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

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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 behavior 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. Proton transfer mass spectrometry 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.

KEYWORDS

fragrance, indoor air quality, mass spectrometry, personal care products, PTR-MS, VOCs

1 | 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.¹ 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.^{2–8} 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,^{9–11} along with several other conditions broadly characterized as “fragrance sensitivity” which includes the effects of both inhalation and

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dermal routes of exposure.¹² 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 labeling 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,^{13–15} 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)¹⁶ 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.¹⁷ Limonene in particular has been reported previously by Carslaw and Shaw (2019)¹⁸ to be one of the most relatively impactful VOCs on indoor chemistry due to its high potential for SOA and formaldehyde formation.^{19–27} World Health Organization Guidelines²⁸ for Indoor Air Quality determine the exposure limit for formaldehyde to be 0.1 mg/m³ (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.⁸ 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,^{29–31} the use of modeling,^{32,33} analysis of air samples,³⁴ direct analysis of consumer products themselves,³⁵ and combinations of these methods.³⁶ 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

Practical Implications

- Showering is a common activity that can use multiple personal care products; each event is seen to release milligram quantities of VOCs such as limonene, benzyl alcohol, and ethanol, and this can perturb transient indoor concentrations.
- Within a shower room, the amount of VOC emitted varies widely between different users even if the raw materials and timing of their use are carefully controlled for.
- A personal care product may not emit all its available VOC content to air when used because of solubility effects and because of limited time for volatilization before being washed away.
- Real-world emissions of VOCs from PCPs used in a shower setting are lower by up to an order of magnitude than would be calculated based on emissions assessed in the laboratory using controlled evaporation rates and knowledge of product formulation.

activities such as showering. Known carcinogens and toxicants, such as trihalomethanes and chloroform, have already been identified as harmful compounds released during showering.^{37,38} 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),³⁹ 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 behaviors. As previous work has measured simplified PCP compositions, we show here, through temporal profiles, the reproducibility between participants while those products are in-use.

1.1 | 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 m³). 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 1.

$$\text{ACH} = \frac{\text{Ventilation Rate} \times 3600}{\text{Volume of Room}} \quad (1)$$

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, moisturizer, 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 1 below.

1.2 | VOC sampling

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^{40–42}; 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 (H₃¹⁸O⁺) and its first cluster *m/z* 37 (H₃¹⁶O H₂¹⁶O⁺) 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 showing 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 H₃O⁺ primary ion count ranged between 1.71 and 8.96 x 10⁶ ion counts per second (cps) with a mean of 3.85 x 10⁶ cps. The *m/z* 37 cps ranged between 1.68 and 8.44 x 10⁵ with a mean of 5.77 x 10⁵, 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 2.

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),⁴³ Wang, Spanel, and Smith (2004),⁴⁴ and Spanel and Smith (1997).⁴⁵

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.⁴¹ Instrument limits of detection (LoDs) for 1 min averaged data were determined by the method outlined by Taipale and colleagues (Taipale et al., 2008)⁴⁶ 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 Supporting Information 1 summarizing the order in which to apply

TABLE 1 Product usage estimates were taken as the median usage assumption data from Yeoman et al (2020)

Product	Amount used (g)	Time of use (s)
Face wash	2	60
Shower gel	4	180
Shampoo	4	120
Conditioner	6	120
Moisturizer	5	120
Aerosol deodorant	-	4

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

TABLE 2 Compound product ions and corresponding significant fragmentation ions, used to calculate fragmentation coefficients

