	1.1 x10^{-1}	5.8	8.8 x10^{-2}
	9	1.0	1.9 x10^{1}	-	4.6 x10^{-1}	1.1 x10^{-1}	1.1 x10^{-1}	2.3 x10^{-1}
	10	6.6 x10^{-1}	6.7	-	5.7 x10^{-1}	3.5 x10^{-1}	1.6 x10^{-1}	1.8 x10^{-1}
	Median	2.0 x10^{-1}	1.1 x10^{-1}	-	3.3 x10^{-1}	3.3 x10^{-1}	5.3 x10^{-1}	2.0 x10^{-1}
Liquid Foundation	1	-	-	-	2.7 x10^{-1}	6.4 x10^{-1}	1.6 x10^{-2}	-
	2	-	-	-	6.8 x10^{2}	7.8 x10^{-1}	3.0 x10^{-1}	-
	3	-	-	-	7.0 x10^{2}	4.3 x10^{-2}	1.9 x10^{-2}	-
	Median	-	-	-	6.8 x10^{2}	6.4 x10^{-1}	1.9 x10^{-2}	-
Conditioner	1	6.6 x10^{-1}	1.5 x10^{1}	5.7 x10^{-1}	1.8 x10^{1}	5.1 x10^{-2}	5.2 x10^{-1}	2.1 x10^{-2}
	2	7.9 x10^{1}	3.7	1.5	5.9 x10^{-1}	5.4 x10^{-2}	3.3	2.1
	3	3.7 x10^{1}	1.0 x10^{-1}	1.4	5.8 x10^{-1}	4.4 x10^{-2}	1.6	9.1 x10^{-1}
	4	2.8	6.3 x10^{-1}	7.4 x10^{-1}	4.5 x10^{-1}	7.2 x10^{-2}	7.6	6.3 x10^{-1}
	5	5.9 x10^{-2}	1.1 x10^{-1}	1.1	3.6 x10^{-1}	2.6	1.5	7.2 x10^{-1}
	Median	2.8	6.3 x10^{-1}	1.1	5.8 x10^{-1}	5.4 x10^{-2}	1.6	7.2 x10^{-1}

Since the range of total VOC emissions found in each product class is highly variable, for the subsequent calculations we report the median emissions of each VOC within each of the PCP classes.

The values in Table 2.3 provide a starting point for possible explicit modelling of the effects of PCP VOC emissions, although further parameters require defining if an overall mass of emission of any given VOC is to be estimated. Using emissions factors on a per unit time and mass of product basis assumes that VOC emissions will scale linearly with additional time that they are in use (exposed to air) and additional mass of product used, up to some total maximum emissions limited by the VOC amount in the PCP dose. We develop here a range of scenarios for each PCP when in use. These various in-use scenarios are then used to scale-up the activity data to a per-person annual estimate of emissions for each product and then scaled further to give an indication of the potential scale of contribution of this source type at a national scale, using the United Kingdom as an example.

There is limited literature guidance on typical in-use scenarios, so we must use our own best-estimates of a plausible range. The range of these scenarios (meaning amount of product used and time-scale for use) is such that this in turn creates a wide range of potential VOC emissions, something that could only be narrowed if more precise information on PCP in-use activity was available to us. For our estimates, shampoo usage is assumed to be proportional to that of conditioner. Moisturiser is the most difficult product class to estimate, as many products fall into this category and are used in a variety of ways, both in terms of amount and frequency (eg, a small amount of eye cream is used daily compared to multiple hand cream applications), and it therefore has the largest estimated range of in-use emissions.

Annual estimates of emissions of VOC from non-aerosol PCPs

The laboratory measured emissions factors are combined with the range of activity scenarios in Table 2.4 to produce a simplified set of potential annual emissions statistics of VOCs from PCPs on a per-person basis. For each PCP class, we have taken the median VOC emissions from the group of products tested. This median emission is then scaled by the three usage scenarios, to give a lower and upper bound and central estimate value for annualized per-person emissions as in Table 2.4. Table 2.5 provides the summary of emissions for each product type and for the seven VOCs in the simplified VOC profile. We show this data in graphical format in Figure 2.6 for each of the products and for each of the seven VOCs within the simplified profile.

Table 2.4: PCP in-use consumption scenarios / activity levels later applied to individual emission factors for each product (L - Low, M – Medium and H - High.)

Product Class		**PCP Used in each Unit of Activity (g)**	**Period of Use (s)**	**Unit Activity (s g)**	**Annual Frequency of Activity (yr^{-1})**
Shampoo	L	2	30	60	52
	M	4	120	480	156
	H†	8	300	2400	364
Shower Gel	L	3	60	180	156
	M	4	180	720	364
	H†	8	300	2400	728
Moisturiser	L	0.5	5	2.5	13
	M	5	120	600	52
	H†	10	600	6000	728
Liquid Foundation	L	2	60	120	13
	M	3	180	540	52
	H†	6	300	1800	364
Conditioner	L	3	30	90	52
	M	6	120	720	156
	H†	12	300	3600	364

†High scenario taken as the complete release of all VOCs contained in each product based on experimental estimates of emissions.

Table 2.5: Annualised estimates of VOC emissions per person from selected non-aerosol personal care products based on the median emission rate product in each class.

	Annualised Emissions (g person^{-1} year^{-1})						
	2-Propanol	Benzyl Alcohol	D4	D5	Ethanol	Limonene	Methanol
Shampoo	4.5 x10^{-4}	3.0 x10^{-3}	6.7 x10^{-3}	1.1 x10^{-3}	5.7 x10^{-4}	7.6 x10^{-2}	1.3 x10^{-3}
	1.1 x10^{-2}	7.1 x10^{-2}	1.6 x10^{-1}	2.6 x10^{-2}	1.4 x10^{-2}	1.8	3.2 x10^{-2}
	1.3 x10^{-1}	8.1 x10^{-1}	1.9	3.1 x10^{-1}	1.6 x10^{-1}	2.1 x10^{1}	3.7 x10^{-1}
Shower Gel	2.1 x10^{-3}	1.3 x10^{-2}	-	-	5.7 x10^{-3}	3.0 x10^{-1}	6.4 x10^{-3}
	2.0 x10^{-2}	1.2 x10^{-1}	-	-	5.3 x10^{-2}	2.8	5.9 x10^{-2}
	1.3 x10^{-1}	7.8 x10^{-1}	-	-	3.6 x10^{-1}	1.8 x10^{1}	4.0 x10^{-1}
Moisturiser	6.2 x10^{-6}	3.6 x10^{-6}	-	2.0 x10^{-5}	1.1 x10^{-5}	1.7 x10^{-5}	6.5 x10^{-6}
	5.9 x10^{-3}	3.4 x10^{-3}	-	1.9 x10^{-2}	1.0 x10^{-2}	1.7 x20^{-1}	6.2 x10^{-3}
	8.3 x10^{-1}	4.8 x10^{-1}	-	2.6	1.4	2.3	8.7 x10^{-1}
Liquid Foundation	-	-	-	1.1	9.9 x10^{-4}	2.9 x10^{-5}	-
	-	-	-	1.9 x10^{1}	1.8 x10^{-2}	5.3 x10^{-4}	-
	-	-	-	4.4 x10^{2}	4.2 x10^{-1}	1.2 x10^{-2}	-
Conditioner	1.3 x10^{-2}	2.9 x10^{-3}	4.9 x10^{-3}	2.7 x10^{-3}	2.6 x10^{-4}	7.3 x10^{-3}	3.4 x10^{-3}
	3.1 x10^{-1}	7.1 x10^{-2}	1.2 x10^{-1}	65 x10^{-2}	6.1 x10^{-3}	1.8 x10^{-1}	8.0 x10^{-2}
	3.6	8.2 x10^{-1}	1.4	7.6 x10^{-1}	7.1 x10^{-2}	2.1	9.4 x10^{-1}

Low
Medium
High

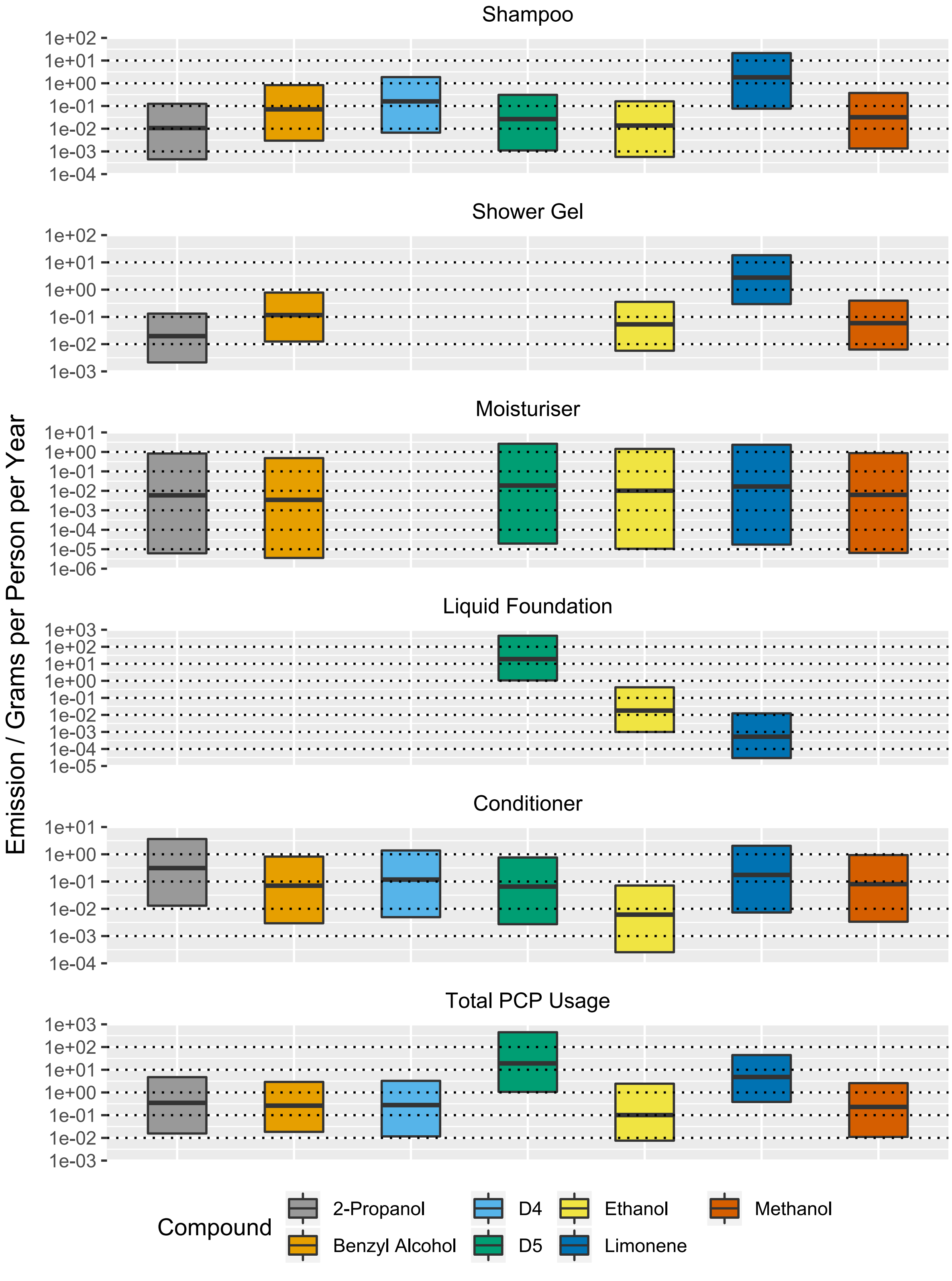

Figure 2.6: Range of potential VOC emissions from various non-aerosol personal care products on an annualised basis covering three activity and frequency scenarios outlined in Table 2.4.

The seven species are selected to represent a simplified speciation based on data from Figure 2.2.

Comparisons against emission inventory estimates

The reporting of VOC emissions forms part of obligations for signatories to the UN-ECE Convention on Long-Range Transport of Air Pollution (CLRTAP, see: http://www.unece.org/env/lrtap/welcome.html.html), where a country is required to provide estimates of annual emissions for the purposes of demonstrating compliance with ceiling targets. Similar obligations exist in the EU under the National Emissions Ceiling Directive (NECD). Reporting of emissions is however generally expressed as a single national total tonnage, and the degree to which speciation of VOCs is available (by compound and emitting sector) in different countries is highly variable. The NECD and CLRTAP defines those VOC sources to be included and excluded from the national inventory, notably VOCs from biogenic sources are excluded, and provides the technical definition of "what is a VOC." They also define how emissions from different sources are categorized between emitting sectors such as energy, transport, industrial and so on.

The EEA/EMEP Guidebook provides estimation methodologies and default emission factors for each source category. Country-specific emission factors can be used where deemed relevant, which may be the case for industrial process emissions, but less so for common sources such as road transport. However, although the reporting of VOCs appears very detailed, the methodologies used are heavily skewed to the dominant sources of VOC emissions as found in the late 1980s and 1990s, the time these treaties and methodologies were being developed. At that point, the overwhelming source of VOCs to air was from fuels and transportation and it is understandable that relatively little emphasis was placed at that time on reporting in detail VOCs from consumer products.

Few countries provide estimates of VOCs emission at a level of speciation, activity, and source sector granularity that would allow for comparison against data of the kind provided in this study. The United Kingdom National Atmospheric Emissions Inventory (NAEI) is possibly the most detailed national emission reporting system of VOC found globally and attempts to make some estimate of emissions of VOCs from sources such as personal care products (NAEI, 2019[55]). The NAEI includes more than 2000 different sources of VOCs and in excess of 600 different VOCs are included. The methodology is described in Passant NR 2002[34].

Using a mid-year 2017 estimate of the UK population of 66 million people[56] some extrapolation of potential national annual emissions of VOCs from non-aerosol PCPs can be made. Of course, to scale further from our per-person estimates carries with it the wide range of scenarios in Table 2.5 providing ultimately a very broad range of potential emissions. Nonetheless, it is potentially useful to place those bottom-up estimates of emissions against the emissions currently included for this source class within the UK NAEI. Table 2.6 shows the activity and frequency scenarios then scaled for the UK as a whole, but with the application of some de-ratings to reflect that not all of the population will be users of each of those product types. We apply a reduction factor of 0.8 to shampoo and shower gel, 0.4 to conditioner, 0.25 to moisturiser, and 0.2 to foundation. For comparison, we then extract from the 2017 UK NAEI the VOC emissions estimated under the EEA/EMEP Guidebook categorization of "Solvent Use," sub-class "Non-aerosol Products – Cosmetics and Toiletries," NFRCode: 2D3a and Source Code: 256.

Table 2.6: Estimated annual UK VOC emissions from non-aerosol PCP use and comparison with 2017 UK NAEI estimates for the 'Non-aerosol Products – Cosmetics and Toiletries' class of emissions. Calculations based on all UK users (following a de-rating to account for non-users) being either High, Medium or Low emissions as set out in product-use scenarios in Table 2.4).

Compound	**Low ($kg\ yr^{-1}$)**	**Medium ($kg\ yr^{-1}$)**	**High ($kg\ yr^{-1}$)**	**UK annual emissions NAEI ($kg\ yr^{-1}$)**
2-Propanol	4.6×10^2	9.4×10^3	1.2×10^5	3.1×10^4
Benzyl Alcohol	7.4×10^2	8.1×10^3	7.1×10^4	5.2×10^1
D4	1.3×10^2	3.1×10^3	3.6×10^4	0
D5	1.4×10^4	2.5×10^5	5.9×10^6	0
Ethanol	3.2×10^2	3.4×10^3	5.0×10^4	‡2.1×10^7
Limonene	1.6×10^4	1.5×10^5	1.1×10^6	0
Methanol	4.2×10^2	6.2×10^3	6.0×10^4	0

‡The national estimate for ethanol within the cosmetics and toiletries category includes perfume which represents the bulk of estimated ethanol emissions in this class.

The most immediate observation to be drawn from Table 2.6 is that of the seven major VOCs found in PCPs, four of these do not currently have any emissions included in the NAEI for this source classification (although all are included in the NAEI and emitted from other sources). Bottom-up extrapolation would suggest that for the central estimate of activity and usage, D5 cVMS (0.25 ktonne yr^{-1}) and limonene (0.15 ktonne yr^{-1}) are the most significant national VOCs by mass of emissions arising from non-aerosol PCP use. For perspective, however, the overall UK emission total for VOCs was estimated at 807 ktonne for 2017 (of which 579 ktonne were solvents), so this VOC contribution from non-aerosol PCPs to overall national emissions is very modest. The significance as a perturbation to indoor air quality where the concentrations would be maximized is explored further in the next section.

Model simulations

The emission rates from Table 2.6 were used to explore ambient concentrations that could arise following a representative use of PCPs within a shower. The median values were used for each of the seven VOCs/VOC classes, and the activity was assumed to be as follows. The shower commenced at 07:30 h, with the first 2 minutes spent using shampoo, followed by 2 minutes using conditioner and a further 3 minutes using shower gel. It was then assumed that there was a 3-minute pause to dry off, followed by 2 minutes spent applying moisturiser. The model was then used to explore the mixing ratios that could arise following the shower. Figure 2.7 shows the concentrations of the primary emissions based on Table 2.3 and focusing on the period from 07:00 to 08:30 hours.

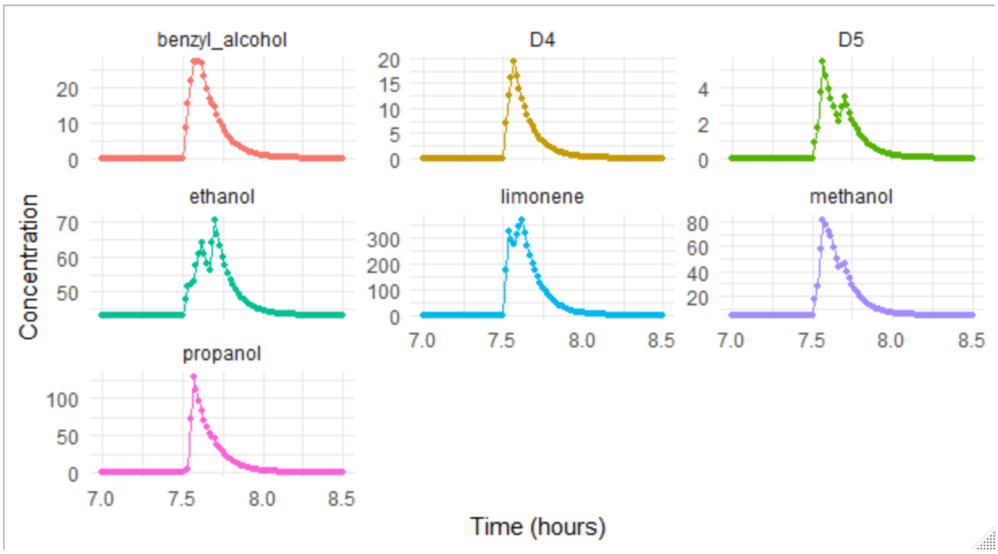

Figure 2.7: Mixing ratios of the seven components of the PCPs investigated following a shower using shampoo, conditioner, shower gel and moisturiser afterwards (units ppb).

Figure 2.7 shows that the mixing ratios of the primary emitted species increase as the shower begins and attain high concentrations, even at the relatively high ventilation rate of 9 h^{-1}. The profiles for the different species show differences according to their emission rates from the different processes, for instance, there is no D4 or D5 in the shower gel, whereas limonene* is present in all the PCPs used. Even though PCP use is only from 7:30-7:39, elevated concentrations are sustained beyond this period. Note that under these conditions, limonene* mixing ratios peak at ~375 ppb.

Figure 2.8 shows some of the species formed through the chemistry. Despite the high concentrations of limonene*, the high ventilation rate limits the potential for secondary chemistry, and formaldehyde and limonaldehyde (oxidation products of limonene) concentrations are only enhanced by about 4 ppb during showering, though they are still slightly elevated an hour or so afterward. Concentrations of PAN-type species in the model are elevated by ~4 ppb during the shower, but higher mixing ratios are sustained for longer than the other secondary species, owing to their much longer lifetimes under these conditions. Fine particle concentrations (not shown) were enhanced by around 1 µg/m^3 as a result of the PCP use, owing to the propensity of limonene oxidation products to form particulate matter[57]. Figure 2.8 also shows the impact of showering on the temporal evolution of the radical concentration. The OH concentration is enhanced as ozonolysis of limonene produces OH radicals, causing the concentration to peak at about 1.3×10^6 molecule cm^{-3}, with HO_2 and RO_2 mixing ratios peaking at 50 and 240 ppt. The OH concentrations are typical for those you might expect outside and show that conditions indoors can lead to significant quantities of radicals, even in the absence of sunlight. The peroxy radical concentrations are enhanced relative to those typically observed outside[58]. Note that some of these species are water-soluble gases[59] and may dissolve in water during showering. These processes are not currently included in the INDCM, so the values we present are likely to be upper limits for such species.

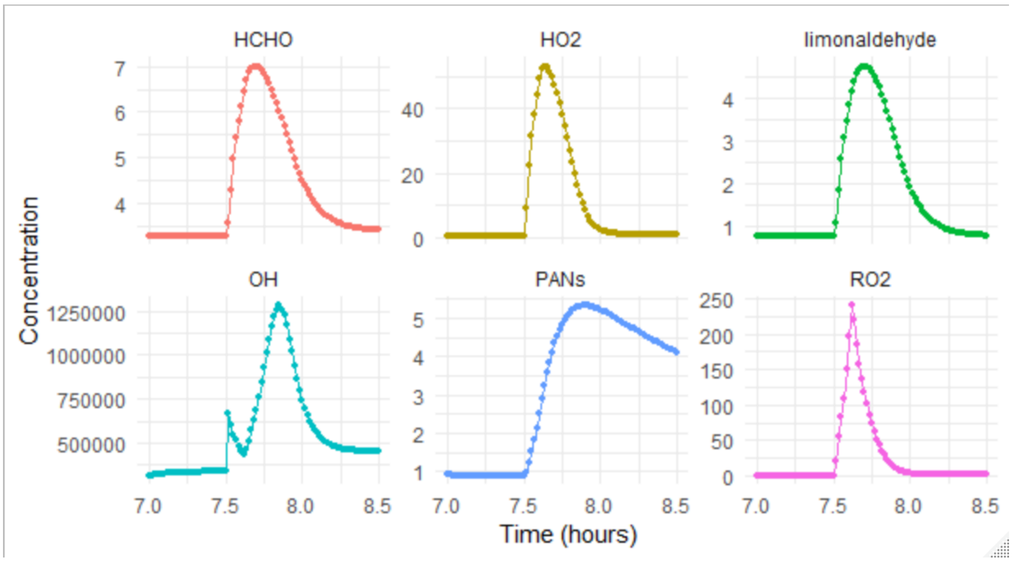

Figure 2.8: Concentration of OH (units molecule cm^{-3}) and mixing ratios of HCHO, limonaldehyde and PANs (sum of all the PAN-type species in the model) in ppb and HO_2 and RO_2 in ppt.

There is evidence that many people do not use their bathroom fans when showering and certainly not to the extent that ventilation rates would be as high as 9 h^{-1} [47]. In order to test model sensitivity to this factor, the model runs were repeated using a ventilation rate of 4.5 h^{-1}. Under these conditions, limonene mixing ratios peaked at around 495 ppb. Higher values were sustained for longer as would be expected with lower ventilation rates. Peak formaldehyde reached similar values under both ventilation rates, but remained elevated for ~1 h longer than shown in Figure 2.8 at the lower ventilation rate.

Comparisons against a proof of concept real-life study

The activity assumptions used in Table 2.4 were assessed during a real-life shower study. Product classes of facewash, followed by shower gel, shampoo, and conditioner were used by participants following the medium unit activity assumptions with measurements made in real time using on-line mass spectrometry of ambient air within the room. After drying off for three minutes, moisturiser and an aerosol deodorant were applied (facewash and deodorant activity assumptions detailed in Table 2.7). To support the assumption that VOC emission will change linearly based on the amount of product used, a single participant showered three times, using each of the low, medium, and high PCP usage amounts (g), where period of use stayed consistent at the central value assumption. The air in the room was sampled while the participant showered using PTR-MS, and the concentration of limonene released was determined after normalizing to a standard limonene calibrant.

Table 2.7: PCP in-use consumption scenarios / activity levels for facewash and aerosol deodorant employed during shower study

Product Class		PCP Used in each Unit of Activity (g)	Period of Use (s)	Unit Activity (s g)
Facewash	L	0.5	30	15
	M	2	60	120
	H	4	120	480
Deodorant	L	-	2	-
	M	-	4	-
	H	-	8	-

For deodorant there is no Unit Activity as an aerosol cannot be weighed out. Therefore product use was controlled by time only as the aerosol will release the same amount of product each time it is used.

Figure 2.9 shows that scaling the amount of PCP used directly changed the limonene concentration in a linear fashion. Clearly, these are very limited experimental data. However, we include them to provide independent reassurance that the emission values calculated bottom-up in this study and then included in the INDCM simulations, generate concentrations that are within an order of magnitude of those generated when the same quantities of PCP materials are used in the real-world.

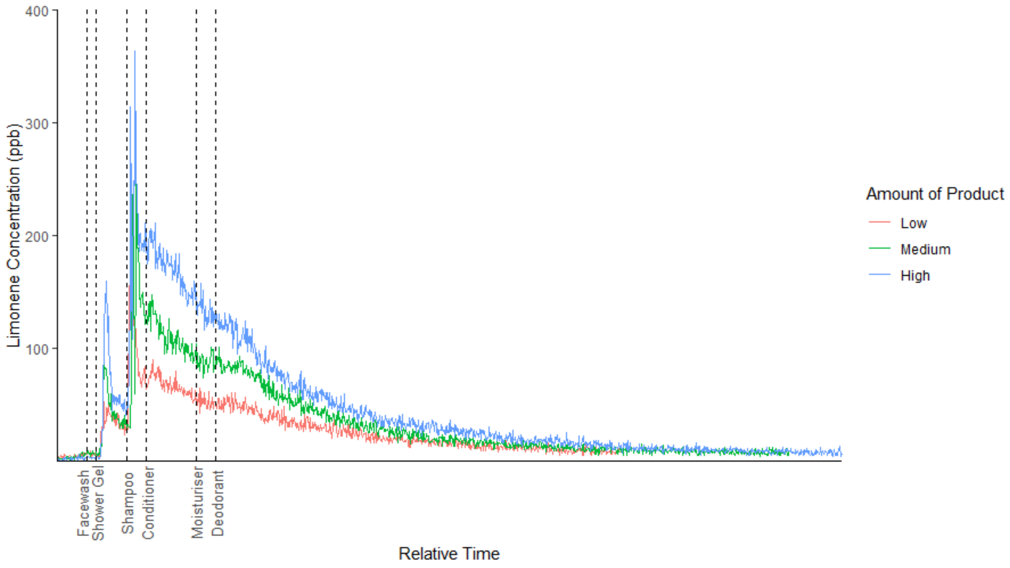

Figure 2.9: Mixing ratio of limonene measured during the real-life shower study in low, medium, and high amount use scenarios.

2.2.5: Conclusions

Online mass spectrometry methods have provided a straightforward method to screen for VOC composition and emission amount in a range of different VOC-containing non-aerosol PCPs. While every product has a unique composition, simplified profiles could be reported using seven common VOCs found in most of the samples screened (four alcohols and two siloxanes, and the lumped value for limonene to represent all monoterpenes). Overall, we find that amounts of individual VOCs released vary considerably between products, but are in the range of a few milligrams to a few grams of each VOC from each product per person per year. Shower gels and liquid foundation were found to have the highest rates of VOC emissions, dominated by limonene (representing all monoterpenes) for the former and D5 cVMS for the latter.

