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Updated speciation of VOCs emitted from European-market aerosol dispenser consumer products

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Aerosol dispensers are a popular format for consumer products that give rise to a substantial fraction of national volatile organic compound (VOC) emissions in high income countries (*e.g.* ~6% to total annual UK VOC emissions). Given a high fraction of usage indoors these emissions can contribute to degraded indoor air quality in rooms with poor ventilation. Characterisation of emissions, both in terms of chemical speciation and amount released is currently poor. This paper presents a method for aerosol dispenser product VOC emission identification and quantification using a custom-built sampling chamber and complementary SIFT-MS and GC-FID-QMS techniques. UK aerosol dispenser production statistics are used to up-scale laboratory data to update the National Atmospheric Emissions Inventory speciation (NAEI) for total UK VOC emissions from aerosol dispenser products. Ethanol, *n*- and iso-butane, and propane were the most abundant VOCs emitted with some species, such as cyclomethicones, identified here that are not currently reported in national emissions inventories. Bottom up estimates of emissions indicate that total VOC emissions from aerosol products are currently overestimated in the UK by ~37 ktonnes per year, particularly from carcare and cosmetics & toiletries sectors. Whilst there have been some widely reported detections of trace amounts of benzene in aerosol products in previous US studies, we do not find benzene in any of the 45 products tested here.

Environmental significance

Aerosol dispenser consumer products are a significant source of volatile organic compounds (VOCs), which can have negative impacts on both indoor and outdoor air quality and health. Despite this, their VOC emissions are not currently well understood or characterised in emissions inventories. Within this study, new analytical methods have been developed to resolve this, providing valuable information for industry regarding product formulations, which in turn can drive positive changes in the sector for both product safety and total VOC reduction. It also contributes to the currently-emerging understanding of the complicated consumer behaviours which influence air quality in the home and determines whether potentially dangerous contaminant species are emitted during use.

Introduction

Aerosol dispenser products are a popular mode of delivery of consumer products with 5.6 billion cans being produced in Europe in 2018.[1] A significant portion of these are personal care products (PCPs), for example deodorants and hairsprays, and household cleaning products (HCPs) such as furniture polish and air fresheners.[2] Both aerosol and non-aerosol PCPs and HCPs emit volatile organic compounds (VOCs), which can contribute to both poor indoor and outdoor air quality, notably due to their ability to react to form secondary organic aerosols, carcinogens (such as formaldehyde) and ozone.[3–5] Exposure to very high concentrations of VOCs from aerosols can be directly harmful and in rare cases, with product misuse, lead to death.[6] As consumer products are generally used indoors this emission sector has a greater primary impact on indoor air quality (IAQ) than other VOC emission sources (*e.g.* transport, fuels, energy), and the dose indoor occupants are exposed to has the potential to be much higher than if the same product was used outdoors. In non-aerosol products (*e.g.* liquids such as shampoos) only a fraction of the total product is ultimately volatised to the gas phase, the majority being deposited on a surface or washed away. Aerosol products on the other hand emit a far greater portion of their contents to the gas phase using propellants to dispense and disperse the active product ingredients.

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Hydrocarbon aerosol propellants (HAPs) are most commonly used, typically comprising a blend of propane, iso-butane, and n-butane, but many other hydrocarbons can also be present. A 2019 study by Heeley-Hill et al. (2021)[7] found that, n-butane, iso-butane, and propane were the highest concentration VOCs found when air sampling was undertaken in 60 UK homes, replicated later by Warburton et al. (2023),[8] which found them highest after ethanol. Aerosol products are therefore greater contributors to indoor VOCs than non-aerosol products due to the emission of HAPs.

On a national scale, HAPs, and thus aerosol products, contribute significantly to total UK anthropogenic VOC emissions. Lewis et al. (2020)[9] identified that solvents had become the largest contributor to UK VOC emissions, a significant change from the dominant exhaust and fugitive fuel sources pre-1990s. Aerosol products are categorised within this solvent source and were estimated by Yeoman and Lewis (2021)[1] to contribute around 6% to total UK VOC emissions in 2018, more than the VOC emissions from all passenger vehicles in the UK. This percentage is likely to have increased since then as vehicle-related emissions continue to decline.

Beyond propellants, there are a multitude of other volatile ingredients used in aerosol formulations, including co-solvents and fragrances and VOCs that serve as denaturants, preservatives, and moisturising agents. The representation of VOCs from consumer products in emissions inventories is of increasing importance as they form an ever-increasing fraction of emissions in high-income countries.[10] The National Atmospheric Emissions Inventory (NAEI) provides a detailed speciation of hundreds of different VOC sources for the United Kingdom. Whilst the absolute amount of VOC emitted from a given sector is updated annually, often based on industry reported sales and/or manufacturing statistics, the speciation of VOCs of those sectoral emissions is only infrequently re-evaluated. For aerosol products specifically, the British Aerosol Manufacturers Association (BAMA) provide detailed annual tonnage estimates for VOC usage in UK aerosol products. However the disaggregation of those emissions into individual VOCs is based on research data from the 1990s.

Alongside the VOCs that are added for aerosol performance there is also the possibility of unintentional contamination of propellants and other ingredients with VOCs from other sources. In the context of this work, contaminants are defined as species which we do not believe have been intentionally added to the products, and include species such as benzene, ethylbenzene, toluene, and xylenes. All of these have associated negative health effects attributed to exposure.[11–14] The detection of contaminant VOCs in aerosol products has been of significant recent interest. Between 2021 and 2022 several aerosol products in the USA were reported to contain elevated amounts of benzene, in excess of 10 times the US Food and Drug Administration limit.[15–17] This led to legal petitions and subsequent voluntary recalls for certain products by the manufacturers. Measuring trace contaminants, particularly common chemicals such as benzene, is not straightforward and the issue of whether aerosols might contain such species is contentious.