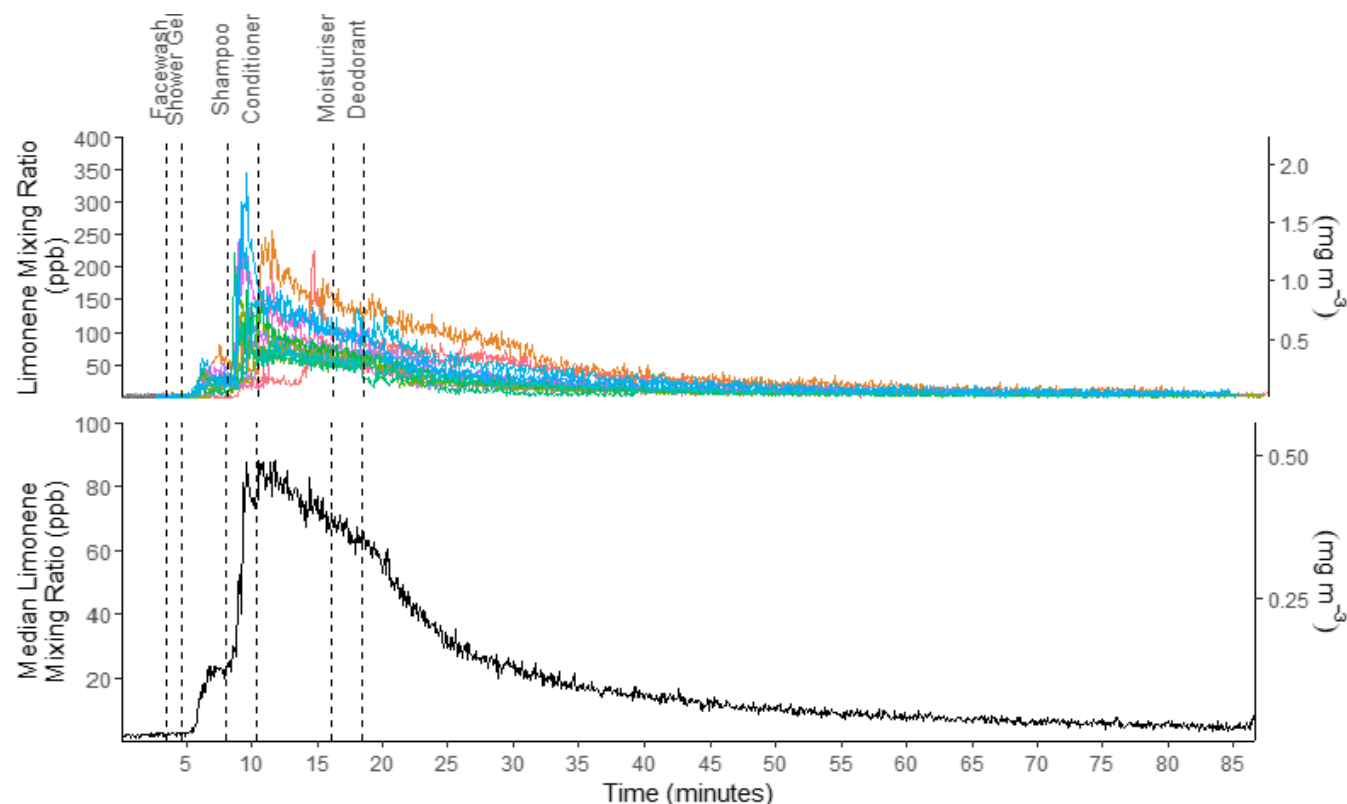


FIGURE 1 VOC evolution profile of limonene. Top: Data from all 18 participants. Bottom: Median participant VOC profile

the products and how long for. They were given 3 min between the use of conditioner and moisturizer 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 (Supporting Information 2) 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)¹⁶ were calculated using Equation 2.

$$\text{Product emitted} = \text{emission factor}^{\dagger} \times \text{amount used}^{\ddagger} \times \text{time of use}^{\S(2)}$$

[†]From Yeoman et al (2020)¹⁶; [‡]From Table 1.

2 | RESULTS AND DISCUSSION

2.1 | 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 Supporting Information 3, showing the