Few countries have a detailed and speciated emissions inventory for VOCs that is constructed at a sufficient level of granularity such that VOCs deriving from non-aerosol PCPs can be uniquely identified. The UK National Atmospheric Emissions Inventory does report at this level of detail, and this is compared to national emission estimates made for each VOC based on the bottom-up data collected here. Four of the seven VOCs in the simplified emissions profile do not have non-aerosol PCP emissions associated with them in the NAEI, and in general, NAEI emissions are considerably lower than would be estimated using the bottom-up figures. The most significant mass emissions per year are D5 cVMS (0.25 ktonne yr^{-1}) and limonene (0.15 ktonne yr^{-1}). Given annual VOC emissions for the UK are of the order ~800 ktonne yr^{-1}, it is clear that the under-representation of non-aerosol PCPs in isolation in the NAEI is unlikely to introduce significant error into the estimates reported under the auspices of CLRTAP or NECD. However, PCPs are only one of many classes of domestic products that potentially release VOCs, most significantly aerosol-based consumer products (eg, cosmetic, glues, car care) and household products (eg, fragrance, cleaning, pesticides), and some of these are also not currently reflected in inventory reporting.

As well as providing information for national emissions inventories, this work highlights the benefits of having product emissions rates in determining individual exposure to indoor air pollutants. On any one day, the exposure of an individual to air pollution is comprised of the sum of short-lived, individual exposures to high concentrations of VOCs from activities such as showering, cooking, cleaning, and walking along a busy road, in addition to low levels of continuous exposure. While measurements both indoors and outdoors have provided us with a reasonable understanding of the latter process, we know very little about exposures from individual indoor activities. Personal exposure measurements are extremely time consuming to make and are typically only carried out on a few individuals at a time, posing issues for representativeness. PCP emission rates for VOCs therefore presents an opportunity to model, based on activity, personal exposure and to start to understand the relative importance of outdoor versus indoor exposure for different individuals.

2.3: Emission rate calculations

Emission rate calculations were carried out in the following way: After peak identification, the relevant compound concentrations detected by the SIFT-MS were calculated by the Labsyft software (using Equation 2.8) in units of mg m^{-3}. These concentrations were applied to Equation 2.9 to calculate aggregate concentration in mg L^{-1} (presented in Table 2.2).

$$Average\ Concentration = \frac{(\sum Concentrations - Last\ Blank\ Reading)}{Total\ Number\ of\ Readings} \tag{2.9}$$

Emissions rates were then determined in units of µg s^{-1} g$_{[product]}^{-1}$ using Equation 2.10, with sweep flow rate calculated using Equation 2.11 in units of L s^{-1}.

$$Emission\ Rate = \frac{Concentration \times Sweep\ Flow\ Rate}{Weight\ of\ Sample} \tag{2.10}$$

$$Sweep\ Flow\ Rate = \frac{Average\ Sample\ Flow}{Average\ Tube\ Pressure} \tag{2.11}$$

2.4: References

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Chapter 3 : Investigating the real-world application of consumer products

3.1: Application of lab-derived conclusions to real-world situations

Following the estimation of emissions rates from lab-based experiments, we are interested in how these compare to the real-life use of PCPs. The isolated and sterile environment in which the lab experiments took place cannot account for such real-world factors as humidity, ventilation, temperature, the presence of water, and the general differences that may arise between consumers using the same products. It may be that these factors cause emissions to be completely unpredictable, and therefore unable to be accounted for by lab-based experiments. Using the same activity assumptions as in the previous chapter (section 2.2.4, Table 2.2), our chosen PCPs were used as intended under realistic showering conditions. A small portion of the work presented in this chapter has already been discussed in section 2.2.4, Figure 2.9, where it was proved that, for a single participant, the amount of product used scales linearly with the amount of compound emitted. Presented here is the full description of that study, which includes the analysis of 18 different participants.

This study seemed the natural progression to consolidate the work carried out in the previous chapter, justifying the assumptions made as being reasonable and true-to-life. The experiments were initially intended to be studied using SIFT-MS, in the same method as previously, however due to technical problems with the instrument a similar technique of PTR-MS was instead utilised.

3.2: Proton-Transfer-Reaction Mass Spectrometry

Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) is a technique very similar to SIFT-MS. Instead of the three reagent ions SIFT-MS employs, PTR-MS uses just H_3O^+, but operates in a very similar way. As such, it benefits from the same advantages as SIFT-MS - minimal fragmentation, no sample collection or pre-concentration required, and the ability to analyse trace gases in real-time.

H_3O^+ reagent ions are produced from pure water vapour by a hollow-cathode discharge ion source. This method produces a high density of high purity ions, and an upstream QMF is therefore not required to preselect the ions. Following that, the process is much the same as with SIFT-MS. The reagent ions react with trace gases introduced into the drift tube, and are analysed by a QMF in conjunction with an electron multiplier for detection[1]. Unlike SIFT-MS, a carrier gas is not employed, with ions being moved down the drift tube by an electric field towards the detector region[2]. H_3O^+ ions and trace gases usually undergo non-dissociative proton transfer reactions[3], as seen in section 2.1.1, Equation 2.1, with the electric field also working to limit the degree of cluster-ion formation. The PTR-MS can operate in both full mass and SIM scan modes, with the in-built software (Ionicon PTR-

MS Suite), analogous to LabSyft software, calculating mixing ratios using Equation 3.1. As the Ionicon PTR-MS Suite does not have the extensive library LabSyft possesses, the kinetic data for each compound must be input manually.

$$[R]_{ppb} = \frac{I(RH^{+}) \times 1 \times 10^{9} \times 1013 \times 22400 \times (273.15 + T_d) \times T(H_3O^{+})}{k \times t \times P_d \times N_A \times 273.15 \times T(RH^{+}) \times I(H_3O^{+})} \tag{3.1}$$

I(x) = Signal intensity / observed ion count rates

T_d = Temperature of drift tube

k = Rate of reaction for H_3O^+ with RH^+

t = Reaction time

T(x) = Transmission of RH^+ (The ratio of ions leaving a region of a mass spectrometer to the number of ions entering that region)

P_d = Drift tube pressure

3.3: Estimating person-to-person variability in VOC emissions from personal care products used during showering

This work was originally published in Indoor Air, February 2021 †

3.3.1: Abstract

An increasing fraction of volatile organic compounds (VOC) emissions come from the domestic use of solvents, contained within myriad commonplace consumer products. Emission rates are often poorly characterized and depend significantly on individual behaviour and specific product formulation and usage. Time-concentration profiles of volatile organic compounds (VOCs) arising from the use of a representative selection of personal care products (PCPs) during showering are generated, and person-to-person variability in emissions calculated. A panel of 18 participants used a standardized set of products, dosages, and application times during showering in a controlled indoor bathroom setting. PTR-MS was used to measure the in-room VOC evolution of limonene (representing the sum of monoterpenes), benzyl alcohol, and ethanol. The release of VOCs had reproducible patterns between users, but noticeable variations in absolute peak concentrations, despite identical amounts of material being used. The amounts of VOC emitted to air for one showering activity were as follows: limonene (1.77 mg ± 42%), benzyl alcohol (1.07 mg ± 41%), and ethanol (0.33 mg ± 78%). Real-world emissions to air were between 1.3 and 11 times lower than bottom-up

estimates based on dynamic headspace measurements of product emissions rates, likely a result of PCPs being washed away before VOC evaporation could occur.

3.3.2: Introduction

There is growing evidence that both aerosol and non-aerosol consumer products, including personal care products (PCPs) and household cleaning products (HCPs), contribute an increasing proportion of anthropogenic VOC emissions in high-income countries. The significance of these products has grown as historically dominant sources of VOCs such as road transport and fuel evaporation decline[5]. While atmospheric emissions of VOCs from fuels and vehicle exhaust have been well-characterized for many decades, both in terms of speciation and amount emitted, estimates of PCP emissions are only now becoming available[6–12]. The environmental and public health motivations to quantify and control VOCs from PCP and HCP sources are no different to other VOC emission sources. Their oxidation in the presence of NO_x leads to the formation of tropospheric ozone, and they can form secondary organic aerosols (SOA), a component fraction of particulate matter. The impacts on health include, but are not limited to, respiratory and cardiovascular diseases[13–15], along with several other conditions broadly characterized as "fragrance sensitivity" which includes the effects of both inhalation and dermal routes of exposure[16]. Symptoms of fragrance sensitivity include headaches, watery eyes, congestion, and contact dermatitis, which can lead to itching, swelling, and redness of the skin. These negative health effects are not limited to those with allergies, as they are not always triggered by an immune response.

A particular challenge associated with the quantification of VOCs from PCPs is that there is no common industry or regulatory standard for the disclosure of VOC ingredients or likely atmospheric emissions. VOCs can be classified in bulk terms, for example, as "parfum" or "fragrance," for reasons of intellectual property protection, but also labelling practicality, since many hundreds of VOCs may be used in a formulation. Steinemann (2009, 2015) and Steinemann *et al.* (2011) report the range of volatile emissions found in consumer products[17–19], which predominantly comprises of terpenoids and alcohols. Headspace speciation of VOCs in consumer products is a useful starting point for assessing possible emissions, but in isolation does not provide sufficient information to assess how much VOC might be released to air from PCPs based on human activity in the real world.

Yeoman et al (2020)[20] described laboratory-based atmospheric emission factors for seven commonly found VOCs in non-aerosol PCPs, two of these (limonene—representing the grouping of monoterpenes—and benzyl alcohol) being fragrance compounds. Of the VOCs released from the products studied, monoterpenes had the highest chemical potential for the formation of secondary products such as formaldehyde and SOA, dependant on the ingress of ozone from outdoors[21]. Limonene in particular has been reported previously by Carslaw and Shaw (2019)[22] to be one of the most relatively impactful VOCs on indoor chemistry due to its high potential for SOA and formaldehyde formation[23–31]. World Health Organization Guidelines[32] for Indoor Air Quality determine the exposure limit for formaldehyde to be 0.1 mg/m^3 (30-min average concentration) and name HCPs and cosmetics among indoor sources, along with textiles, insulating materials, and other consumer items.

While bottom-up estimates provide a standardized laboratory method for assessing the possible scale and composition of VOC emissions from individual products, they do not quantify the emissions variability arising from how individuals use those consumer products in the real world. There is likely to be variability based on amount of PCP used, duration and frequency of use, method of application, and so on. PCPs are predominantly an indoor VOC emission source, the bathroom being a location where they most commonly used, followed by the bedroom[12]. Showering is one activity, which for many people is a daily occurrence, that can include the use of a range of different products, and by extension is likely a significant component of daily VOC emissions from use of PCPs. There are several previous works describing exposure to VOCs from a range of consumer products, using both top-down and bottom-up approaches. These include product-use studies[33–35], the use of modelling[36,37], analysis of air samples[38], direct analysis of consumer products themselves[39], and combinations of these methods[40]. Despite these numerous previous works, there is no research specifically into the variability of VOC emissions from PCPs when in real-world use during specific activities such as showering. Known carcinogens and toxicants, such as trihalomethanes and chloroform, have already been identified as harmful compounds released during showering[41,42]. They are, however, contaminants and resulting reaction products of the water supply and are not a result of personal product choices or an individual's bathing habits. For consumer products specifically, there has been most emphasis in the research literature on quantifying real-world VOC emissions from domestic cleaning activities, potentially because in practical terms these are experiments that are somewhat easier to simulate, control, and measure. This is illustrated by Rossignol et al (2013)[43], where studies in an experimental house were used to identify and quantify VOCs emitted from a single HCP used in a real-life scenario.

The research presented here also takes a real-life approach to calculating emissions and concentrations of VOCs generated during showering across a cohort of volunteers using a single controlled showering facility. A common set of experimental parameters, for example, product types, dosages, duration, and ventilation were used, allowing an evaluation of the inherent variation in emissions between individuals based on their real-world behaviours. As previous work has measured simplified PCP compositions, we show here, through temporal profiles, the reproducibility between participants while those products are in-use.

3.3.3: Experimental

Shower Facility

A single shower facility was used for all experiments located in the Wolfson Atmospheric Chemistry Laboratories, Chemistry Department, University of York. As this study was focused on quantifying VOCs emitted, the shower facility chosen had no windows to minimize compound photochemical loss. The room dimensions were 2.59 m x 2.46 m x 0.93 m (5.96 m^3). The ventilation rate of the room was controlled using an extractor fan continuously operating at a flowrate of 6.3 L/s (measured directly using a handheld Kestrel 5500 anemometer). The room exchange rate was calculated as 0.06 air changes per min (3.8 air changes/h) using Equation 3.2.

$$ACH = \frac{Ventilation\,Rate\ \times 3600}{Volume\ of\ Room} \tag{3.2}$$

The 18 participants were a mixture of both male and female researchers from the Wolfson Atmospheric Chemistry Laboratories who volunteered to take part in these experiments.

The temperature and humidity within the room were measured using a HM1500LF probe (TE Connectivity). Participants were issued with pre-measured doses of commonly available PCPs selected from the general range available in UK supermarkets in 2019. A face wash, shampoo, conditioner, shower gel, moisturiser, and aerosol deodorants (male and female equivalents) were selected for the participants to use. All fragranced wash-off products were “citrus” based, with the expectation they would contain limonene, which was adopted as an easy to measure tracer of emissions. Participants were given the choice of two deodorants, which although differed in scent, had the same bulk VOC propellant. Each product to be used was pre-weighed in advance and is summarized in Table 3.1.

Table 3.1: Product usage estimates were taken as the median usage assumption data from Yeoman et al (2020) (Table 2.2)

Product	Amount Used (g)	Time of Use (s)
Facewash	2	60
Shower Gel	4	180
Shampoo	4	120
Conditioner	6	120
Moisturiser	5	120
Aerosol Deodorant	-	4

Concentrations of selected VOCs were measured using an Ionicon (GmbH, Innsbruck, Austria) high-sensitivity Proton-transfer-reaction mass-spectrometer (PTR-MS). This instrument has three Varian turbo-molecular pumps and a stainless-steel ringed drift tube (9.6 cm). The instrument has been described elsewhere[2,3,44]; therefore, only a brief description of the instrument set-up will be included here.

Air for analysis by PTR-MS was sampled from the shower facility at a flowrate of 0.4 L/min through a 1.5 m length of 1/8" PFA transfer line (Swagelok) heated to 100°C. The PTR-MS was operated with the quadrupole scanning through 10 pre-determined masses (ion dwell time 0.1 s per *m*/*z*) at a cycle time of 0.8 s in selected ion monitoring mode (SIM). The targeted protonated masses and likely contributing compounds were as follows: *m*/*z* 31 (formaldehyde), *m*/*z* 45 (acetaldehyde), *m*/*z* 47 (ethanol), *m*/*z* 91 (benzyl alcohol), and *m*/*z* 81, 137 (limonene). In addition to these masses, both the primary ion count *m*/*z* 21 ($H_3{}^{18}O^+$) and its first cluster *m*/*z* 37 ($H_3{}^{16}O\ H_2{}^{16}O^+$) were recorded. Cyclic volatile methyl siloxanes (cVMS) were not selected for analysis due to unreliability in detecting compounds with high *m*/*z* values (cVMS are over 200). Omitting these compounds does not hinder the study's aim to better understand the variability in VOC emissions between people undertaking the same activity, but we recognize that cVMS likely do make a notable contribution to the absolute of VOC emitted per showering activity. Prior to each participant entering the room, the instrument background was measured by sampling air from the shower facility which has first passed through a custom-built platinum catalyst heated to 380°C. During the experimental period of 34 days, the PTR-MS drift tube pressure, temperature, and voltage were held constant at 1.80 mbar, 60°C and 500 V. This maintained an E/N ratio of ~133 Td. The H_3O^+ primary ion count ranged between 1.71 and

8.96 x 10^6 ion counts per second (cps) with a mean of 3.85 x 10^6 cps. The *m/z* 37 cps ranged between 1.68 and 8.44 x 10^5 with a mean of 5.77 x 10^5, which represented 15% of the primary ion signal.

Limonene calibrations were carried out daily using a secondary gas standard (37.5 ppb in zero air). This secondary standard was quantitatively determined using a thermal desorption-gas chromatograph-flame ionization detector (TD-GCFID) against a National Physical Laboratory certified stock standard (1 ppm). Certified gas standards of 2-propanol, benzyl alcohol, and ethanol were not available for calibration. Hence, benzyl alcohol, 2-propanol, and ethanol gas standards (approximately 1 ppm) were made from liquid standards (Sigma-Aldrich) in 3 L Tedlar bags (Cole Palmer) and sampled individually by the PTR-MS to determine the fragmentation coefficients for each compound. These are summarized in Table 3.2.

Table 3.2: Compound product ions and corresponding significant fragmentation ions, used to calculate fragmentation coefficients

Compound	**Main Product Ion** ***m/z***	**Significant Fragmentation Ion(s)** ***m/z***	**Fragmentation Coefficient**
Limonene	137	81, 95	0.36
Benzyl Alcohol	91	79	0.37
Ethanol	47	45, 46	0.9

Mixing ratios were then determined using the instrument-specific transmission coefficients and reaction rate constants (*k*) taken from the LabSyft kinetic library, which are taken from Wang, Spanel, and Smith (2003)[45], Wang, Spanel, and Smith (2004)[46], and Spanel and Smith (1997)[47].

Despite careful calculation of transmission coefficients, using a range of gas standards under laboratory conditions, mixing ratios may be subject to systematic errors, which, in some instances, can be as much as a factor of two[2]. Instrument limits of detection (LoDs) for 1 min averaged data were determined by the method outlined by Taipale and colleagues (Taipale et al., 2008)[48] and were 2.7, 6.4, and 3.7 ppt for limonene, benzyl alcohol, and ethanol, respectively. Precision of the measurements, assessed as the 1 standard deviation of the measured zero value over 60 s, was typically 0.1 ppb for a PTR-MS VOC measurement. At higher abundances (ppb-level and greater), uncertainty in reported measurement is determined largely by the uncertainty in the gravimetric gas standards, reported as 5% by the supplier.

Participants were asked to follow instructions shown in section 3.4.3 summarising the order in which to apply the products and how long for. They were given 3 min between the use of conditioner and moisturiser to turn the shower off and dry. A stop clock located in the room allowed participants to time themselves, and products had already been weighed out and placed into capped pots prior to each experiment. Afterward, they were asked to complete a questionnaire (section 3.4.3) regarding how well the amount and time assumptions matched their personal PCP use.

Aggregate VOC emissions were calculated from the integral of the concentration-time profile using R software and a cubic spline function to determine the area under each transient time-concentration plot for the 15-min showering activity window for limonene, benzyl alcohol, and ethanol. These mole fraction values were converted from ppb into mg/m^3, and then accounting for room size and ventilation over the measurement period, integrated to give total amount of VOC emitted as an overall mass during the activity. The activity window is considered to begin when the first product is applied and ends around 2 min after the last product is applied.

Comparisons to bottom-up estimates made in Yeoman et al (2020)[20] were calculated using Equation 3.3.

$$Product\ emitted = emission\ factor^{\dagger} \times amount\ used^{\ddagger} \times time\ of\ use^{\ddagger} \tag{3.3}$$

† From Yeoman et al (2020)[20]

‡ From Table 3.1

3.3.4: Results and Discussion

VOC time-concentration profiles

Single-user reproducibility can be determined by a participant showering multiple times under the same conditions (time and dosage). An example is presented in Figure 3.1, showing the concentrations arising indoors from a single participant that is reproducible to within a factor of two for most VOCs.

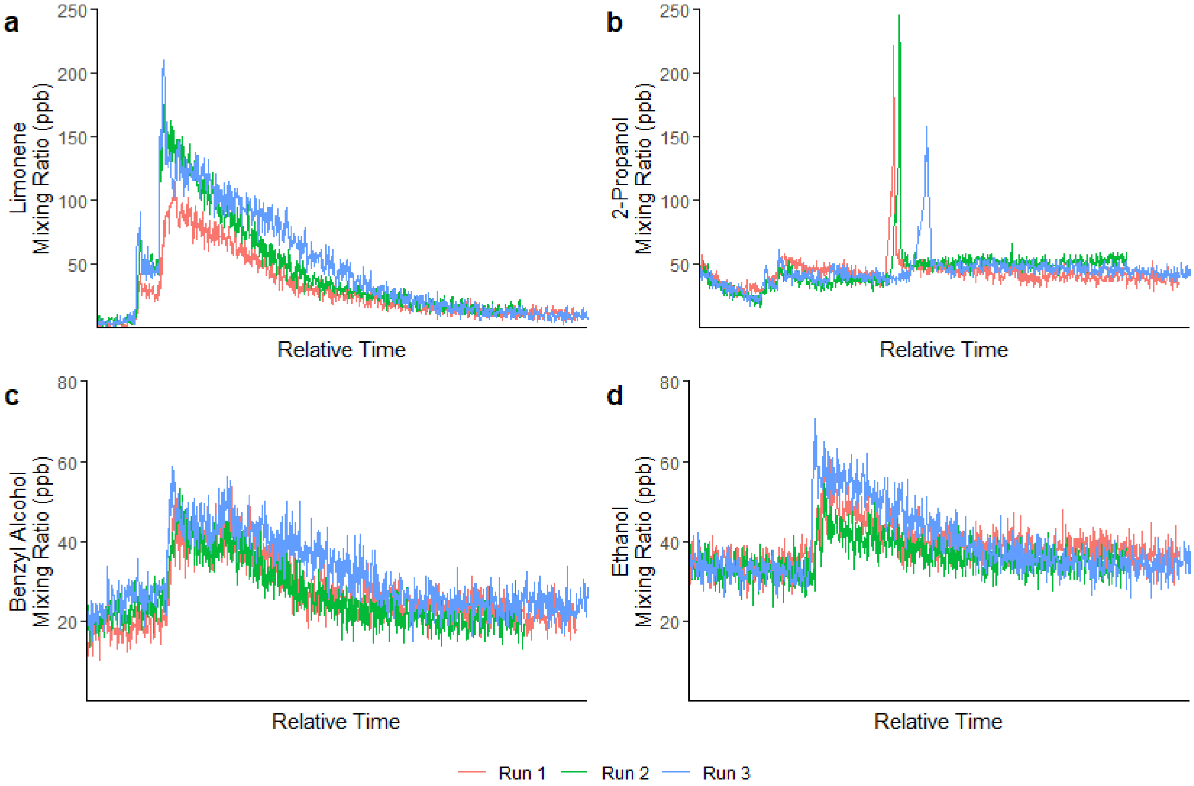

Figure 3.1: Single-participant reproducibility experiment; a) Limonene b) 2-Propanol c) Benzyl alcohol d) Ethanol

The shower data from all 18 participants are presented as temporal profiles for each compound (Figures 3.2-3.4) where each coloured line represents one of the 18 participants. Mixing ratios are presented on the left-hand y-axis, and a concentration in mg/m^3 on the right-hand y-axis.

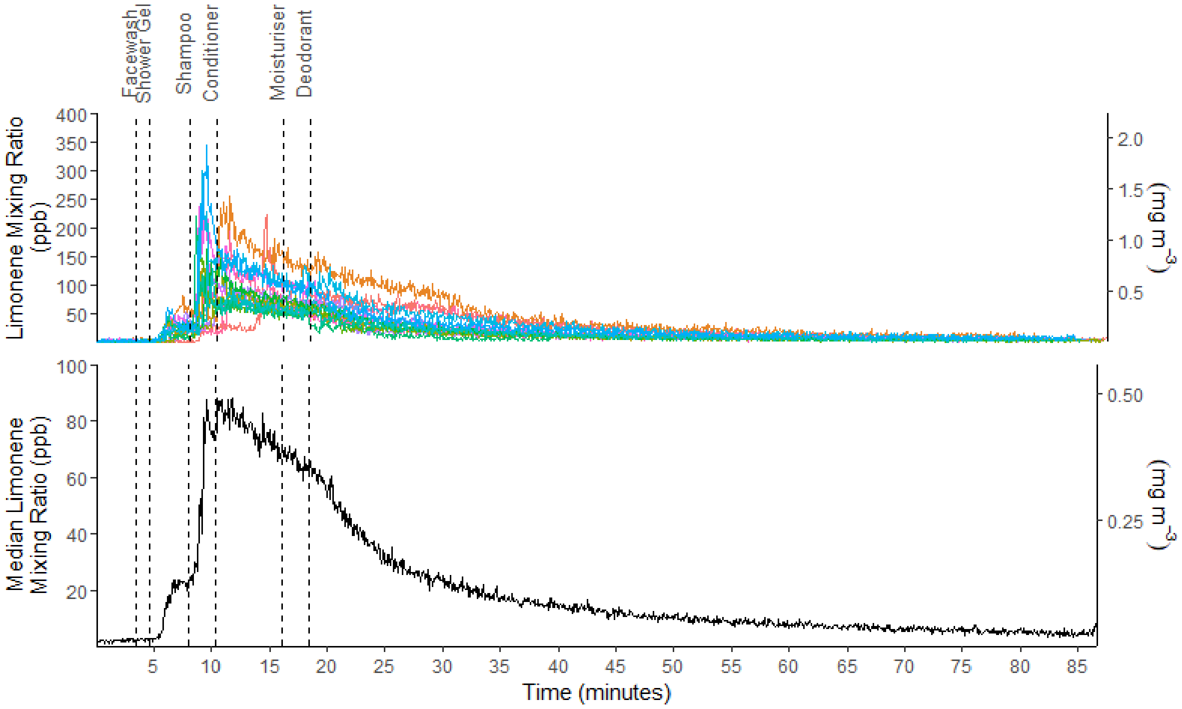

Figure 3.2: VOC evolution profile of limonene; Top: Data from all 18 participants, Bottom: Median participant VOC profile.

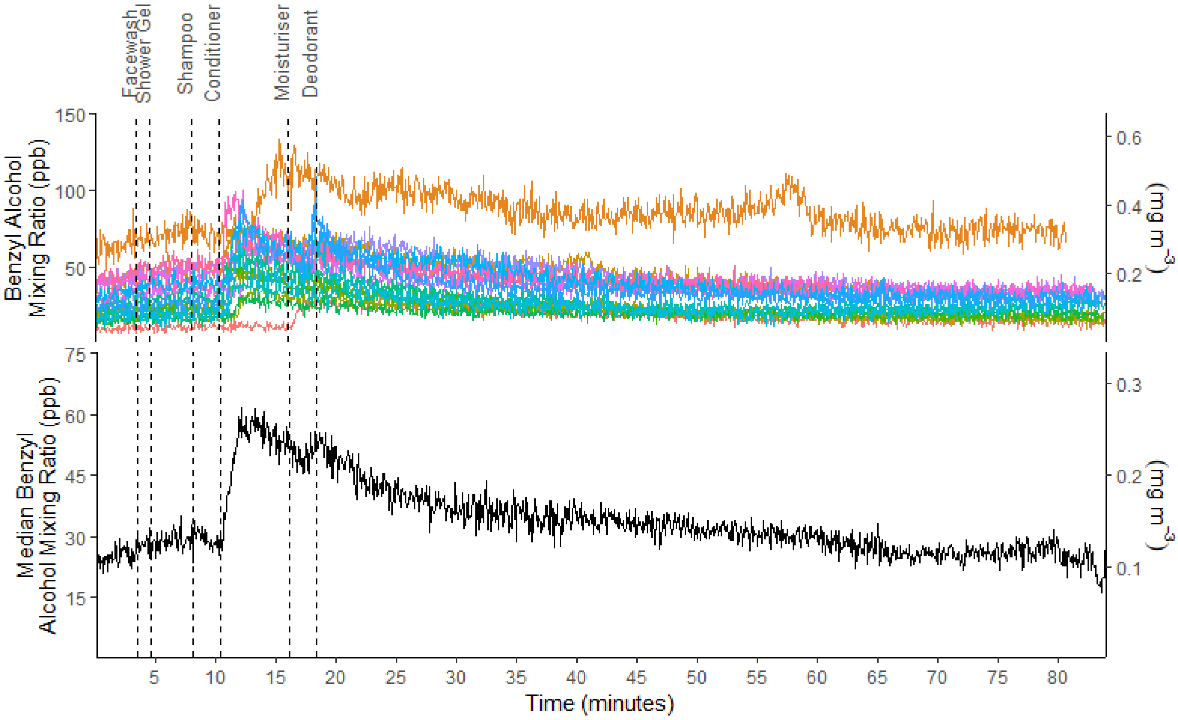

Figure 3.3: VOC evolution profile of benzyl alcohol. Top: Data from all 18 participants, Bottom: Median participant profile.

