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Inhalation of VOCs from facial moisturizers and the influence of dose proximity

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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-moisturizers 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 moisturizer can lead to a much larger inhaled VOC dose than would be inhaled from typical indoor ambient air over 24 h (e.g., limonene up to ~×16 greater via facial application, ethanol up to ~×300). Emissions from facially applied PCPs typically decayed to background concentrations over periods ranging from 5 to 150 min.

KEYWORDS
indoor air quality, mass spectrometry, personal care products, public health, SIFT-MS, VOCs

1 | 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 oxidized 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 while online 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 moisturizers 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 absorption[12–15] and the direct application of products,[16–23] including the impact of PCPs on skin chemistry.[24] Biesterbos et al.[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.

While the air quality implications of PCP inhalation may not, as of yet, be at the forefront of consumers' minds, an increasing popularity for eco-friendly, "green" products, and a rise in sustainable consumption, has been seen. Eighty-five percent of retailers in a European study reported increased sales of sustainable products over the past 5 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.[38] reported that 95% of fragranced baby products analyzed, both green and non-green, emitted at least one potentially hazardous VOC (under Australian or World Health Organization 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 moisturizers (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.

Practical Implications

- Personal care products emit volatile organic compounds, including alcohols and fragrance compounds in the number of milligrams, which are potentially harmful if inhaled in large amounts.
- Facially applied personal care products, such as moisturizers, have the potential to deliver enhanced VOC doses via inhalation due to close proximity of the nose and mouth to the emission source.
- The potential inhaled dose of VOC from the facial application of personal care products can be much larger than the dose inhaled from ambient room air.
- Products marketed as "green" generally emit the same volatile compounds as regular products, and at comparable emission rates.
- VOC emissions and inhaled dose may be approximately inferred from a product ingredients list, based on its relative listing position.

TABLE 1 SIFT-MS SIM method targeted scanned m/z values, and their corresponding ions, for each of the three reagent ions H_3O^+, NO^+, and O_2^+

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 ($C_7H_8O^+$)

2 | EXPERIMENTAL

2.1 | 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 setup are detailed here.

The first series of experiments were used to assess VOC product emissions under standardized headspace conditions following a methodology reported previously in Yeoman et al.[1] This initial screening of products identifies the compounds to target in subsequent experiments. Sixteen commercially available day-moisturizers 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 was 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 min, with an ion dwell time of 100 ms per *m/z*, and a cycle time per reagent ion mass spectra of 38 s, 114 s overall. Over the 120 min 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. 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 subsampled into the SIFT-MS with a flow rate of 15 ml min^{-1}, the remainder of gas sent to waste. The SIFT-MS subsample 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 setup run as a blank, prior to product application. Approximately 0.45 g of each of the 16 day-moisturizers were applied across the face onto the Parafilm using gloved hands, replicating real-life moisturizer application methods and amounts. The mass of 0.45 g was selected based on two usage studies. Hall et al.[17] found the mean mass of facial moisturizer used to be 0.906 g per day, which assuming two daily applications, is 0.453 g per application. Biesterbos et al.[25] found 0.4g to be the mean application of day cream. The mannequin head was not heated and presumed to be ~21°C, 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).

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 1.

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 min and the longest 180 min.

2.2 | 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 aerosolize and fully evaporate the liquid into a temperature-controlled mixing region. The liquid was pressurized 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 vapor 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 deionized 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 was conditioned for ~48 h at 45°C, 0.6 H_2O g h^{-1}, and 2 L min^{-1} air.

The same SIFT-MS SIM method was run as previously. Calibration sampling lasted for ~7 h as the H_2O liquid flowrate was changed from 0.2 g h^{-1} to 2.0 g h^{-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.

2.3 | Data workup and analysis

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

Figure S1 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 vapor present, it was not necessary to calibrate in this more extreme humidity region. We assume a room water concentration of 1.098×10^{-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 h^{-1} was determined. Correction factors for each compound were calculated at this value using the calibration curves and then applied to the data.