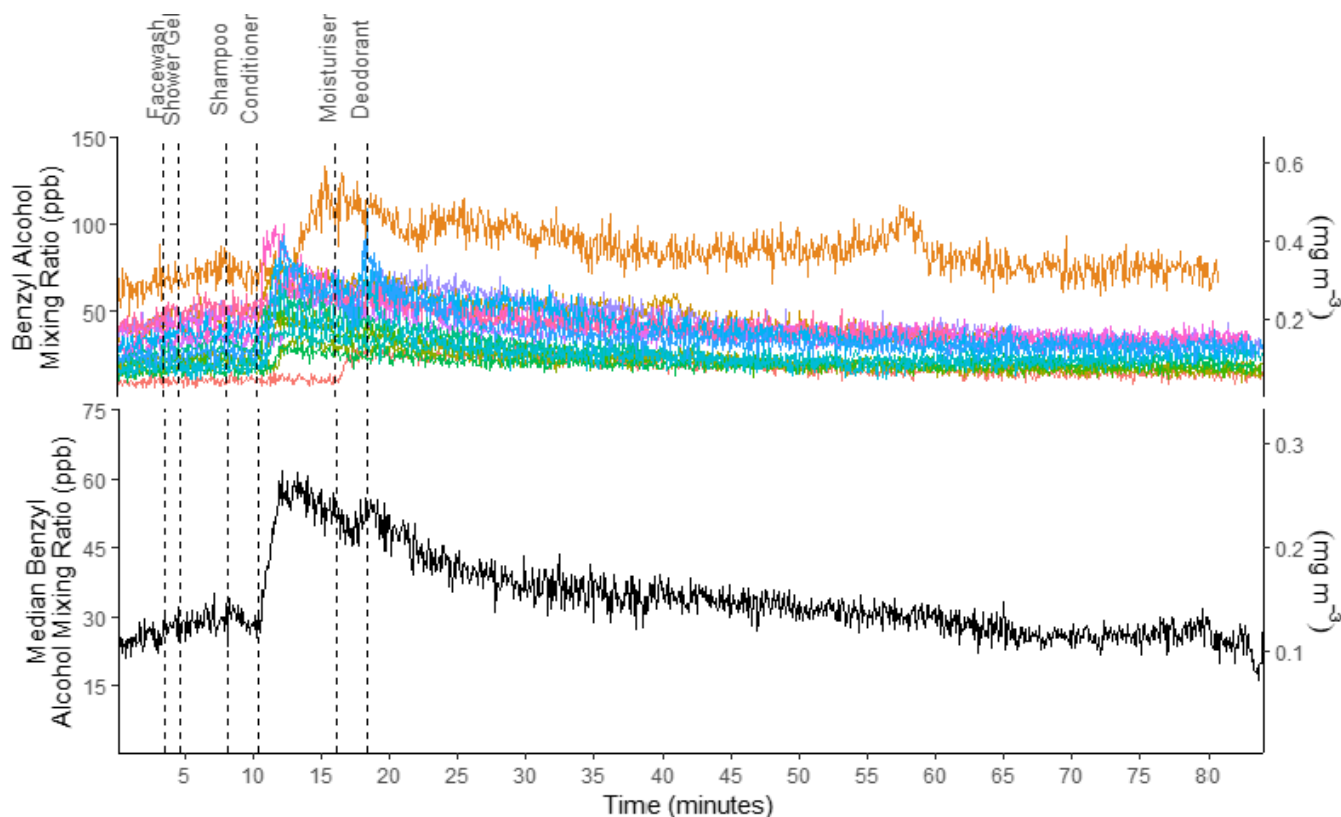


FIGURE 2 VOC evolution profile of benzyl alcohol. Top: Data from all 18 participants, Bottom: Median participant profile

concentrations arising indoors from a single participant that is reproducible to within a factor of two for most VOCs.

The shower data from all 18 participants are presented as temporal profiles for each compound (Figures 1-3) where each colored 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.

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 Supporting Information 4, with Figure 4 displaying the variation between participants, and a summary in Table 3.

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 modeled in Yeoman et al (2020).¹⁶ In Table 4, we calculate the estimated “bottom-up” emissions of limonene and benzyl alcohol based on emissions in Yeoman et al (2020)¹⁶ using Equation 2, 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.

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 1. The main benzyl alcohol peak can be attributed to conditioner (Figure 2), with moisturizer seeming to be the main contributor to the emission of ethanol (Figure 3). 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)³⁹ report up to $0.07 \text{ mg}/\text{m}^3$ emitted from the use of a high-emitting HCP, while another real-life product-use study, Singer et al (2006),³⁶ reports much higher limonene, as 1-h average concentrations, from the use of surface cleaner ($0.96\text{--}2.5 \text{ mg}/\text{m}^3$) and a floor cleaner ($1.13\text{--}6.2 \text{ mg}/\text{m}^3$) at different dilutions. Residential and workplace air-sampling studies report maximum limonene concentrations of $0.49 \text{ mg}/\text{m}^3$ (Edwards et al, 2001⁴⁷) to as low as $0.05 \text{ mg}/\text{m}^3$ (Su et al,