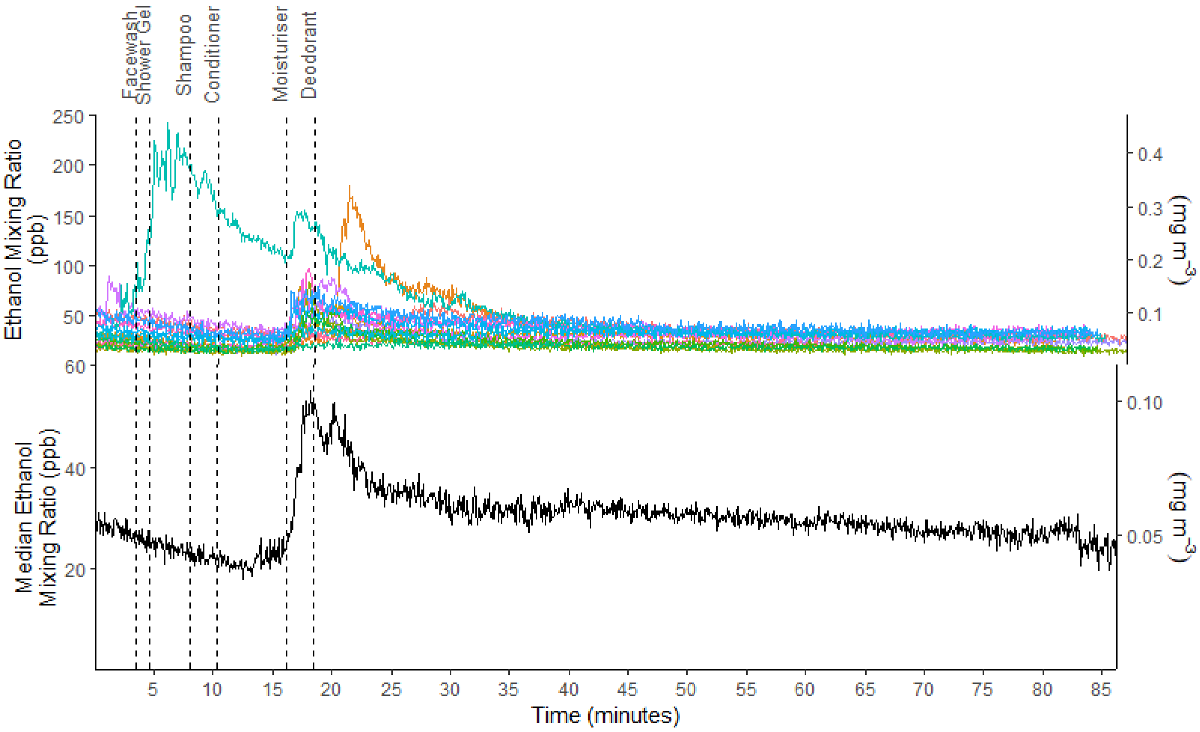

Figure 3.4: VOC evolution profile of ethanol. Top: Data from all 18 participants, Bottom: Median participant profile.

In order to assess the overall amount of VOCs emitted from fixed amounts of products, we consider the concentration over one 15-min shower activity. Data for individual participants are presented in Table 3.3, with Figure 3.5 displaying the variation between participants, and a summary in Table 3.4.

Table 3.3: Table of total VOC mass emitted from all 18 participants over 15-minute activity window

	VOC Emitted (mg) for 15 Minute Activity		
	Limonene	Benzyl Alcohol	Ethanol
Participant 1	1.941	0.866	0.462
Participant 2	3.634	2.332	0.524
Participant 3	1.892	0.465	0.428
Participant 4	1.488	1.518	0.317
Participant 5	1.816	1.464	0.277
Participant 6	1.882	1.110	0.503
Participant 7	1.723	1.361	0.328
Participant 8	2.903	1.429	0.449
Participant 9	1.487	1.436	0.236
Participant 10	1.662	0.856	0.206
Participant 11	1.654	0.614	0.242
Participant 12	1.490	0.853	0.272
Participant 13	4.538	0.549	0.224
Participant 14	1.448	1.030	0.218
Participant 15	1.555	0.703	1.662
Participant 16	1.577	0.861	0.330
Participant 17	2.992	1.387	0.378
Participant 18	3.162	1.205	0.466
Mean	2.158	1.113	0.418
Median	1.770	1.070	0.329

Lowest

Highest

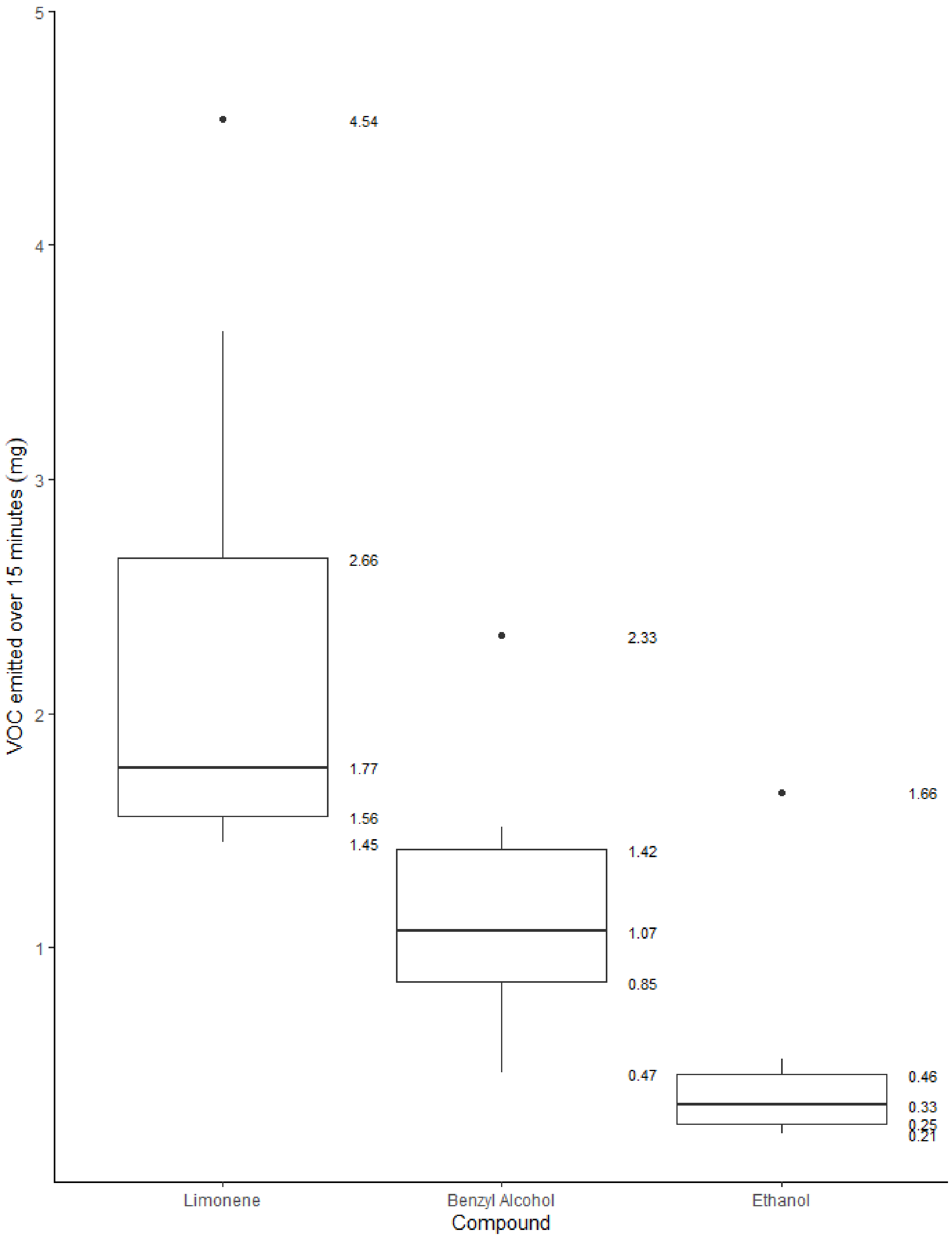

Figure 3.5: Variation in total mass of limonene, benzyl alcohol, and ethanol emitted to air over the 15 - minute activity window, having taken ventilation rate and room size into consideration.

Table 3.4: Summary of variation between participants

	Median concentration (mg m^{-3})	Median Emission (mg)	Relative Standard Deviation (%)	Interquartile Range (mg)
Limonene	0.23	1.77	42	1.10
Benzyl Alcohol	0.18	1.07	41	0.57
Ethanol	0.06	0.33	78	0.21

Generally, the temporal pattern of concentrations is consistent between participants and the concentrations measured are broadly compatible (same order of magnitude) as a bottom-up estimate of likely in-room emissions modelled in Yeoman et al (2020)[20]. In Table 3.5, we calculate the estimated "bottom-up" emissions of limonene and benzyl alcohol based on emissions in Yeoman et al (2020)[20] using Equation 3.3, during dynamic headspace analysis and compare to the "top-down" assessment in this study. Both methods have their limitations but can be used in a complementary fashion. The top-down approach highlights the importance of accounting for real-world variability in how products are used, and wider environmental effects, like wash-off and solubility. These show the possible over-estimation of emissions that would arise if those estimates were based solely on laboratory-based experimentation on raw materials.

Table 3.5: Bottom-up and top-down estimates using emission factors calculated in Yeoman et al (2020)[20] (Table 2.3) product usage estimates found in Table 3.1, and the median real-world emission value.

Product	Limonene (mg)	Benzyl Alcohol (mg)
Shampoo	12.0	0.5
Shower Gel	7.9	0.3
Moisturiser	0.3	0.1
Conditioner	1.2	0.5
Total (bottom-up)[†]	21.4	1.4
Median (top-down)[‡]	1.8	1.07

[†] Sum of shampoo, shower gel, moisturiser, and conditioner, calculated using Equation 3.3

[‡] Values taken from Figure 3.5

It is important to bear in mind that as citrus-based products were selected for this investigation, the limonene emission estimates reported here do not represent all PCPs used and may represent a worst-case emission scenario in terms of total mass of VOC emitted. Having said this, a high proportion of PCPs are citrus scented, and those that are not still contain a combination of monoterpenes to create a desired scent, even if it is not explicitly citrus.

Relative amounts of each VOC emitted between products in real-world use are consistent with the median in-use emission factors previously reported. A notable peak arises for limonene from the use of shampoo, with the smaller peak before it correlating to emissions from the shower gel product, as seen in Figure 3.2. The main benzyl alcohol peak can be attributed to conditioner (Figure 3.3), with moisturiser seeming to be the main contributor to the emission of ethanol (Figure 3.4). The ethanol peak also coincides with the water being turned off and may be linked to the decrease in liquid water content in the room, something that is further discussed in a later section.

In other literature, limonene concentrations reported during the use of consumer products are very varied. Rossignol et al (2013)[43] report up to 0.07 mg/m^3 emitted from the use of a high-emitting HCP, while another real-life product-use study, Singer et al (2006)[40], reports much higher limonene, as 1-h average concentrations, from the use of surface cleaner (0.96–2.5 mg/m^3) and a floor cleaner (1.13–6.2 mg/m^3) at different dilutions. Residential and workplace air-sampling studies report maximum limonene concentrations of 0.49 mg/m^3 (Edwards et al, 2001[49]) to as low as 0.05 mg/m^3 (Su et al, 2018[38]). Our shower activity experiments yield results toward the higher end of this range; Figure 3.2 shows a median limonene peak of around 0.5 mg/m^3, with a maximum of 2 mg/m^3 reached.

Table 3.6 presents both the median and per person emissions rate for each compound.

Table 3.6: Emission rates calculated for all 18 participants using total mass emissions data found in Table 3.3.

	Emission Rate (µg s^{-1})		
Participant	**Limonene**	**Benzyl Alcohol**	**Ethanol**
1	2.21	9.63 x10^{-1}	5.14 x10^{-1}
2	4.15	2.59	5.82 x10^{-1}
3	2.16	5.17 x10^{-1}	4.75 x10^{-1}
4	1.70	1.69	3.52 x10^{-1}
5	2.07	1.63	3.08 x10^{-1}
6	2.15	1.23	5.59 x10^{-1}
7	1.97	1.51	3.64 x10^{-1}
8	3.31	1.59	4.99 x10^{-1}
9	1.70	1.60	2.62 x10^{-1}
10	1.90	9.51 x10^{-1}	2.29 x10^{-1}
11	1.89	6.83 x10^{-1}	2.68 x10^{-1}
12	1.70	9.48 x10^{-1}	3.02 x10^{-1}
13	5.18	6.10 x10^{-1}	2.49 x10^{-1}
14	1.65	1.14	2.42 x10^{-1}
15	1.77	7.81 x10^{-1}	1.85
16	1.80	9.56 x10^{-1}	3.67 x10^{-1}
17	3.41	1.54	4.20 x10^{-1}
18	3.61	1.34	5.18 x10^{-1}
Median	2.02	1.19	3.65 x10^{-1}

The data presented here indicate that the overall emissions of VOCs from a single measured dose of PCP are affected by person-to-person variations in how the products are used, even when application amount and time is controlled for. Variations arising from different interpretations of timing instructions with regard to rinsing were assessed in a further experiment. The experimental details and results from this can be found in Figure 3.6 and Table 3.7. Briefly, it was found that lower VOC concentrations were detected when the participants spent a longer period rinsing the products. This explained how small deviations in how products are used can yield significant differences in emissions, and likely accounts for some of the variation in participant data. This is reflected in the spread in the interquartile range, 0.89 mg, which implies that emissions in real-world settings for controlled amounts could be estimated to within a factor of around two.

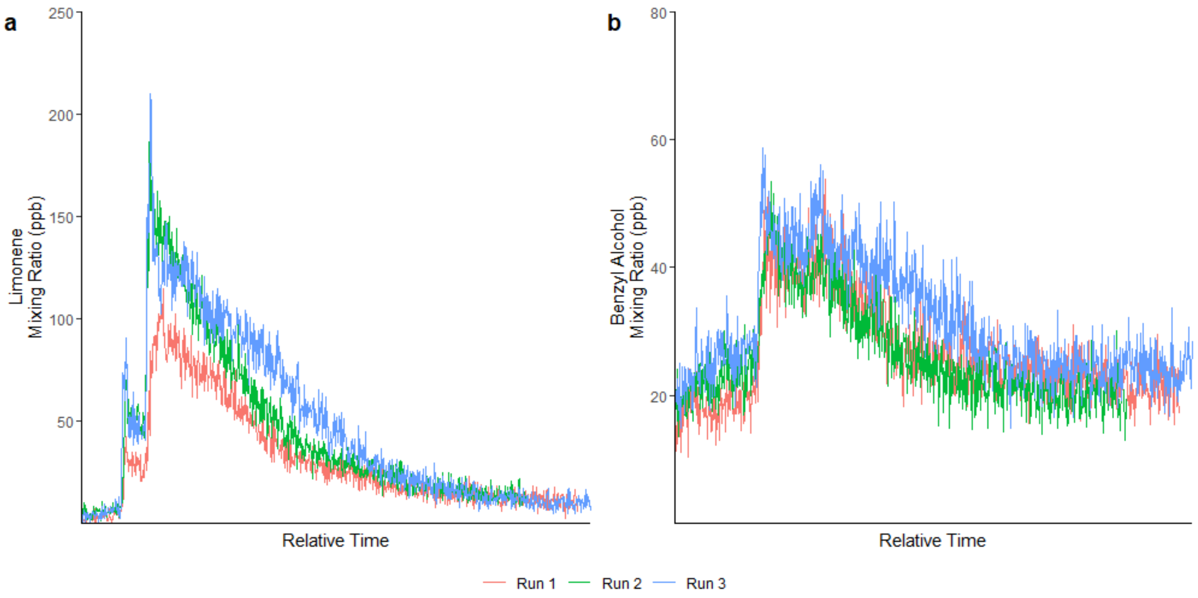

Figure 3.6: Rinsing time variation experiment a) Limonene, b) Benzyl alcohol, where Run 1 is a longer rinse time, Run 2 is standard rinse time, and Run 3 is less rinse time.

Table 3.7: Wash-off product usage alterations for rinsing time experiment

Product	Run	Time Applying (s)	Time Rinsing (s)
Facewash†	More Rinse	30	30
	Standard	30	30
	Less Rinse	30	30
Shower Gel	More Rinse	30	150
	Standard	90	90
	Less Rinse	150	30
Shampoo	More Rinse	30	90
	Standard	60	60
	Less Rinse	90	30
Conditioner	More Rinse	30	90
	Standard	60	60
	Less Rinse	90	30

†Facewash timings could not be altered

Although this is a relatively large source of uncertainty in emissions, it is small compared to the variability associated with the total amount of product used by individual consumers, the frequency of use, or indeed product to product formulation differences. It would suggest that to narrow further the uncertainties in PCP emissions it is the overall consumption and content of VOCs that would benefit from additional study, in advance of further data on variability in use between individuals.

Concentrations profiles and links to VOC properties

There is link between VOC solubility in water and its concentration profile; the less soluble a compound is, the more defined and higher its concentration during showering. Limonene is the best example of this; it has a relatively high octanol/water partition coefficient ($log\mathrm{K}_{ow}$) and two distinct concentration maxima arising from shower gel and shampoo applications. Conversely, ethanol decreases in concentration when the shower starts, and only peaks after the water is turned off, when moisturiser and deodorant are used. The liquid water content during showering itself had a temporary effect on concentration, with concentrations increasing once liquid droplets were removed (an example humidity profile can be found in Figure 3.7). The behaviour of VOCs and interactions with the wider in-house environment are therefore potentially important. While a simple bottom-up evaluation of VOCs from many of these PCPs would indicate substantial VOC emissions, when used in practice the low *log*K_{ow} of some VOCs led to efficient scavenging to the aqueous phase. This potentially represents a route by which those VOCs may be overestimated in terms of atmospheric emissions based solely on their presence in the raw product itself. This was observed for both 2-propanol and methanol (Figures 3.8 and 3.9), which were determined to be present in consumer products by Yeoman et al (2020)[20], but displayed inconsistent temporal profiles from this study. As the peaks do not correlate to a change in the humidity profile, temperature profile, or any non-experimental activity such as opening the shower room door, we are left to believe that the release of 2-propanol is associated with other impurities in the environment. It is not a known contaminant of tap water, nor is it commonly found in water pipes. As such, we have no explanation other than it being carried into the shower room by the participants (on clothing, towels, PCPs they had already used, etc.) and is released at times when they had finished following the showering instructions and that we were unable to monitor.

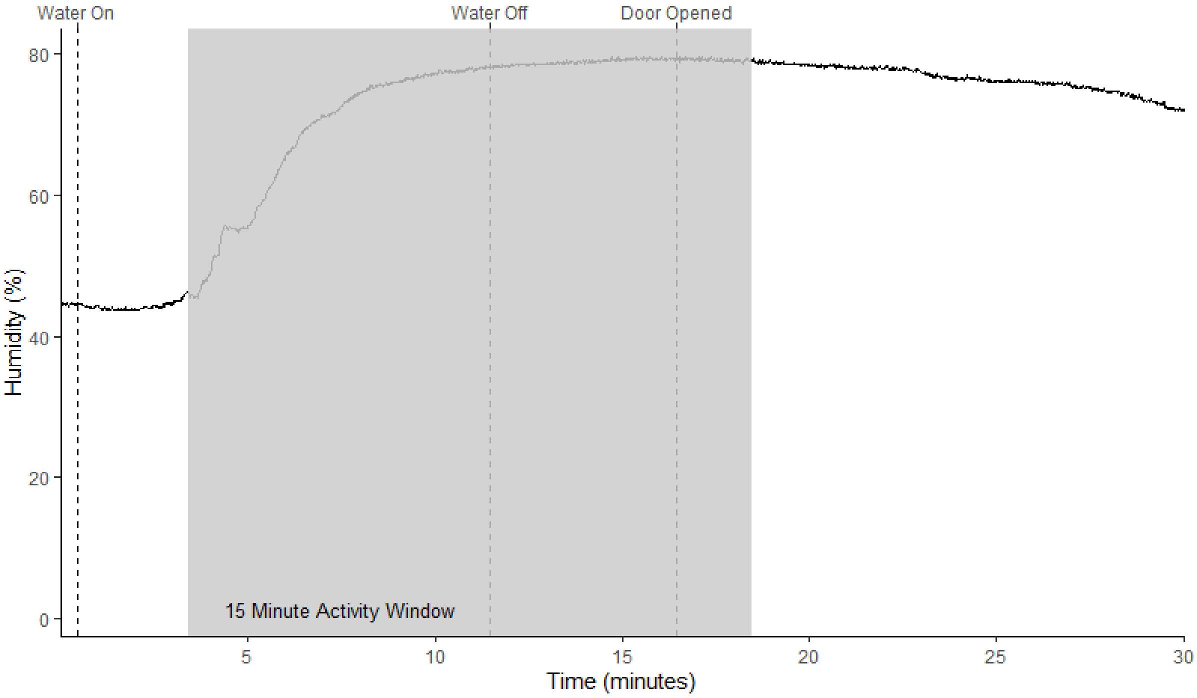

Figure 3.7: Humidity profile of randomly selected experimental run

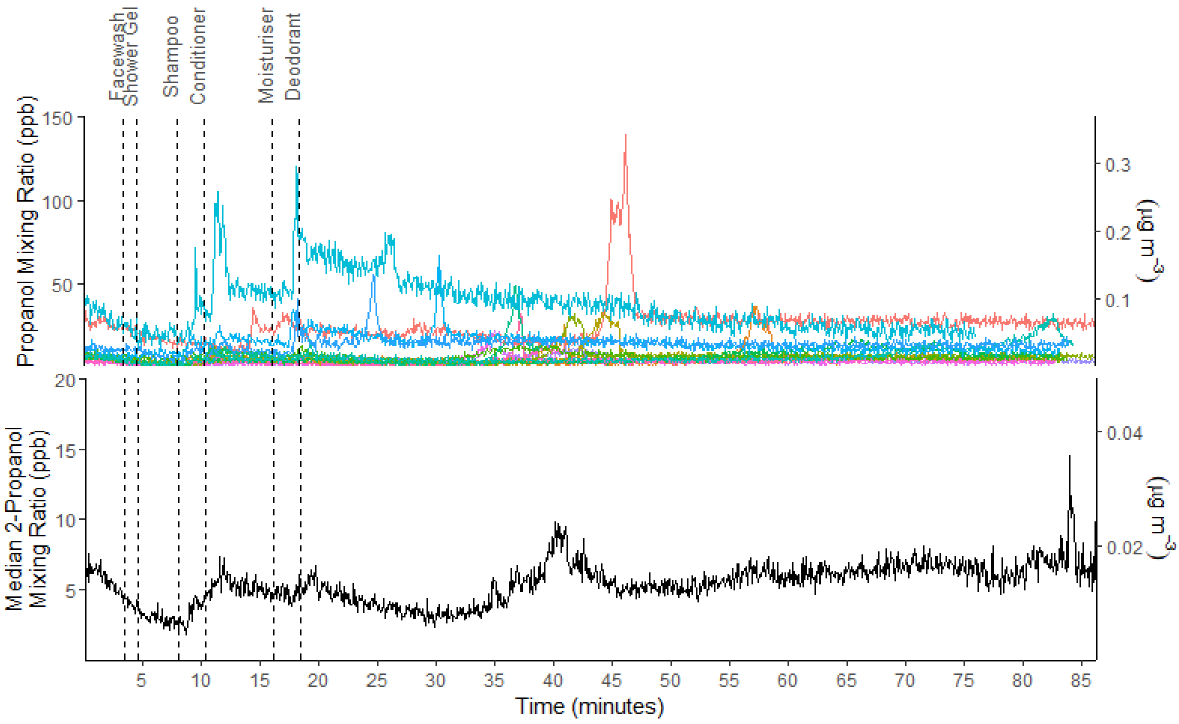

Figure 3.8: VOC evolution profile of 2-propanol Top: Data from all 18 participants Bottom: Median

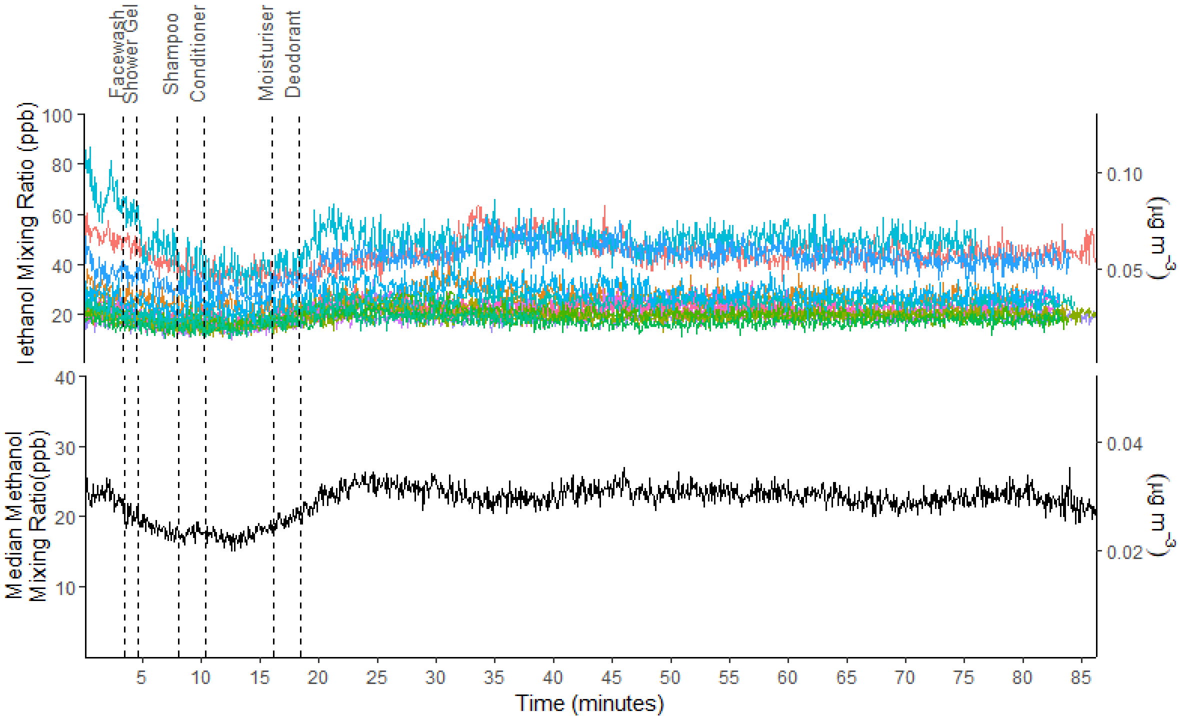

Figure 3.9: VOC evolution profile of methanol Top: Data from all 18 participants Bottom: Median

A compound's potential for dermal absorption through skin lipids may also be an influencing factor on concentration, and there is potential for all of the products used in this study to be dermally absorbed, even if this is just through hands while applying to the hair in the case of conditioner.

Limonene is very effective at penetrating the skin[50], and there is evidence it could be used as an enhancer for drug delivery for this reason[51,52]. Consequently, this may have a pronounced effect on the amount of limonene available for evaporation. Although also dermally absorbent[53], benzyl alcohol does not have the drug delivery enhancement potential limonene does, which may explain why the bottom-down calculations for limonene have been overestimated to a much greater degree, as seen in Table 3.5.

The production of secondary pollutants is possible, formaldehyde in particular from the reaction of limonene with OH radicals, and subsequent unimolecular decomposition[31]. OH radicals are present in indoor air and are produced in a variety of ways, including in the reaction of limonene with ozone, making limonene both a source and sink for hydroxyl radicals, with ozone driving the production of OH[54]. It might therefore be expected that formaldehyde be present in this microenvironment during or after showering has occurred as a secondary product. The measured formaldehyde profile in Figure 3.10 is different in both its shape and magnitude to that modelled in Yeoman et al (2020)[20], where levels reached 7 ppb. Formaldehyde has a *log*K_{ow} value of 0.35, indicating the liquid water may be an effective scavenger mechanism from the air in the room, coupled to air exchange. In this case, although limonene was clearly present in substantial amounts, the bathroom microenvironment did not lead to any detectable formaldehyde formation inside.