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.

3 | RESULTS AND DISCUSSION

3.1 | Volatile organic compound emissions from regular and "Green" moisturizers

Establishing the differences in VOC emissions from regular and green day facial moisturizers first requires the determination of the most prevalent VOC species from a selection of both types of products and a standardized 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 1 (data in Table 2) are the standardized 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 methylsiloxanes (cVMS) in these products, despite results from Yeoman et al.[1] suggesting that they would likely be present in moisturizers. However, that study was carried out on a wider range of moisturizing 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-moisturizers (rather than cyclic siloxanes), and no siloxanes at all were listed in the green product ingredients.

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 copreservative 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 moisturizers, 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 stabilizer, conditioning agent, and humectant. Benzyl alcohol has the widest range of skincare uses: as a preservative, stabilizer, 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 3) between the two product classes, with all three compounds being found in higher quantities in the regular products.

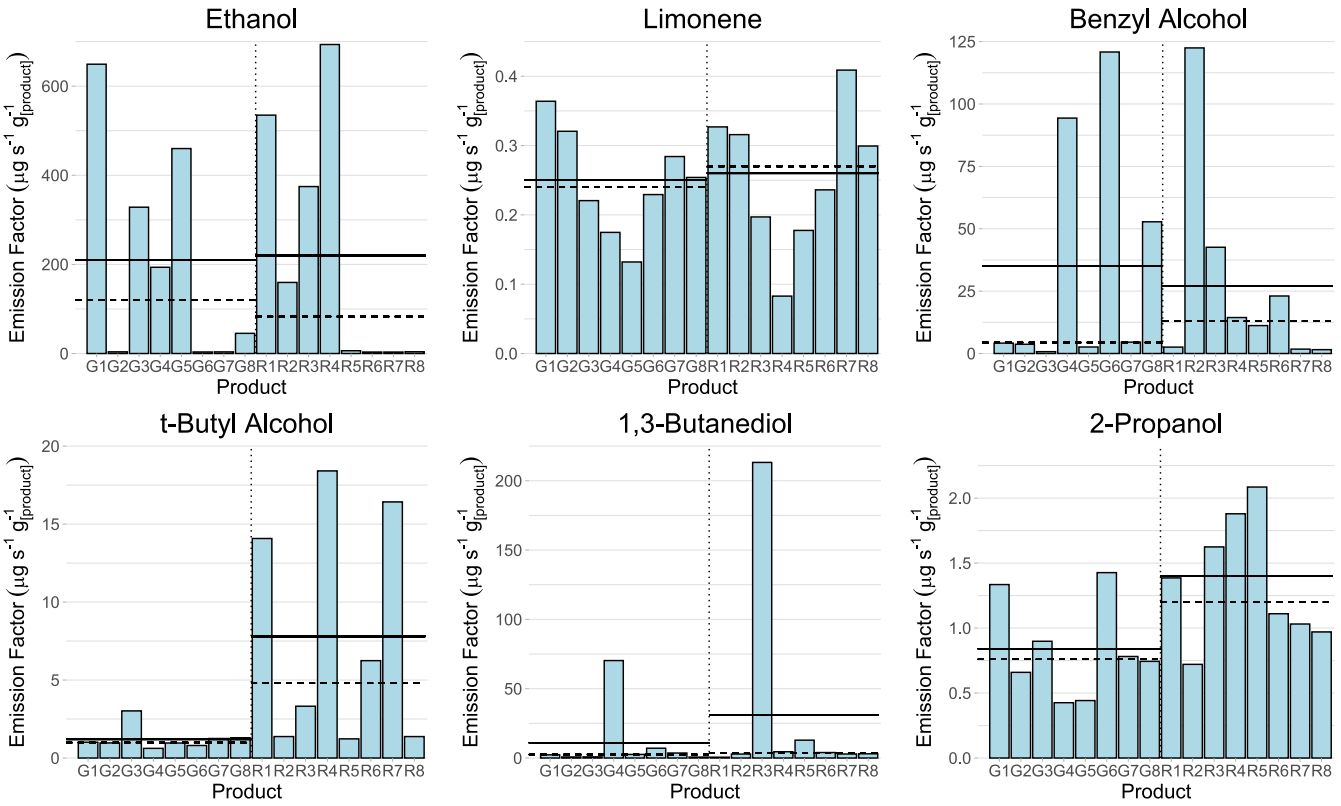

FIGURE 1 Standardized headspace emission rates of 6 key ingredient VOCs identified by SIFT-MS from 16 moisturizing products. R denotes regular, G denotes green-marketed products. Solid lines – mean values, dashed line–median value