Aerosol products in their final packaged form are technically difficult to sample. To get a true measure of what is released to the gas phase indoors the product must be discharged into a large volume. Only a few lab-based studies have been conducted on VOC emissions from compressed aerosol consumer products. Work by Guo and Murray (2001)[18] determined total VOC emissions from an aerosol furniture polish using head-space gas chromatography/flame ionisation detection (GC/FID) in a small glass chamber ($\sim$0.013 m^3). Nourian et al. (2021)[19] analysed the chemical components of aerosol propellants using a sampling chamber and GC-MS (gas chromatography mass spectrometry) from a range of PCPs and HCPs, determining that they make up between 30-90 wt% of the product, whilst Lin et al. (2022)[20] found low moisture content and high VOC content (average of 82 wt%) in three aerosol spray products as opposed to liquid and gel products during similar GC-MS experiments.

Whilst many different sampling and analysis methods have been employed to attempt to determine aerosol product formulation and contaminants, there has yet to be a systematic study detailing VOC speciation from final purchased aerosol products when used as intended by the public. This paper presents the most a complete assessment to date combining selected ion flowtube mass spectrometry (SIFT-MS) and gas chromatography-flame ionisation detection-quadrupole mass spectrometry (GC-FID-QMS) for compound identification, and with testing across a wide range of different product types. Whilst the primary aim of the study is to provide an updated speciation of VOCs emitted by contemporary aerosol products, a by-product is a comprehensive assessment of whether any contaminant species are present. The updated speciation, weighted by consumption and use statistics across different product types, should allow for a more accurate inventory reporting and provide the basis of an improved parameterisation of emissions for indoor and outdoor air pollution models.

Materials and methods

Sample selection

A representative range of 45 aerosol consumer products across multiple different manufacturers (including supermarket own-brand products) were purchased from two large UK retailers.

The products were as follows: 4 air fresheners (AF), 1 antibacterial surface spray/disinfectant (AD), 4 furniture polishes (FP), 1 insecticide (I), 1 miscellaneous medical spray (MM), 2 shoe odour sprays (SO), 2 insect repellents (IR), 1 water spray (WS), 3 body sprays (non-antiperspirant) (BS), 9 deodorants (antiperspirant) (D), 5 dry shampoos (DS), 5 hairsprays (HS), 2 moisturisers (M), 2 after sun sprays (AS), and 3 sunscreens (S).

Particularly complex products, such as shaving foam, hair mousse, and fake tanning spray, and potentially hazardous or corrosive products, such as oven cleaner, were excluded from the sample selection.

We note that throughout the paper we use standard UK classifications for body sprays and deodorants – deodorant being a product that contains antiperspirant, and a body spray a product that does not contain antiperspirant.
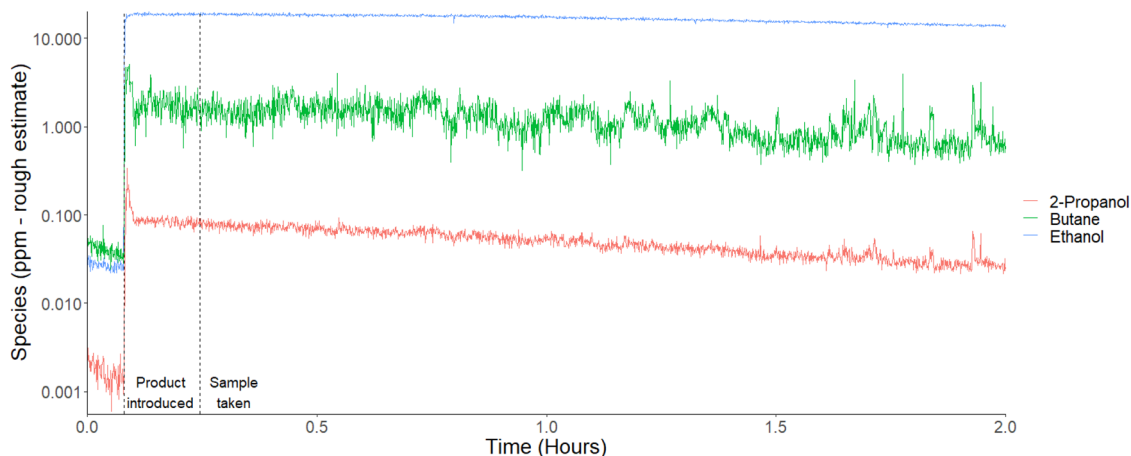
Fig. 1 Chamber VOC mixing profile before and after sample introduction measured using SIFT-MS. Dashed lines indicate points at which product is introduced and GC takes a sample.

Test chamber

A 2 m^3 in-house custom-built chamber was used for sampling. This comprised a framework built from aluminium extrusion profiling, with 4 mm tempered glass panels sealed with inert thermoplastic elastomer seals (Bosch Rexroth, Germany). 40 cm aluminium panels 1 m from the bottom of the chamber housed four $\frac{1}{4}''$ unions, with one central $\frac{1}{2}''$ union on three sides. On the front of the chamber, a hinged door was fitted, which was itself sealed with inert thermoplastic elastomer draught excluders fitted around the door (Bosch Rexroth, Germany). 1 m from the floor on the door panel, a glove box was fitted, which comprised two 192 mm holes cut into a 40 cm aluminium panel and fitted with two glove ports and nitrile glove box gloves (Nitri-Box, Honeywell, USA), all sealed with thermoplastic elastomer draught excluders.

In order to aid mixing within the chamber, two small fans were placed in the front right and back left corners of the chamber on the floor pointing upwards at a ~60° angle from the floor. The fans were run at a wind speed of 17.4 mph. A diagram of the set up can be found in SI Fig. 1.

Fig. 1 presents the concentration profile measured using SIFT-MS to confirm that the dispensed product was rapidly well mixed in the chamber following introduction. Indicated by the dashed line on the right, concentrations within the chamber were stable at the time of sampling. Full SIFT-MS parameters and methodology can be found in the instrument methodology later in the text.

Sampling setup

Ambient outdoor air was pumped into the chamber using a diaphragm pump (MPC 301 Z, Welch, Germany) at a rate of 20 L min^{-1} through a 7 μm inline filter (Swagelok, OH, USA). Ambient outdoor air was used to flush the chamber due to outdoor air having lower ambient VOC concentrations than indoor air.