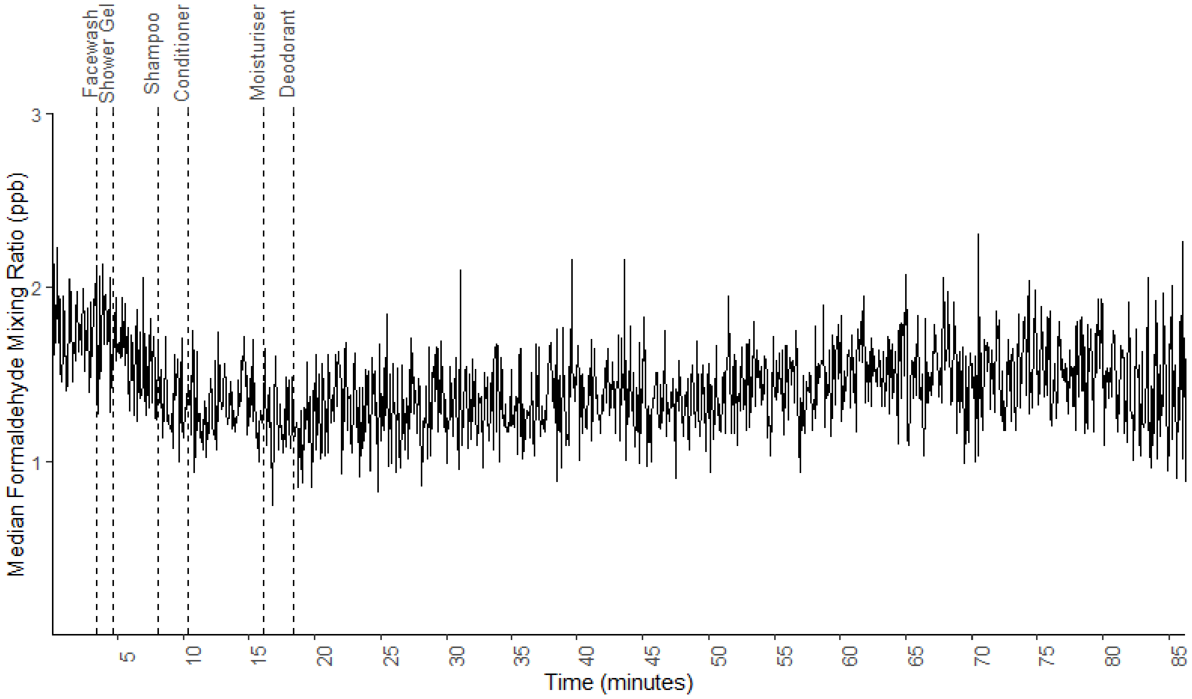

Figure 3.10: Formaldehyde emission profile produced from median emission concentrations. As a standard was not run for formaldehyde, the assumed fragmentation coefficient is 1, which is the Labsyft kinetic library value[47].

The influence of ventilation on VOC profiles over the course of sampling must also be considered. The air in the room would have been replenished about 4 times (once every 15 min), meaning the initial release and measurement of compounds should be accurate, but their persistence dependent on air exchange rate. A bathroom with a lower ventilation rate would allow for higher accumulated concentrations in the room. Many situations can be envisaged where ventilation is lower than the values reported here: People may not open bathroom windows, or turn extractor fans on, especially in the winter months.

3.3.5: Conclusions

Having observed the emissions from the real-life usage of PCPs during showering, we find that personal differences in product-use behaviour result in variations in VOC emissions and in-room concentrations. Maintaining consistent time and dosage does not eliminate differences in absolute peak concentrations, and most notable of the factors introducing variability is the presence of liquid water and the effect of rinsing time. This makes predicting emissions during this activity more complex as compound solubility must be taken into consideration, along with the amount of liquid water that may be present. Other consumer product usage circumstances where liquid water is involved, washing-up or doing laundry for example, would be affected by this.

These data are informative in terms of the peak concentration of VOCs individuals may be exposed to during a single, common activity. For context, in 1998 the World Health Organization (WHO) reported no indication of inhalation risk from limonene due to limited data on the rate in which a harmful concentration can be reached on evaporation[55]. Although this paper does not attempt to address this specifically, it provides a possible timescale for reaching high concentrations during one activity. As previously described, fragrance sensitivity, and the health risks associated with it, can occur through routes other than that of inhalation, such as the dermal route. Contact dermatitis usually relates to direct application of a compound to the skin and is known to occur with limonene as it is oxidized[56–58]. However, if exposure levels are high enough in the gas-phase, there may also be potential for a dermal reaction to be triggered, particularly to the eyes which can be especially sensitive[59].

As limonene is relatively unaffected by the presence of liquid water, it can be used as a “tracer” for the variability and uncertainty in emissions of other compounds from PCPs when dosage and time are closely controlled. Hence, it can be assumed that in the absence of liquid water, benzyl alcohol and ethanol are emitted consistently within a factor of 2.

Although variable between individuals, there is modest agreement between emissions estimated from the real-world activity and the bottom-up emission values for PCPs reported in Yeoman et al (2020)[20]. For both limonene and benzyl alcohol, the median real-world shower emissions were lower, by a factor of 1.3 and 11, than the bottom-up estimate. This is potentially rationalized through product being washed away before vapour exchange could occur, in contrast to laboratory estimates which quantify VOC emissions assuming vapour exhaustion. The loss of compound through dermal absorption should also be noted as a potential contributing factor.

Although there remain considerable uncertainties in PCP emissions, and this field of work is in its infancy, it seems plausible that greatly improved domestic VOC emissions estimates could be constructed. These could be based on a knowledge of typical product composition (based on bottom-up laboratory emissions screening), the total amount of materials sold (and industry reported trade figure), and a correction factor for real-world use, accounting for the reality that only a fraction of the VOC content in a product is released to air when used. Although scaling up emissions from a very small study such as this carries with it large uncertainties, using a median emission of 1.8 mg limonene per showering activity, and assuming this activity is replicated by half the UK population each day, would lead to an annualized emissions of around 13 tonnes of limonene per year from showering.

3.4: Supplementary information

3.4.1: Data analysis

As mentioned in section 3.3.2, the PTR-MS can calculate mixing ratios of desired compounds using Equation 3.1. However, due to the fact the heating element in the PTR-MS was not working efficiently, more water clustering than usual occurred. This meant that all data processing and calculations had to be carried out by hand in order to take the contribution of $H_3O{\bullet}H_2O^+$ as a reagent ion into consideration[60]. This was the only cluster ion we saw in enhanced concentrations; therefore any others present did not need to be taken into account.

$H_3O{\bullet}H_2O^+$ acts as a proton donor in the same way H_3O^+ does (Equation 3.4)[2], however this changes variable *k* as a second rate of reaction needs to be included. This is done by averaging the rate of reaction for H_3O^+ and $H_3O{\bullet}H_2O^+$ for each compound.

$$H_3O{\bullet}H_2O^+ + R \longrightarrow RH^+ + 2H_2O \tag{3.4}$$

We also factor in a fragmentation coefficient, for added accuracy. As PTR-MS is more energetic than SIFT-MS, the Labsyft library fragmentation values for each compound cannot be used here, and must therefore be experimentally determined. Gas standards were made up for limonene, 2-propanol, benzyl alcohol, methanol, and ethanol of ~50ppb in nitrogen and sampled using the PTR-MS for ~ 4 cycles. Fragmentation coefficients were calculated using Equation 3.5. Raw signal intensities of the main product ion and any significant fragmentation ions were totalled and divided by the main product ion for each cycle, then averaged to yield a single fragmentation coefficient. These values are detailed in Table 3.8.

$$Fragmentation\ Coefficient = \frac{\sum \frac{Main\ product\ ion + Fragmentation\ ion(s)}{Main\ Product\ Ion}}{Number\ of\ cycles}$$

(3.5)

Table 3.8: Main product and significant fragmentation ions, and calculated fragmentation coefficients of the five compounds of interest

Compound	Main Product Ion *m/z*	Significant Fragmentation Ion(s) *m/z*	Fragmentation Coefficient
Limonene	137	81, 95	0.36
2-Propanol	43	-	1
Benzyl Alcohol	91	79	0.37
Methanol	33	31	0.99
Ethanol	47	45, 46	0.9

Equation 3.6[48] includes the fragmentation coefficient and $H_3O{\bullet}H_2O^+$ reagent ion. Combining this with the original PTR-MS Equation (3.1) results in Equation 3.7, which was used for all data workup in this study in units of ppb.

$$[R] = \frac{1}{k \times t} \times \frac{T(H_3O^+)}{F(RH^+) \times T(RH^+)} \times \left(\frac{T(H_3O^+)}{I(H_3O^+)} + \frac{T(H_3O \bullet H_2O^+)}{I(H_3O \bullet H_2O^+)}\right)$$

(3.6)

$$[R]_{ppb} = \frac{I(RH^+) \times 1 \times 10^9 \times 1013 \times 22400 \times (273.15 + T_d)}{k \times t \times P_d \times 6.022 \times 10^{23} \times 273.15 \times T(RH^+) \times F(RH^+)} \times \left(\frac{T(H_3O^+)}{I(H_3O^+)} + \frac{T(H_3O \bullet H_2O^+)}{I(H_3O \bullet H_2O^+)}\right)$$

(3.7)

The value of $I(H_3O^+)$ was taken as the PTR-MS calculated concentration for *m/z* 21, rather than the raw signal intensity of *m/z* 19. As *m/z* 19 is in high concentrations it is not directly measures as this would shorten the life of the detector. When the PTR-MS calculates the concentration of m/z 21 it corrects for this, and therefore is a more accurate value for raw H_3O^+ signal intensity. Reaction time, *t*, was not made available in the PTR-MS data files and had to be derived manually by plotting experimental data against that which had been hand calculated using Equation 3.1. The term *t* was adjusted for the hand calculated data until it fit the PTR-MS experimentally calculated data.

3.4.2: Standards and calibration

A 37.5 ppb limonene gas standard (determined by GC-MS) was made up and sampled at the end of each day of experiments, and worked up using Equation 3.7. Correction factors for each day were determined based on the known concentration of 37.5 ppb and applied to both shower and pre-shower data to correct for daily changes in the PTR-MS sensitivity.

The limit of detection (LoD) for limonene, benzyl alcohol, and ethanol were calculated using Equation 3.8[48], selecting a representative period of 1 minute before sampling began.

(~ 60 PTR-MS cycles).

$$LoD = 2\sigma_{zero}$$

(3.8)

3.5: References

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Chapter 4 : Examining the relationship between product application site and inhalation risk

4.1: The relationship between product application site and inhaled dose

Chapters 2 and 3 have demonstrated how both lab-based and real-life experiments are useful and informative when researching VOC emissions from PCPs. The complementary method of first screening products to identify their key VOCs, and then validating the results using true-to-life application techniques enhances the reliability of the work. Therefore, this method has been replicated for the next investigation, which considers the exposure risks associated with the application of products close to the inhalation pathway. Thus far, emissions into a room have been the focal consideration, with inhalation exposure risk being a secondary factor based on those room emissions. However, the idea that an applicant is at greater risk of VOC inhalation than a room occupant has not been considered, nor has the fact that application site will have a proximity-based risk influence. As an additional consideration for this study, the differences between products marketed as `green` and those that are not has been investigated.

Utilising the SIFT-MS for a second time, this chapter considers a different PCP usage scenario, employing a novel application replica for experimental use. Day facial moisturisers have been chosen for analysis as they are applied in close proximity to the inhalation pathway. The following paper makes comparisons between emissions into a room and potential inhaled dose, whilst also discussing the information consumers are provided, and the transparency of labelling.

4.2: Inhalation of VOCs from facial moisturisers and the influence of dose proximity

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4.2.1: Abstract

Volatile organic compound (VOC) emissions from personal care products (PCPs) contribute to poor indoor air quality. Exposure to indoor VOCs is typically determined through ambient concentration measurements, however for some PCPs the proximity of use to the nose and mouth may lead to disproportionately large inhaled doses. In this paper, we quantify emission factors for six common PCP ingredient VOCs (ethanol, 2-propanol, benzyl alcohol, 1,3-butanediol, t-butyl alcohol, and the grouping of monoterpenes as limonene) from 16 facial day-moisturisers using headspace analysis and selected-ion flow-tube mass spectrometry. A wide range of emissions rates were observed across the range of products tested (e.g. ethanol 3.3 - 6.9 $\times 10^{2}$ µg s^{-1} $g_{[product]}^{-1}$, limonene 1.3 $\times 10^{-1}$ – 4.1 $\times 10^{-1}$ µg s^{-1} $g_{[product]}^{-1}$). We use a mannequin head with reconstructed nose and mouth airways to sample VOCs from facial application at typical respiration volumes. A single facial application of moisturiser can

lead to a much larger inhaled VOC dose than would be inhaled from typical indoor ambient air over 24 hours (e.g. limonene up to ~ x16 greater via facial application, ethanol up to ~ x300). Emissions from facially applied PCPs typically decayed to background concentrations over periods ranging from 5 to 150 minutes.

4.2.2: Introduction

Personal care products (PCPs) are a class of consumer products used for hygiene or cosmetic purposes. They contain a range of volatile organic compounds (VOCs)[1–7] which are released to air when the product is used. VOCs in PCPs are typically very safe at low ambient concentrations, but can be readily oxidised to form more harmful secondary pollutants, such as ozone and secondary organic aerosols (a sub-class of respirable particles)[8]. VOCs are considered to be a major factor that affects air quality indoors where they can accumulate from multiple sources, particularly if ventilation is poor. Indoor exposure to VOCs is typically quantified using time-integrated ambient measurements which quantifies the resulting concentrations arising from all sources indoors that are well-mixed internally in the room. Measurements made using diffusion tubes or whole air canisters typically sample room air over several hours to days whilst on-line MS methods can track concentrations in real-time[9]. However, human exposure can potentially be influenced by proximity to the point of emission; for VOC-containing products applied to the face, such as moisturisers and sunscreens, the potential exists for a higher VOC dose than might be inferred from ambient room measurements, or a consumption-based metric such as mass of product used per day.

The personal care industry is valued at around £400 billion a year worldwide (as of 2021) and is expected to grow by 4.8% annually. Around £75 billion of this, just under 20%, is from facial skincare, comprising of products designed for the care and protection of the face. This includes face and eye creams, face scrubs, masks, and lip balms[10]. This multi-billion-pound industry comes under close scrutiny from both consumers and regulatory boards, nationally and internationally. Factors at the forefront of regulation are product safety, ingredient transparency, and, more recently, environmental sustainability, focussing on both human and ecological concerns that arise from their use.

There are three major possible acute toxicity exposure routes for compounds found in PCPs: dermal, oral, and inhalation[11]. Of these three, PCP labels (by legal requirement) generally concern themselves with the dermal and oral exposure routes, typically warning that a product is not for oral use, and what to do if contact with eyes or an adverse skin reaction occurs. This is not unexpected as many PCPs are applied directly to the skin, and hence the majority of research into exposure routes and safety assessments surrounds dermal absoption[12–15] and the direct application of products[16–23], including the impact of PCPs on skin chemistry[24]. Biesterbos et al. (2013)[25] assumed that inhalation exposure from PCPs would be relatively low when used in a ventilated area. The Scientific Committee on Consumer

Safety (SCCS) have also indicated that repeated VOC exposure from an inhalation route lacks relevance for the majority of consumer products[11]. Pauwels and Rogiers (2010)[26] had only a single reference to inhalation in their evaluation of human health and safety of cosmetics. This is surprising as the amount of VOC potentially inhaled is potentially much higher than the amount that is dermally absorbed, especially if a product is applied to the face. There have been some limited studies quantifying the inhalation route[27–29] noting that it should be taken into account when considering product safety, but dermal safety remains the major influence on PCP testing and regulation.

Whilst the air quality implications of PCP inhalation may not, as of yet, be at the forefront of consumer's minds, an increasing popularity for eco-friendly, `green` products, and a rise in sustainable consumption, has been seen. Eighty-five% of retailers in a European study reported increased sales of sustainable products over the past five years[30] as people begin to consider the environmental impacts of the products they buy[31]. Factors influencing how manufacturers justify the `green` classification of their products include: sustainability of packaging, toxicity concerns surrounding waste both from manufacturing and post-application (predominantly relating to water[32–34]), the use of animal-derived ingredients, cruelty-free testing, and the source of ingredients (which may include organic/sustainability certifications). As the scope for claiming a product is `green` is so vague, within this paper a green product will refer to any product that claims sustainable, organic, or natural sources relating to its formulation only. These products often have certification from bodies such as NATRUE (The International Natural and Organic Cosmetics Association), the Soil Association, and ECOCERT. There is a perception that in addition to environmental benefits (which can to a degree be quantified) 'green' advertising can also infer indirectly that a product is healthier or safer (both for the consumer and the environment). There is generally little qualitative evidence to support this, and products of all kinds must meet the same regulatory standards.

One chemical class of VOCs that is particularly contentious in PCPs (and other domestic products) are fragrances. Klaschka (2016)[35] describes the potential health hazards of natural ingredients in PCPs. Fragrance compounds, such as monoterpenes, have the potential to contribute to the formation of secondary pollutants indoors which may cause respiratory irritation through reactions with ozone[36,37]. A study by Nematollahi et al. (2018)[38] reported that 95% of fragranced baby products analysed, both green and non-green, emitted at least one potentially hazardous VOC (under Australian or World Health Organisation guidelines), concluding that emissions from the two types of products were not significantly different.

In this paper we consider the potential exposure to VOCs via inhalation from PCP use, testing both regular skincare products and those marketed as 'green' or 'eco' products. The methodology uses selected-ion flow-tube mass spectrometry (SIFT-MS) to quantify the real-time evaporation of key VOCs from day facial moisturisers (meaning those not designed for use at night), and the likely inhaled dose, when tested using sampling systems built into a mannequin head and at typical human respiration rates. These dose values were then compared against typical in-room concentrations to identify any enhancement arising from proximity of application.

4.2.3: Experimental

Data Acquisition

A Voice200 SIFT-MS was used to identify and quantify VOC concentrations and emissions, using both full mass scan and SIM (selected ion monitoring) modes. The details of the instrument have been well-described in previous publications[39,40], and as such only the specific details of the experimental set-up are detailed here.

The first series of experiments were used to assess VOC product emissions under standardised headspace conditions following a methodology reported previously in Yeoman et al. (2020)[1]. This initial screening of products identifies the compounds to target in subsequent experiments. Sixteen commercially available day-moisturisers were tested, 8 green and 8 regular, across a range of brands and formulations, all available from UK retailers. Approximately 20 mg of each product was weighed onto a section of filter paper and placed into a 50 mL stainless steel gas-tight sample vessel, which was then thermostatted at 25 °C for the first hour of sampling and 40 °C for the second. The sample was drawn into the SIFT-MS at a flowrate of 15 mL min^{-1} under atmospheric pressure from the headspace of the sample vessel, with the inlet to the vessel connected to a supply of high purity N_2. Prior to each measurement a blank sample of the empty vessel was carried out, and any trace residual signal for VOCs later subtracted from the data collected. A full mass scan mode using reagent ions H_3O^+, NO^+, and O_2^+ were used to scan sequentially over a mass range of *m/z* 18 and 400. Data acquisition lasted for 120 minutes, with an ion dwell time of 100 ms per *m/z*, and a cycle time per reagent ion mass spectra of 38 seconds, 114 seconds overall. Over the 120 minute analysis period this provided an average 63 mass spectra per reagent ion.

Real-life application and exposure were studied using the Beauty-product Application Replica and Basic Airway Reconstruction Accessory (BARBARA). A stand-alone mannequin head was fitted with 1/8" PFA gas lines inserted through apertures in the mouth and nose, connected together at the back of the head with a Swagelok T piece (Figure 4.1). A scroll pump (Edwards 6i) and mass flow controller (0-10 slpm, Alicat) were used to control a flowrate of ~6 L min^{-1} of air through the nose and mouth in order to replicate average human rate of respiration[41,42]. The mannequin sample air, drawn through the nose and mouth, was then sub-sampled into the SIFT-MS with a flow rate of 15 mL min^{-1}, the remainder of gas sent to waste. The SIFT-MS sub-sample thus representing 1/400th of the flow that a person would inhale (assuming 6 L min^{-1}). The face-portion of the mannequin was covered with a clean sheet of Parafilm (a flexible, chemically resistant film made from a blend of waxes and polyolefins) for each experiment, clipped together at the back, and this experimental set-up run as a blank, prior to product application. Approximately 0.45 g[17,25] of each of the 16 day-moisturisers were applied across the face onto the parafilm using gloved hands, replicating real-life moisturiser application methods and amounts. The mass of 0.45g was selected based on two usage studies. Hall et al. (2007)[17] found the mean mass of facial moisturiser used to be 0.906g per day which, assuming two daily applications, or 0.453g per application. Biesterbos et al. (2013)[25] found 0.4g to be the mean application of day cream. The mannequin head was not heated, and presumed to be ~21℃, the average controlled temperature of the room. Room size measured 199.65 m^3, fitted with a standard laboratory ventilation system typically running at ~5 air changes per hour (ACH).

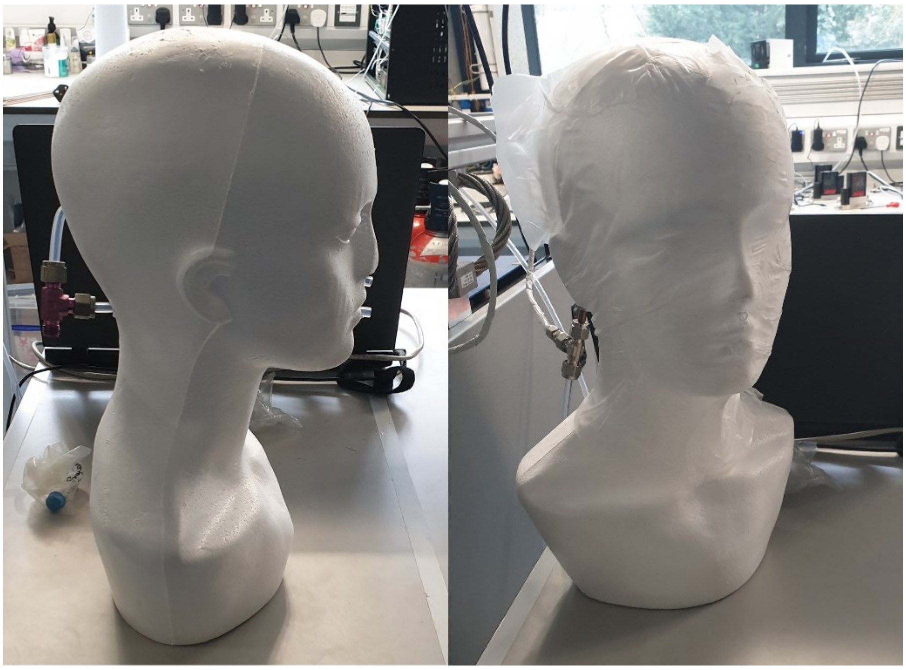

Figure 4.1: Mannequin head experimental setup (BARBARA)

During sampling, the SIFT-MS was run in SIM mode. Targeted scanned masses selected prior to sampling, based on results from the headspace analysis, are detailed in Table 4.1.

Table 4.1: SIFT-MS SIM method targeted scanned m/z values, and their corresponding ions, for each of the three reagent ions H3O$^+$, NO$^+$, and O2$^+$

Compound	**H_3O^+ *m/z***	**NO^+ *m/z***	**O_2^+ *m/z***
Ethanol	47 ($C_2H_7O^+$)	45 ($C_2H_5O^+$) 63 ($C_2H_5O^+.H_2O$)	
2-Propanol	43 ($C_3H_7^+$),	59 ($C_3H_7O^+$)	
t-Butyl Alcohol	57 ($C_4H_9^+$)		
Limonene (representing monoterpenes)	137 ($C_{10}H_{17}^+$) 155 ($C_{10}H_{17}.H_2O^+$)	136 ($C_{10}H_{16}^+$)	93 ($C_7H_9^+$) 136 ($C_{10}H_{16}^+$) 137 ($C_{10}H_{17}^+$).
1,3-Butanediol		89 ($C_4H_9O_2^+$)	72 ($C_4H_8O^+$)
Benzyl Alcohol		107 ($C_7H_7O^+$) 108 ($C_7H_8O^+$)	108 ($C_7H_8O^+$)

The overall experimental data acquisition time varied, and sampling was continued until each of the selected compounds had decayed down to ambient background concentrations, as seen before product application. The shortest run time was 60 minutes, and the longest 180 minutes.

Calibrating the SIFT-MS measurement

The calibration was performed using an in-house dynamic liquid calibration system. This comprised of a Bronkhorst Controlled Evaporator and Mixer (CEM) unit: a proportional liquid-gas mixing valve, controlling the mass flow of liquid measured by a mini-Coriolis flow meter and introducing a mass flow controlled zero-air dilution gas to aerosolise and fully evaporate the liquid into a temperature controlled mixing region. The liquid was pressurised without gas contact, using a custom-built pneumatic cylinder with wetted materials of glass and PTFE. In the case of water, the system can output liquid concentrations ranging from around 0.1% up to its vapour pressure at the outlet conditions. Using aqueous solutions of water-soluble compounds, the system can deliver almost any concentration of analyte in a flow rate of 1-4 SLPM of diluent gas.

An aqueous solution was made up of four water-soluble target compounds in deionised water, with target mixing ratios of 1 000 ppb for ethanol, benzyl alcohol, and 1,3-butanediol, and 500 ppb for 2-

propanol. This solution was added to the in-house liquid calibration system, and the line conditioned for ~48 hours at 45 °C, 0.6 H_2O g hr^{-1}, and 2 L min^{-1} air.

The same SIFT-MS SIM method was run as previously. Calibration sampling lasted for ~7 hours as the H_2O liquid flowrate was changed from 0.2 g hr^{-1} to 2.0 g hr^{-1} by intervals of 0.1, providing 19 calibration points per compound. The SIFT-MS measured concentration for each compound was allowed to settle between each H_2O liquid flowrate change.

Data Workup and Analysis

All primary data workup was carried out using the SIFT-MS instrument LabSyft software.

Figure 4.2 shows the liquid calibration curves for 1,3-butanediol, 2-propanol, benzyl alcohol, and ethanol. A linear regression was applied to this data, omitting points 1.9 and 2.0 for 1,3-butanediol to account for its non-linearity at higher H_2O flowrate concentrations, likely due to partitioning into liquid water condensing on the flow path . As our experiments were not carried out in environments with very high water vapour present, it was not necessary to calibrate in this more extreme humidity region. We assume a room water concentration of 1.098 x10^{-2} g L^{-1} based on a 21°C average room temperature and 60% room relative humidity. With an experimental "air" flowrate of 2 L min^{-1}, a H_2O flowrate of 1.308 g hr^{-1} was determined. Correction factors for each compound were calculated at this value using the calibration curves and then applied to the data.

