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Does green mean clean? Volatile organic emissions from regular *versus* green cleaning products†

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Cleaning products emit a range of volatile organic compounds (VOCs), including some which are hazardous or can undergo chemical transformations to generate harmful secondary pollutants. In recent years, "green" cleaners have become increasingly popular, with an implicit assumption that these are better for our health and/or the environment. However, there is no strong evidence to suggest that they are better for indoor air quality compared to regular products. In this study, the VOC composition of 10 regular and 13 green cleaners was examined by headspace analysis. Monoterpenes were the most prevalent VOCs, with average total monoterpene concentrations of 8.6 and 25.0 mg L^{-1} for regular and green cleaners, respectively. Speciated monoterpene emissions were applied to a detailed chemical model to investigate the indoor air chemistry following a typical cleaning event. Green cleaners generally emitted more monoterpenes than regular cleaners, resulting in larger increases in harmful secondary pollutant concentrations following use, such as formaldehyde (up to 7%) and PAN species (up to 6%). However, emissions of the most reactive monoterpenes (α-terpinene, terpinolene and α-phellandrene), were observed more frequently from regular cleaners, resulting in a disproportionately large impact on the concentrations of radical species and secondary pollutants that were formed after cleaning occurred.

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Environmental significance

Increased consumer interest in cleaning products which are safer for our health/the environment has resulted in the advent of products marketed as "green". Cleaning products are large sources of volatile organic compounds (VOCs) indoors, including species which react with oxidants to form hazardous secondary pollutants. Here, the VOC emissions from regular and green cleaners are determined experimentally, and the secondary pollutant formation is estimated using an indoor air chemistry model. This work reveals that green cleaners are larger emitters of monoterpenes, though some regular cleaners are larger sources of very reactive monoterpenes, impacting the formation of hazardous secondary pollutants. Our results will provide pointers to influence how fragranced products can be formulated to improve indoor air quality.

1 Introduction

In developed countries, it is estimated that we spend approximately 90% of our time indoors. As a result, a large proportion of our personal exposure to air pollutants occurs in indoor environments. There are many sources of gaseous and particulate air pollutants indoors, including building materials and furnishings (wood, plastics, floorings, *etc.*[1–3]), personal care products,[4] household appliances (stoves, photocopiers, fires, *etc.*[3,5]) and occupant activities such as cooking and cleaning.[6–8]

Household cleaning products are widely used in the built environment to promote cleanliness and hygiene.[9] Cleaning products generally constitute complex mixtures of chemicals including water, solvents, surfactants, preservatives and fragrances. Depending on the usage purpose, other compounds can be included such as disinfectants, acids, bases, bleaching agents, abrasives, or enzymes.[10] Many of the components of cleaning products are volatile, and therefore cleaning products can be a major source of volatile organic compounds (VOCs) in indoor environments.

The fragrance component of household cleaners is a key selling point to consumers, promoting the perception of a clean environment through the concealing of malodours.[11] Natural and synthetic fragrance ingredients used in scented products are chemically complex mixtures containing terpene and terpenoid compounds. Consequently, cleaning products have been identified as one of the largest sources of terpenes indoors.[12] In a study of 25 UK homes, highly variable indoor concentrations of limonene and α-pinene were measured at

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much higher concentrations than outdoors (mean indoor/outdoor ratios of 8 and 6, respectively), following the intermittent use of fragranced products such as household cleaners indoors.[12]

Many terpenoid species are susceptible to oxidation by oxidants present indoors such as ozone (O_3), and hydroxyl (OH) and nitrate (NO_3) radicals. Such chemistry results in the production of a wide range of secondary pollutants, such as organic nitrates, carbonyls (such as formaldehyde), peroxyacetyl nitrates (RCO_3NO_2, henceforth PAN) and particulate matter (PM).[13] Some secondary pollutants from terpenoid oxidation have been associated with adverse health effects,[14–18] although the toxicology of many secondary pollutants remains poorly characterised. Evidence suggests that occupant exposure to pollutants from cleaning products may cause adverse respiratory effects and asthma prevalence in cleaning staff.[19] Some secondary pollutants are more detrimental to health than the parent VOC,[20] hence it is important to study both the primary VOC emissions from cleaning and the chemical transformations that follow to improve indoor air quality and reduce occupant health risks.

The chemical composition of cleaning product formulations is often unclear from the product labels, as manufacturers are not required to disclose all formulation ingredients. This was illustrated in a study of 134 common consumer products, where fewer than 4% of the identified VOCs were listed as product ingredients.[21] The fragrance component of consumer products is often listed as "parfum", or an equivalent term, with no chemical detail about the fragrance components. Under regulation (EC) 648/2004, disclosure of specific fragrance compounds is only required if they are allergenic and at a concentration exceeding 0.01%. As such, there is large variability and uncertainty in the current knowledge of primary VOC emissions and secondary pollutants from indoor cleaning activities.

An increasing awareness surrounding the environmental and health impacts of household products has driven a recent shift in consumer choice towards "green" products, with the assumption that they are less polluting and therefore less harmful than their regular counterparts.[22] However, owing to the ambiguity surrounding the chemical composition of cleaning products, it is not possible to substantiate these consumer perceptions with relation to indoor air pollution. Additionally, there is no official designation of "green" and no standard certification to ensure that products marketed as "green" have lower concentrations of chemicals of concern.[23] Research comparing the VOC emissions from regular and green cleaners remains limited. Several studies suggest that there is no significant difference between regular and green cleaners,[21,24–26] however other studies have observed reduced air concentrations of hazardous VOCs from green cleaners.[23,27,28] To our knowledge, there currently exists no studies investigating the secondary pollution from fragranced regular and green cleaners.

Therefore, the aim of this study was to investigate the primary VOC emissions and resultant secondary pollutant formation from 10 regular and 13 green cleaning products. The VOC composition of the cleaners was determined by headspace analysis techniques, and results were used to estimate VOC emission rates during a typical cleaning event on a realistic scale. The chemical transformations of reactive monoterpene emissions were investigated using an indoor chemical model, and the resulting key harmful secondary pollutants were identified. This is the first study to investigate the chemical processing of complex mixtures of reactive terpene emissions relevant to commercially available products, including those marketed as "green".

2 Methods

2.1 Cleaning products

Twenty-three commercially available household cleaning products were selected for comparison (Table 1). Four product categories (surface cleaner, bathroom cleaner, floor cleaner and dishwashing detergent) were identified as the most frequently used household cleaners based on results from a European household survey on the use of domestic products.[29] Within each product category, multiple "regular" products (those which do not make a claim to be "green" in any way) and "green" products (those which make a claim such as "green", "environmentally friendly", "natural", "plant-based", "nontoxic" *etc.*) were selected. The products included market leading brands selected from market size data (Household Cleaners UK Generated by Mintel Market Sizes, 2019), budget brands and upmarket brands.

Table 1 Product details of household cleaning products tested in this study

ID	Class	Regular	Green	Scented
SR1	Surface cleaner	✓		✓
SR2	Surface cleaner	✓		✓
SR3	Surface cleaner	✓		✓
SR4	Surface cleaner	✓		✓
SG1	Surface cleaner		✓	✓
SG2	Surface cleaner		✓	✓
SG3	Surface cleaner		✓	✓
SG4	Surface cleaner		✓	
BR1	Bathroom cleaner	✓		✓
BR2	Bathroom cleaner	✓		✓
BG1	Bathroom cleaner		✓	✓
BG2	Bathroom cleaner		✓	✓
BG3	Bathroom cleaner		✓	
FR1	Floor detergent	✓		✓
FR2	Floor detergent	✓		✓
FG1	Floor detergent		✓	✓
FG2	Floor detergent		✓	✓
FG3	Floor detergent		✓	✓
FG4	Floor detergent		✓	✓
DR1	Dishwashing detergent	✓		✓
DR2	Dishwashing detergent	✓		✓
DG1	Dishwashing detergent		✓	
DG2	Dishwashing detergent		✓	✓

2.2 Experimental

2.2.1 Equilibrium headspace GC-TOF-MS. Equilibrium headspace GC-TOF-MS was used to qualitatively characterise the volatile fraction of the cleaning product formulations. Floor and dishwashing detergent samples were prepared (as per manufacturer instructions) by diluting with deionised water, while surface and bathroom cleaners were analysed as the neat product formulation. 1 mL aliquots of sample were dispensed into 20 mL glass headspace sample vials. Analysis was performed using a 7890B gas chromatograph (Agilent Technologies, USA) coupled to a 7200 Accurate-Mass Q-TOF GC/MS mass spectrometer (Agilent Technologies, USA), with a MultiPurpose Sampler MPS Dual Head autosampler (GERSTEL GmbH & Co. KG, Germany) operated in headspace mode with a pre-heating module.