The recirculation line comprised a 14 m length of $\frac{1}{2}''$ per-fluoroalkoxy alkane (PFA) tubing which pumped chamber air using a metal bellows pump (MB-41 Metal Bellows pump,

Senior Metal Bellows, MA, USA) to the gas chromatograph-flame ionisation detection-quadrupole mass spectrometer (GC_FID_QMS) instrument used in this study. A stainless steel $\frac{1}{2}'' \times \frac{1}{2}'' \times \frac{1}{8}''$ tee fitting (Swagelok, OH, USA) was installed to connect the recirculation line to a pre-concentration thermal desorption unit (TDU, in-house built) upstream of the GC-FID-QMS. Background air samples were taken immediately before each aerosol sample was sprayed using 6 L stainless steel, internally silica-treated canisters (Restek, PA, USA and Entech, CA, USA), prepared by evacuating to 0.01 Pa. Samples were drawn through 1/4″ PFA tubing, through a 7 μm inline filter (Swagelok, OH, USA), into the canister.

A sampling run would see the chamber closed with a sample aerosol canister placed inside, and the sampling method started. After 5 minutes, a background sample would be collected into an evacuated 6 L canister, immediately followed by the aerosol being sprayed into the centre of the chamber. The aerosol can was weighed before and after being sprayed to determine the weight of product dosed into the chamber. One spray lasted approximately 1 second and released, on average, 0.6 g of product.

The sample would be allowed to mix in the chamber for 10 minutes, after which a 20 mL chamber sample would be drawn. The chamber would then be opened, the fans repositioned to point outward, and all internal chamber surfaces wiped thoroughly with dry tissue paper. The chamber would then be left to vent until the next sample, between 45 and 50 minutes. The fans would be placed in their initial inward position before the chamber door was next closed.

Instrument methodologies

A Voice200 ultra SIFT-MS (Syft Technologies, Christchurch, New Zealand) was employed for characterisation of the mixing and concentration profile within the chamber, and to confirm that full mixing had occurred at the point of sampling. The SIFT-MS was operated in selected ion monitoring (SIM) mode. Details of the reagent and product ion masses can be found in SI Table 1. Sample was drawn from the chamber at a flow rate of 100

Table 1 BAMA product categories and total number of cans filled in 2022 in the United Kingdom, and estimated corresponding proportion using different propellant types

Product category	Cans filled	HAP	Alternative	BOV	DME
Insecticide sprays excluding insect repellents or pet flea sprays	8 514 000	1	0	0	0
Paints and lacquers automotive, household, clear varnish and decorative	37 705 000	0.65	0.05	0	0.3
Air fresheners	1.75×10^8	0.95	0.05	0	0
Furniture polish	10 321 000	0.9	0.1	0	0
Shoe and leather treatment	3 607 000	0.95	0	0.05	0
Starches, fabric finish sprays	3 347 000	1	0	0	0
Oven cleaners	5 066 000	1	0	0	0
Hard surface cleaners	18 899 000	0.9	0.1	0	0
Other household products	57 183 000	1	0	0	0
Shaving soaps, creams, lathers and gels	1.56×10^8	0.5	0	0.5	0
All types of haircare products	1.69×10^8	0.4	0	0.1	0.5
Hairspray					0.5
Dry shampoo		0.4			
Styling mousse		0.05		0.05	
Perfumes and colognes	8 050 000	1	0	0	0
Deodorants/body sprays	2×10^8	1	0	0	0
Antiperspirants	4.27×10^8	1	0	0	0
Other personal care products	15 558 000	0.95	0	0.05	0
Suntan and bronzing products	1 957 000	0.8	0	0.2	0
Sunscreen		0.4			
After sun		0.4			
Artificial tanning		0.1		0.1	
Medical and pharmaceutical products	30 730 000	0.8	0	0.1	0.1
Flea sprays and all veterinary products	345 000	1	0	0	0
All products for the car or cycle – EXCEPT paints and lacquers	16 416 000	0.95	0	0.05	0
Industrial aerosols	45 614 000	0.9	0	0.1	0
Food products excluded pet products	117 000	0.7	0	0.3	0
Miscellaneous	1 473 000	1	0	0	0

mL min^{-1}. Three representative VOCs, ethanol, butane, and 2-propanol were chosen to evaluate the aerosol product emission and mixing profile. We note that butane concentrations cannot be quantitatively determined using SIFT-MS due to the presence of isobaric interference from other alkanes potentially in the sample, but the measurements provide qualitative information on mixing.

In isolation SIFT-MS does not provide sufficient analytical resolution to confidently assign detected masses to all individual VOCs in aerosol products so a separate parallel method of analysis was used based on GC.

The GC-FID-QMS instrumental methodology has been described in detail in Warburton *et al.* (2023).[8] Briefly, an Agilent 7890A Gas Chromatograph (Agilent Technologies, CA, USA)

Table 2 BAMA aerosol product categories apportioned into three NAEI categories that meet NECD/EMEP reporting norms