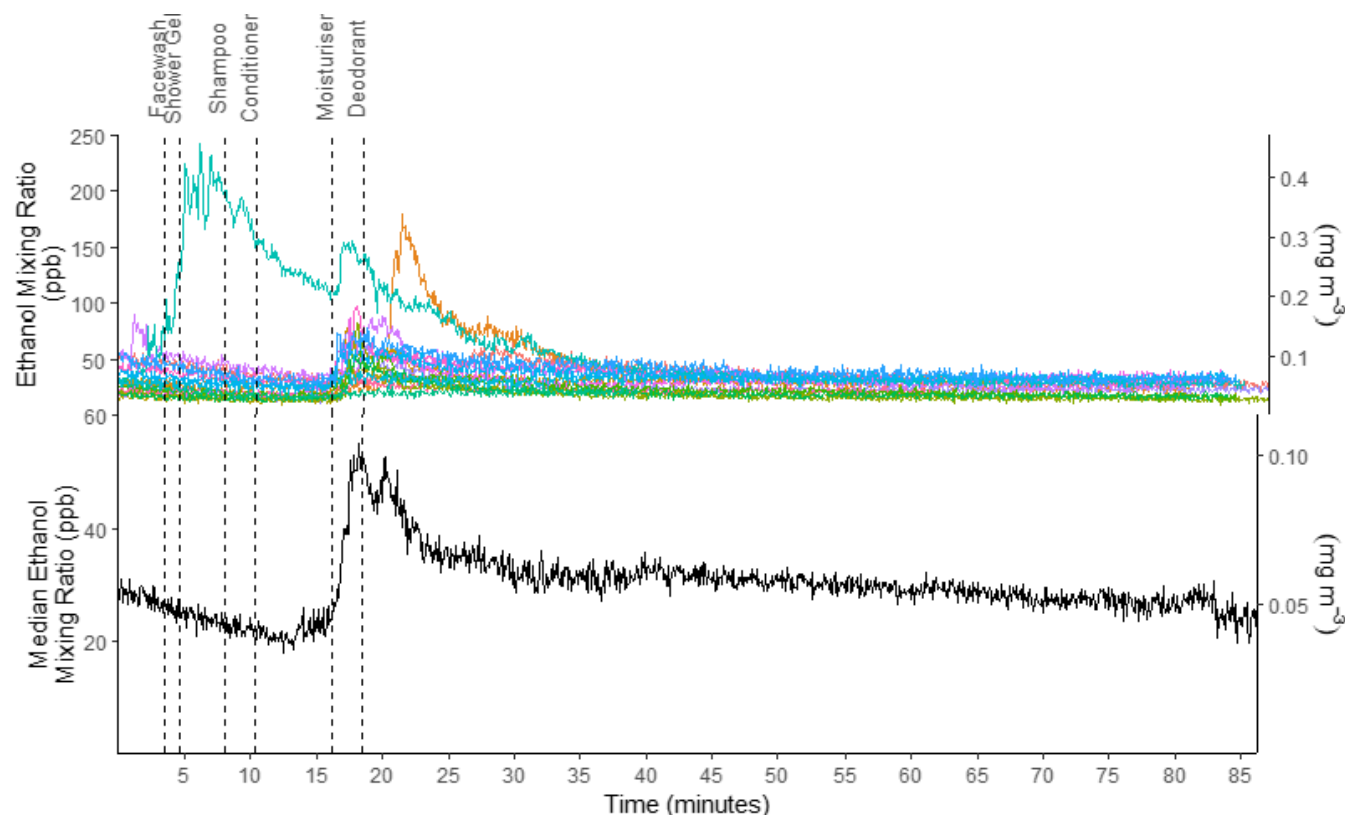


FIGURE 3 VOC evolution profile of ethanol. Top: Data from all 18 participants. Bottom: Median participant profile

2018³⁴). Our shower activity experiments yield results toward the higher end of this range; Figure 1 shows a median limonene peak of around 0.5 mg/m^3 , with a maximum of 2 mg/m^3 reached.

Table 5 presents the median emission rate for each compound, with full per person emissions rates detailed in Supporting Information 5.

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 Supporting Information 6 and 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.

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.

2.2 | 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 ($\log K_{ow}$) 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 moisturizer 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 Supporting Information 8). The behavior 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 (Supporting

FIGURE 4 Variation in total mass of limonene, benzyl alcohol, and ethanol emitted to air over the 15-min activity window, having taken ventilation rate and room size into consideration