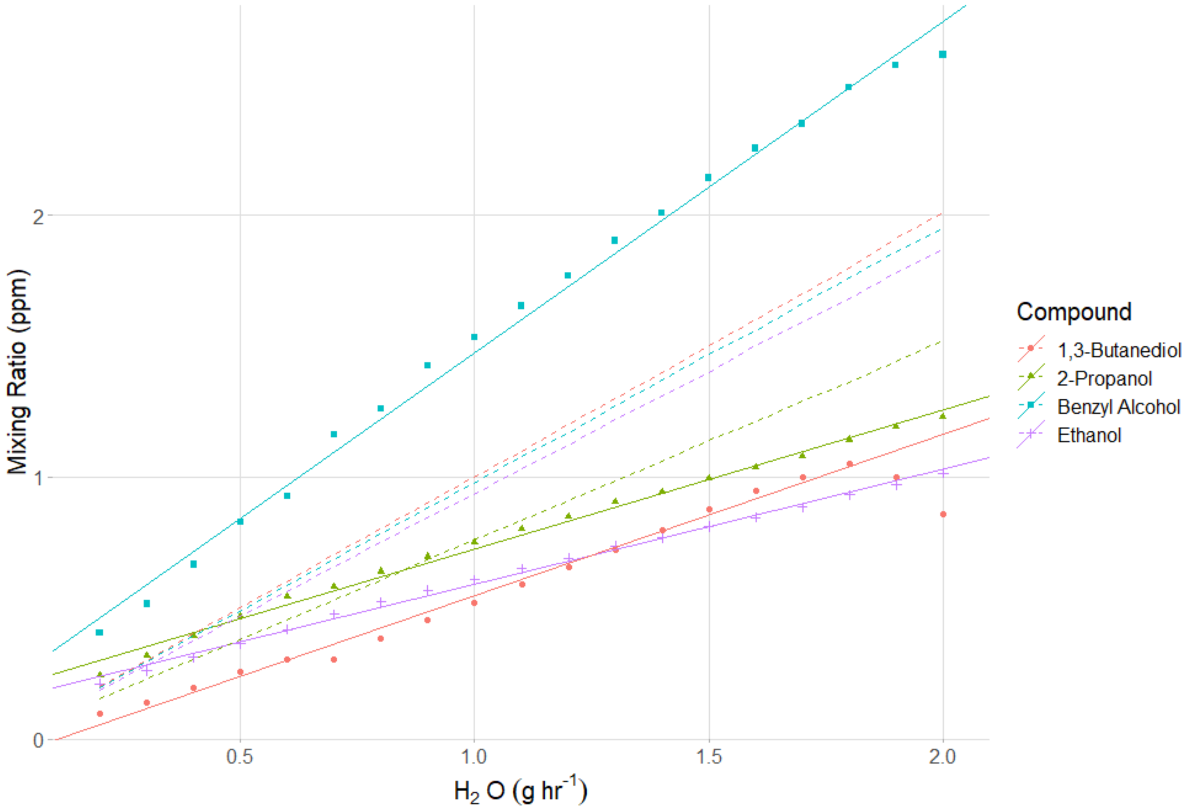

Figure 4.2: Liquid calibration curves for four compounds. Points represent SIFT measured mixing ratio. Solid line represents linear regression for SIFT measured mixing ratios. Dashed lines represent delivered mixing ratio.

Residual standard error in ppm, as calculated by the lm() function in programming software R were: Benzyl alcohol ± 0.057, ethanol ± 0.016, 2-propanol ± 0.024, and 1,3-butanediol ± 0.028.

4.2.4: Results and Discussion

VOC Emissions from Regular and 'Green' Moisturisers

Establishing the differences in VOC emissions from regular and green day facial moisturisers first requires the determination of the most prevalent VOC species from a selection of both types of products and a standardised estimation of emission rate. SIFT-MS full mass scan detected six key VOC species that were either present in the majority of products or, most notably for 1,3-butanediol, highly emitting in at least one product. Presented in Figure 4.3 (data in Table 4.2) are the standardised emission rates for each of the products based on thermostatted dynamic headspace analyses, expressed as mass released per unit time per gram of product. Limonene has been used to represent the grouping of all monoterpene species since they give similar mass spectra. There were no cyclic volatile methylsiloxane (cVMS) in these products, despite results from Yeoman et al. (2020)[1]

suggesting that they would likely be present in moisturisers. However, that study was carried out on a wider range of moisturising products, including more than just facial products. According to the ingredient lists, linear dimethicone (polydimethylsiloxane) appeared to be the siloxane of choice in the regular day-moisturisers (rather than cyclic siloxanes), and no siloxanes at all were listed in the green product ingredients.

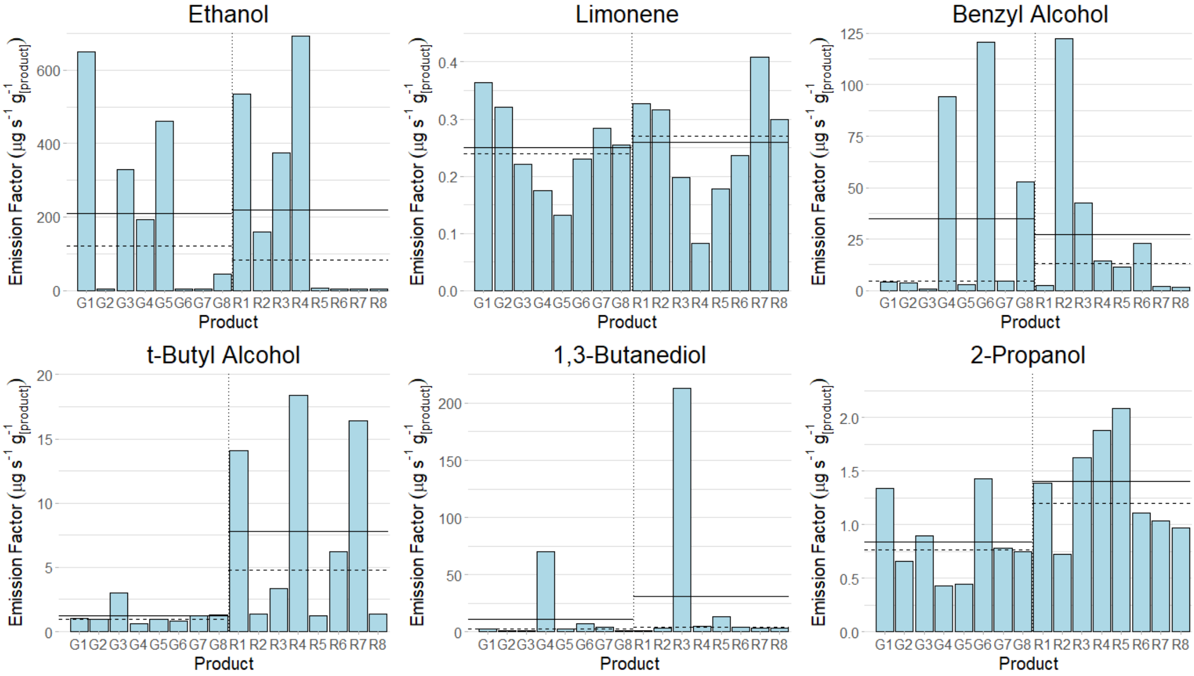

Figure 4.3: Standardised headspace emission rates of 6 key ingredient VOCs identified by SIFT-MS from 16 moisturising products. R denotes regular, G denotes green-marketed products. Solid lines – mean values, dashed line – median value.

Table 4.2: Emission rates of 6 key VOCs identified by SIFT-MS from 16 products.

Product	**Emission rate (µg s^{-1} g$_{[\text{product}]}^{-1}$)**					
	Limonene	**Ethanol**	**Benzyl Alcohol**	**t-Butyl Alcohol**	**1,3-Butanediol**	**2-Propanol**
G1	3.6 x10^{-1}	6.5 x10^{2}	4.2	1.0	2.3	1.3
G2	3.2 x10^{-1}	3.8	3.7	9.7 x10^{-1}	7.6 x10^{-1}	6.6 x10^{-1}
G3	2.2 x10^{-1}	3.3 x10^{2}	7.5 x10^{-1}	3.0	8.0 x10^{-1}	9.0 x10^{-1}
G4	1.7 x10^{-1}	1.9 x10^{2}	9.4 x10^{1}	6.2 x10^{-1}	7.0 x10^{1}	4.3 x10^{-1}
G5	1.3 x10^{-1}	4.6 x10^{2}	2.6	9.6 x10^{-1}	2.6	4.4 x10^{-1}
G6	2.3 x10^{-1}	3.5	1.2 x10^{2}	8.0 x10^{-1}	7.1	1.4
G7	2.8 x10^{-1}	3.7	4.6	1.3	3.6	7.8 x10^{-1}
G8	2.5 x10^{-1}	4.5 x10^{1}	5.3 x10^{1}	1.3	6.7 x10^{-1}	7.4 x10^{-1}
R1	3.3 x10^{-1}	5.3 x10^{2}	2.6	1.4 x10^{1}	5.9 x10^{-1}	1.4
R2	3.2 x10^{-1}	1.6 x10^{2}	1.2 x10^{2}	1.4	2.9	7.2 x10^{-1}
R3	2.0 x10^{-1}	3.7 x10^{2}	4.3 x10^{1}	3.3	2.1 x10^{2}	1.6
R4	8.3 x10^{-1}	6.9 x10^{2}	1.4 x10^{1}	1.8 x10^{1}	4.5	1.9
R5	1.8 x10^{-1}	6.3	1.1 x10^{1}	1.2	1.3 x10^{1}	2.1
R6	2.4 x10^{-1}	3.3	2.3 x10^{1}	6.2	4.0	1.1
R7	4.1 x10^{-1}	3.3	1.8	1.6 x10^{1}	2.9	1.0
R8	3.0 x10^{-1}	4.0	1.6	1.4	3.0	9.7 x10^{-1}

Four of the six key species identified are alcohols, and there are several reasons they are added to skincare products. Predominantly alcohols aid the transdermal delivery of active skincare ingredients by breaking down the skin barrier. This makes the product fast absorbing and fast drying, adding a weightless feeling which is considered desirable for this type of product. Additionally they can be used as a mattifying (degreasing) ingredient and as a co-preservative along with other compounds. For this role, ethanol is the most commonly used alcohol. European Union (EU) regulations require alcohols to be at least partially denatured if they are to be used in cosmetics. A foul smell and taste is introduced to ensure it is not fit for human consumption, which also then leads to exemption from excise duty (Directive 92/83/EEC Article 27)[43]. From our analyses it appears that *t*-butyl alcohol is the denaturant of choice for facial moisturisers, with 2-propanol being often used in trace amounts as a chemical analytical marker, added to denatured alcohol as an anti-fraud measure. Limonene / monoterpenes are regularly added to skincare products for their fragrance, while 1,3-butanediol acts as a non-drying solvent, viscosity stabiliser, conditioning agent, and humectant. Benzyl alcohol has the widest range of skincare uses: as a preservative, stabiliser, solvent, and fragrance compound.

The origin of these compounds is inconsequential, as whether they are added in their natural form (for example limonene and benzyl alcohol from plant extracts), are organically sourced, or synthetically produced does not alter their chemical properties. The only practical difference between the green and regular products comes down to whether each compound is 'naturally' sourced. Organic ethanol for example can be produced by fermentation and limonene and benzyl alcohol can be extracted from essential oils derived from plants.

For ethanol and limonene we see no substantial differences in emission rates between the green-marketed and regular products. The variation in benzyl alcohol between the two product categories is less straightforward as its use is very variable depending on product and manufacturer. As there are no natural sources of 1,3-butanediol, and few instances of 2-propanol and t-butyl alcohol being found in nature, here we see greater range in both mean and median (Table 4.3) between the two product classes, with all three compounds being found in higher quantities in the regular products.

Table 4.3: Statistical analysis of emission rates from headspace experiments

Compound		Mean	Median	Range	Relative Standard Deviation (%)
			($\mu g\ s^{-1}\ g_{[product]}^{-1}$)		
Ethanol	Regular	2.2 x10^{2}	8.3 x10^{1}	6.9 x10^{2}	116
	Green	2.1 x10^{2}	1.2 x10^{2}	6.5 x10^{2}	109
Limonene	Regular	2.6 x10^{-1}	2.7 x10^{-1}	3.3 x10^{-1}	38
	Green	2.5 x10^{-1}	2.4 x10^{-1}	2.3 x10^{-1}	29
Benzyl Alcohol	Regular	2.7 x10^{1}	1.3 x10^{1}	1.2 x10^{2}	139
	Green	3.5 x10^{1}	4.4	1.2 x10^{2}	127
t-Butyl Alcohol	Regular	7.8	4.8	1.7 x10^{1}	88
	Green	1.2	9.9 x10^{-1}	2.4	57
1,3-Butanediol	Regular	3.1 x10^{1}	3.5	2.1 x10^{2}	227
	Green	1.1 x10^{1}	2.5	7.0 x10^{1}	204
2-Propanol	Regular	1.4	1.2	1.4	33
	Green	8.4 x10^{-1}	7.6 x10^{-1}	1.0	41

With the exception of limonene, these experiments yielded higher emission factors than those estimated in Yeoman et al (2020)[1]. Facial moisturisers, especially those designed for use during the day which have been tested here, typically dry more quickly than moisturisers designed for the rest of the body or for use at night. They also tend to contain more active ingredients than body moisturisers, which may necessitate a larger quantity of solvent. These are plausible reasons for observing higher ethanol emission factors here and may also explain the larger 2-proponal emission factors, as alcohol content is directly linked to denaturing / tracer compounds.

Real-life Exposure and Inhalation

Whilst many PCPs contain VOCs, and give rise to emissions that lead to a rise in ambient in-room concentrations (for example aerosol sprays, shampoos etc), facially applied products are somewhat unusual as the emission occurs very close to the inhalation pathways of nose and mouth. Using our application method on a mannequin head with representative nose and mouth respiration the mass of VOCs inhaled from a single facial application was determined.

Figure 4.4 shows the raw time vs concentration plots of 6 selected products and their typical concentration-time profiles. The experiments were run for as long as was necessary for all VOCs to reach close to their pre-application background level. Figure 4.4 illustrates just how variable the emission of VOCs are from different products even within the same PCP sub-class – some giving rise to very rapid spikes in volatile solvents such as ethanol lasting only a few seconds, others leading to slower emission of less volatile species such as benzyl alcohol and 1,3-butanediol over tens of minutes. Presented in Table 4.4 are the average release times of each species. These values are based on an assessment of when concentrations returned to baseline values, although there is a degree of imprecision in this since there was some small natural variability in background concentrations. We note that the average emission time of 1,3-butanediol is also influenced by some retention on both the PFA and the SIFT-MS sampling lines. In real-life there would be no such obstructions, and the emission may be faster that estimated here.

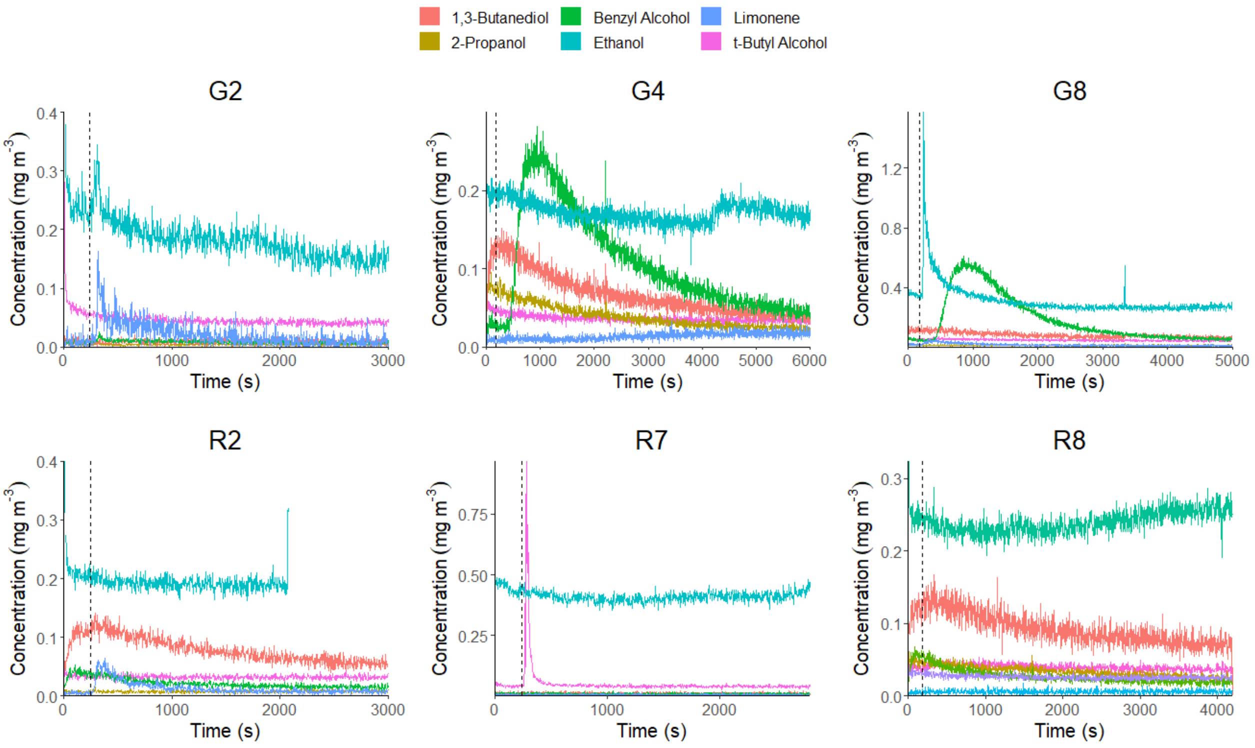

Figure 4.4: Time concentration profiles of 6 example facial moisturising products. Top row are 'green-marketed' products, bottom row are regular products. The dashed line indicates time of product application.

Table 4.4: Average volatilisation times for 6 key compounds when facially applied, representing time from application to point at which inhaled concentrations return to ambient background.

Compound	Time (minutes)
t-Butyl Alcohol	4.9
2-Propanol	32
1,3-Butanediol	151
Benzyl Alcohol	44
Ethanol	32
Limonene	32

Presented in Figure 4.5 and Table 4.5 are the total amounts of each VOC `inhaled` for one standard application of the product to the face. Aggregate dose was calculated as the integral of the concentration – time profile, from the time of application until return to background levels. This has been expressed as a mass of VOC (in mg) per gram of product used.

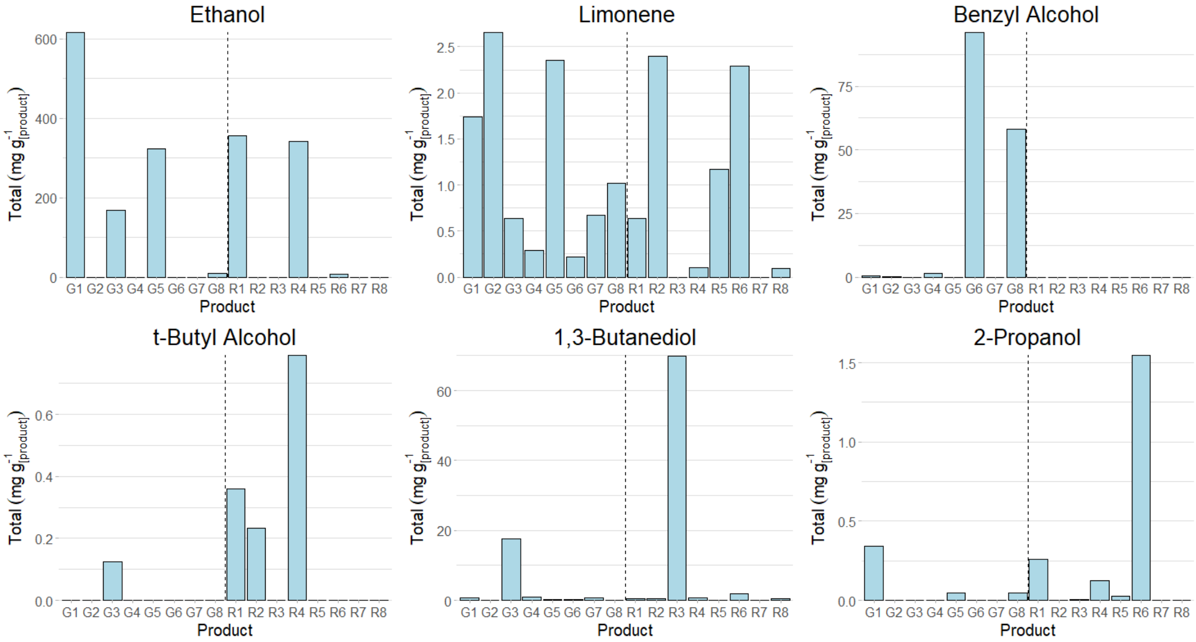

Figure 4.5: Integrated inhaled dose of 6 key VOCs from 16 products for one facial application (~0.45 g) at a standard respiration rate of 6 L min^{-1} combined through mannequin nose and mouth. Dotted line – separates green and regular products. R denotes regular, G

Table 4.5: Aggregate inhaled doses in mg $g_{[product]}^{-1}$ of 6 key VOCs identified by SIFT-MS from 16 products for one facial application (around 0.45 g) at a respiration rate of 6 L min^{-1} combined through mannequin nose and mouth.

Product	**Aggregate Inhaled (mg $g_{[product]}^{-1}$)**					
	Limonene	**Ethanol**	**Benzyl Alcohol**	**t-Butyl Alcohol**	**1,3-Butanediol**	**2-Propanol**
G1	1.7	6.2×10^{2}	6.5×10^{-1}	0	6.3×10^{-1}	3.4×10^{-1}
G2	2.7	0	1.9×10^{-1}	0	0	0
G3	6.3×10^{-1}	1.7×10^{2}	0	1.2×10^{-1}	1.8×10^{1}	0
G4	2.9×10^{-1}	0	1.6	0	9.0×10^{-1}	0
G5	2.4	3.2×10^{2}	0	0	1.5×10^{-1}	4.8×10^{-2}
G6	2.2×10^{-1}	0	9.6×10^{1}	0	1.3×10^{-1}	0
G7	6.7×10^{-1}	0	0	0	7.3×10^{-1}	0
G8	1.0	8.6	5.8×10^{1}	0	0	4.5×10^{-2}
R1	6.3×10^{-1}	3.6×10^{2}	8.0×10^{-3}	3.6×10^{-1}	5.3×10^{-1}	2.6×10^{-1}
R2	2.4	0	0	2.3×10^{-1}	5.6×10^{-1}	2.5×10^{-4}
R3	0	0	0	0	7.0×10^{1}	7.9×10^{-3}
R4	1.1×10^{-1}	3.4×10^{2}	0	7.9×10^{-1}	6.5×10^{-1}	1.2×10^{-1}
R5	1.2	0	0	0	0	2.5×10^{-2}
R6	2.3	8.2	0	0	1.9	1.5
R7	0	0	0	0	1.1×10^{-2}	0
R8	9.5×10^{-2}	0	1.4×10^{-2}	0	5.1×10^{-1}	0

An important point for consideration is that the facial sampler was only held at room temperature, and whereas skin temperature is higher at 32-34 °C[44]). A likely consequence is on a human evaporation may have been somewhat faster than estimated here. Additionally, the effects of dermal absorption have not been taken into account, of which there is known potential for limonene, benzyl alcohol, ethanol, 2-propanol, and t-butyl alcohol[45-47].

There is greater variability between inhaled doses between products when applied to the mannequin than is seen from the controlled emission rate experiments in Figure 4.3. In the headspace analysis, where a sealed container was utilized, all VOCs are driven into the gas phase at saturation concentration, and in turn pass to the SIFT-MS. The substantial differences seen, for example, between the headspace and mannequin data for R2 benzyl alcohol are therefore likely a function of the performance of the moisturiser matrix in free air, where the liquid-gas partitioning of VOC to air does not follow the simple saturation seen in the headspace analysis. These observed differences show up the limitations of assessment of emissions based purely on headspace analysis alone, and identify the need for real-life experiments when studying consumer product emissions.

A small number of the 16 products, in particular G1, have high aggregate inhaled doses suggesting that ethanol makes up the majority of their total content. As product ingredients are listed in order of decreasing weight (required by EU regulation No 1223/2009[48]), the relationship between the aggregate inhaled ethanol dose (Table 4.5) and ethanol ingredient list position can be examined as a qualitative method for assessing VOC emissions. Product labelling of PCPs does not require exact amounts (either mass of percentage) to be reported. The relationship between position on ingredient list and amount of ethanol inhaled is visualised in Figure 4.6. Not all of the 16 products had ethanol or denatured alcohol listed (despite containing this VOC), therefore the position of `parfum`, or similar, has been used instead as ethanol would be included in the fragrance blend as a solvent. Figure 4.6 suggests that whilst labelling is only qualitative in nature, it can provide a helpful guide to possible VOC emissions to the consumer. There is reasonable agreement between the positioning on the ingredients lists and the measured downstream inhaled dose.

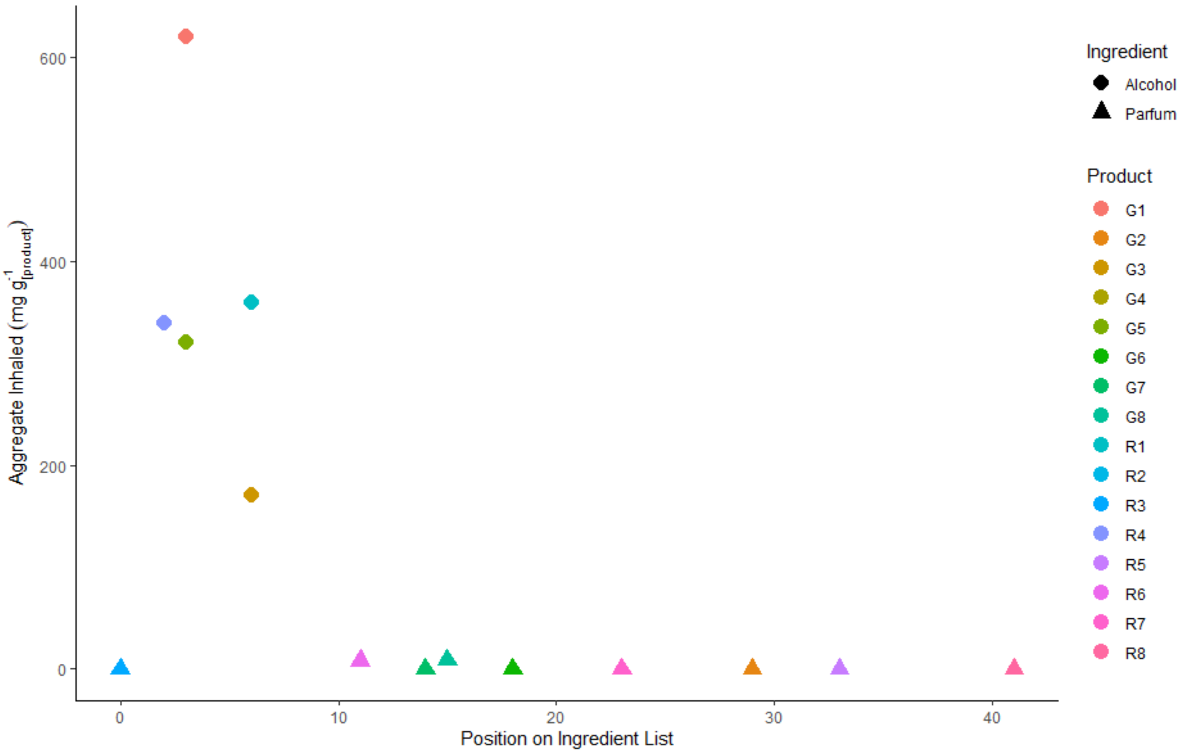

Figure 4.6: Aggregate inhaled ethanol dose from Table 4 relative to ethanol / parfum ranking position on product ingredient list, used a proxy for amount contained in each product.

Facial Exposure vs Ambient Inhalation

A day-moisturiser would usually be applied just once a day, in the morning (with the second daily application being a night-moisturiser)[19]. It is possible to place the VOCs inhaled via this route in context with ambient inhalation. Here we compare the mass of VOCs inhaled from one application of 0.45 g, a modest average application assumption[17,25], with the average mass inhaled of the same VOCs from a typical domestic living room in the UK (Table 4.6). Median ambient indoor concentrations are taken from Heeley-Hill et al. (2021)[49] for ethanol and limonene; these are 40.1 µg m^{-3} and 3.8 µg m^{-3} respectively. (This was a study of 60 private UK homes in 2020). Over 24 hours, at a rate of 6 L min^{-1}, a person will inhale 8.6 m^{3} of air, or 0.34 mg of ethanol and 0.033 mg of limonene inhaled over 24 hours spent inside a typical UK residence. Outdoor concentrations and amounts inhaled would be expected to be considerably lower than indoor. In Table 4.6 we contrast the facial moisturiser dose against 24 hours of ambient air indoors.