Each sample was heated to 50 °C and intermittently agitated at 250 rpm for 5 minutes in the pre-heating module to allow equilibration of the headspace. Equilibration temperatures of 40, 50, 60 and 70 °C and times of 1, 3, 5, 7, 9 and 15 minutes were tested to optimise sensitivity of the qualitative headspace analysis (Fig. S1†). Following the equilibration period, 250 μL of gaseous headspace was injected into the GC-MS system with a split ratio of 1 : 10 and an inlet temperature of 290 °C. A BPX5 column (50 m × 320 μm × 1 μm) was used for chromatographic separation, with a helium carrier gas at flow rate 1.5 mL min^{-1}. The duration of the method was 34 minutes, with the following oven temperature program: 40 °C (2 min), 10 °C min^{-1} to 125 °C (3 min), 10 °C min^{-1} to 300 °C (3 min). The detector temperature was 310 °C.

Visualisation and processing of the GC-MS data were performed using MassHunter Workstation Software (Version 7.0 Qualitative Analysis, Agilent Technologies). The background-subtracted mass spectra of the peaks were extracted, and compounds were tentatively identified by spectra library matching using the National Institute of Standards and Technology (NIST) Mass Spectral Search Program (version 2.3, NIST) and an R match factor of >700. Inter-comparison of peak identification results relative to retention time was performed to improve confidence in identification.

2.2.2 Dynamic headspace SIFT-MS. A Voice200 SIFT-MS (Syft Technologies) was used to quantify volatile components of the cleaning product formulations by dynamic headspace sampling, as described by Yeoman *et al.*[4] The principles of Selected-Ion Flow-Tube Mass Spectrometry (SIFT-MS) are discussed in detail elsewhere,[30,31] with only the operating conditions listed here. The SIFT-MS was operated with a flow tube temperature of 120 °C, pressure of 460 mTorr, a voltage of 25 V, a sample flow rate of 5 sccm, and a nitrogen (N_2, Research grade, BOC) carrier gas flow of 120 sccm which was maintained throughout the measurement period. The microwave ion source current was operated at 40 mW at 400 mTorr pressure.

The SIFT-MS was operated in selected ion monitoring mode (SIM), dynamically measuring 15 VOCs with a time resolution of 6 seconds (54 masses scanned, 0.1 second ion dwell time). The compounds measured by SIFT-MS and the corresponding reagent ions, molecular masses and product ion molecular formulae are given in Table S1.† Due to the low mass resolution of SIFT-MS, it was not possible to differentiate between the product ions of isobaric species such as monoterpenes (m/z 136) and sesquiterpenes (m/z 205). Therefore, these are reported as total monoterpenes and total sesquiterpenes, respectively.

A 50 cm^3 gas-tight vessel was used as a headspace sampling chamber, which comprised of a stainless-steel screw-down lid and Viton O-ring seal and two 1/16 in stainless steel Swagelok bulkhead connectors to provide an inlet and outlet.[4] VOC-free N_2 diluent gas was supplied to the chamber from a Teflon bag connected to the inlet. The SIFT-MS was connected to the chamber outlet and was supplied with a 5 mL min^{-1} flow of sample gas *via* a mass flow controller. The sampling chamber was thermostatically controlled at 25 °C to achieve a stable ambient temperature throughout the experiment.

For each sample, background measurements of the headspace chamber were acquired for about 10 minutes prior to sample introduction. 1 μL of sample was then decanted onto a small open vial and placed into the sampling chamber immediately. The headspace gas was then measured for a further 60 minutes, or until VOC concentrations stabilised at background concentrations.

Background VOC concentrations, defined as the mean concentration of a 2 minutes period immediately prior to sample introduction, were subtracted from the data. Data were calibrated for acetaldehyde, benzene, ethanol, methanol, and total monoterpenes using calibration factors determined from gas standards (1 ppm in nitrogen, National Physical Laboratories) (Fig. S3†). For all other species, concentrations were determined using literature compound specific rate constants and ion transmission data, which was obtained weekly. For details regarding the uncertainty in SIFT-MS measurements, see ESI, Table S3.†

The concentration (C) of species i in the cleaning product formulation (μg μL^{-1}) was calculated from the integral of the calibrated, background subtracted SIFT-MS data using eqn (1). The concentration profiles showed a peak shortly after sample introduction followed by a decline back to baseline concentrations in most cases, indicating that the VOC source was depleted within the duration of the sampling time. The integral of the VOC peak was therefore assumed to be equivalent to the total amount of that VOC emitted from the sample under the given conditions. VOC concentration profiles which showed no or insignificant peaks were identified by visual inspection of the data and were discounted from subsequent analysis.

$$C_i = \frac{\int_{t_0}^{t} C_i \mathrm{d}t \times \nu}{V_{\mathrm{sample}}} \quad (1)$$

where $\int_{t_0}^{t} C_i \mathrm{d}t$ is the integral of C_i with respect to time, t_0 and t are the times at which the sample was introduced to the headspace chamber and the end of the sampling period, respectively, ν is the sample flow rate (8.3×10^{-7} m^3 s^{-1}), and V_{sample} is the sample volume (1 μL).

The VOC concentrations were used to estimate emission rates during a typical cleaning event in an indoor environment. The following assumptions were made:

• Product volume: the volume of cleaning product used during a realistic cleaning event was assumed to be 10 mL for surface and bathroom cleaners (based on semi-realistic cleaning experiments), 107 mL for floor cleaners (based on an assumed floor surface area of 8.4 m^2 and a floor solution application of 12.82 mL m^{-2} [32,33]), and 50 mL for dishwashing detergent.

• Dilution factor: manufacturer guidance was used to calculate a dilution factor where possible. Otherwise, dishwashing detergents were assumed to have a dilution factor of 0.001 (0.1% v/v).

• Room volume: an average kitchen volume of 25 m^3 was assumed based on a detailed study of the surface areas of 9 kitchens.[32]

• Emission period: an emission period of 3 minutes was assumed, based on previous cleaning activity experiments.

Using these assumptions, VOC emission rates ($k_{Em(i)}$, molecule cm^{-3} s^{-1}) were determined using eqn (2):

$$k_{Em(i)} = \frac{C_i \times V_{product} \times F_{dil} \times N_A}{t \times V_{room} \times M_w} \quad (2)$$

where $V_{product}$ is the volume of cleaning product used in a cleaning event (μL), F_{dil} is the dilution factor for cleaning products used as a dilute solution, t is the emission period (seconds), V_{room} is the volume of the room (cm^3), N_A is Avogadro's constant, 6.022×10^{23} mol^{-1}, and M_w is the molecular weight of species i (μg mol^{-1}).

Estimating realistic-scale VOC emissions in this way has limitations. Emission rates were calculated based on the assumption that all VOCs were emitted from the cleaning product during a cleaning activity period of 3 minutes. However, there is evidence to suggest that indoor emission sources such as cleaning products can emit VOCs for a period following the activity due to reversible surface partitioning and emissions from product residues.[8,34] Complex emission dynamics including multiphase interactions (*i.e.*, partitioning of VOCs to organic or aqueous surface films) and the effects of different product application modes are not taken into consideration here. Finally, it is acknowledged that the VOC species targeted for this analysis do not account for all volatile components of the cleaning products, and some VOC emissions are not accounted for. However, our results do provide a comparative study between the different cleaners and importantly, between the green and regular products. The approach used in this study to estimate VOC emission rates from product formulation compositional data was evaluated by applying it to data reported in a previous study,[33] see ESI.†

2.2.3 Speciated monoterpene emission rates. The total monoterpene emission rates calculated from dynamic headspace SIFT-MS measurements were quantitatively speciated per product using equilibrium headspace GC-TOF-MS. Each sample was prepared and analysed using the same instrumentation and methodology specified in Section 2.2.1, with the exceptions of: (i) the sample volume (550 μL), (ii) the inclusion of an internal standard (550 μL dimethylaniline, 10 μg L^{-1}), (iii) the sample incubation temperature (35 °C), and (iv) splitless injection. The sample incubation temperature was reduced to align more closely with the SIFT-MS analysis conditions and realistic room temperatures, lessening the impact of temperature on the liquid–gas partitioning of monoterpenes. The inclusion of an internal standard normalised the data, thus compensating for variability in instrument response, sample preparation, and matrix effects of the different formulations.