| Carcare	Household	Cosmetics and toiletries
All products for the car or cycle – EXCEPT paints and lacquers	Insecticide sprays excluding insect repellents or pet flea sprays	Shaving soaps, creams, lathers and gels
	Paints and lacquers automotive, household, clear varnish and decorative	All types of haircare products
	Air fresheners	Perfumes and colognes
	Furniture polish	Deodorants/body sprays
	Shoe and leather treatment	Antiperspirants
	Starches, fabric finish sprays	Suntan and bronzing products
	Oven cleaners	Medical and pharmaceutical products
	Hard surface cleaners	
	Other household products	
	Flea sprays and all veterinary products	
	Industrial aerosols	
	Food products excluded pet products	
	Miscellaneous	
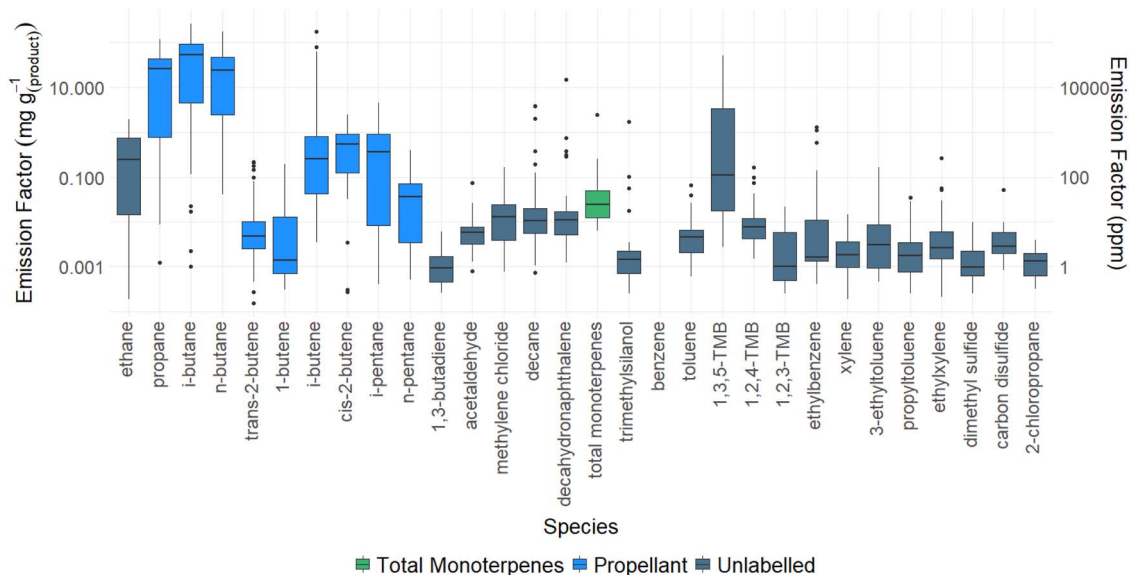
Fig. 2 Range of emission factors for 45 aerosol products tested using a specific trace benzene-tailored methodology with Nafion membrane. Unlabelled – compounds not found on the product ingredients lists. Total monoterpenes represents the summed total of 22 species. Xylene – sum of o-, m-, and p-xylene.

coupled to a custom thermal desorption unit (TDU) and fitted with flame ionisation detectors (FID) and an Agilent 5977A Quadrupole Mass Spectrometer (QMS) (Agilent Technologies, CA, USA) was used to identify and quantify VOC concentrations. The test chamber was connected directly to the TDU, whilst the background canisters were connected to the TDU through a sampling manifold comprising 16 pneumatically actuated solenoid valves (Swagelok BN series, OH, USA) connected together into one sampling line which then attached directly to the TDU. 20 mL was withdrawn for both chamber and background canister samples. Following drying through a −40 °C water trap and after pre-concentration at temperatures no higher than −110 °C, samples were finally re-focussed on a capillary trap at temperatures no higher than −110 °C and subsequently desorbed at ~200 °C onto the GC column following trap desorption. Analytes were initially separated on a 60 m long, 150 μm internal diameter (ID) VF-WAX column with a film thickness of 0.50 μm (Agilent Technologies, CA,

USA). Unresolved analytes were diverted onto an Na_2SO_4-deactivated Al_2O_3 porous-layer open tubular (PLOT) column (50 m × 320 μm ID, with a film thickness of 5 μm, Agilent Technologies, CA, USA) using a Deans switch, (Agilent Technologies, CA, USA), for separation and detection by FID. At 8.3 minutes, once the unresolved analytes had passed through, the Deans switch was deactivated and resolved analytes continued onto a length of fused silica tubing (2 m × 150 μm ID), which was subsequently split between the second FID and the QMS for simultaneous detection through sections of 150 μm ID fused silica tubing of length 0.91 m and 2.1 m, respectively. Quantification of VOCs was largely based on FID peak integration with MS data used when mass resolution was required to deconvolve overlapping or coeluting peaks. A thirty-component mix of 4 ppb non-methane hydrocarbons (NMHC) in nitrogen provided by the National Physical Laboratory, Teddington, UK, cylinder number D933515 (hereafter referred to as 'NPL 30'), was used for quantification of the components contained therein while
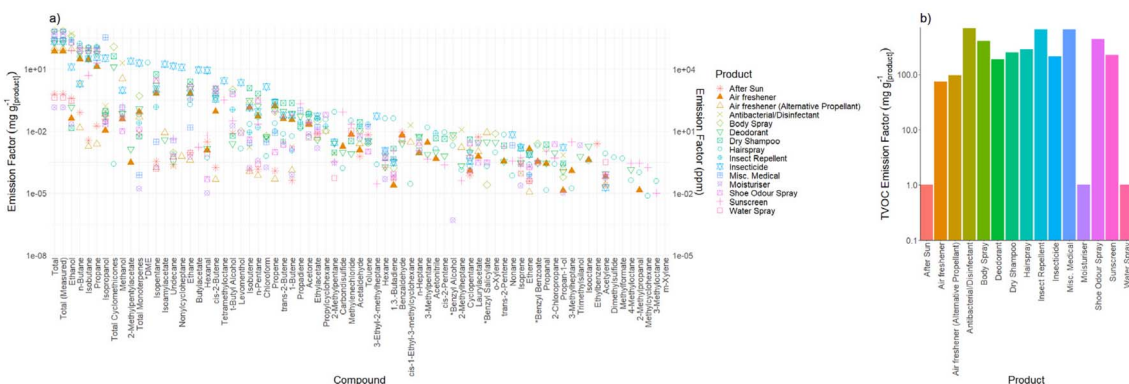