TABLE 2 Emission rates of 6 key VOCs identified by SIFT-MS from 16 products

	Emission rate ($\mu g\ s^{-1}\ g_{[product]}^{-1}$)					
Product	**Limonene**	**Ethanol**	**Benzyl Alcohol**	**t-Butyl Alcohol**	**1,3-Butanediol**	**2-Propanol**
G1	3.6×10^{-1}	6.5×10^{2}	4.2	1.0	2.3	1.3
G2	3.2×10^{-1}	3.8	3.7	9.7×10^{-1}	7.6×10^{-1}	6.6×10^{-1}
G3	2.2×10^{-1}	3.3×10^{2}	7.5×10^{-1}	3.0	8.0×10^{-1}	9.0×10^{-1}
G4	1.7×10^{-1}	1.9×10^{2}	9.4×10^{1}	6.2×10^{-1}	7.0×10^{1}	4.3×10^{-1}
G5	1.3×10^{-1}	4.6×10^{2}	2.6	9.6×10^{-1}	2.6	4.4×10^{-1}
G6	2.3×10^{-1}	3.5	1.2×10^{2}	8.0×10^{-1}	7.1	1.4
G7	2.8×10^{-1}	3.7	4.6	1.3	3.6	7.8×10^{-1}
G8	2.5×10^{-1}	4.5×10^{1}	5.3×10^{1}	1.3	6.7×10^{-1}	7.4×10^{-1}
R1	3.3×10^{-1}	5.3×10^{2}	2.6	1.4×10^{1}	5.9×10^{-1}	1.4
R2	3.2×10^{-1}	1.6×10^{2}	1.2×10^{2}	1.4	2.9	7.2×10^{-1}
R3	2.0×10^{-1}	3.7×10^{2}	4.3×10^{1}	3.3	2.1×10^{2}	1.6
R4	8.3×10^{-2}	6.9×10^{2}	1.4×10^{1}	1.8×10^{1}	4.5	1.9
R5	1.8×10^{-1}	6.3	1.1×10^{1}	1.2	1.3×10^{1}	2.1
R6	2.4×10^{-1}	3.3	2.3×10^{1}	6.2	4.0	1.1
R7	4.1×10^{-1}	3.3	1.8	1.6×10^{1}	2.9	1.0
R8	3.0×10^{-1}	4.0	1.6	1.4	3.0	9.7×10^{-1}

With the exception of limonene, these experiments yielded higher emission factors than those estimated in Yeoman et al.[1] Facial moisturizers, especially those designed for use during the day which have been tested here, typically dry more quickly than moisturizers designed for the rest of the body or for use at night. They also tend to contain more active ingredients than body moisturizers, which may necessitate a larger quantity of solvent. These are plausible reasons for observing higher ethanol emission factors here and may