The monoterpene fraction of the cleaning products was quantified using calibration standards to account for different sensitivities of the monoterpene compounds. A standard solution of α-pinene, camphene, β-myrcene, α-phellandrene, D-limonene, γ-terpinene and terpinolene in 50 : 50 H_2O : methanol (2 μg L^{-1}) was prepared. Calibration standards were analysed in the range 125–1000 ng L^{-1} with the addition of internal standard. The concentrations of monoterpenes in the samples were quantified using the resultant calibration curve (Fig. S2†). For monoterpene species which were not present in the analytical standard, an average of the instrument response to all monoterpenes in the standard was assumed. For β-pinene and α-terpinene, the instrument response was assumed to be equivalent to that of their isomers, α-pinene and γ-terpinene, respectively.

The quantified monoterpene fraction was used to calculate the relative abundance ratios of monoterpenes in each cleaning product, which were applied to the total monoterpene emission rates determined from SIFT-MS to calculate individual monoterpene emission rates for each cleaner.

2.3 Model simulations

INCHEM-Py v1.2 was used to model the indoor air chemistry following the emission of VOCs from cleaning. INCHEM-Py is an open-source box-model that has been re-factored from the indoor detailed chemical model (INDCM).[35,36] The model creates and solves a series of ordinary differential equations (ODEs) to estimate indoor species concentrations over time, assuming a well-mixed environment. The model utilises the near-explicit Master Chemical Mechanism (MCM)[37,38] which describes the gas-phase chemical degradation of 142 non-methane VOCs to H_2O and CO_2 end-products. Additional reaction mechanisms for species unique to the indoor environment, and therefore not included in the MCM, have been (and continue to be) developed and included in the model.[13,36,39–41]

The general equation for the ODEs created and solved by INCHEM-Py to calculate the concentration C of species i through time is as follows:

$$\frac{dC_i}{dt} = \sum R_{ij} + (\lambda_r C_{i,out} - \lambda_r C_i) - \nu_{d_i}\left(\frac{A}{V}\right) C_i \pm k_t C_i \quad (3)$$

where R_{ij} is the sum of the reaction rates of species i with all other species j, λ_r is the air change rate (ACR, h^{-1}), $C_{i(out)}$ is the indoor (outdoor) concentration of species i (molecule cm^{-3}), ν_{d_i} is the deposition velocity of species i (cm s^{-1}), A/V is the surface area to volume ratio (SAV, cm^{-1}), and k_t is the emission rate (molecule cm^{-3} s^{-1}) of species i. The first term in the equation includes all MCM and additional chemical reaction mechanisms, including photolysis reactions. Photolysis rate coefficients are calculated considering attenuated outdoor light

(dependent on latitude of simulation location and emissivity of glass windows) and artificial indoor light (dependent on lighting type). The second term in the equation represents the exchange of pollutants between indoors and outdoors (dependent on outdoor species concentrations and ACR). The third term represents irreversible surface deposition at a rate which is species-specific and dependent on the SAV of the room. Finally, the fourth term accounts for user-defined emissions of specific species at a given rate and for a given time period.

The irreversible deposition of species onto indoor surfaces is described in INCHEM-Py for 3371 species by species-specific deposition velocities. The rate of irreversible loss to indoor surfaces is independent of the surface material and does not consider subsequent emission of secondary pollutants from surface chemistry. However, for key species O_3 and H_2O_2 deposition mechanisms have been developed which include the deposition and secondary pollutant emissions from specific indoor surface materials.[42] Loss rates of O_3 and H_2O_2 to indoor surfaces and subsequent emission of aldehydes is calculated from the specific deposition velocities and SAVs of the following materials: metal, glass, wood, plastic, linoleum, paint, paper, concrete, soft furnishings, and skin.

To investigate the production of secondary species from cleaning activities in a realistic environment, the model was parameterised using a 'typical' kitchen setting. Based on Manuja *et al.*,[32] a room volume of 25 m^3 and a total surface area of 63.27 m^2 was assumed. The surface area to volume ratios for each of the materials considered in the model were as follows, assuming one adult (2 m^2) is in the room: soft furnishings = 0.081 m^{-1}; paint = 0.992 m^{-1}; wood = 0.665 m^{-1}; metal = 0.311 m^{-1}; concrete = 0.048 m^{-1}; paper = 0.008 m^{-1}; plastic = 0.220 m^{-1}; linoleum = 0.070 m^{-1}; glass = 0.058 m^{-1}; and skin = 0.080 m^{-1}. The temperature and relative humidity of the room were assumed to be 20 °C and 53.5%, respectively.

The background concentrations of VOCs indoors were determined in part from the indoor–outdoor exchange of species, controlled by the outdoor concentrations and the ACR. The ACR was assumed to be 0.5 h^{-1} based on a review of residential dwelling ventilation.[43] Outdoor concentrations of 110 VOCs were defined as static concentrations sourced from published literature and measurement databases, while outdoor O_3, NO and NO_2 were defined as diurnal concentrations. The diurnal concentrations of O_3, NO and NO_2 were provided by the 'London suburban' profile, which is calculated from hourly average concentrations measured over a 3 months period (July, August, September) by a monitoring station in a suburban London location (data provided by the European Air Quality Database). Additional background concentrations of acetone, ethanol, methanol, isopropanol and isoprene were contributed to by constant indoor emissions from the breath of one adult occupant.[42]

The total indoor photolysis conditions were determined from a combination of attenuated light and artificial indoor light. Attenuated light was defined using a latitude of 51.45 °N, a date of 21/06/2020, and low emissivity glass (transmittance wavelength range 330–800 nm [44]). Artificial indoor lighting was assumed to be incandescent and was on between 07 : 00 and 19 : 00.

To simulate a cleaning activity, the speciated monoterpene emission rates were applied to the model per cleaner as timed emissions at midday for an assumed cleaning period of 3 minutes. All other VOC emission rates determined from SIFT-MS analysis were not included in these simulations, because the VOCs were either not available in the model, or they exhibit low reactivity and therefore were not considered important drivers of indoor air chemistry. Cleaners with no observed monoterpene emission (SG4, BR2, BG3, DG1) were discounted from all subsequent analyses.

The chemical degradation of nine monoterpene species were represented in the model, see Fig. S4† for their chemical structures. Species α-pinene, β-pinene, and D-limonene were included as fully explicit reaction schemes, provided by the MCM.[37,38,45] Proxy-schemes for camphene, carene and γ-terpinene, developed by Carslaw *et al.*,[36] were utilised which use the rate coefficients for the preliminary oxidation steps using data from the literature and then mapping oxidation products onto existing MCM species. For the purpose of this study the same approach was used to develop degradation schemes for α-phellandrene, α-terpinene, and terpinolene. Inclusion of these nine monoterpenes accounted for over 95% of the total amount of monoterpenes identified from GC-MS analysis. Other monoterpenes identified (tricyclene, cyclofenchene, allocimene, α-thujene, α-fenchene, β-myrcene, sabinene, β-ocimene, β-phellandrene) were not included in the model because either their oxidation rate coefficients were not available in the literature, or they were not present in significant abundance.

3 Results and discussion

3.1 Characterisation of VOCs

High resolution gas chromatography mass spectrometry (GC-MS) was used to analyse the headspace composition of the cleaning products selected for this study. A total of 317 VOCs occurrences were observed, representing 97 VOC identities emitted from 23 cleaning products. Of the 317 VOCs emitted from the cleaners, 44 VOCs were detected just once, 18 VOCs were detected twice, and 36 VOCs were detected in three or more cleaners. The green cleaners exhibited a 6% greater number of VOC occurrences and a 36% greater number of VOC identities compared to the regular cleaners, demonstrating the variety in VOC composition of the green product formulations. The identified VOCs included 18 monoterpenes, 23 monoterpenoids, 8 sesquiterpenes, 17 alcohols, 17 esters, 6 aldehyde/ketone species and 8 other hydrocarbons (aromatics, alkanes, alkenes). The prevalence of the main chemical classes identified from regular and green cleaners is shown in Fig. 1.