Fig. 3 (a) Average emission factor per gram of product for each product class. * – estimated compounds. Left-hand axis in units of mg $g_{[product]}^{-1}$, right-hand axis in units of ppm. (b) TVOC for each product class in units of mg $g_{[product]}^{-1}$.
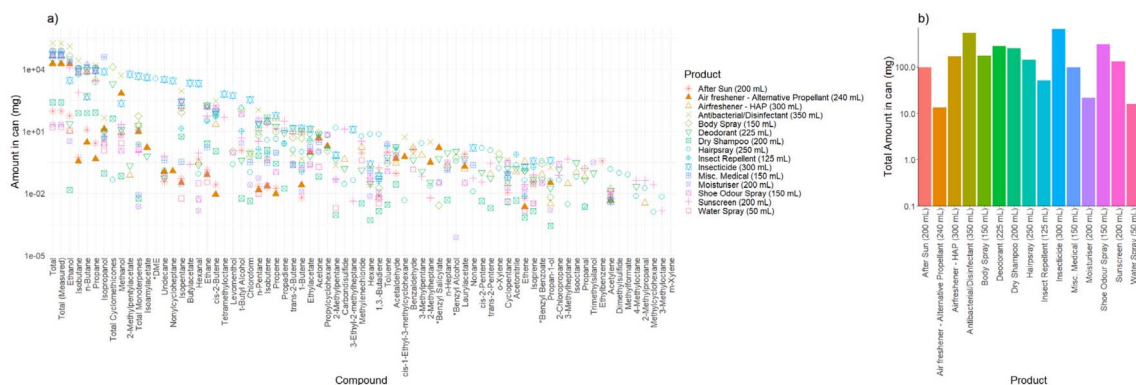
Fig. 4 (a) Average VOC emission per can for each product class in mg. * – estimated compounds. (b) Total VOC per can for each product class in mg.

equivalent carbon responses were used to quantify other species. System and carrier gas contamination was quantified using a sampling method which drew no sample through the TDU ports, but left carrier gas flowing through the TDU traps for the same time duration as would normally be used in a sample method ('no flow blank').

Trace benzene method

A specific set of analytical conditions were needed to determine the presence or absence of trace levels of benzene within sample aerosols. A challenge in quantifying very small amounts of benzene in aerosols is potential co-elution with ethanol when using GC methods; ethanol is often found at a much higher concentration within the aerosol. The use of SIFT-MS in isolation is also inadequate for benzene confirmation due to its potential isobaric interference in complex mixtures since the

diagnostic ion is also produced *via* fragmentation of many other VOCs and subject to interference. To support FID quantification of benzene at ppt mixing ratios, a Nafion MD-070-96 coil (Perma Pure LLC, NJ, USA) was added to the chamber sample recirculation line to remove most ethanol from the sample stream. Other oxygenates such as other alcohols, esters, aldehydes and ketones were also removed or experienced significant reduction in concentration. Chamber samples were passed through the Nafion at a rate of 2.5 L min^{-1}, while dry, highly purified air free of VOCs ('blank gas') was used as a purge gas at a rate of 6 L min^{-1}. Blank gas was produced by passing compressed air dried to a −35 °C dew point through a bed of platinum beads at 400 °C. With most ethanol removed from the sample a custom Dean switching method was used to isolate benzene and allow for FID quantification on the PLOT column, with detection limit of 0.004 ppb.

Table 3 Calculated annual UK TVOC for each product category in ktonne. The full dataset detailing every compound can be found in SIE 3

Product category	Total UK VOC emission (ktonnes)
Insecticide sprays excluding insect repellents or pet flea sprays	0.23
Paints and lacquers automotive, household, clear varnish and decorative	1.08
Air fresheners	1.60
Furniture polish	0.29
Shoe and leather treatment	0.11
Starches, fabric finish sprays	0.10
Oven cleaners	0.16
Other household products	1.75
Shaving soaps, creams, lathers and gels	3.34
All types of haircare products	3.37
Perfumes and colognes	0.25
Deodorants/body sprays	10.87
Antiperspirants	6.87
Other personal care products	0.18
Suntan and bronzing products	0.02
Medical and pharmaceutical products	0.77
Flea sprays and all veterinary products	0.01
All products for the car or cycle – EXCEPT paints and lacquers	0.49
Industrial aerosols	1.31
Food products excluded pet products	0.002
Miscellaneous	0.05
Hard surface cleaners	1.52
Total	34.37

A-C: Aerosols – Carcare
A-C&T: Aerosols – Cosmetics and Toiletries
A-H: Aerosols – Household
NA-Ad: Non-aerosol – Adhesives
NA-Au: Non-aerosol – Automotive
NA-C&T: Non-aerosol – Cosmetics and Toiletries
NA-H: Non-aerosol – Household
NA-PT: Non-aerosol – Paint Thinner
P-R: Paint – Retail
P-T: Paint – Trade

2-Prop: 2-Propanol
But: Butane
Dec: Decane
Eth: Ethanol
Lim: Limonene
Meth: Methanol
Non: Nonane
Prop: Propane
TC: Total Cyclomethicones
Und: Undecane
US: Unspeciated

Fig. 5 (a) NAEI current estimate of consumer product sector contributions to UK annual TVOCs. (b) Consumer product sector contributions to UK annual TVOCs using measured data for aerosol sectors. Pink – aerosol products. Blue – non-aerosol products. The consumer product sector is made up of aerosols (carcare, household, and cosmetics and toiletries), non-aerosols (automotive, cosmetics and toiletries, household, and paint-thinner), and paint (trade and retail).

Data processing methods

SIFT-MS data acquisition and analysis was carried out using Labsyft Pro (version 1.8.1, Syft Technologies).

Chromatograms were integrated using GCWerks software (GC Soft Inc., CA, USA) and using the NPL 30 standards with concentrations for each species reported in µg m^{-3}, converting from a mixing ratio to mass concentration using the ideal gas

law (temperature 298 K, pressure 1 atm, assuming ideal gases), correcting for background VOC concentrations and no flow blanks. Emission factors were then reported in units of mg g$_{[product]}^{-1}$.