Table 4.6: Amount inhaled from one application of 0.45 g of day-moisturiser to the face. Indoor/application ratios are calculated based on median indoor concentrations[49] over a period of 24 hours (ethanol 0.34 mg, limonene 0.033 mg).

Product	Ethanol Inhaled directly from product (mg)	Ethanol Ratio of product dose to 24 hr ambient air	Limonene Inhaled directly from product (mg)	Limonene Ratio of product dose to 24hr ambient air
G1	2.8×10^{2}	804	7.8×10^{-1}	24
G2	0	0	1.2	37
G3	7.5×10^{1}	219	2.9×10^{-1}	9
G4	0	0	1.3×10^{-1}	4
G5	1.5×10^{2}	421	1.1	32
G6	0	0	1.0×10^{-1}	3
G7	0	0	3.0×10^{-1}	9
G8	3.9	11	4.6×10^{-1}	14
R1	1.6×10^{2}	466	2.8×10^{-1}	9
R2	0	0	1.1	33
R3	0	0	0	0
R4	1.5×10^{2}	445	4.8×10^{-2}	1
R5	0	0	5.3×10^{-1}	16
R6	3.7	11	1.0	32
R7	0	0	0	0
R8	0	0	4.3×10^{-2}	1
Mean	1.2×10^{2}	339	5.2×10^{-1}	16

One application of a day-moisturiser appears therefore to provide a notably higher inhaled mass of VOC than would regularly be inhaled simply from being indoors in a typical home. As there is potential for two applications of this product, or one with similar ingredients such as a night-moisturiser, in one day, this would result in double the expected inhaled dose calculated here.

For ethanol that mass inhaled due to the moisturiser application is on average over 300 times higher than ambient 24-hour inhalation, and for limonene 16 times. Although the use of this particular class of PCPs contributes only modestly to overall indoor air VOC concentrations, the user themselves inhales a substantially greater amount. Examined purely on the basis of VOC content and tonnage of product sold, facial moisturisers would appear to be a small contributor in the wider scheme of national emissions inventories, where VOCs come from a vast range of different sources. However the unusual application mode of these products to the face gives them a disproportionately significant role in controlling dose inhaled for ingredient VOCs such as ethanol and limonene.

Inhaled dose and proximity has been explored by the concept of `intake fraction`. First conceived by Bennett et al. (2002)[50], it describes the emission to intake relationship of pollutants: the ratio of the mass intake of pollutant by an individual and the mass of pollutant released into the environment over a specified time period (iF). Although usually summed over the population (iF_s), individual exposure can be expressed by an individual intake fraction (iF_i). Jolliet et al. (2015)[51] define an additional exposure metric, product intake fraction PiF. This is the chemical mass within a product eventually taken in by humans via all possible exposure pathways (inhalation, dermal, and ingestion) per unit of chemical mass within that product. These intake fractions express the increased exposure risk to pollutants when they are released in close proximity to people. This paper takes this idea a step further, conveying the increased inhalation exposure risk from specific PCP application area for a single user, which could perhaps be developed into an individual product intake fraction (PiF_i), a combination of these two metrics.

Public Health England's most recent (2019) air quality guidelines document[52] gives the maximum exposure limit for limonene to be 90 mg m^{-3} over 30 minutes, and 9 mg m^{-3} over 24 hours. One daily application of a day-moisturiser would not result in the applicant exceeding that daily exposure limit, nor the 30-minute limit (the period over which limonene emits, as seen in Table 4.4). However, it could be conceivable that someone using multiple products, more than once a day (for example morning and night, as previously mentioned) may exceed the daily recommended exposure limit.

An additional consideration is the ACH during the experiment, which was higher than the average air exchange rate found in homes (typically in the range of 0.5–1.5 ACH[53,54] depending on the season). As a consequence, it must be noted the results from these experiments may represent a lower inhaled dose that occurs in typical home environments. However, as sampling occurred directly from the product application site, rather than the lab air, in order to simulate the proximity of inhalation, ACH impacts would not be substantial as there would be little time for ventilation to effect emissions.

4.2.5: Conclusions

Using on-line mass-spectrometry we have been able to implement a novel technique for the study of proximity-based inhalation risks from a range of day-moisturisers. After first screening the selected products for their VOC content, we have been able to quantify the VOC dose an applicant would receive from one use, and the relative increase this would represent compared against simply breathing typical room air. The experiments indicated that facial application leads to large VOC doses when compared against typical amounts of some VOCs inhaled in ambient air indoors over a 24 hour period. They also suggest that facially applied products may be a more important source of VOCs for personal air quality exposure than might be inferred from total solvent consumption statistics. Additionally, we conclude that there are no significant differences in VOC inhalation when using green or regular branded products.

Whilst product labelling is only qualitive and provides a list of ingredients in rank order, that rank order is useful in highlighting products that may lead to high inhaled doses and may help guide consumer decision-making. We highlight the inhalation route as being equally, if not more, important than dermal and oral routes for exposure to VOCs from PCPs, particularly for compounds such as limonene that are implicated in respiratory irritation for sensitive individuals[55]. The inhalation of VOCs from facially applied PCPs has the potential to confound studies of indoor air quality and health, since these are typically based on ambient measurements only and would not account for enhanced VOC doses arising from directly applied products.

4.3: Supplementary information

4.3.1: Calibration

H_2O flowrate of the in-house dynamic liquid calibration system is calculated, in units of g hr^{-1}, using Equation 4.1, to be applied to the calibration curve in Figure 4.2.

$$H_2O\ flowrate = \ H_2O\ concentration\ \times air\ flowrate \tag{4.1}$$

4.3.2: Experimental data analysis

Emission rates for the headspace analysis were calculated using the same method as in Chapter 2 (Sub-chapter 2.3) and Equations 2.9, 2.10, and 2.11.

The mannequin experiment data workup employed similar methods as used in Chapter 3 (Section 3.3.3). Aggregate emissions were calculated between the time of product application to the end of the emit time from the time-concentration profiles (Figure 4.4) using R software and a cubic spline function to determine the area under the curve (AUC). Equation 4.2 uses the AUC to calculate total product inhaled, in units of mg $g_{[product]}^{-1}$, as presented in Table 4.5 and Figure 4.5. Equation 4.2 includes a correction factor of 400 to account for the SIFT-MS sampling only 15 mL min^{-1}, 1/400th of the air inhaled at 6 L min^{-1}. Air inhaled is determined by Equation 4.3.

$$Product\ inhaled = \frac{\left(\frac{AUC}{Emit\ time} - Basline\right)}{Product\ used} \times Air\ inhaled\ \times 400$$

(4.2)

$$Air\ inhaled = Time\ \times pump\ flowrate$$

(4.3)

4.4: References

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Chapter 5 : An analysis of the world-wide use of aerosol consumer products

5.1: Introduction to aerosol products and available data

Having assessed the potential health, environmental, and inventory implications of the use of non-aerosol consumer products, we move our attention to aerosolised products. The VOC emission potential is much higher for aerosol products, as they are composed almost entirely of volatile solvents. Therefore, reasonable conclusions regarding the scale of their emissions can be drawn without the need to determine emissions factors from laboratory experiments. There are also limited solvent formulation choices for manufacturers, another factor for which there is data, meaning detailed identification of species is also not required for this assessment.

Presented in this chapter is a literature review-style project, published as a policy bridge article to establish, and then put into context, the extent of aerosol product solvent emissions both nationally and globally. A widespread search was undertaken for all available aerosol can fillings data globally, going back in date as far as possible. Industry data on aerosol units sold are behind paywalls, and would likely only give the same, limit, information as fillings data does on product size, and no indication of the amount of solvent in each can. In order to make plausible predictions on global aerosol use, and then convert this to amount of solvent emitted, we have had to make a series of assumptions regarding consumer habits, solvent quantity per can, and other variables.

5.2: Global Emissions of VOCs from compressed aerosol products

This work was originally published in Elementa: Science of the Anthropocene, April 2021 †

5.2.1: Abstract

Disposable compressed gas aerosols have been a ubiquitous part of life since the mid-1950s. The signing of the Montreal Protocol in 1987 led to aerosol propellants changing from halocarbons to less damaging replacements; around 93% of current aerosol emissions by mass are volatile organic compounds (VOCs), with small contributions from compressed air (6.6%) and fluorocarbons (0.4%). The global consumption of aerosol units has increased significantly since the signing of the Montreal Protocol, increasing by an order of magnitude in some countries. In high-income countries, annual consumption increased through the 1990s and 2000s, typically reaching a plateau of approximately 10 ± 3 units person^{-1} year^{-1} dependant on product preferences. The largest contributors of both units and mass emissions are personal care products (PCPs). Consumption of aerosols in lower- and upper-middle income countries are growing rapidly, for example, Brazil, Mexico, China, Thailand, all tripling reported consumption since 2006. Based on evidence drawn from national production

estimates, product specifications and formulations, and interpolation of usage between countries of similar economic status, we estimate global emissions of VOC from aerosol propellants were approximately 1.3 ± 0.23 Tg year^{-1} in 2018. The fraction of anthropogenic VOC emissions accounted for by aerosols has in some countries increased significantly as emissions from vehicles and fuels have declined. For example, in the UK, 6.1% of anthropogenic VOC emissions were from aerosols in 2017, more than were released from gasoline passenger cars. Should low- and middle-income economies grow consumption per capita in line with recent trends, then we project global aerosol consumption may reach approximately $4.4 \pm 0.96 \times 10^{10}$ units year^{-1} in 2050. Should existing national and international policies on aerosol product formulation remain unchanged, and VOCs remain the dominant propellant, compressed aerosols could account for a global emission of approximately 2.2 ± 0.48 Tg year^{-1} in 2050.

5.2.2: Introduction

Aerosols dispensers have been extensively used in professional and consumer products across the globe for over 70 years. Their ease of use and effectiveness for product application has aided their popularity, with 5.6 billion units of aerosols being manufactured in 2018 in Europe alone[1]. Norwegian chemical engineer Erik Rotheim patented the first aerosol spray can and valve, which was capable of both holding and dispensing products in 1927[2]. However, it wasn't until the end of World War II that aerosol products began to be mass produced, with the American government creating the first insect repellent, known as the "bug bomb," to help protect servicemen from diseases such as malaria. After that, the commercial use of aerosols quickly expanded to include hair spray, air freshener, deodorant, and shaving foams, all manufactured for general public use. These products soon became available in Europe, creating the first boom in aerosol product popularity in the 1960s and their use has continued globally in the 21st century[3].

There are three chemical components to an aerosol product: the active ingredient, a solvent, and a propellant. The active ingredient is the portion of the product intended for application and is concentrated in the form of a solution, suspension, emulsion, or powder[4]. The propellant dispenses the product while sometimes also acting as a cosolvent. The propellant can be a liquefied or compressed gas and can comprise anywhere from 5% to 90% of the total product mass depending on its intended use. The aerosol propellant forces the product out of the can when the nozzle is depressed. The difference in pressure between the propellant inside and the pressure of the outside air triggers product release. Additionally, propellants can act to disperse the product into a fine mist on evaporation as the active ingredients are broken up. These particles can be expelled in the form of droplets, foam, paste, or powder depending on the dispersing ability of the propellant and the force with which they are dispensed[5].

Initially chlorofluorocarbons (CFCs) were used as aerosol propellants; their non-flammable and odourless properties and chemical stability made them ideal for use in consumer products. However, concerns associated with their environmental impact were catalysed by Molina and Rowland's 1974[6] paper detailing the possible destruction of ozone arising from halogens released through CFC photodissociation in the stratosphere. The CFCs used in aerosols proved to be extremely potent ozone-depleting substances and having high global warming potentials (GWPs) between 1,100 and 14,000 for a 100-year time period[7]. The establishment of the Montreal Protocol (signed 1987, effective 1989) led to all United Nations (UN) member states agreeing to regulate the production and consumption of almost 100 man-made chemicals including CFCs[8]. This was later amended (The Montreal Amendment 1997) to include the phasing out of hydrochlorofluorocarbons (HCFCs), which were also being used as aerosol propellants, and several other amendments shortening the time frame for the overall phase out of these chemicals from use. The most recent, the Kigali Amendment (signed 2016, effective 2019) goes further still in curbing ozone-depleting substances. All signing parties have agreed to reduce the production and consumption of hydrofluorocarbons (HFCs), another aerosol propellant, by more than 80% by 2047[9]. The current status of the amendment is that 112 parties have signed out of 193 member states[10].

The implementation of the Montreal Protocol was extremely successful and led to the rapid replacement of halocarbon-containing propellants with simple short lifetime volatile organic compounds (VOCs), replacement chemicals that were of considerably lower (although not zero) environmental impact. The role of VOCs in promoting tropospheric ozone and photochemical smog was established at the time of the Montreal Protocol; however, the air quality degradation arising from their use as aerosol replacements was considered as far less significant than the negative impacts of stratospheric ozone depletion. Since VOCs were introduced as halocarbon replacements in aerosols, there has been limited reassessment of the impacts of that policy decision from an air quality perspective or the future trajectory and appropriateness of VOCs as replacements for the coming decades.

5.2.3: Aerosol propellants currently in use

The changes required by the Montreal Protocol were not technically problematic for aerosol manufacturers since CFC and HCFC alternatives were already being used in countries where pre-Montreal Protocol bans of ozone-depleting substances were in place, such as the United States and Sweden[11]. A majority of manufacturers elected to use hydrocarbon blends as a replacement propellant, and this remains the most common formulation today. Most hydrocarbon aerosol propellant (HAP) blends are made up of propane, *n*-butane, and *iso*-butane, with other hydrocarbons such as *iso*-pentane and *n*-pentane, sometimes included. There are no standard HAP formulae, and many different manufacturer-specific blends are found in consumer products, each with a different vapour pressure—a key factor controlling aerosol performance. Generally, a blend of propane and *n*-butane will have a lower vapour pressure than one of propane and *iso*-butane[12], and this will have an effect on its dispensing properties. Despite their range of uses, hydrocarbons are not always an appropriate propellant. Some PCPs, which can be defined as any cosmetic or hygiene product available to the public for personal use[13], require a very pure and odourless propellant for which dimethyl ether (DME) is the most common solvent used. Another alternative is compressed gas (e.g., N_2 or air), which is considered the most environmentally friendly option.

Table 5.1 gives an outline of the three main propellant types, highlighting the properties which manufacturers consider in their selection. Choosing an appropriate propellant ultimately depends on two things: the vapour pressure and purity required (although cost may be an influencing factor). The higher the vapour pressure, the higher the degree of dispersion from the aerosol can, and the finer and drier the product mist. High vapour pressure products include air freshener, flying insect spray, and spray paint, whereas lower vapour pressure products include shaving cream, gels and mousse, and perfume[11]. A medium vapour pressure product, for example, hair spray, deodorant, or furniture polish, has a wet application and moderate dispersion. Product dispersion is also controlled by the percentage of propellant in the can, with lower vapour pressure products having a low ratio of propellant to active ingredient. These are important factors considered in the following section on emissions (see Table 5.2).

Table 5.1: Compressed aerosol propellant properties[11,14,15]

	Propellant Properties			
Propellant Type	**Flammable?**	**Pressure**	**Purity***	**Co-Solvent Required?**
Hydrocarbons	Yes	High	Varies	Yes
DME	Yes	High	High	Rarely
Compressed Gas	No	Low	Varies	Yes

*Odourless

Table 5.2: Simplified aerosol product volume and pressure assumptions[13].

Product	Average Size (mL)	Pressure
Air fresheners	300	High
Automotive	500	Medium
Colognes/perfumes	75	Low
Deos/body sprays/anti-perspirant	250	Medium
Hairspray products	300	Medium
Hard-surface cleaners	750	Low
Industrial	300	High
Insecticides	300	Medium
Medical (excluding inhalers)	300	Medium
Miscellaneous	300	Medium
Other household	300	Medium
Other personal	300	Medium
Oven cleaner	300	Medium
Paints/lacquers	400	High
Shaving products	200	Low
Shoe/leather cleaners	250	Low
Starches	300	Medium
Suntan/bronzing products	200	Medium
Veterinary/pet care	300	Medium
Waxes/polishes	400	Medium

The breakdown of the types of propellants used for aerosol products is shown in Figure 5.1 with hydrocarbon-based propellants dominating the mass of emissions, and particularly the C_4 alkane isomers[13]. Although these data are from 2012, we assume in this work, and later calculations, that there has not been a significant change in distribution between these broad chemical classes over the last decade. We assume that without any major policy change on aerosol composition and usage, this would also hold for the foreseeable future. In combination, hydrocarbon-based propellants and DME make up 93% of emissions, which we describe collectively henceforth as "VOC emissions" labelled on Figure 5.1 as "Total VOC" Products using compressed air makes up 6.6% of mass, and 0.4% is from products using fluorocarbons (largely medical devices such as inhalers). Since compressed air has no direct environmental impacts once emitted, and HCFCs make up an insignificant amount of mass of emissions (e.g., 0.4% of approximately 1–6% of VOC in most countries), in the remainder of this article, we discount this mass in subsequent calculations and report mass emissions from aerosols as they relate to VOCs.

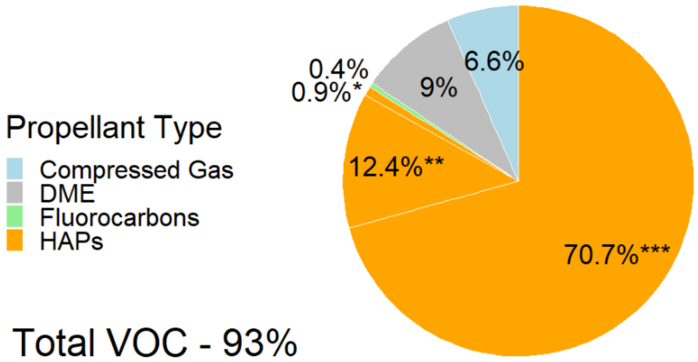

Figure 5.1: Consumption of aerosol propellants by type (2012)[13]. HAP speciation has been made using the reported composition of aerosol products included within the UK National Atmospheric Emissions Inventory available at www.uk-air.defra.gov.uk. HAPs and DME have been combined as total VOC. HAP = hydrocarbon aerosol propellant; DME = dimethyl ether; VOC = volatile organic compound. *Pentane. **Propane. ***Butane

5.2.4: Atmospheric impacts and health effects

To assess the atmospheric impact of aerosol propellant emissions beyond stratospheric ozone depletion, which was considered in the Montreal Protocol, two major additional impacts from propellants are examined: (i) the GWP of the gas once released and (ii) impact on health (toxicity), either directly or *via* the contribution of those emissions to secondary air pollutants such as ozone or $PM_{2.5}$. Indirect impacts on the atmosphere can also arise from the manufacturing activities that produce the propellant and other supply-chain impacts from raw material extraction, through production to distribution. The fluorocarbons, made up primarily of HFCs as they have only recently been targeted by the Montreal Protocol, are undoubtedly the most impactful of the four propellant groups by the metric of GWP. However, HFCs are only used in a very small range of products, typically health-related, and many are likely to be converted to alternative propellants as a consequence of the Kigali Amendment. In terms of GWP, VOCs are significantly more environmentally acceptable (e.g., DME compared to HFCs in Good et al. 1998), and while they do not have a large direct effect on radiative forcing, they do undergo photooxidation that generates tropospheric ozone, itself a greenhouse gas. As for the compressed gas propellants, carbon dioxide and nitrous oxide are both well known as greenhouse gases, but the mass associated with their aerosol use is insignificant compared to other anthropogenic sources.

The health impacts of VOCs that are used as propellants are either through direct inhalation toxicity or through a contribution to degraded ambient air quality. Solvent/inhalant abuse[16], the triggering of asthma attacks[17], and fire risks from flammable propellants and pressurized cans are the direct health risks that usually coincide with short-term, high-concentration releases or exposure. When propellants are inhaled, they can take the place of oxygen in the lungs, causing nausea, vomiting, rapid breathing, and in severe cases, comas and death[18]. These hazards are associated with inappropriate and unsafe use by users, yet even with careful and appropriate use, there remains potential for negative health impacts. The physiological response to hydrocarbon propellants was first studied in 1978[19]. Although acute, single exposure (250, 500, and 1,000 ppm) to propellants, *iso*-butane and propane were shown to have "no untoward physiological effects" on pulmonary and cognitive function or cardiac rhythm, repetitive exposure to 1,000 ppm did cause minor cognitive decline. Additionally, participants had detectable traces of propellants in their blood and on their breath. Possible long-term toxic health effects could be caused by propellants making their way into the respiratory and cardiovascular systems; however, there have been no long-term studies on the inhalation of propellants from the continuous use of aerosol consumer products to evaluate this.

There are no current UN, European Union, or World Health Organization regulations or exposure limits for any of these compounds in ambient outdoor or indoor air. However, there are several workplace exposure limit guidelines from a range of organizations/agencies as presented in Table 5.3.

Table 5.3: Recommended exposure limits

Propellant Type	Recommended Exposure Limits
Propane	TLV 1,000 ppm[20]
	AEGL 5,500 ppm[21]
Butane	STEL 750 ppm[52]
	TWA 600 ppm[52]
	AEGL 5,500 ppm[21]
DME	STEL 500 ppm[52]
	TWA 400 ppm[52]

DME = dimethyl ether; TLV = threshold limit values; AEGL = acute exposure guideline levels (over 1 h); STEL = short-term exposure limit; TWA = time weighted average (over 8 h).

The more significant health impact of VOCs is their contribution to poor air quality. Propane and *n*-butane are the second and third most abundant nonmethane hydrocarbons in the atmosphere, with atmospheric lifetimes of approximately 13 and 7 days, respectively[22]. In the presence of sunlight and NO_x tropospheric ozone can form[23]. The contribution of VOCs to ozone is well-described (e.g., Derwent et al., 1996[24]), as is the formation of other more harmful secondary aldehydes[25]. Significant attention has been paid to reducing emissions as part of air quality management at national and continental scales (as an example EC Directive 1999/13/EC[26]). The formation of secondary organic aerosols (SOAs) is also possible from propellants, although the by-products from their oxidation generate species with relatively limited SOA potential compared to other classes such as monoterpenes and aromatic compounds[27].

5.2.5: Emissions of VOCs from individual aerosol products

Since aerosols are used for a very wide variety of applications, unsurprisingly the emissions arising from each product are highly variable. For example, a high vapour pressure product will have a high mass dispense rate and will therefore emit more propellant and smaller particles over a short period of time[28]. The overall emission of propellant is therefore the result of the propellant concentration, dispense rate, and the time in use or “spray time.” Figure 5.3 shows the relationship between dispense rate, typical spray time, and the amount of propellant released per application[28]. The products in the “most significant” segment of the plot emit more per aerosol application, combining high dispense rates and longer spray times. This figure shows only the potential from each product type, the absolute emitted by each product class is dependent on how frequently each product is used and by how many people, and it is recognized that some items on this plot would be used only infrequently (e.g., oven, carpet cleaner) compared to others that may be used multiple times per day (e.g., deodorants, hair spray).

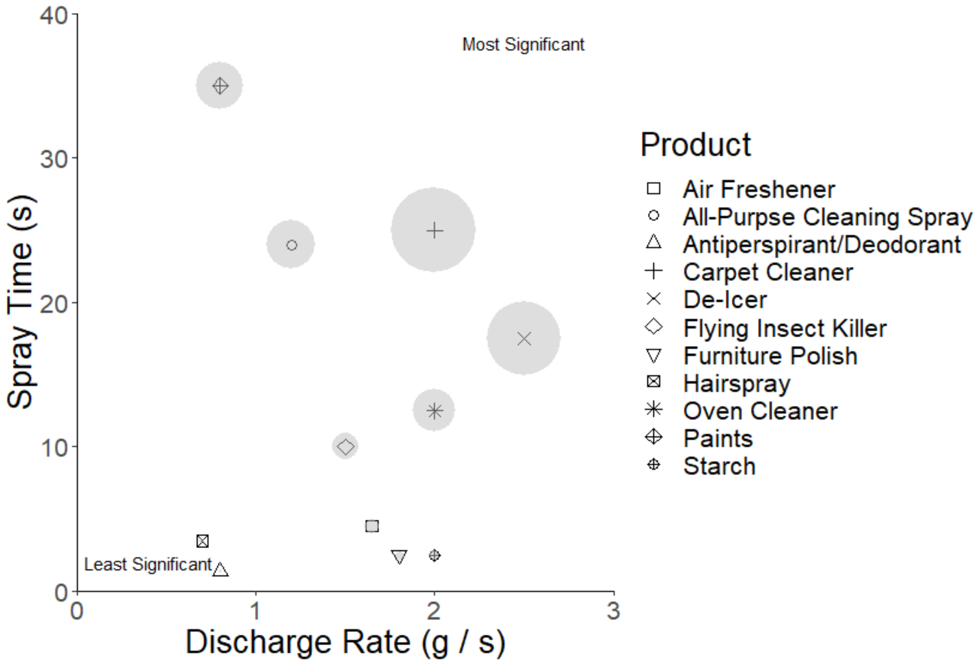

Figure 5.2: Propellant emission potential for a range of domestic products per unit of application by a user. Plot based on discharge rates and typical spray time, showing the median value where a range was given[28]. The grey circles are sized to be proportional to the amount of aerosol propellant release per usage.

5.2.6: VOC propellant emissions at a national scale

A more complete assessment of the emissions from aerosol products can be derived from consumption statistics, and this can be evaluated using a combination of manufacturing and sales data along with information on the aerosol products themselves. In this section, we examine in detail aerosol propellant emissions for the UK, using this as a reasonable case study that is likely to be broadly representative of other high-income industrialised countries. In later sections, we look more widely at trends in other countries. We note however the significant heterogeneity in how data are reported between countries and that it is very difficult to generate exact like-for-like comparisons. Figure 5.3 shows UK aerosol fillings from the year 1960 onward, with each unit of aerosol filling representing one can of product. Each unit is not however of a standard size/mass or volume of propellant; instead the graph shows only unit consumption rather than trends in mass of propellant emissions. For the avoidance of doubt, in this study, we are considering only emissions from individual disposable aerosol canisters. This is a quantity of VOC that is distinct from the total emission of VOCs that might be used as a propellant, for example, industrial car paint spraying may use hydrocarbons from bulk tanks.

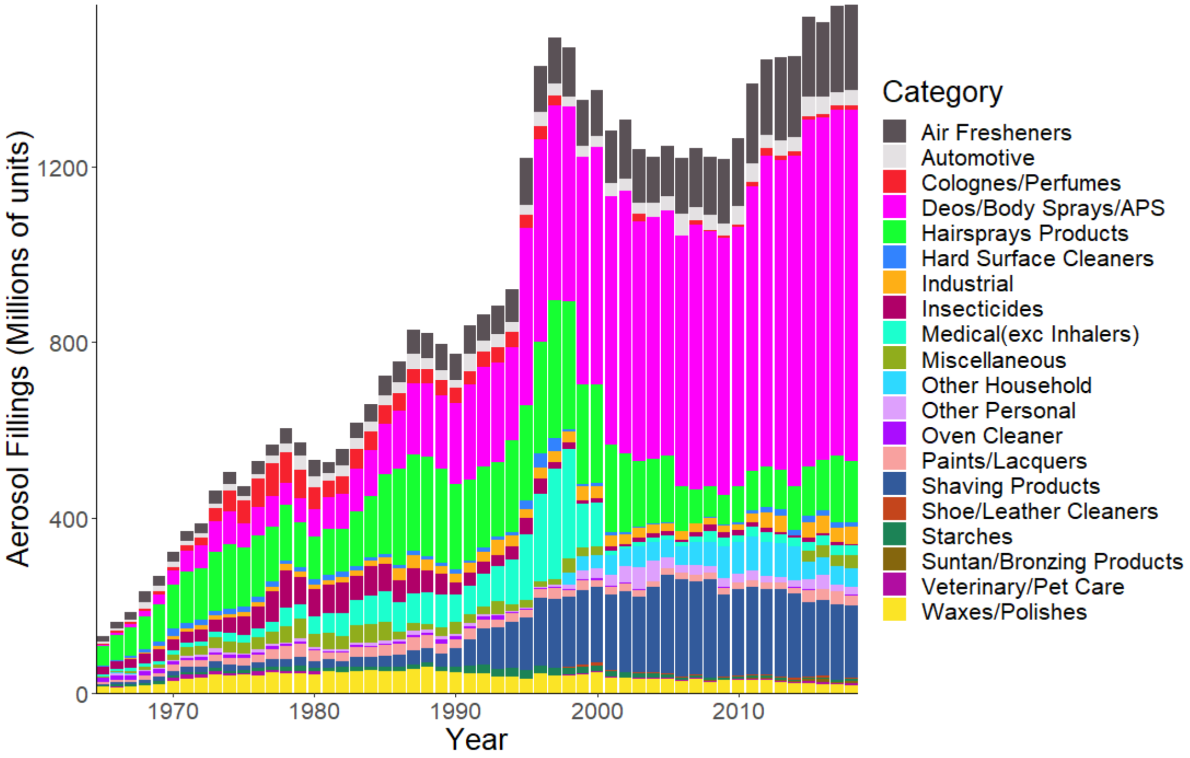

Figure 5.3: UK aerosol filling statistics by product class for the period 1965–2019 (British Aerosol Manufacturers' Association, data aggregated and combined from reports in 2015[29], 2018[30], 2019[31]).