Monoterpenes and monoterpenoids were the most commonly identified species in both regular and green cleaners, with five monoterpenes/monoterpenoids being identified in over 50% of the cleaners tested: limonene, eucalyptol, β-pinene, 3-carene and linalool. Limonene was the most prevalent VOC identified in regular and green cleaners, which is consistent with other studies of fragranced consumer

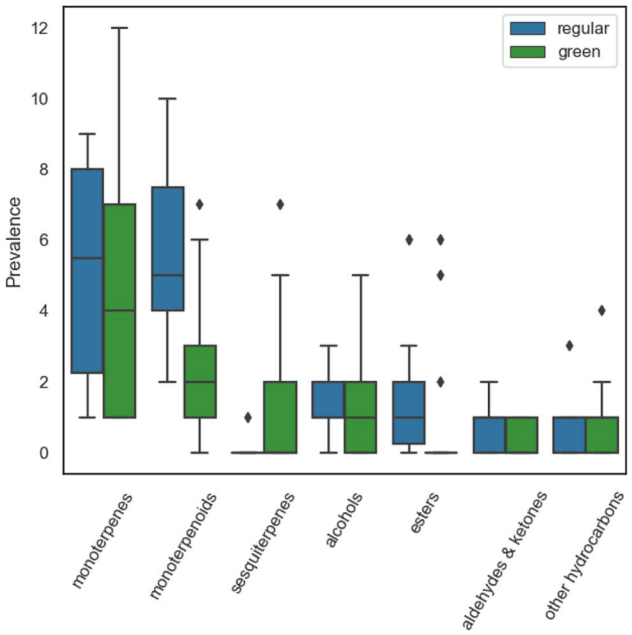

Fig. 1 The distribution of the number of VOCs of different chemical classes detected from regular ($n = 10$) and green ($n = 13$) cleaners by equilibrium headspace GC-TOF-MS. Boxes show median (central mark), 25th percentile and 75th percentile (box limits). Whiskers extend to the data points that are within the range of the 25th percentile minus 1.5 times the IQR and the 75th percentile plus 1.5 times the IQR. Diamond-shaped markers represent outliers.

products.[25,27] The detected monoterpenoid species included 8 alcohols, 8 esters, 4 ethers, 2 ketones and 1 aldehyde. The monoterpene alcohols were common in both regular and green cleaners, while monoterpene esters were twice as prevalent in the regular cleaners. The median number of monoterpenes and monoterpenoids was greater for the regular cleaners compared to the green cleaners, although the spread of monoterpenes was greater for green cleaners. This can be explained by the inclusion of 3 non-fragranced green cleaners in the analysis, which contained only 1 monoterpene, D-limonene. The monoterpenes α-thujene, β-ocimene, β-myrcene and allocimene were identified in green cleaners only, while α-fenchene was only identified in a regular cleaner ("ocean" scented). The greater variety of monoterpene compounds in green cleaners could be an indication that naturally derived fragrance ingredients (such as essential oils, which usually contain more than 100 different chemical substances[46]) are more commonly used in the formulation of green cleaners.

A greater number of green cleaners contained sesquiterpenes compared to regular cleaners, while esters, aldehydes and ketones were more prevalent in the regular cleaners. A possible explanation for this difference could be that green cleaners typically use natural fragrances such as essential oils or plant extracts which consist largely of biologically synthesised terpene compounds (including monoterpenes and sesquiterpenes) and oxygenated terpene derivatives.[47,48] Conversely, regular products typically incorporate synthetically derived fragrance mixtures, which utilise synthetic aroma chemicals such as esters and other carbonyls to replicate a "natural-identical" scent (although the exact chemical composition of synthetic fragrances is often proprietary information).[46]

3.2 Targeted quantification of VOCs

SIFT-MS was used with dynamic headspace sampling to directly quantify a targeted subset of VOCs in the cleaning product formulations. The compounds targeted in this analysis were selected based on the information obtained from the product ingredient lists, results from GC-MS analysis, and common VOCs reported in the literature regarding cleaning product emissions.

The headspace VOC concentrations increased immediately after the sample was introduced into the sample chamber, as the VOCs partitioned from the liquid to the gas phase. Over the duration of the 60 minutes measurement period the VOC concentrations peaked and then declined as the emission source was depleted, finally returning to background concentrations. An example of the VOC concentration profiles measured from a green surface cleaner (SG2) is shown in Fig. 2. This characteristic VOC concentration profile supported the assumption that the total amount of each VOC in the product formulation was released within the measurement period.

The mass concentrations of VOCs in the cleaning product formulations are reported in Table 2. The total VOC mass concentrations measured in this study ranged from 9.3 to 25 441 mg L^{-1}, which is comparable to a study by Temkin *et al.*, who reported mass concentrations ranging from 0.97 to 38 035 mg L^{-1} (μg g^{-1}) from 30 regular and green cleaning products.[27] DR1, SG1, and SG3 contained the largest total mass concentration of VOCs, with the measured compounds accounting for 2.5%, 2.0% and 1.3% of the total sample (w : v%). Ethanol was the greatest contributor to total VOC concentration for these cleaners, and was identified in 15 of the 23 samples, suggesting that it may be used as a common solvent in cleaning product formulations. Ethanol was explicitly listed as an ingredient in only one product (FG2), although a further 8 included 'alcohol' in the ingredient list. Methanol was also identified as a component of most of the cleaning product formulations, with quantifiable measurements made from 17 of the 23 cleaners ranging from 1418 to <10 mg L^{-1}.

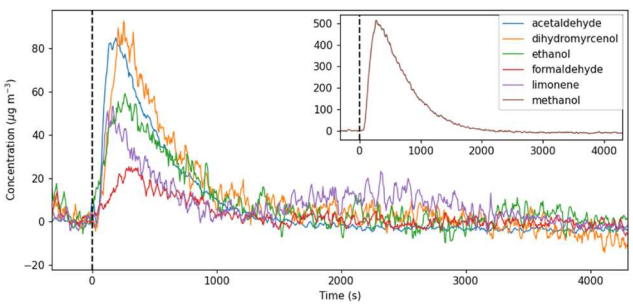

Fig. 2 The concentration profile of VOCs measured by SIFT-MS with dynamic headspace sampling of cleaner SG2. t_0 = time when sample was introduced to the headspace chamber (black dashed line).

Table 2 VOC mass concentrations measured from cleaning product formulations by headspace SIFT-MS (mg L^{-1})