Calculation of total UK VOC emissions from aerosolised consumer products

Whilst the combination of SIFT-MS and GC-FID-MS was comprehensive for speciation, there are a number of other VOCs (found in a small number of products) that could not be quantified using either method but are known to be present in aerosol products. These are dimethyl ether (DME), benzyl alcohol, benzyl benzoate, and benzyl salicylate. In order to capture them in later calculations of emissions their amounts must be estimated based on likely fractional composition of product relative to other quantified species. Since exact chemical compositions are not provided on labelling, ingredient lists were used to infer unmeasured compound amounts to likely alternative VOCs. For DME the mass amount was mapped to ethanol, and for benzyl alcohol, benzyl benzoate, and benzyl salicylate to a fragrance compound (either isoamyl acetate, total monoterpenes, lauryl acetate, or benzaldehyde, dependent on what was present in the sample).

Analytical measurements yielded data in the form of mg of VOC per gram of product used (mg g$_{[product]}^{-1}$), calculated by dividing the data acquired by the amount of product dosed into the chamber. In order to calculate total VOC mass from an individual canister the density of the product had to be determined as product filling is expressed as a volume in units of mL. Six new aerosol products were purchased (furniture polish, hairspray, deodorant, dry shampoo, insecticide, and air freshener), weighed, their contents emptied, and then weighed again. Product densities for each product type were then calculated using eqn (1) and (2).

$$\text{Weight of contents (g)} = \text{weight of full can (g)} \\ - \text{weight of empty can (g)} \quad (1)$$

$$\text{Product density}(\text{g mL}^{-1}) = \frac{\text{weight of contents(g)}}{\text{filling volume(mL)}} \quad (2)$$

These data can be found in SI Table 2.

The overall amount of VOC from each aerosol canister was then calculated using eqn (3). For product classes where density was not calculated, an average density of 0.75 g mL^{-1} was used. Data on average canister size can be found in SI Table 3.

$$\text{TVOC in can (mg)} = \text{species concentration (mg g}_{[product]}^{-1}) \\ \times \text{product density (g mL}^{-1}) \times \text{average can size (mL)} \quad (3)$$

Publicly available data on the number of aerosol cans filled in the UK has been used to scale total VOC (TVOC) emissions from each product type to yield a bottom up total UK VOC emission estimate from all aerosol products. These fillings data can be found on the British Aerosol Manufacturers' Association website (https://bama.co.uk/library/232), Annual Reports and Accounts 2022–2023, page 13, 2022 BAMA FILLING

Table 4 NAEI Category TVOC emissions from aerosol products for 2022, values calculated in this paper, and differences between these two values

Category	NAEI data (ktonne)	This work (ktonne)	Difference (ktonne)
Carcare	20.12	0.49	−19.63
Household	7.07	8.22	+1.15
Cosmetics and toiletries	44.59	25.67	−18.92
Total aerosols	71.78	34.37	−37.41

FIGURES.[21] Fillings are reported in 22 categories (Table 1, columns 1 and 2). For each of these categories, an average TVOC emission is estimated considering the varied VOC speciation and composition differences that exist between product classes. The product categories 'all types of haircare products' and 'suntan and bronzing products' have been split into sub-categories: hairspray/setting spray, dry shampoo, and styling mousse, and sunscreen, aftersun and artificial tanning respectively, as we have more detailed product speciation data for these based on our measurements.

Not all aerosols use HAP however, so alternative propellants need to be taken into account in the overall inventory estimations. Alternative propellants include N_2, CO_2 and compressed air. Some products are bag-on-valve (BOV) where the product is contained within a separate bag within the canister, which itself is surrounded by an alternative, non-HAP propellant. BOV is mostly used for products requiring 360° application, where the product can be sprayed upside down, such as sunscreen. For each product class, we have estimated the proportion of those products which use each of the propellant types (Table 1, columns 3–6).

For product categories where there was viable measurement data (insecticide, air fresheners, hard surface cleaner, body sprays, antiperspirants (labelled as deodorants), hairspray, dry shampoo, sunscreen, and after sun) an average speciation was taken of all the products sampled from each category, and an average total to represent an HAP filling for that product category. These individual product characteristics were then multiplied by the corresponding filling statistics and HAP/non-HAP proportion (eqn (4)). One alternative propellant air freshener was also sampled, and this data used as the alternative propellant speciation for that product category. The medical and pharmaceutical HAP category was calculated using averages from the shoe odour spray and insect repellent measurement data. Moisturiser aerosol data was used as a proxy for the other personal care products category BOV calculations.

All other category/propellant filling not estimated directly using measurements, were assigned as having an averaged speciation calculated. HAP average was calculated by using the mean of insecticide, air freshener, dry shampoo, deodorant (antiperspirant), sunscreen, shoe odour spray, insect repellent, hairspray (not including the product containing DME), and antibacterial surface spray/disinfectant. Moisturiser, aftersun, and misc. medical measurement data was used to calculate the average BOV speciation. We are assuming these are BOV based on the absence of HAP propellants. Alternative propellant air freshener measured product was used to calculate the average alternative propellant speciation. Average DME speciation was
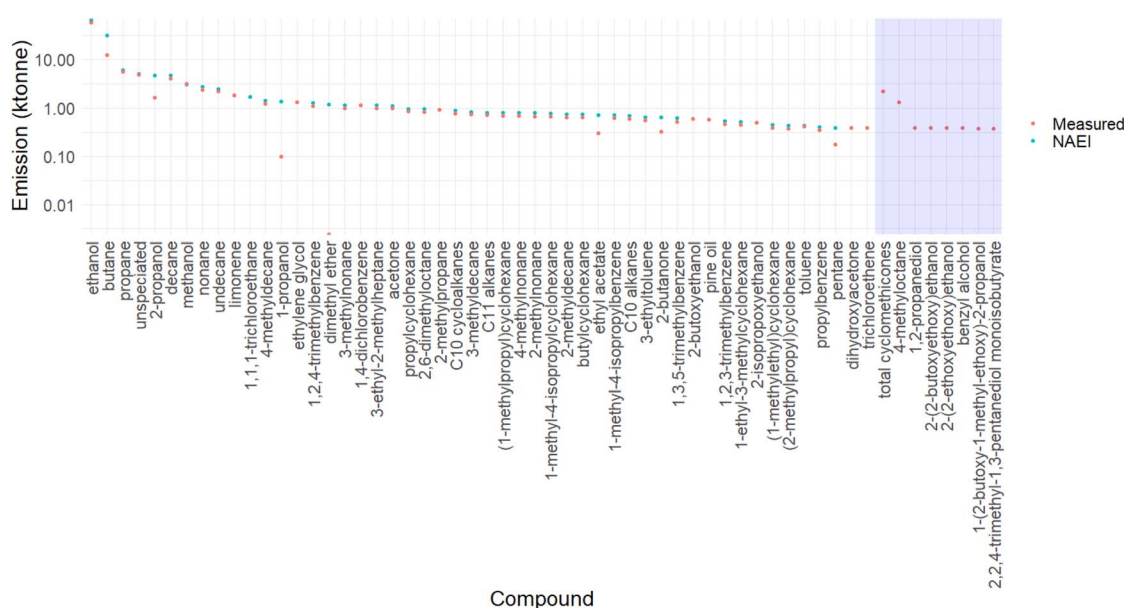
Fig. 6 Highest 50 VOCs from indoor sources 2022 as reported in the NAEI. Both data from the NAEI and our measurements are plotted. Compounds in the blue square are not present in the NAEI highest 50, but are when measurements from this paper are included.