To convert data on aerosol unit fillings into values representative of an atmospheric mass emission of propellant requires assumptions to be made about the average chemical composition of each unit, size, and pressure (which determines the amount of propellant in each).

Using recently published laboratory test data from Nourian et al. 2021[32] as a guide for our calculations, a 300 mL high-pressure aerosol product contains on average 83 g of propellant; differences in both volume (average product size) and pressures can then be scaled accordingly. A medium-pressure product will contain approximately 70% of the propellant of a high-pressure product and a low-pressure product approximately 25%. For example, air fresheners are typically sold in a 250 mL canister and are a medium-pressure product. Therefore, they will contain, on average, approximately 48 g of propellant per can (69 g in 250 mL, scaled down to 70%). Table 5.2 shows the estimated aerosol product ratings to support a conversion of national unit–consumption statistics into a national atmospheric emission of propellant. Aerosol VOC emissions by mass and by-product for the UK are then shown in Figure 5.4.

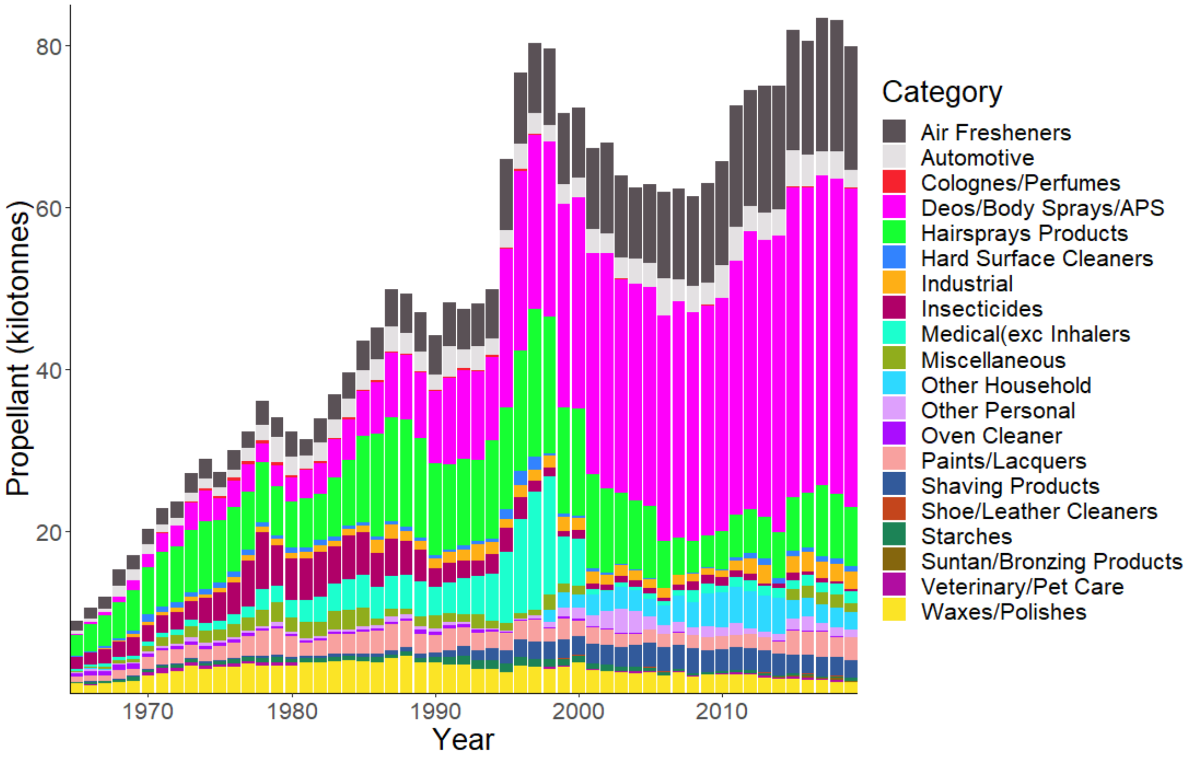

Figure 5.4: Estimated UK aerosol emissions in kilotons for all propellant types, constructed using industry fill reporting statistics from Figure 5.3 and corrected for mass emissions specific to individual products based on fill assumptions (volume and pressure) from Table 5.2.

The upward trends in Figure 5.4 reflect several different factors, some related simply to population growth in the UK (from 52 million in 1960 to 67 million in 2020[33]) and some to consumer trends and habits. The consumption of some aerosol products is in decline, such as hair spray, whereas others show increasing trends, such as aerosol deodorants and air fresheners. Overall PCPs, and in particular deodorants, body sprays, antiperspirants, and hair spray, are consistently responsible for the largest portion of the aerosol market by both filling number and total mass of VOC emissions. In total, using this bottom-up methodology, an estimated ~80 kt of propellant, overwhelmingly as VOCs in the form of either simple hydrocarbons or DME, is emitted from the UK each year. Statistics and long-term data at this level of granular product detail are not available on a global scale, or indeed regional scale, but we consider these trends are likely broadly reflective of patterns in other European countries. Recent industry reported aerosol consumption patterns for Europe are shown in the supplementary material (Figure 5.5). Although European data are not reported using the same aerosol product taxonomy as the UK data, they show a similar pattern with PCPs forming the largest class of aerosol products. Although only covering 3 years of production, this demonstrates that the year-to-year demand and production for each product is reasonably constant, a fact that is further highlighted in the Impact Assessment Study on the Adaptation to Technical Progress of the Aerosol Dispensers Directive, figure 2.2[13].

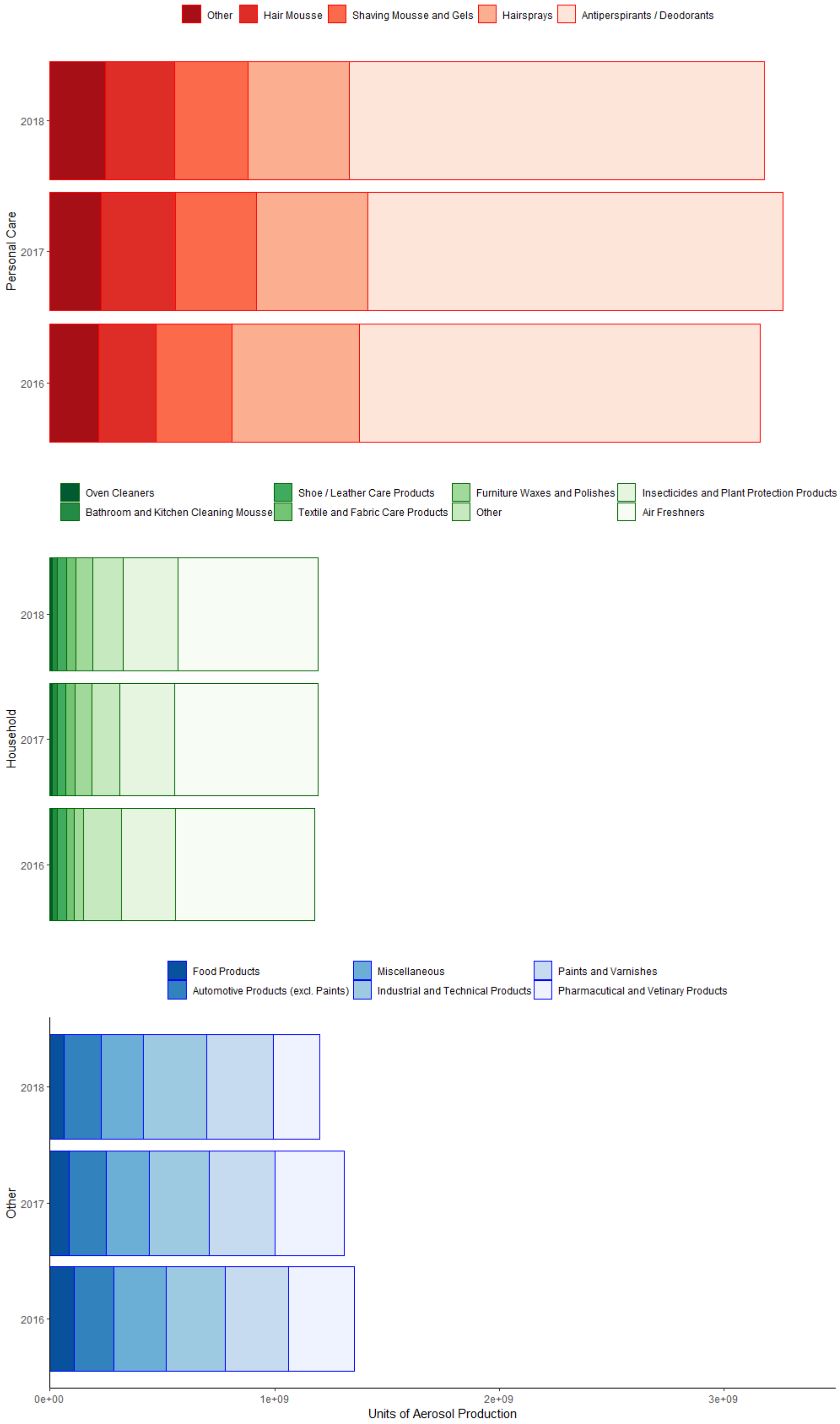

Figure 5.5: European aerosol production breakdown for the years 2016-2018, using data provided by the European Aerosol Federation (FEA).

5.2.7: Contributions to national VOCs emission budgets

During the period following the Montreal Protocol and the phase out of CFCs and HCFCs from aerosols, anthropogenic VOC emissions were, in most industrialized countries, dominated by emissions from road transport, fossil fuels and the associated extractive and refining industries. For example, see a recent analysis of multiyear sectoral VOC emissions trends in Lewis et al. (2020)[34] for the UK. Although the emissions of VOCs from aerosols have generally been accounted for in emissions inventories, until the early 2000s propellant VOCs made up only a small fraction of any individual country's national emissions. Policies designed to reduce photochemical ozone pollution from the 1980s onward focused predominately on sources such as gasoline vehicle exhaust and fugitive emissions, and significant reductions occurred in many industrialized countries in the 1990s and 2000s. As transport and fossil fuel VOC emissions declined, other sectors such as solvents from household products have grown in significance in terms of their fractional contribution to VOC emissions (e.g., for the United States, see McDonald et al., 2018[35]).

As an example, the emissions of VOCs from anthropogenic sources in the UK is shown in Figure 5.6 showing the total VOC from all sources, with aerosols highlighted individually as a source. These downward trends in estimated emissions are also reflected in ambient data (e.g., Dollard et al., 2007[36]; Lewis et al., 2020[34]). The UK National Atmospheric Emissions Inventory (NAEI), from which the data in Figure 5.6 are drawn, is highly detailed by sector and also by VOC species. Further details are described in Passant (2002)[37]. Taking the UK as likely representative of other countries in Europe in terms of consumer behaviour and habits, the fraction of UK national emissions represented by aerosol propellants grew from around 2.0% of national emissions in 1990 to around 6.1% in 2017. Although this may superficially appear to be still a relatively modest contribution, put in perspective, the official inventory estimated UK emissions of VOCs from aerosol use in 2017 (approximately 60 kt pa) were greater than the total VOC emissions arising from all passenger cars in the UK (estimated as approximately 30 kt pa in 2017[38].

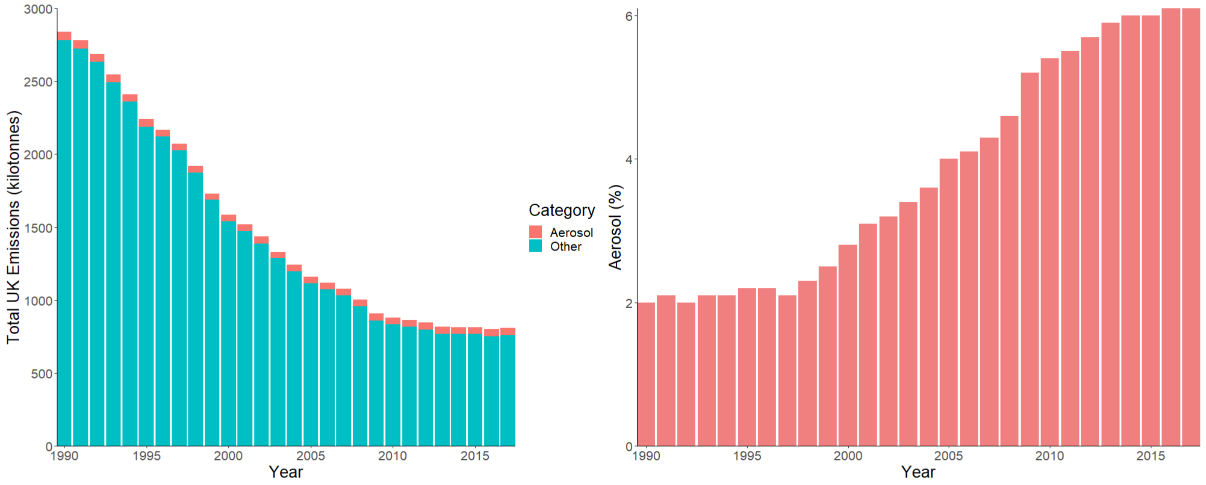

Figure 5.6: Total annual UK anthropogenic VOC emissions (excluding aerosols and biogenic) and VOCs from aerosols. Presented on the left-hand plot is the contribution of aerosols to total UK anthropogenic emissions, and on the right-hand plot, the percentage of the total it represents. VOC speciation and sectoral analysis have been made using the reported composition of aerosol products included within the UK National Atmospheric Emissions Inventory available at www.uk-air.defra.gov.uk. VOC = volatile organic compound

5.2.8: Global consumption and future projections

Industry reported data on aerosol products are generally from trade bodies and at a national level. In high-income countries, this shows frequently that a broadly stable and consistent rate of production/consumption was reached in the mid-2000s. Countries for which long-term and internally consistent production data are available include the United States, Australia, Japan, China, Argentina, Thailand, Brazil, Mexico, South Africa, and the continent of Europe grouped. We assume here that at a national level, production is a reasonable surrogate for consumption and emissions in high-income countries, although it is likely that some component of national production may be exported outside of the country of production. Reported data on aerosol unit production from a range of countries are shown in Figure 5.7 along with a projection of the trend for each to 2050. There is evidence that since the start of the time series in 2005, most high-income countries have seen relatively little change in aerosol use. In Figure 5.8 the same data are expressed as a per capita value, correcting for population change over time in 1 year time steps. We produce per capita estimates by including the whole population (all ages) of a country since more specific data, for example, breaking this down as use by age demographic, do not exist.

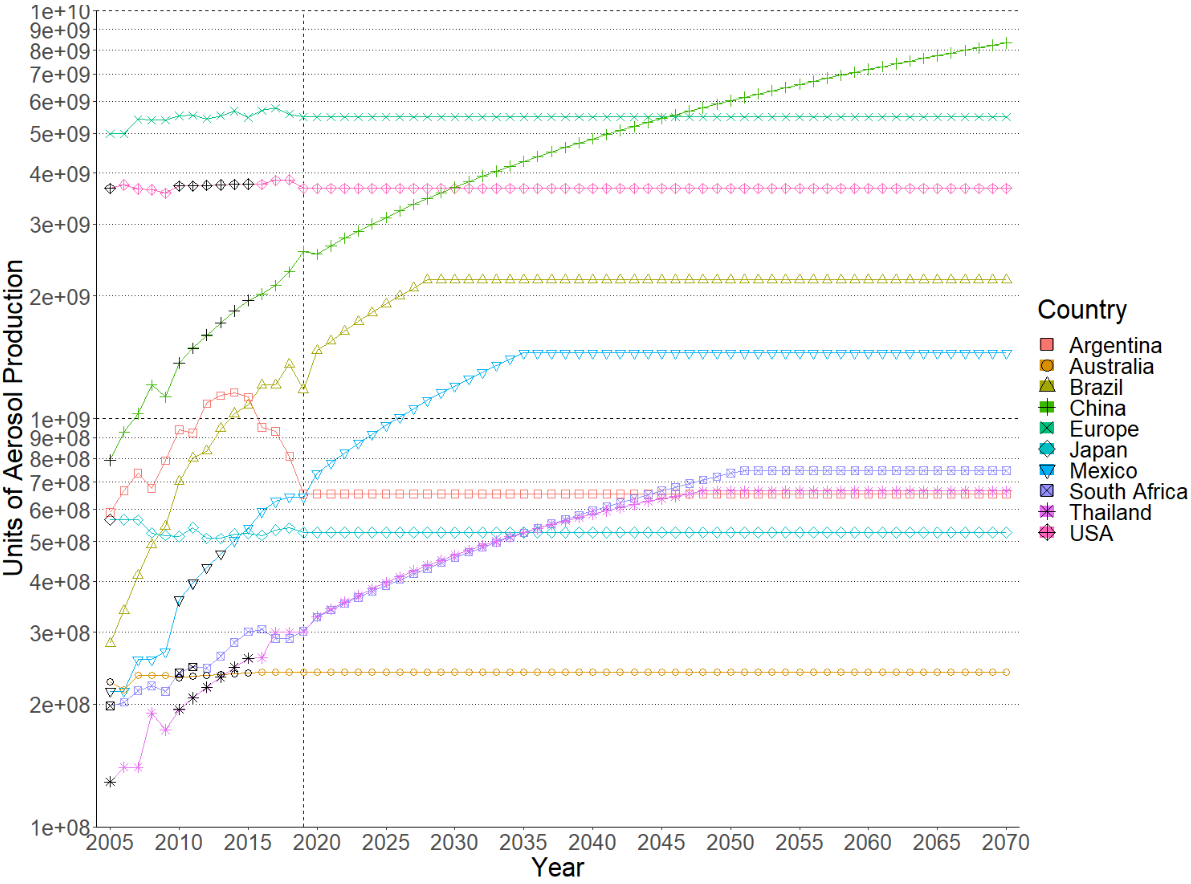

Figure 5.7: Global aerosol use by country and future projections based on recent trends. Where national reporting statistics are available, corrected for projected population growth indicated by the dashed line. Points in black where there are gaps in reporting data have been estimated using a linear regression[1,39–47].

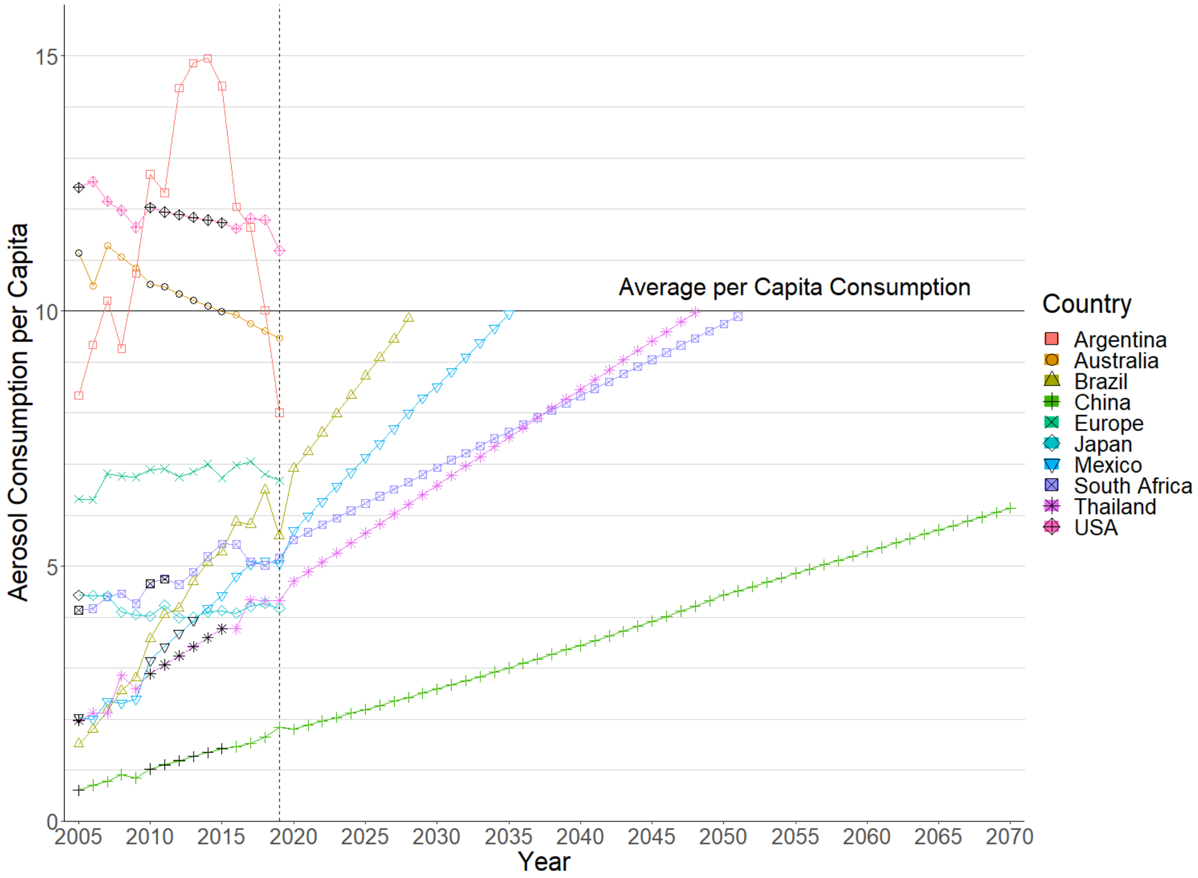

Figure 5.8: Aerosol production per capita. Points in black have been estimated using the same linear regression as to predict future production figures. Unit data are taken from Figure 5.7 and population data used to create per capita values from The World Bank[33]. A typical high-income consumption rate of 10 unit per person per year is marked with the black solid line

Expressed per capita, there are notable absolute differences between countries, the United States being the highest per capita user of aerosols. The average annual per capita production from high-income countries is approximately 10 ± 3 aerosol units person^{-1} year^{-1}. The per capita use data for Argentina has been calculated as 55% of production, as it has been reported that they export 45%[39]. With this adjustment, Argentinian per capita consumption rate is comparable with that of high-income countries and, as such, is an example of how an upper-middle income country can reach this value of 10 aerosol cans per person per year consumption rate.

Both figures also show the industry reported trends in aerosol production for a number of expanding middle-income economies (Argentina, Brazil, China, Mexico, South Africa, and Thailand). In each case, there is a significant growth in consumption over the reference period both in absolute number and as a per capita value. These recent trends are extrapolated as simple forward projections to 2050 but do not exceed a high-income 10 units person^{-1} year^{-1} value. Figure 5.8 is annotated with a line marking of this high-income limit. We predict the year in which this will occur assuming that the future rate of production follows recent past trends. This per capita forecast data have been calculated using population predictions and are corrected for the expected large population growth in some emerging economies. First to reach 10 units person^{-1} year^{-1} would be Brazil in 2028, followed by Mexico in 2035, Thailand in 2048, and South Africa in 2051. China is not predicted to reach 10 cans per person plateau point in this time frame. Despite this, China will become the largest consumer of aerosol products in the world in the 2040s. We have assumed that once a country has reached the 10 units person^{-1} year^{-1} plateau, production and consumption remain constant since there is no historical precedent for a population using aerosols substantially above this rate per person.

The potential scale of future global aerosol consumption can be evaluated by first assessing the gross national income (GNI) of all nations, which tracks their wealth on an annual basis and then applying representative aerosol usage assumptions and trends to each GNI group. Every country has been categorized into one of the four following groups by the World Bank based on their GNI per capita (2019 data) using the World Bank Atlas Method[48]; low-income (less than US$1,035), lower-middle income (US$1,036–US$4,045), upper-middle income (US$4,046–US$12,535), or high-income (more than US$12,536) countries. A breakdown of these economy classifications can be found in Table 5.4. The majority of European countries fall within the high-income category, and as such, the whole of Europe has been classified as being high-income. We assume that all high-income nations have reached a consumption plateau, and the current and future average aerosol units consumed annually per person at 10 ± 3. The current average annual units per person for upper-middle income countries is estimated as 5 ± 2, although we note that our estimate is based on a relatively small number of countries in that GNI group that report annual statistics. We exclude China and Argentina from this group and treat them individually. We apply this estimate to all upper-middle income countries that do not report their usage data for the years up to 2020 and follow the projection that shows based on the extrapolation of past trends, that they will reach the maximum of 10 units per person per year by approximately 2050. Lower-middle income countries have been estimated to currently consume 2 ± 1 units per person annually and will reach 3 ± 1 by 2050. Low-income countries are assumed to currently have no annual consumption and will not increase consumption on the 2020–2050 time frame. These last two assumptions mean our estimates of both current and future global use are potentially conservative.

Table 5.4: Economic classifications according to The World Bank. Data determined using the World Bank Atlas method.