sample ID	acetaldehyde	total monoterpenes	methanol	dihydromyrcenol	2-tert-butylcyclohexyl acetate	ethanol	formaldehyde	citral	lactic acid	2-phenethyl acetate	1,2,4-trimethylbenzene	total sesquiterpenes	m-xylene	cinnamaldehyde	eugenol	benzyl benzoate	benzene	total
DR1	194.7	30.7	1418.4	236.9	56.2	22439.8	255.3	54.0	728.2	-	5.9	16.4	-	4.8	-	-	-	25441.3
SG1	160.3	19.0	-	151.3	11.6	18727.2	188.1	5.1	666.0	-	-	3.5	-	-	-	-	-	19932.1
SG3	173.8	8.9	-	57.1	40.3	12047.9	199.4	14.4	270.4	14.9	10.8	-	12.3	-	0.9	-	-	12850.9
FG4	139.2	167.4	13.4	218.8	43.2	-	79.7	110.4	9206.0	6.2	6.1	41.5	1.9	86.6	-	-	-	10120.4
FG2	83.8	6.1	111.0	44.2	15.7	6198.9	71.8	14.2	164.7	1.9	1.3	21.1	-	66.9	-	9.6	-	6811.3
BG2	7.4	13.2	337.1	12.8	6.2	506.8	18.3	11.2	-	1.8	-	-	-	-	-	4.0	-	918.8
BG1	4.9	7.4	-	6.6	-	607.0	11.3	13.0	0.2	-	-	-	-	-	-	-	-	650.4
DG2	11.5	11.1	2.9	31.1	9.8	493.2	9.6	3.8	1.9	-	1.9	-	1.0	-	-	-	0.5	578.3
SR4	3.1	1.8	4.5	-	-	115.4	2.2	-	-	-	-	-	-	-	-	-	-	127.0
DR2	7.1	26.8	12.3	37.6	6.5	3.9	-	6.3	-	1.6	-	-	-	-	-	-	-	101.9
FG1	4.8	9.1	7.3	48.3	-	4.7	4.6	-	-	-	-	-	1.2	-	-	-	-	79.9
SG2	4.4	5.1	44.8	5.9	3.7	5.4	1.8	-	-	1.9	-	-	-	-	-	-	-	73.0
SR3	0.8	3.5	5.6	9.3	41.3	-	-	-	-	-	-	-	-	-	-	-	-	60.5
FR2	1.6	1.8	4.6	36.5	7.4	-	-	5.3	-	-	-	-	-	-	1.2	-	-	58.5
SR1	3.1	1.3	21.3	12.7	3.7	1.5	-	1.9	-	-	-	-	-	-	-	-	-	45.5
BR1	0.2	2.8	-	9.9	16.6	6.0	1.0	-	-	-	-	-	-	-	-	-	-	36.5
DG1	3.8	-	32.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	35.8
BR2	0.6	-	1.6	9.8	20.4	-	-	-	-	0.6	-	-	-	-	-	-	-	33.1
FR1	0.6	6.0	8.5	5.4	2.8	3.6	-	-	-	-	-	-	-	-	-	-	-	26.8
FG3	2.8	2.6	-	-	-	11.9	-	-	-	-	-	-	-	-	-	-	-	17.3
BG3	1.2	-	15.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	17.0
SR2	0.9	2.8	2.4	-	4.4	-	-	-	-	-	-	-	-	-	-	-	-	10.5
SG4	-	-	-	-	-	-	-	-	9.3	-	-	-	-	-	-	-	-	9.3

Formaldehyde (methanal, HCHO) and acetaldehyde (ethanal, CH_3CHO) were also emitted from most of the cleaning products at mass concentrations as high as 255.3 mg L^{-1} and 194.7 mg L^{-1}, respectively. These results are consistent with Temkin *et al.*, who observed formaldehyde and acetaldehyde emissions from over 30% of a range of regular and green cleaning products in the U.S. market.[27] Short chain aldehydes such as HCHO and CH_3CHO are pollutants of concern in the indoor environment due to their known or suspected toxicity, carcinogenicity and mutagenicity.[14,49] These results suggest that while they were not listed ingredients for any of the formulations, some cleaning products may be primary sources of HCHO and CH_3CHO in the built environment.

Lactic acid was identified as a component of 7 green cleaners and 1 regular cleaner. This compound was included in the ingredient list of 5 of the green cleaners including SG1 and SG3, for which relatively large mass concentrations were measured (660.0 and 270.4 mg L^{-1}, respectively). However, the largest mass concentrations of lactic acid were measured from FG4 (9206.0 mg L^{-1}) and DR1 (728.2 mg L^{-1}), which did not state lactic acid as an ingredient. Lactic acid is used in the green cleaning industry as a descaling and antimicrobial agent, which is produced by fermentation based on natural and renewable resources, and is an alternative to synthetic agents such as inorganic acids.[50]

Of the 23 cleaners studied, 20 of them listed fragrance components (usually non-specific *e.g.*, 'parfum') in their ingredients, with 10 explicitly listing limonene. The results from SIFT-MS were in good agreement with this observation, as monoterpenes were measured in 19 of the fragranced cleaners. Monoterpenes were undetected in the 3 unfragranced cleaners (DG1, BG3, SG4), as well as fragranced cleaner BR2. Of the fragranced cleaners, the average mass concentration of total monoterpenes was 8.6 and 25.0 mg L^{-1}, respectively. Although there is limited information available regarding liquid composition of cleaning products, this value is low compared to those reported in other studies. Singer *et al.*, reported a mass concentration of 44850 mg L^{-1} (44.85 mg mL^{-1}) of monoterpenes in a pine oil-based general-purpose cleaner,[33] while Angulo Milhem *et al.*, reported mass concentrations ranging from 15.0 to 992.6 mg L^{-1} (μg g^{-1}) of monoterpenes from 6 essential oil-based cleaners.[51] However, it is worth noting that the chemical formulation of cleaning products is likely to vary widely depending on the type of cleaning agent, the manufacturer, and regional regulations and policies regarding product formulation (with the latter likely changing over time, making it particularly hard to compare between studies separated by significant time periods). Additionally, both of these past studies focussed on cleaning products which were essential oil-based (*i.e.*, an essential oil was listed as an ingredient of the cleaner), whereas this was not a requirement for product selection in this study. Essential oils are mainly composed of terpenes and terpenoids:[52] formulations containing these ingredients are likely to have a larger concentration of monoterpenes compared to other products.

Other fragrance compounds identified in the product formulations included dihydromyrcenol ($C_{10}H_{20}O$, found in 17 cleaners), citral ($C_{10}H_{16}O$, found in 11 cleaners), sesquiterpenes ($C_{15}H_{24}$, found in 4 cleaners), cinnamaldehyde (C_9H_8O, found in 3 cleaners) and eugenol ($C_{10}H_{12}O_2$, found in 2 cleaners). It is

Table 3 Rate coefficients for the reactions of monoterpenes relevant to this study with OH, NO_3, and O_3 at 298 K, the yield of OH formed from the reactions between the terpenes and ozone and the OH production/loss metric described in the text[a]. The rate coefficients and OH yields of D-limonene, α-pinene and β-pinene are from the MCM.[56] All other rate coefficients and OH yields are from IUPAC Atmospheric Chemical Kinetic Data Evaluation[57] preferred values where possible

	Rate coefficient (cm^3 $molecule^{-1}$ s^{-1})				
Monoterpene	k(OH)	k(NO_3)	k(O_3)	OH yield(%)	OH production/loss
α-Terpinene	3.5×10^{-10}	1.8×10^{-10}	1.9×10^{-14}	0.38	1.77
Terpinolene	2.2×10^{-10}	9.7×10^{-11}	1.6×10^{-15}	0.70	0.44
α-Phellandrene	3.2×10^{-10}	7.3×10^{-11}	2.9×10^{-15}	0.32	0.25
α-Pinene	5.3×10^{-11}	6.2×10^{-12}	9.4×10^{-17}	0.80	0.12
D-Limonene	1.6×10^{-10}	1.2×10^{-11}	2.1×10^{-16}	0.87	0.10
γ-Terpinene	1.7×10^{-10}	2.9×10^{-11}	1.6×10^{-16}	0.81	0.07
3-Carene	8.8×10^{-11}[b]	9.1×10^{-12}	4.9×10^{-17}	0.86	0.04
β-Pinene	7.9×10^{-11}	2.5×10^{-12}	1.9×10^{-17}	0.35	0.01
Camphene	5.3×10^{-11}[c]	6.6×10^{-13}	5.0×10^{-19}	0.18	0.00

[a] The final column shows an estimate of the ratio of OH production: loss calculated as $k(O_3)[O_3] \times$ OH yield/k(OH)[OH], where $[O_3] = 1.06 \times 10^{11}$ molecule cm^{-3} and $[OH] = 1.23 \times 10^6$ molecule cm^{-3} (simulated indoor concentrations at 12 : 00). [b] *Atmos. Chem. Phys.* 2021, **21**, 12665–12685, DOI: https://doi.org/10.5194/acp-21-12665-2021. [c] *Atmospheric Environment, Part A: General Topics*, 1990, **24**(10), 2647–2654.

worth nothing that monoterpene alcohols ($C_{10}H_{18}O$) were not measured by SIFT-MS, and therefore concentrations of species such as linalool and eucalyptol, which were identified in the formulations using GC-MS, were not quantified.

Emission rates of the measured VOC species from a typical cleaning activity on a realistic scale were estimated using the approach outlined in the Methods section. The emission rates were used to initialise an indoor air chemistry model to gain a better understanding of the chemical fate of VOC emissions following cleaning, and the potential for harmful secondary pollutant formation.