determined by using the average HAP speciation for all compounds except for DME, iso-butane, n-butane, and propane. These compounds used the speciation from the one DME product measured, a hairspray product.

Total VOC for each product category was determined using eqn (5) (summing the VOC estimations for each propellant type).

$$\begin{aligned}\text{Average VOC emissions for propellant type}\\ \times \text{ product category filling amount}\\ \times \text{ proportion of propellant type for}\\ \text{product category}\end{aligned} \quad (4)$$

$$\begin{aligned}\text{Total for product category}\\ = \text{HAP} + \text{BOV} + \text{DME} + \text{alternative propellant}\end{aligned} \quad (5)$$

The fillings figures reported in the BAMA Annual Reports and Accounts are for aerosol products produced in the UK, rather than consumed. 70% of this production total are exported, leaving 30% to be used/dispensed in the UK. Products manufactured in the UK comprise 60% of the total consumed in the UK. Lab measurements are of a basket of products that include UK manufactured and imported and so the speciation averages reflect this mix. Overall mass amounts emitted in the UK are then corrected for these import/export flows.

The bottom-up estimation of emissions reported here are then compared with those currently estimated in the NAEI (2022 reporting inventory). To allow for comparability, a matching is needed between three NAEI inventory categories and BAMA industry reporting (22 product categories). This is shown in Table 2.

Results and discussion

Is there evidence for trace benzene in UK aerosol products?

Fig. 2 shows the combined hydrocarbon speciation from all 45 aerosol products screened in this study using a method tailored for trace benzene quantification. No benzene was found in any of the samples of UK-purchased aerosol products above a method detection limit of 0.004 ppb (0.012 ppb limit of quantification). Whilst the role and purpose of some VOCs is clear – labelled for example as propellant or fragrance, many other VOCs are present at low concentrations, but that are unlikely to be deliberately included for functional reasons and that are not listed on the ingredients list.

Measuring furniture polish aerosols

There were difficulties in analysing the four furniture polish products due to the large quantity of hydrocarbons present in the formulations. The hydrocarbons caused a large baseline drift on the chromatogram at retention times where species such as ethanol, methanol, and monoterpenes usually eluted. These may have artificially inflated the concentrations of these species due to coelution that only occurs with said hydrocarbons. Therefore, the furniture polish data has been removed from the following data sets, and has not been used for any of the TVOC calculations.

Full aerosol product speciation

Fig. 2 showed a speciation that deliberately excluded some oxygenated VOCs in order to support benzene detection. In Fig. 3 and 4 the averaged speciation for each product class is shown using a GC methodology that includes more polar species. Full emission factors and the TVOC emitted per can for each individual product can be found in SI Spreadsheets 1 and 2. A total of 70 measured and four estimated (DME, benzyl alcohol, benzyl salicylate, and benzyl benzoate) VOC species are reported across the 41 products sampled and reported (furniture polish not reported here).

Results from the full speciation chamber experiments are presented in Fig. 3 as an average per gram product, and in Fig. 4 as a total amount (mg) emitted from each aerosol canister used. Both monoterpenes and cyclosiloxanes have been reported as totals due to uncertainty reporting individual compounds, as compound rearrangement is common. Monoterpenes were mostly dominated by eucalyptol and limonene.

Unsurprisingly, HAP products emit the most TVOCs, followed by those propelled by DME. We note that only one DME product was sampled, 3 BOV and 1 alternative propellant, so these datasets are limited.

Three product classes have noticeably lower VOC emission factors per can of product used: aftersun, moisturiser and water spray. The first two we believe to be BOV due to their low HAP content, and the latter known to be propelled by nitrogen (which we classify as alternative propellant). We highlight this since it demonstrates that products using alternative propellant methods can have low emissions and that regular evaluation of products in use is needed in order to keep inventory estimates current. The estimated total VOC emitted per can of aerosol for the four different propellant technology types, calculated are as follows – HAP 61.32 g, alternative propellant 19.00 g, BOV 24.30 g and DME 54.94 g.

Table 3 presents the data calculated for annual UK TVOC for each product category using consumption statistics and provides an estimate of annual UK VOC emissions from different categories of aerosol product. The full dataset detailing every compound can be found in SI Spreadsheet 3.

VOC product to species flows

To place data on VOC emissions from aerosol products in a wider context, Fig. 5 shows the current UK annual total emissions inventory data for all indoor sources (including non-aerosol), and then 'flows' that product-type mass of emissions into a VOC-mass speciation, showing how each sector contributes to emissions ordered from highest to lowest species abundance. Fig. 5a provides flows based on current total amounts and speciation, and Fig. 5b is an updated estimation using the aerosol data collected here. Two changes are immediately visible; firstly, that the contribution of compressed aerosol dispenser products to overall consumer product VOC emissions is lower than the 2022 inventory (24% of emissions, rather than 40%), and secondly, that a greater fraction of those emissions are as ethanol, rather than butane. These differences are detailed further in Table 4.