Low	Lower Middle	Upper Middle	High
Afghanistan	Angola	Albania [a]	Andorra [a]
Burkina Faso	Algeria	American Samoa	Antigua and Barbuda
Burundi	Bangladesh	Argentina	Aruba
Central African Republic	Benin	Armenia	Australia
Chad	Bhutan	Azerbaijan	The Bahamas
DR Congo	Bolivia	Belarus [a]	Bahrain
Eritrea	Cabo Verde	Bosnia and Herzegovina [a]	Barbados
Ethiopia	Cambodia	Botswana	Belgium [a]
Gambia	Cameroon	Brazil	Bermuda
Guinea	Comoros	Bulgaria [a]	British Virgin Islands
Guinea-Bissau	Rep Congo	China	Brunei Darussalam
Haiti	Cote d’Ivoire	Colombia	Canada
PDR Korea	Djibouti	Costa Rica	Cayman Islands
Liberia	AR Egypt	Cuba	Channel Islands [a]
Madagascar	El Salvador	Dominica	Chile
Malawi	Eswatini	Dominican Republic	Croatia [a]
Mali	Ghana	Equatorial Guinea	Curacao
Mozambique	Honduras	Ecuador	Cyprus [a]
Niger	India	Fiji	Czech Republic [a]
Rwanda	Kenya	Gabon	Denmark [a]
Sierra Leone	Kiribati	Georgia	Estonia [a]

Low	Lower Middle	Upper Middle	High
Somalia	Kyrgyz Rep	Guatemala	Faroe Islands [a]
South Sudan	Lao PDR	Guyana	Finland [a]
Sudan	Lesotho	Indonesia	France [a]
Syrian AR	Mauritania	Iran Islamic Rep	French Polynesia
Tajikistan	Micronesia Def Sts	Iraq	Germany [a]
Togo	Moldova [a]	Jamaica	Gibraltar [a]
Uganda	Mongolia	Jordan	Greece [a]
Yemen	Morocco	Kazakhstan	Greenland [a]
	Myanmar	Kosovo [a]	Guam
	Nepal	Lebanon	Hong Kong SAR [b]
	Nicaragua	Libya	Hungary [a]
	Nigeria	Malaysia	Iceland [a]
	Pakistan	Maldives	Ireland [a]
	Papua New Guinea	Marshall Islands	Isle of Man [a]
	Philippines	Mexico	Israel
	Sao Tome and Principe	Montenegro [a]	Italy [a]
	Senegal	Namibia	Japan
	Solomon Islands	North Macedonia [a]	Korea Rep
	Sri Lanka	Paraguay	Kuwait
	Tanzania	Peru	Latvia [a]
	Timor-Leste	Russian Federation [a]	Liechtenstein [a]
	Tunisia	Samoa	Lithuania [a]
	Ukraine [a]	Serbia [a]	Luxembourg [a]
	Uzbekistan	South Africa	Macao SAR [b]

Low	Lower Middle	Upper Middle	High
	Vanuatu	St. Lucia	Malta [a]
	Vietnam	St. Vincent and the Grenadines	Mauritius
	West Bank and Gaza	Suriname	Monaco [a]
	Zambia	Thailand	Nauru
	Zimbabwe	Tonga	Netherlands [a]
		Turkey [a]	New Caledonia
		Turkmenistan	New Zealand
		Tuvalu	Northern Mariana Islands
		Venezuela RB	Norway [a]
			Oman
			Palau
			Panama
			Poland [a]
			Portugal [a]
			Puerto Rico
			Romania [a]
			Qatar
			San Marino [a]
			Saudi Arabia
			Seychelles
			Singapore
			Sint Maarten

Low	Lower Middle	Upper Middle	High
			Slovak Republic [a]
			Slovenia [a]
			Spain [a]
			St. Kitts and Nevis
			St. Martin
			Sweden [a]
			Switzerland [a]
			Taiwan [b]
			Trinidad and Tobago
			Turks and Caicos Islands
			United Arab Emirates
			United Kingdom [a]
			United States
			Uruguay
			Virgin Islands (U.S)

[a] Included within the grouping of Europe

[b] Included in China's total

Having classed each country by income level and having then assigned that country to an aerosol projection pathway, we then estimate absolute consumption by correcting for future population. Population projections taken from the World Bank[33] have been combined with the production trends from Figure 5.7 and are presented in Figure 5.9 in units of aerosol consumption on the left-hand *y*-axis. We must assume that countries will remain in their GNI group and follow that aerosol trend over the next 30 years. Import and export must be taken into consideration as not all countries consuming aerosols will be producing them themselves, nor will high-producing countries consume all that they make. As such, the production value for Argentina has, again, been decreased by 45% and the United States and Europe by 10% to account for export. (Industry data suggest that the majority of European and United States production is consumed within those borders, hence the lower export value.) By focusing our calculations on aerosol usage per person, global estimates of VOC emissions are in essence unaffected by cross border trade, since all aerosols are at some point used by someone. One potential issue to account for would be the "banking" of remnant VOCs in used or partially used products in storage or sent for disposal. In general, aerosols are designed to dispense a large fraction of their contents, and if disposed of through recycling, when crushed, any remaining content would be released. For canisters sent to landfill (or stored very long term), it is possible that unreleased VOC would lead to an overestimate in our emissions in the short term (e.g., in year), but over a decadal timescale, those landfill units would ultimately degrade and leak out their contents.

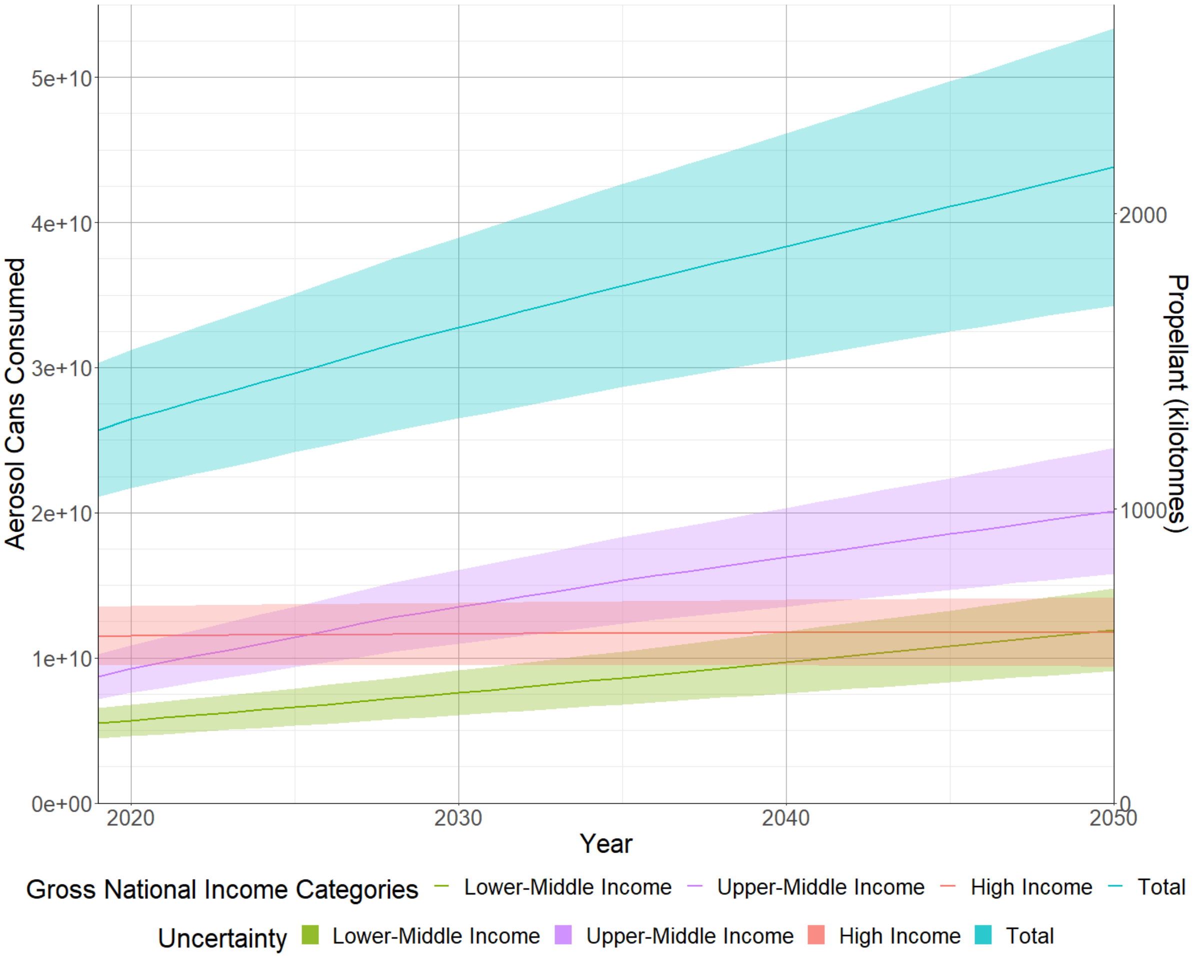

Figure 5.9: Estimated trends in global aerosol consumption. Expressed as units of aerosol cans consumed and converted to mass of VOC propellant based on the aerosol composition from Figure 5.1 the product templates shown in Figure 5.3, and growth curves extrapolated using recent trends seen in representative GNI groups where statistics were available. Shaded uncertainties incorporate population uncertainties and the range generated from a Monte Carlo simulation of possible per capita consumption rates and product distributions. VOC = volatile organic compound; GNI = gross national income

The approach described in Figures 5.3 and 5.4 has been used as a template to convert from unit fillings (which is the metric for industry reported data) to a propellant emission by mass. We have used the detailed UK inventory and manufacturer reporting data (1,567 million cans filled with an estimated 83 kt of propellant in 2018) to derive an average of 53 g per aerosol filling across an averaged profile of all aerosol product types. As we are interested in the filling of VOCs specifically (and not compressed air), this figure has been scaled to 49 g per aerosol filling to account for the combined 93% HAP and DME consumption as seen in Figure 5.1. This "propellant factor" has been applied to the global fillings data (left-hand axis of Figure 5.9) to give data as kilotons of propellant on the right-hand *y*-axis.

The uncertainties have been assessed for both the projections of population and aerosol use and emission values. The UN Population Division provides data on uncertainties[49] in the form of 95% prediction intervals, reported as World Bank income groups, which is converted to uncertainty using data for the "medium variant" population trajectory. As these data are only given in 5-year intervals, the intervening years were interpolated in a linear fashion. Percentage uncertainty in population growth is small for the high-income classification as census data are often more up-to-date and reliable and is unsurprisingly greater for the lower-middle income category. The prediction interval increases for all three income categories from 2020 to 2050 as population estimates become more uncertain the further into the future predictions are made.

There are many obvious uncertainties associated with the aerosol unit estimates and the conversion to VOC emissions. These are predominantly linked to the conversion of aerosol units into mass emissions (e.g., the process described in Table 5.2), and critically the likely final plateau usage in each country, since the use of aerosols (meaning which products and how many in total) in each country is a function of national habits and preferences. This does not follow any common variable like GDP, and notably the richest countries by per capita GDP do not necessarily have the highest aerosol usage. We assume that the plateau value varies around 10 ± 3 in an entirely random manner. The range here is based purely on the per capita values that have been reported in the past by individual high-income countries. We use a 10,000-step Monte Carlo simulation to evaluate a range of uncertainties in typical per capita usage in each country and the distribution of aerosol units between subproduct types. When combined with the uncertainties in the population projections, this inevitably leads to a spread in estimates, shown as the shaded bands on Figure 5.9.

Projecting per capita aerosol consumption across countries in the same GNI group if specific reporting data do not exist (and that is most countries) gives an estimate of current global VOC emissions from compressed aerosols of 1.3 ± 0.23 Tg year^{-1} for 2018. By applying projections of current usage trends into the future and including all countries in a GNI group, we estimate global aerosol production could reach approximately 4.4 × 10^{10} units year^{-1} generating an emission of 2.2 ± 0.48 Tg year^{-1} an increase of around 70% in VOC propellant emissions by 2050 from present day.

Estimates of the current global anthropogenic emissions of VOCs from *all* anthropogenic sources are also rather uncertain, but some recent estimates place total emissions in the range 98–156 Tg year^{-1}. Set against that global value (for 2013, taken from IPCC estimates), aerosol propellant VOCs currently represent around 1% of global anthropogenic emissions. If anthropogenic emissions reductions in middle-income countries follow those of high-income countries, with reducing emissions from gasoline vehicles and related fuel evaporation, then the fractional contribution to global emissions is likely to rise further, potentially approaching a value similar to that seen in a typical high-income country like the UK where propellants represent 6% of national VOC emissions.

5.2.9: Conclusions

The annual per person consumption of aerosols has broadly stabilized in most high-income countries; however, there is evidence for a rapid rise in consumption in middle- and low-income countries. On current trends, it appears reasonable to assume that as economies and wealth grow that consumption patterns may converge on the historically stable figure of approximately 10 aerosol units per person per year, a value derived from past reporting in high-income countries. Accounting for the distribution of different aerosol products used allows for consumption statistics to be translated into amounts of propellant released, where that propellant is dominated by VOCs, a combination of simple hydrocarbons and DME. Not all countries report their aerosol use, but there is sufficient information across representative income levels to make some informed estimates of consumption in each of the four World Bank GNI categories. Based on this and projected growth in population in each country, some global estimates of aerosol use have been made. We estimate that globally around 1.3 ± 0.23 Tg of VOC propellant is currently released each year in the form of hydrocarbons and DME. The central value is lower than that estimated in Nourian et al. 2021[32]; 1,437.8 kt, no uncertainties given, estimate based on a market report of the number of aerosol valves sold in 1 year. We note that our calculation has taken aerosol can size, fill pressure, and percentage of propellant into account. The method used here also makes use of a wider and more detailed breakdown of product consumption for annual global estimates. Assuming patterns of use continue forward on the trajectories seen in the recent past for middle- and low-income countries, then global VOC emissions from aerosols may reach around 2.2 ± 0.48 Tg per year in 2050.

To assess the scale of downstream impact of aerosol VOC emissions would need a complex and comprehensive modelling study since the effects would be dependent on the wider local and regional pollution conditions, geography, season, and so on. This is well beyond what we can include in this article. However, to give a scale of effect on ozone formation, we use a simple box model (MCM 3.1, www.mcm.york.ac.uk) run over a 3-day period and constrained to VOC, NO_x and other supporting ambient data from the 2012 Clearflo air pollution research project in central London 2012[50]. We use a baseline model initialized using the observed average ambient VOC, CO, HCHO, and NO_x concentrations, followed by a second counterfactual where we reduce the amount of ambient propane, *n*-butane, and *iso*-butane by the proportions reported as originating from aerosol propellants in the NAEI[38]. For reference, this uses conditions of NO: 3 ppb and NO_2: 10 ppb, along with a full range of VOCs (Top 10 were ethanol: 10.7 ppb, ethane: 8.3 ppb, acetone: 8.1 ppb, methanol: 6.8 ppb, *n*-butane: 5.2 ppb, propane: 4.9 ppb, *iso*-butane: 2.6 ppb, *iso*-pentane: 3.5 ppb, toluene: 2.6 ppb, and butanol: 2.5 ppb). For the counterfactual, 48% of *n*-butane emissions in the UK were estimated to be from an aerosol source, so this model was run with *n*-butane reduced from 5.2 ppb to 2.6 ppb. 14% of propane emissions were estimated to be from aerosol sources and so on. Over a 3-day UK summertime photochemical trajectory reducing the initializing ambient VOCs concentrations by the proportion accounted for by aerosol emissions in the NAEI resulted in a decrease in ozone of around 2.2–2.8 ppb after 72 h. We would suggest that in many other locations, the replacement of aerosol propellant with non-VOC alternatives would also lead to potentially meaningful reductions in surface ozone when measured over multiday timescales.

Although at present aerosol VOC propellants make up approximately 1% of global anthropogenic VOC emissions, their contribution as a fraction of emissions appears likely to rise. Substantial reductions in VOC emissions from road transport, gasoline vehicles, and evaporative losses have been reported in many high-income countries, and it seems likely that this will ultimately propagate through to middle- and low-income countries over time, particularly should transport fleet electrification become widespread by 2050. Although projections of VOCs in the future at a global scale are uncertain, in some more ambitious air quality and emission scenarios, for example, presented by Amann et al. (2020)[51], global emissions of VOCs from all anthropogenic sources could decline to approximately 37.9 Tg year^{-1} in 2040. If aerosols consumption follows the patterns shown here and the propellant remains as of today, then they would represent approximately 6% of all global VOC emissions—a value consistent with the current day UK contribution. We note that there are currently few downward pressures on the emissions of VOCs from aerosols specifically, indeed, there is some evidence that aerosolization is being applied to products that were previously dispensed as liquids—for example, suntan lotions and moisturisers.

Policy implications

The replacement of halocarbons with hydrocarbons in the 1987 Montreal Protocol was clearly a landmark environmental change. There may, however, be a case that the subsequent global growth in aerosol consumption was not foreseen at the time of the signing of the Protocol, when aerosol usage was lower per capita in high-income countries than today (roughly 50% of current use), and usage was very low in middle- and low-income countries such as China and India. Given that VOCs contribute to tropospheric ozone pollution, international policy revision may be required and the continued support of VOCs as the preferred replacement for halocarbons potentially not sustainable for aerosol products longer term. Although there are a few notable exceptions, such as the California Air Resources Board product regulations, the general absence of controls on aerosol formulation or consumption appears in tension with the often highly regulated nature of VOC emissions from other industry sectors. Road transport (both evaporative and tailpipe), buildings materials (e.g., timber, furniture), and decorative products (e.g., paints and varnishes) are all subject to specific emissions regulation in many countries. The cost–benefit of implementing new technologies to further reduce emissions of VOCs from gasoline vehicles may be disproportionately poor when compared to the equivalent air quality gains from VOC reduction that might be achieved more straightforwardly by a lowering of consumption of aerosols or the replacement of VOCs with less harmful compressed air/N_2 as the propellant.

Although this article is not intended to provide policy prescriptive solutions, we would stress the need for much improved collection of statistics on annual aerosol consumption by product type and by country. Without robust data of this kind, the full impacts of the Montreal Protocol remain uncertain to calculate, as are the possible future benefits of replacement of hydrocarbons with alternatives. We are not experts in the manufacture of consumer products but would note that many technological options exist for the reduction of aerosol VOC emissions. As identified earlier, for some products, the use of compressed air or N_2 may be a viable alternative propellant. Perhaps more significantly for very many personal care and household cleaning products, a clear solution would be product de-aerosolization. Many consumer products can be (and are) applied in their liquid or solid forms, for example, as roll-on deodorant, hair gel, solid furniture polish, bronzing lotion, room fragrance, to name but a few. In some cases, the continued use of aerosols when non-aerosol alternatives exist is simply down to the continuation of past consumer preferences and habits.

More generally the role played by aerosol VOC emissions in air pollution needs to be much more clearly articulated in messaging on air pollution and its management to the public. The association of VOC emissions with gasoline and vehicles is heavily entrenched, and even among air quality professionals, there is limited knowledge of the scale of aerosol product impact. Approaches to emissions reduction from PCPs could potentially be communications-led, with individuals encouraged to switch to non-aerosol alternatives or moderate consumption. Product labelling of consumer products as high VOC emitting—and clearly linking this to poor air quality—may drive change away from aerosols to their alternatives as has been seen previously with the labelling of paints and varnishes. Although behavioural change appears to have considerable potential to reduce emissions, other more direct interventions could also be envisaged. Fiscal approaches such as variable taxation on aerosol products would be a more drastic measure for effecting change, as would regulatory phase out and banning of aerosols products containing HAPs or DME.

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Chapter 6 : Summary and conclusions

Traditionally, IAQ concerns have centred around the burning of fuels indoors for cooking and heating, which is something that does not often occur in the UK and other synonymous nations. Instead, VOCs from sources such as building materials, tobacco smoke, and other domestic activities are the more dominant pollutants. These indoor pollutants can cause health problems, particularly respiratory, to building occupants and even have the potential to contribute to outdoor air pollution. The UK Government's current plans for improving IAQ, and tackling IAP, are focussed more on removing these potentially harmful pollutants from indoor environments by improving ventilation, particularly in new homes, rather than curbing emissions from their source. This thesis is motivated by the limited knowledge and interest in, what we believe and have proven to be, a significant source of IAP, consumer products, with the objective of promoting the idea that these pollutants can be reduced at the source, and potentially influencing new government policies.

The use of consumer products globally is widespread, with a trend of increasing popularity and innovation for new products of all kinds (PCPs and HCPs). The consumer product industry has never been immune to criticism and examination, with all products sold being subjected to regional government regulations regarding product safety, however there is very little currently curbing their VOC emissions. Presented in this thesis is a comprehensive investigation of the role of consumer products as significant contributors to IAP. This includes both top-down and bottom-up laboratory analyses, the review of ingredient lists, product formulations, government guidelines, manufacturer's requirements, and emissions inventories, and the evaluation of potential public health concerns, environmental impacts, and consumer habits. Prior to this review, neither consumers, regulatory bodies, nor policy makers had access to any particularly detailed information surrounding consumer product VOC emissions and their links to IAP.

Presented in Chapters 2, 3, and 4 are on-line mass spectrometry analyses of non-aerosol PCPs. Chapter 2 describes the initial product headspace analysis that developed the basis for subsequent work. An initial screening of commonly used PCPs by SIFT-MS allowed the determination of the seven most prevalent VOC species, which comprised solvents, fragrance compounds, and cyclosiloxanes (monoterpenes - grouped and represented as limonene -, benzyl alcohol, ethanol, methanol, 2-propanol, D4, and D5). There were noticeable differences in the VOC emissions between product classes, for example cyclosiloxanes were not present in the shower gels, and ethanol and limonene were observed in all product classes tested. Within product classes, however, differences in brand and formulation did not appear to influence variation in VOC emission profiles, allowing them to be generalised, both in terms of VOCs emitted and the rates at which they do so. Emission rates were easily calculated for each product with the aid of Labsyft instrument software, expressed as micrograms per second per gram of product used, and then averaged for each product class providing a simplified profile for understanding the impact of each product class's VOC emissions, which differ widely. These emission rate calculations have proved a valuable part of this initial investigation, as they can be used for model simulations and personal exposure estimations. Annual UK emissions from PCPs have been estimated based on these emissions rates and low, medium, and high per-person usage assessments, scaled up to represent the nation as a whole. When comparing the medium usage assessment to 2017 NAEI estimates for the "Non-aerosol Products – Cosmetics and Toiletries" class of emissions, which are only reported for 2-propanol, benzyl alcohol, and ethanol, we observe that values may have been underpredicted.

Following this, Chapters 3 and 4 describe the realistic experimental techniques used to provide context for the lab based work carried out, and see if it translates reliably into real-life emissions from consumer products. Six PCPs (facewash, shower gel, shampoo conditioner, moisturiser, and an aerosol deodorant) were selected for use in a shower study, where said products were applied by 18 participants who had volunteered to take part. Clear application time instructions were given, with products weighed out in advance in order to control product use as far as possible. PTR-MS was utilised to measure VOC emissions in real-time, allowing time-concentration evolution profiles to be constructed for each, having targeted VOCs based on the headspace analysis described in Chapter 2. Average profiles for one 15 minute showering activity were produced for ethanol, limonene (again representing all monoterpenes), and benzyl alcohol, the only targeted compounds which were measurable in the humid environment. These profiles were mostly consistent between participants, showing clear peaks for different products used. The total mass of each measurable compound from the 15 minute activity was calculated from the emissions of all 18 participants, showing variability (albeit the same order of magnitude) between users – a factor that we cannot control or predict. These small deviations, which lab-based experiments could not account for, were attributed to rinsing time differences. These real-world, top-down emissions were 1.3-11 times lower than the bottom-up headspace analysis estimates. It was concluded that the presence of liquid water (as a solvent for water-soluble compounds and as a physical remover of products, washing them down the drain before they have a chance to finish volatising) and dermal absorption were responsible for this. These results also provide estimates of the peak exposure to VOCs we may expect during one common activity (taking a shower).

A single-user reproducibility showering experiment proved that the amount of product used scales linearly, meaning the product-use assumptions made previously for total annual PCP emissions are realistic, and that this is a reliable method for making personalised usage scenario assumptions based on time and amount of product used, if correction factors determined by real-life experiments are taken into consideration. This led to the understanding that complimentary use of the two methods (top-down real-life, and bottom-up lab-based) is best for accurate consumer product VOC emission analysis.

This approach is used in Chapter 4, considering a different PCP application scenario and the unique health risks it poses to consumers. Products such as facial moisturiser are applied almost directly to site of the inhalation exposure pathway, leading to potential increased exposure risks than from non-facially applied products. As previously, headspace analysis using SIFT-MS was employed for an initial screening of 16 day facial moisturisers, half of which were marketed as being `green`, to identify their most prominent VOC emissions. Four of the six key species identified were alcohols (ethanol, benzyl alcohol, 2-propanol, and *t*-butyl alcohol), with fragrance compound limonene (monoterpenes) and conditioning agent 1,3-butanediol making up the other two. The same method for emission rate calculation was used as for the previous headspace analysis. It was observed that there were no distinguishable differences between the `green` and regular marketed products, the only distinction being where the ingredients were sourced.

Real-life application was measured using a novel mannequin head experimental setup with representative nose and mouth respiration to replicate proximity-based inhalation risk, producing emission time profiles for the targeted VOCs. An initial observation was that the six VOC species emit over vastly different time scales, ranging from 5 (ethanol) to 150 (1,3-butanediol) minutes. The amount of each VOC `inhaled` from one standard application was determined, expressed as mass of VOC in mg, and used for facial exposure vs ambient inhalation comparisons. Data for median ambient room concentration over 24 hours from a typical domestic living room in the UK is available for limonene and ethanol. Using these values, mass inhaled was calculated as being ~ 16x and ~ 300x greater respectively via facial application than from breathing typical room air.

A crucial finding from these on-line mass spectrometry investigations into non-aerosol PCPs is that real-world influences must be taken into consideration when measuring, estimating, and subsequently reporting their VOC emission contributions. The complementary approach of lab-based and real-life experiments outlined in this thesis is both reproducible and generates reliable results. Additionally, screening products of their VOC emissions highlights the importance of ingredient list transparency, and the relationship between consumer awareness and their ability to make informed decisions about the products they use.

Aerosolised consumer products are just as popular as non-aerosol products, and it is therefore imperative that their VOC emissions, which make up around 93% of current aerosol emissions by mass, are included in consumer product pollution analyses. Whilst non-aerosol consumer product VOC emissions are relatively easy to measure, it is not feasible to carry out the same method on compressed aerosol products when there is information available on filling data and manufacturer solvent choices. Chapter 5 is the resulting literature review of an extensive investigation to obtain as much of said data as possible. Initially, UK statistics were reviewed, looking at consumption patterns over the past 6 decades and determining the solvent contributions of aerosol consumer products to national anthropogenic emissions totals. The British Aerosol Manufacturers' Association (BAMA) report production data in units of aerosol cans filled for 20 product categories, which reached over 1 500 million in 2018. Using this data, and assumptions made on propellant mass in grams based on can size and pressure for each category, we estimate that this equates to 83 kt of propellant. This solvent contribution represents around 6% of UK national emissions, having grown from around 2% in 1990, greater than the total VOC emissions arising from all passenger cars in the UK. This is due to an increase in demand for aerosol products, but also from the successful reduction in transport sector emissions over the past few decades.

After acquiring similar fillings data from other nations (Argentina, Australia, Brazil, China, Europe – including the UK –, Japan, Mexico, South Africa, Thailand, and the USA) global aerosol consumption was estimated, and future projections made, taking exports into consideration. Nations classified as high-income have reached a plateau in their national consumption, around 10 cans per person per year, with upper-middle income nations currently consuming approximately half at 5 cans. However, the upward trajectory of production data for upper-middle income countries suggests they will reach 10 cans annual consumption per person by the year 2050. Without any data for lower-middle income nations a modest current estimation of 2 cans per person per year, increasing to 3 by 2050, has been made. Applying these assumptions to all nations, based on their GNI classification and population estimates, the global prediction for aerosol product VOC solvent emissions for 2018 is 1.3 ± 0.23 Tg year^{-1}, increasing to approximately 2.2 ± 0.48 Tg year^{-1} in 2050, an increase of around 70%. The significance of this study is the rate of increase we are likely to encounter from aerosol product solvent VOC emissions. This information may be crucial in changing public opinion on aerosols, as it would seem there is not currently much aversion to them, or to the idea of increased aerosolization as this mode of product delivery is easy and convenient.

If the current predicted solvent contribution from aerosol products in the UK is ~ 6%, then a prediction for all VOC emissions from consumer products, aerosol and non-aerosol, solvent, fragrance, and other compounds, will be considerably higher. To conclude in short; consumer products are an important and significant source of VOC emissions, and therefore pollution. Whilst it can be generalised that all consumer products are substantial in exacerbating poor IAQ, this thesis shows how variable the polluting effects of different products can be depending both on their formulation and how they are used.

6.1: Future work

The work presented in this thesis can be easily expanded upon, continuing the screening of consumer products, particularly HCPs, and building a larger emissions database. I believe the future of this research will result in a full inventory that can be used for predicting VOC emissions and exposure on both a personal and national level. This could be based on individual profiles for how each product is used, including factors such as water, time, amount of product, and application site, bringing together all of the aspects discussed and developed in this thesis for non-aerosol products, with the possibility of including aerosol products as well once the VOC contribution from fragrance, and other non-solvent compounds, has been determined.

As this work is very much routed in population and consumer habits, finding a way to reliably predict usage will be key to advancing this work. Collaboration with manufacturers, sellers, consumers, or social scientists may be required to obtain this information.

6.2: Final remarks

Consumer products emit a range of VOCs which contribute to poor IAQ. As they continue to grow in popularity, changes must be made in order for the UK to reach its emissions targets. This work gives a detailed insight into the scale of consumer product emissions from both aerosol and non-aerosol products, identifying key species emitted and quantifying their emission rates. Additionally, it advises solutions to the problems raised, which include formulation changes driven by regulation and shifts in consumer opinion influencing buying and usage habits, in order to reduce IAP and harmful VOC exposure.