TABLE 3 Statistical analysis of emission rates from headspace experiments

Compound		Mean	Median ($\mu g\ s^{-1}\ g_{[product]}^{-1}$)	Range	Relative Standard Deviation (%)
Ethanol	Regular	2.2×10^{2}	8.3×10^{1}	6.9×10^{2}	116
	Green	2.1×10^{2}	1.2×10^{2}	6.5×10^{2}	109
Limonene	Regular	2.6×10^{-1}	2.7×10^{-1}	3.3×10^{-1}	38
	Green	2.5×10^{-1}	2.4×10^{-1}	2.3×10^{-1}	29
Benzyl Alcohol	Regular	2.7×10^{1}	1.3×10^{1}	1.2×10^{2}	139
	Green	3.5×10^{1}	4.4	1.2×10^{2}	127
t-Butyl Alcohol	Regular	7.8	4.8	1.7×10^{1}	88
	Green	1.2	9.9×10^{-1}	2.4	57
1,3-Butanediol	Regular	3.1×10^{1}	3.5	2.1×10^{2}	227
	Green	1.1×10^{1}	2.5	7.0×10^{1}	204
2-Propanol	Regular	1.4	1.2	1.4	33
	Green	8.4×10^{-1}	7.6×10^{-1}	1.0	41

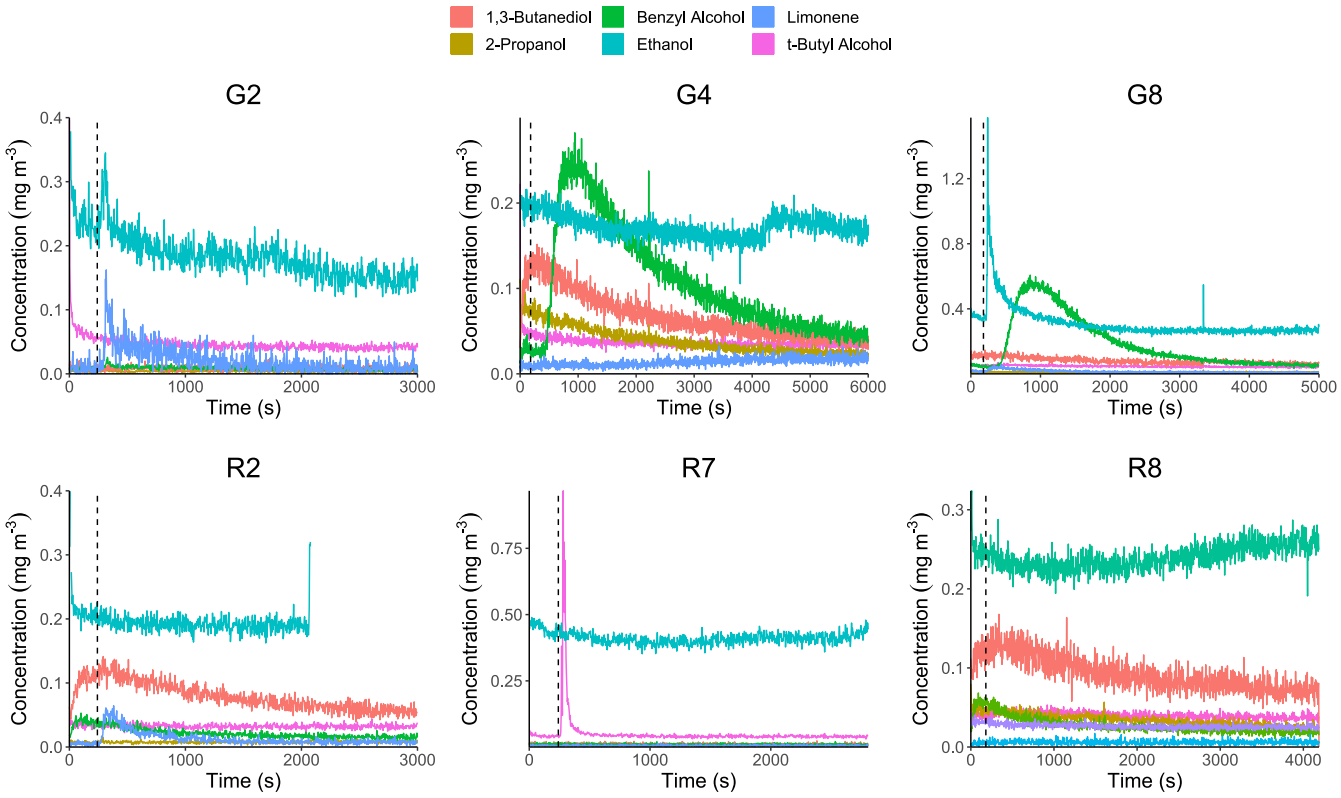

FIGURE 2 Time concentration profiles of 6 example facial moisturizing products. Top row are "green-marketed" products, bottom row are regular products. The dashed line indicates time of product application

also explain the larger 2-proponal emission factors, as alcohol content is directly linked to denaturing/tracer compounds.

3.2 | Real-life exposure and inhalation

While many PCPs contain VOCs, and give rise to emissions that lead to a rise in ambient in-room concentrations (e.g., 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 2 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 2 illustrates just how variable the emission of VOCs are from different products even within the same PCP subclass—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 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 than estimated here.

Presented in Figure 3 and Table 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.

An important point for consideration is that the facial sampler was only held at room temperature, 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 are 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 1. In the headspace analysis, where a sealed container was utilized, all VOCs are driven into the gas phase at saturation concentration, in turn, passed 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 moisturizer 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 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 or percentage) to be reported. The relationship between position on ingredient list and amount of ethanol inhaled is visualized in Figure 4. 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 suggests that while 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.

TABLE 4 Average volatilization times for 6 key compounds when facially applied, representing time from application to point at which inhaled concentrations return to ambient background

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

3.3 | Facial exposure vs ambient inhalation

A day-moisturizer would usually be applied just once a day, in the morning (with the second daily application being a night-moisturizer).[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 6). Median ambient indoor concentrations are taken from Heeley-Hill et al.[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 h, 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 h spent inside a typical UK residence. Outdoor concentrations and amounts inhaled would be expected to be considerably lower than indoor. In Table 6, we contrast the facial moisturizer dose against 24 h of ambient air indoors.

One application of a day-moisturizer 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-moisturizer, in one day, this would result in double the expected inhaled dose calculated here.

For ethanol that mass inhaled due to the moisturizer application is on average over 300 times higher than ambient 24-h 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 based on the VOC content and tonnage of product sold, facial moisturizers would appear to be a small contributor in the