Fig. 6 presents the 50 most abundant VOCs emitted from indoor sources (as seen in Fig. 5) in the UK as reported in the NAEI in order of magnitude. By including a new aerosol emission speciation based on these species, eight new compounds enter the top 50 (highlighted in blue in Fig. 6), either due to their presence in substantial amounts in aerosols, or due to the overestimation of other species in previous assessments being reduced. They are: total cyclomethicones, 4-methyloctane, 1,2-propanediol, 2-(2-butoxyethoxy)ethanol, 2-(2-ethoxyethoxy) ethanol, benzyl alcohol, 1-(2-butoxy-1-methyl-ethoxy)-2-propanol, and 2,2,4-trimethyl-1,3-pentanediol mono-isobutyrate. Cyclomethicones are compounds which are often identified in non-aerosol consumer products,[22,23] and the NAEI is not currently reporting them. It can also be seen on Fig. 6 that 2-propanol, 1-propanol, 1,1,1-trichloroethane, ethyl acetate, 2-butanone, pentane, and DME drop lower in the rank order when the updated aerosol measurement data is used.

Comparing methods for reporting aerosol dispenser product VOC emission to the NAEI

$$\text{VOC emissions} = \sum N \times m \times \% \times S_g \qquad (6)$$

N = sales data for each subcategory, provided by market research company. m = average can fill for each subcategory, provided by market research company. $\%$ = average VOC content for each subcategory, based on generic information from formulators. S_g = average specific gravity (relative density), based on generic information from formulators.

Eqn (6) is the method currently used by BAMA to report their annual aerosol dispenser product emissions to the NAEI. The method in this paper uses a very similar calculation, but more accurate and up-to-date lab data. The information provided by manufacturers is generic so as to protect their formulations, and is limited to the TVOC content of the can. This does not provide accurate enough detail to inform the inventory in the way that our measured data does. This method also does not take into account different propellant types within the product subcategories, which may explain the overestimation of TVOC in the current NAEI.

Potential user exposure to VOCs

Potential exposure dose to aerosol dispenser products for users is dependent on a myriad of influential factors. These include the variable conditions of the room in which they are used (predominantly room size and ventilation), the site of product application (which influences the distance between the product being dispensed and the inhalation exposure pathway (nose and mouth)), and the amount of product used on application. These variables will differ significantly between product types, as they are formulated for different purposes, but also on user behaviour which is even more difficult to predict and account for.

The data presented in this paper (average emission factor per gram of product for each product class in mg $g_{[product]}^{-1}$, shown in Fig. 3 and within the SI Spreadsheet 1) could be used to calculate user exposure and inhalation dose if the aforementioned variables are known, or if they have been calculated.

Conclusions

Given the relatively large fraction of national VOC emissions that can arise from aerosolised products in high income countries, measurements of aerosol dispenser product VOC speciation and amounts are an important prerequisite to accurate inventory reporting. Whilst the UK NAEI inventory is considered internationally state of the art in terms of its detail and representation of VOCs, a number of VOCs are found to be emitted in substantial amounts in these measurements that are not reported in the inventory. This likely arises because of continual reformulation of products and changes since the last inventory speciation more than two decades ago. We note that using a bottom up approach to estimate emissions highlights that some previous iterations of the UK inventory likely over-estimated the emissions from aerosol products, and we note that very recent inventory recalculations of emissions are closer to those estimated here.

Since aerosol formulations are varied and change as new technologies are developed there should be a regular re-appraisal of product VOC emissions, needed to help support accurate international inventory reporting, but also to ensure that accurate emissions are included in indoor and outdoor modelling of air quality.

This study has tested for VOCs released at point of use and highlights that some VOCs are present that likely were not intentionally included in the original ingredients and can be classed as contaminants or degradation products. For example, it is known that some bulk VOC raw ingredients may contain feedstock contaminants. It is likely that the aromatic VOCs identified in this paper are most likely from feedstocks rather than from product packaging, or from reactions occurring inside the canister. However, further work would be required to confirm this.

Whilst there is industry-wide acknowledgement of the need for the long-term reduction of VOCs emitted from aerosol products it should be noted that simply replacing the HAP with BOV or alternative propellants may not reduce overall the total amount of VOC released, although it may change the speciation. Some products require a solvent for performance purposes beyond aerosolization, where simple alkanes such as butane may be replaced with ethanol or another solvent. Some products, however, may be technically reformulated to replace HAPs without the need for an alternative organic solvent. Reducing HAP emissions from those products that can be reformulated offers a route to reduce VOC emissions from the aerosol and household/personal care product sector as a whole.

Author contributions

A. M. Y. conceived the experiments, conducted the experiments, analysed the results, interpreted the data, and drafted the work. T. W. conceived the experiments, conducted the experiments,

analysed the results, and drafted the work. N. K. S. conducted the experiments, analysed the results, and drafted the work. S. J. A. provided technical support, designed and built the TDU and GC analytical systems, substantively revised the work. M. S. provided technical support and substantively revised the work. J. R. H. provided technical support and substantively revised the work. A. C. L. conceived the experiments, interpreted the data, and drafted the work. All authors have reviewed and approved the manuscript.

Conflicts of interest

The authors declare no competing interests.

Data availability

The data presented in this study are available in supplementary information (SI), accessible at https://pure.york.ac.uk/portal/en/persons/amber-yeoman/datasets/. Supplementary information: spreadsheets - updated speciation of VOCs emitted from European-market aerosol dispenser consumer products, DOI: https://doi.org/10.15124/d2cc4117-e30c-4fa7-b2cb-af1805a8e269. Further data available on request. See DOI: https://doi.org/10.1039/d5ea00102a.

Acknowledgements

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