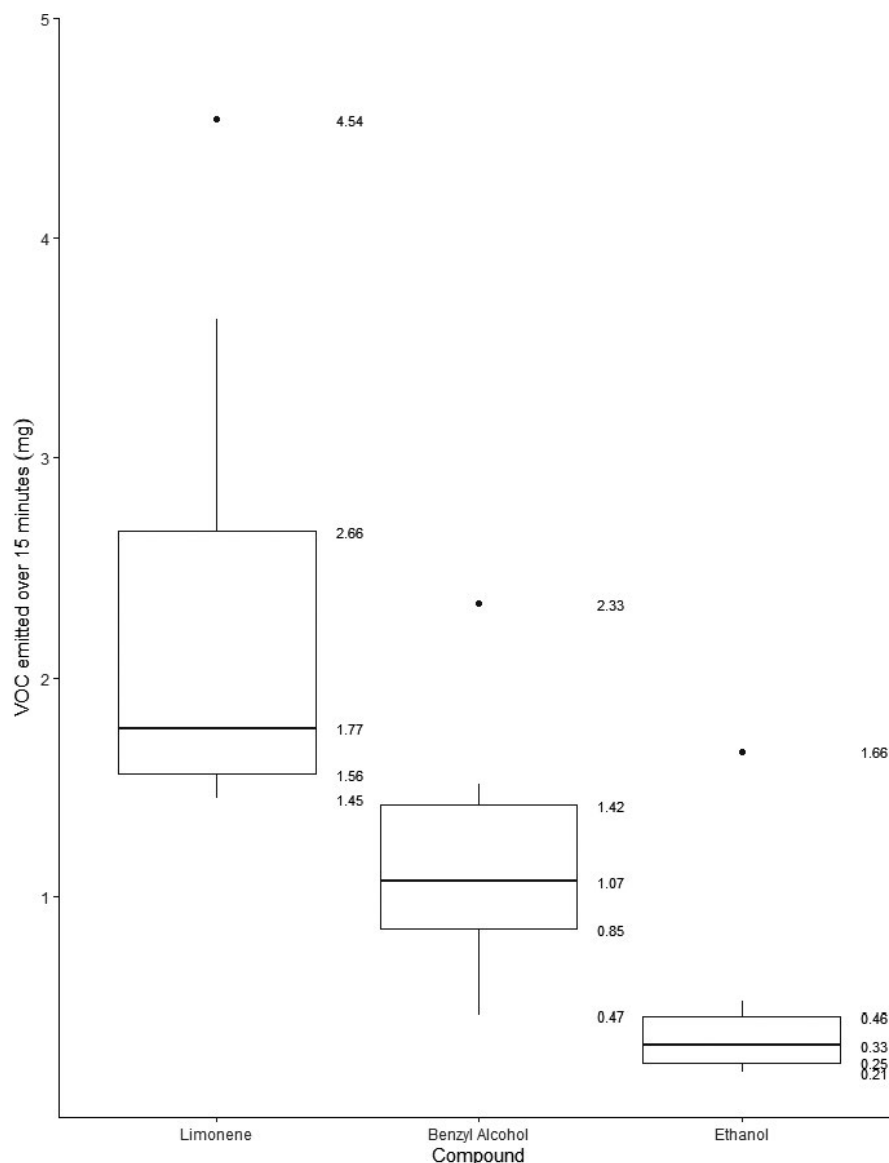


TABLE 3 Summary of variation between participants

	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

Information 9 and 10), which were determined to be present in consumer products by Yeoman et al (2020),¹⁶ 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.

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,⁴⁸ and there is evidence it could be used as an enhancer for drug delivery for this reason.^{49,50} Consequently, this may have a pronounced effect on the amount of limonene available for evaporation.

TABLE 4 Bottom-up and top-down estimates using emission factors calculated in Yeoman et al (2020),¹⁶ product usage estimates found in Table 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
Moisturizer	0.3	0.1
Conditioner	1.2	0.5
Total (bottom-up) ^a	21.4	1.4
Median (top-down) ^b	1.8	1.07

^aSum of shampoo, shower gel, moisturizer, and conditioner, calculated using Equation 1.

^bValues taken from Figure 4

TABLE 5 Median emission rates calculated from all 18 participants using total mass emissions data found in Supporting Information 4

	Emission Rate (μg/s)		
	Limonene	Benzyl alcohol	Ethanol
Median	2.02	1.19	3.65 × 10 ⁻¹

Although also dermally absorbent,⁵¹ 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 4.

The production of secondary pollutants is possible, formaldehyde in particular from the reaction of limonene with OH radicals, and subsequent unimolecular decomposition.⁵² 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.⁵³ 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 Supporting Information 11 is different in both its shape and magnitude to that modeled in Yeoman et al (2020),¹⁶ 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.

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 | CONCLUSIONS

Having observed the emissions from the real-life usage of PCPs during showering, we find that personal differences in product-use behavior 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.⁵⁴ 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.⁵⁵⁻⁵⁷ 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.⁵⁸

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).¹⁶ 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 vapor exchange could occur, in contrast to laboratory estimates which quantify VOC emissions assuming vapor 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.

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CONFLICT OF INTEREST

There are no conflicts of interest to disclose. The project complies with the ethical research approval processes at the University of York which require prior ethics assessment and independent approval at project conception, and are captured as part of the annual ethical approval process for the NCAS research program delivered at York.

PEER REVIEW

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section.

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