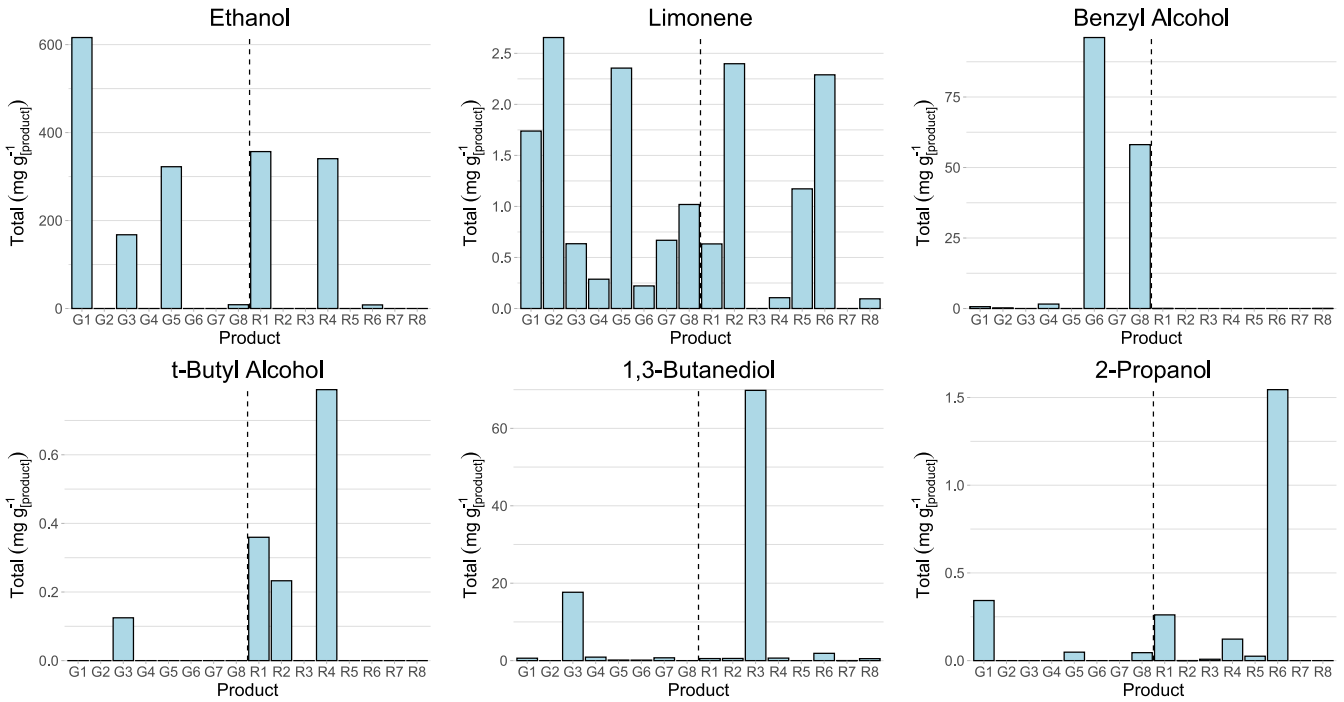

FIGURE 3 Integrated inhaled dose of 6 key VOCs from 16 products for one facial application (~0.45 g) at a standard respiration rate of 6 L min^{-1} combined through mannequin nose and mouth. Dotted line – separates green and regular products. R denotes regular, G denotes green

TABLE 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

	Aggregate Inhaled (mg $g_{[product]}^{-1}$)					
Product	**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

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 have been explored by the concept of "intake fraction". First conceived by Bennett et al.,[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).