3.3 Monoterpene emissions and implications for indoor air chemistry

The presence of monoterpenes in indoor environments is potentially important, because these compounds are chemically reactive towards indoor oxidants, such as O_3, and OH and NO_3 radicals.[36,38] Through multiple oxidation steps, monoterpenes can produce a range of secondary pollutants, including carbonyls, organic acids, peroxide species, organic nitrates and particulate matter.[13] There is evidence to suggest that the secondary pollutants from terpene oxidation chemistry are more hazardous to human health than the terpenes themselves. For example, Wolkoff *et al.* found that exposure of mice to an O_3/limonene mixture resulted in sensory irritation of the upper airways at concentrations below the no-observed-effect-levels (NOELs) of the parent compounds.[53] Additionally, the detrimental health effects of some terpene/O_3 reaction products are well documented such as HCHO, which is accepted to be a sensory irritant and human carcinogen.[14]

To investigate the production of secondary pollutants from terpene oxidation chemistry following cleaning, the measured monoterpene emission rates were used to drive the indoor air chemistry model, INCHEM-Py.[35] It was anticipated that the different combinations of monoterpene emissions in the cleaning simulations would give rise to different concentrations of secondary pollutants. This was observed by Carslaw *et al.*, who found that emissions of a 50 : 50 mix of limonene and α-pinene resulted in more efficient production of formaldehyde than the same concentration of the individual terpenes, while emissions of each monoterpene individually resulted in more efficient production of radical species and particulate matter.[54] Therefore, the secondary chemistry resulting from the complex terpene mixtures contained within fragranced cleaning products is likely to depend not only on the chemical reactivity of the individual species towards indoor oxidants, but also on the interplay between the chemical transformations and relative concentrations of each compound emitted from the cleaner.

The chemical reactivity of the nine monoterpenes included in the model simulations is described in Table 3. For each monoterpene the rate of reaction is generally fastest with OH, followed by NO_3. The rate of reaction with O_3 is much slower, with rate coefficients of the order of 10^{-14} to 10^{-19}. However, due to the high reactivity and instability of radical species, OH and NO_3 are short lived and are present in indoor environments at much lower concentrations compared to O_3, which has a longer lifetime and originates mostly from outdoor environments.[55] Therefore, initial oxidation of monoterpenes is generally more likely to occur *via* ozonolysis. The most reactive monoterpene towards O_3 is α-terpinene, while the least reactive is camphene.

Oxidation of a monoterpene can lead to net OH production or loss, depending on the balance between OH formation through ozonolysis, *versus* OH loss through reaction with the monoterpene. At any time, this balance depends on the ratio of the rate coefficients for reactions with OH and O_3 and the OH yield following ozonolysis for a particular monoterpene, and the OH and O_3 concentrations. Table 3 shows a proxy for this metric in the final column, which represents the balance between formation and loss of OH for each monoterpene using the O_3 and OH concentrations estimated by the model at midday.

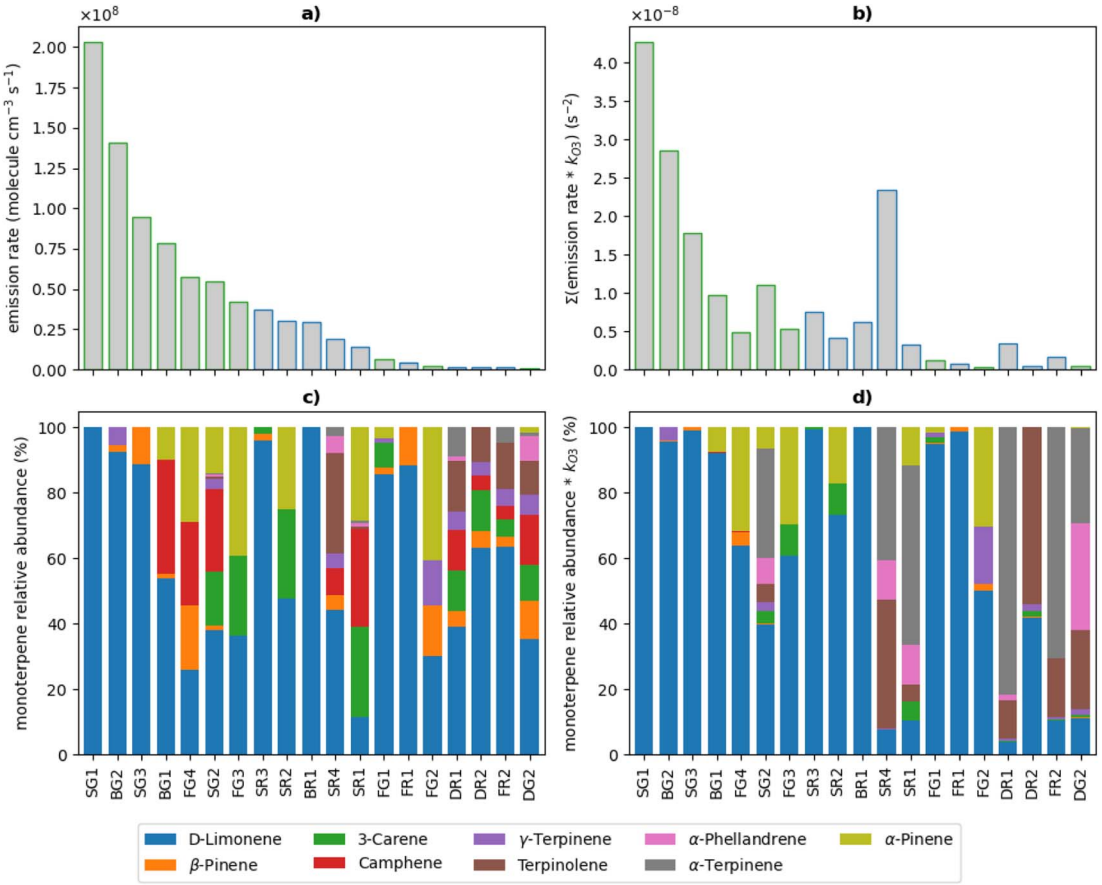

Fig. 3 (a) Estimated total monoterpene emission rates per product, as determined from SIFT-MS measurements (green edge bars = green cleaners, blue edge bar = regular cleaners). (b) The relative abundance (%) of monoterpenes determined from GC-MS analysis used to speciate the total monoterpene emission rates. (c) The sum of the monoterpene emission rates scaled to the monoterpene O_3 rate coefficient per product. (d) The relative abundance (%) of monoterpenes scaled to their respective O_3 rate coefficients.

Under these conditions, α-terpinene will contribute most to OH production indoors, due to its large O_3 rate coefficient compared to the OH rate coefficient. Camphene is the least important for OH production due to its very low O_3 rate coefficient. Depending on the mixtures of these monoterpene species indoors, one might expect quite different oxidation chemistry and hence secondary pollutant formation indoors.

The total monoterpene emission rates applied to the model are shown in Fig. 3A. Emission rates ranged from 5.9×10^5 to 2.0×10^8 molecule cm^{-3} s^{-1} (equivalent to 85 ppt h^{-1} and 29 ppb h^{-1}, respectively) with the top 7 emitters being green cleaners. Dishwashing liquids were the lowest emitters of monoterpenes, likely owing to the large dilution upon use of these products. The relative abundance ratios of monoterpene isomers used to speciate the total monoterpene emissions are shown in Fig. 3B. Limonene was the most abundant monoterpene in most cleaners, with 2 cleaners emitting 100% limonene. Other cleaners consisted of unique monoterpene profiles relating to the specific formulation ingredients of each product.

To illustrate the differences in reactivity towards indoor oxidants, the speciated monoterpene emission rates and relative abundance ratios for each cleaner were scaled to their corresponding O_3 rate coefficients (Table 3) in Fig. 3C and D, respectively. A similar approach has been taken to evaluate the differences in reactivity of the speciated monoterpene emissions from each cleaner towards OH radicals, shown in Fig. S5.† This process is illustrative given that monoterpenes react readily with O_3 and OH indoors.

The relative magnitude of the k_{O_3}-scaled emission rates increased or decreased in comparison to the total monoterpene emission rates per cleaning product, depending on the concentration and chemical reactivity of the different mixtures of monoterpene species emitted. SG1 had the highest monoterpene emission rate of all the cleaning products, consisting entirely of limonene, and also gave the largest value when scaled to k_{O_3}. Cleaning products which contained the most reactive monoterpenes α-terpinene, α-phellandrene and terpinolene typically resulted in an increase in the relative magnitude of the k_{O_3}-scaled emission rate. This was particularly observed for cleaners SG2, SR4, DR1, and FR2, which were the 4 largest emitters of these compounds. Interestingly, the cleaners containing the most reactive monoterpenes were mainly regular products. Conversely, when there were greater contributions to the total monoterpene emission rate from less reactive species such as camphene, β-pinene and 3-carene, a decrease in the relative magnitude of the k_{O_3}-scaled emission rate was observed.