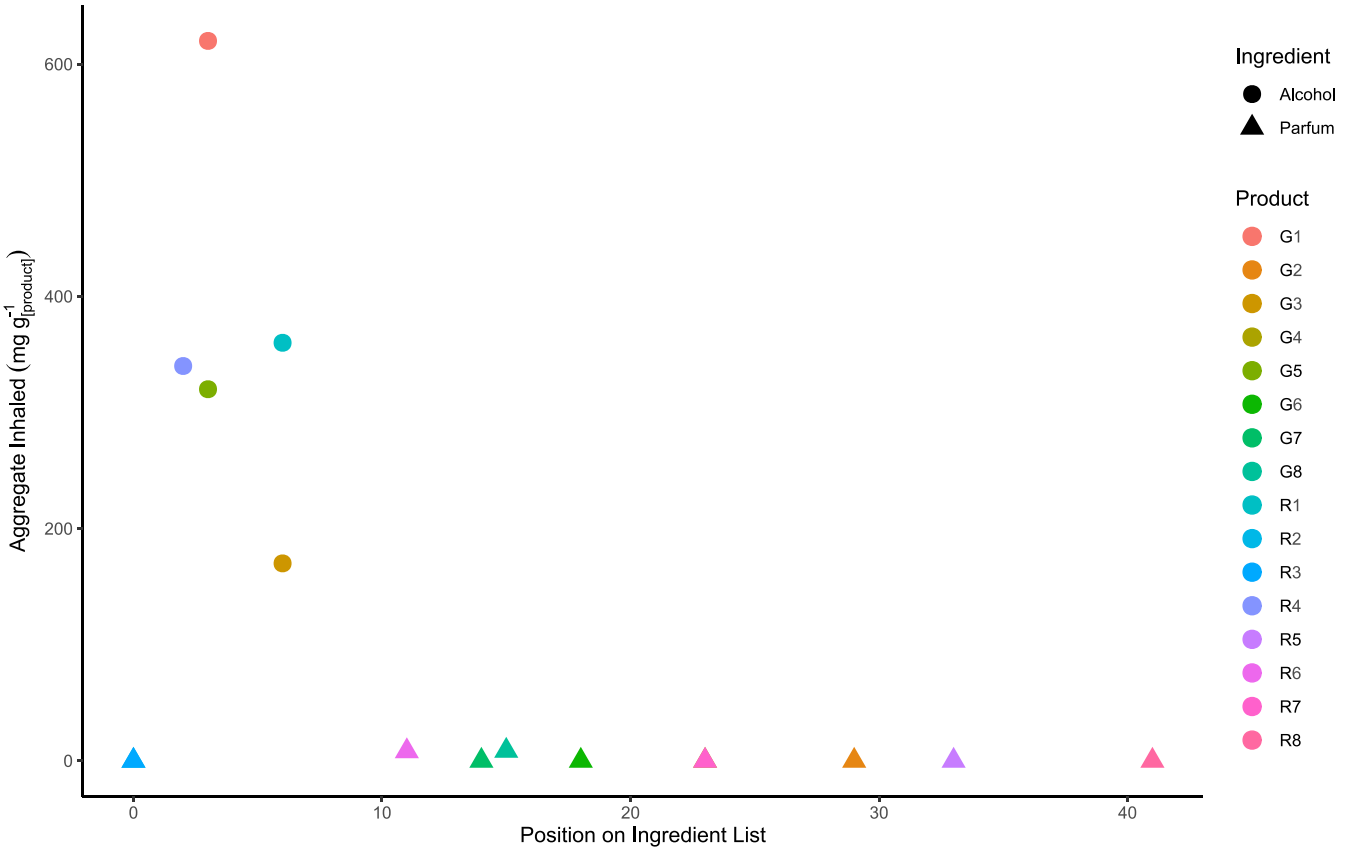

FIGURE 4 Aggregate inhaled ethanol dose from Table 5 relative to ethanol/parfum ranking position on product ingredient list, used a proxy for amount contained in each product

TABLE 6 Amount inhaled from one application of 0.45 g of day-moisturizer to the face. Indoor/application ratios are calculated based on median indoor concentrations[49] over a period of 24 h (ethanol 0.34 mg, limonene 0.033 mg)

Product	Ethanol Inhaled directly from product (mg)	Ethanol Ratio of product dose to 24 h ambient air	Limonene Inhaled directly from product (mg)	Limonene Ratio of product dose to 24 h 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

Although usually summed over the population, individual exposure can be expressed by an individual intake fraction (iF_i). Jolliet et al.[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 min, and 9 mg m^{-3} over 24 h. One daily application of a day-moisturizer would not result in the applicant exceeding that daily exposure limit, nor the 30-min limit (the period over which limonene emits, as seen in Table 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 | 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-moisturizers. 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 with simply breathing typical room air. The experiments indicated that facial application leads to large VOC doses when compared with typical amounts of some VOCs inhaled in ambient air indoors over a 24 h 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.

While product labelling is only qualitative 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.

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CONFLICT OF INTEREST

There are no conflicts of interest to disclose.

AUTHOR CONTRIBUTIONS

Amber M Yeoman contributed to conceptualization, data curation, formal analysis, investigation, methodology, visualization, writing—original draft, and writing—review and editing. Aiden C Heeley-Hill contributed to data curation and investigation. Marvin Shaw contributed to conceptualization, investigation, methodology, resources, validation, and writing—original draft. Stephen J Andrews contributed to conceptualization, investigation, methodology, resources, validation, and writing—original draft. Alastair C Lewis contributed to conceptualization, methodology, project administration, funding acquisition, writing—original draft, and writing—review and editing.

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SUPPORTING INFORMATION

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