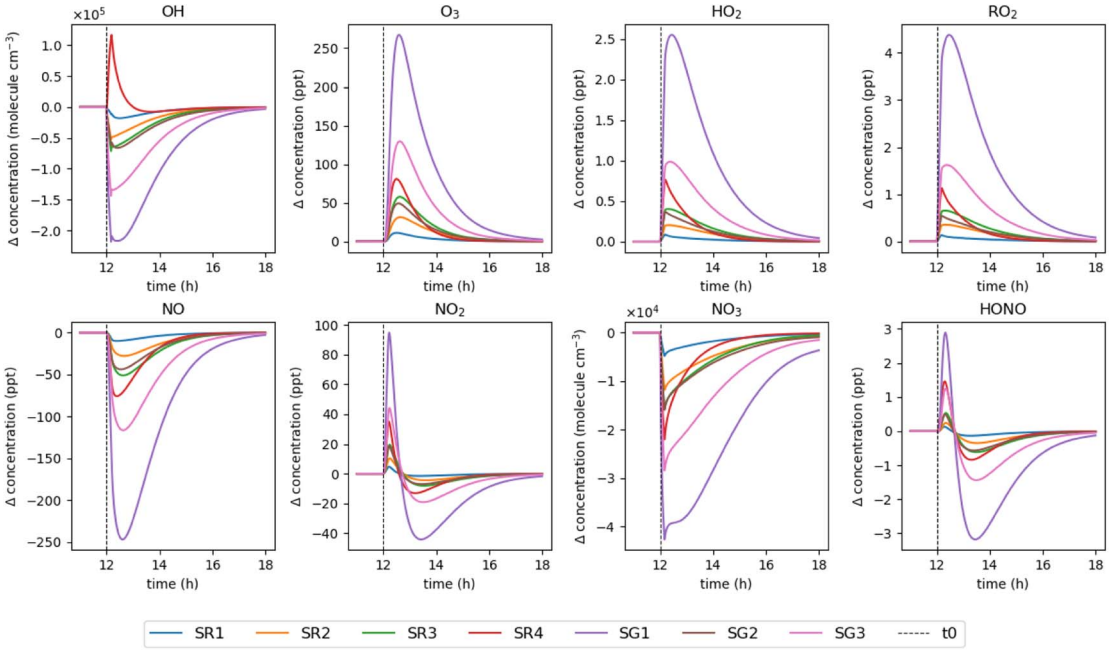

Fig. 4 Relative change in concentration of key indoor species from 11–18 h for each surface cleaner simulation, compared to a baseline simulation (no emissions).

This was the case for cleaners FG4, FG3 and SR2, which were among the highest emitters of these relatively low-reactivity monoterpenes.

The total monoterpene emission rates of the regular surface cleaners SR4 and SR1 were of similar magnitude (1.87×10^7 molecule cm^{-3} s^{-1} and 1.43×10^7 molecule cm^{-3} s^{-1}, respectively), however the magnitude of the k_{O_3}-scaled emission rates were considerably different for these two cleaners. The monoterpene emissions from SR1 consisted of 2% the most reactive monoterpenes and 58% of the less reactive monoterpenes, while those from SR4 consisted of 38% of reactive monoterpenes and 13% of low-reactivity monoterpenes. When scaled to the O_3 rate coefficients, the reactive monoterpene emissions contributed 72% and 91% for SR1 and SR4, respectively, despite these species only making up 2% of the overall monoterpene emission rate for SR1. This demonstrates that the more reactive species will dominate the chemistry and sequester the most O_3 from the indoor atmosphere, thus limiting the reactions of other monoterpenes with O_3. Therefore, reactive species such as α-terpinene, α-phellandrene and terpinolene will have a greater impact on the indoor air chemistry and resulting secondary pollutant concentrations, compared to less reactive species such as camphene, β-pinene and 3-carene.

In the simulated cleaning events, the peak total monoterpene mixing ratio following the timed emissions ranged from <0.2 to 4.8 ppb. These concentrations are low compared to a study performed by Singer *et al.*, who reported an average concentration of 2857 μg m^{-3} (513 ppb) monoterpenes in the first 60 minutes after mopping the floors of a 50 cm^3 chamber with a pine oil-based general-purpose cleaner.[33] By contrast, in the House Observations of Microbial and Environmental Chemistry (HOMEChem) campaign, an increase in limonene concentration of roughly 3 ppb was reported when mopping the floors of an experimental house with a terpene cleaner, much closer to our observed results.[58] The results reported in the literature demonstrate the large variability in terpene emissions from cleaning, likely arising from differences in product composition, dependencies on behavioural factors such as how the product is used/applied and how long for, and environmental factors such as ventilation conditions. These dependencies result in wide variations in experimental methodologies used to assess the VOC emissions from cleaning activities, thus limiting the ability to make meaningful comparisons of the reported results.[51]

The effect of monoterpene emissions on oxidant and radical species concentrations were investigated in greater detail to understand the chemical transformations that take place following a cleaning event. Fig. 4 shows the relative change in concentration of various species compared to a baseline simulation for the regular and green surface cleaners only, for simplicity. Following cleaning, OH concentrations undergo a rapid decrease as they react with the monoterpenes introduced to the system. The exception is SR4, which shows an increase in OH radicals following cleaning. Fig. 3 shows that this product contains α-terpinene, which is very effective at producing OH (see Table 3). SG1 shows the biggest decrease in OH concentration, which is composed entirely of limonene. Under these conditions, limonene effectively removes the OH.

For all cleaning simulations, the concentration of O_3 increases compared to the baseline simulation despite the occurrence of monoterpene-O_3 reactions. This is due to the production of peroxy (RO_2) and hydroxy (HO_2) radicals from monoterpene oxidation chemistry which react with nitric oxide (NO) to generate nitrogen dioxide (NO_2), as evidenced by the

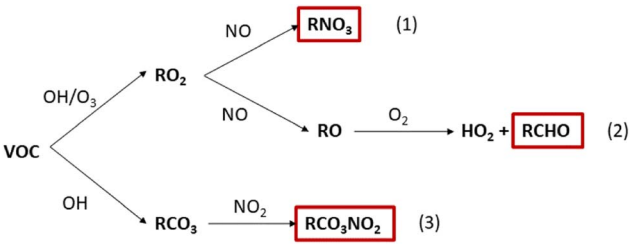

Fig. 5 The general VOC oxidation chemistry leading to the formation of key secondary pollutants: organic nitrates (RNO_3), formaldehyde (HCHO) and PAN species (RCO_3NO_2).

changes in these species' concentrations shown in Fig. 4. NO_2 undergoes photolysis to generate an oxygen atom, which then rapidly reacts with O_2 to generate O_3. Additionally, the sequestration of NO by reaction with RO_2 and HO_2 limits O_3 loss *via* reaction with NO, thus enhancing O_3 concentrations in the system compared to baseline. The greatest increase in O_3 concentration is observed for SG1 and SG3 which are the two largest monoterpene emitters, both consisting of over 85% limonene. SR4 causes the next largest increase in O_3, despite having the second smallest monoterpene emission of the surface cleaners. Fig. 3C shows that this product contains highly reactive monoterpenes (30% terpinolene, 3% α-terpinene and 5% α-phellandrene) resulting in efficient HO_2 and RO_2 production, hence more efficient NO_2 production and NO removal, favouring an overall increase in O_3 concentration.

The concentrations of NO_2 and nitrous acid (HONO) both show an initial increase following cleaning, followed by a rapid decrease to concentrations lower than the baseline simulation a few hours after cleaning. The main pathway of NO_2 production in the model is *via* the NO + O_3 reaction, therefore the concentration of NO_2 will depend critically on the concentrations of NO and O_3. Initially after cleaning, the NO and O_3 concentrations are sufficient for efficient production of NO_2. However, as time proceeds NO concentrations decline due to the increasing concentrations of RO_2 and HO_2 radicals, thus NO concentration becomes the limiting factor for NO_2 production, causing a decline in NO_2 concentrations relative to the baseline simulation. The main production pathway for HONO in the model is *via* heterogeneous chemistry of NO_2 on indoor surfaces

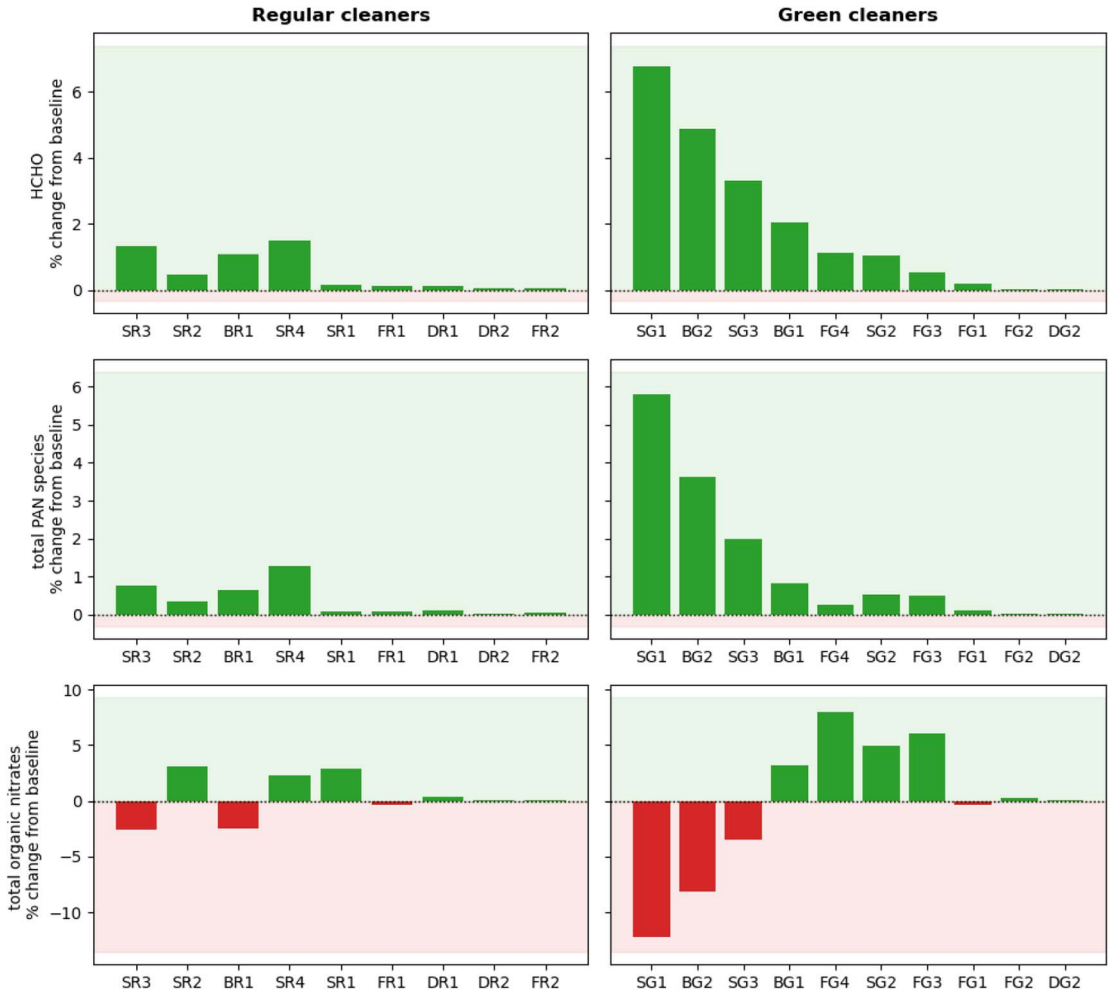

Fig. 6 Percentage difference in 3 hours post-emission average concentrations of secondary pollutants HCHO, total PAN species, and total organic nitrate species, compared to the baseline simulation for regular (LHS) and green (RHS) cleaners.

at a rate of $(2.9 \pm 1.8) \times 10^{-3}$ m min^{-1},[59,60] hence the concentration of HONO is strongly coupled to the concentration of NO_2 under these conditions.

The concentration of NO_3 radicals was low and decreased in all simulations owing to its high reactivity towards VOCs, particularly unsaturated compounds such as monoterpenes.[45] This chemistry further contributes to the production of RO_2 and nitrooxy-substituted RO_2 radicals and organic nitrates, which are an important precursor for secondary organic aerosol (SOA).[39]

The impact of the chemistry following cleaning on the production of secondary pollutants was evaluated for each cleaner. The percentage change in concentration of HCHO, PAN species and organic nitrates (RNO_3) are shown in Fig. 6. These species have been selected based on their known or suspected health impacts. HCHO is well understood to be a carcinogen[14,15] and is produced *via* the reaction of methoxy radicals (CH_3O) with ambient oxygen (Fig. 5, pathway 2). There is less evidence regarding the detrimental health effects of PAN species and organic nitrates, although they are both suspected of being irritants.[16–18,61] PAN species are formed by reaction of peroxyacetyl radicals (RCO_3) with NO_2 (Fig. 5, pathway 3), while organic nitrates are formed as minor reaction products of RO_2–NO chemistry (Fig. 5, pathway 1).

HCHO was produced in all cleaning simulations as a product of monoterpene oxidation. The extent of HCHO production varied from <0.1 to 6.8% relative to the baseline simulation over an average of 3 hours following cleaning. This relates to absolute HCHO mixing ratios of <2 ppb for all simulations, which is well below the safe exposure limits.[14] However, it is worth noting that while HCHO concentrations fall well below the recommended exposure limit of 0.1 ppm under these conditions,[62] larger concentrations are likely to arise from cleaning events involving multiple products and/or for longer cleaning periods. This is a particularly important consideration when evaluating occupational exposure to hazardous pollutants from cleaning, as professional cleaners will likely be exposed to higher concentrations of pollutants and for a much longer time than considered in this study.

Increases in HCHO concentration remained below 2% for all regular cleaners, while larger changes were observed for some green surface and bathroom cleaners (SG1, BG2, SG3, BG1). The increase in HCHO concentration correlates well with the magnitude of total monoterpene emissions. The exception is SR4, which produced a similar increase in HCHO concentration as FG3 (1.5% and 1.1% increase in HCHO, respectively), despite SR4 having a total monoterpene emission rate of less than half that of than FG3 (1.9×10^7 molecule cm^{-3} s^{-1} and 4.2×10^7 molecule cm^{-3} s^{-1}, respectively). Again, this can be attributed to the high reactivity of the monoterpenes emitted from SR4 towards indoor oxidants, leading to efficient RO_2 formation. When the RO_2 radical formed is CH_3O_2, HCHO is produced *via* reaction pathway 2 in Fig. 5.

PAN species were produced in all cleaning simulations, owing to the oxidation of emitted monoterpenes by OH to produce RCO_3 species which further react *via* pathway 3 in Fig. 5. The formation of PAN species following cleaning was small for most cleaners, with only three cleaners resulting in a 3 hours average change of >1% from the baseline simulation. SG1 was the largest producer of PAN species, resulting in a 3 hours average absolute mixing ratio of 25 ppt. SG1 was the largest emitter of total monoterpenes, consisting consisted entirely of limonene which has a relatively high OH rate coefficient (Table 3). The formation of PAN species was dependant on the magnitude of monoterpene emissions from the cleaning event and the reactivity of the emitted monoterpenes towards OH.

Finally, the concentration of organic nitrate compounds showed positive and negative changes in the simulations of both regular and green cleaning emissions. The formation of organic nitrates is dependent on the branching ratio of RO_2 + NO reactions to form RO ($\geq$80%) or organic nitrate species ($\leq$20%).[7] Hence, the specific RO_2 species formed by initial oxidation of monoterpene species determines the yield of organic nitrate *via* pathway 1 in Fig. 5. This is further evidence of how the complex mixture of different VOCs in cleaning products can influence the indoor air chemistry and the concentrations of potentially hazardous air pollutants.

4 Conclusions

Mass spectrometric techniques coupled with headspace sampling have been implemented to characterise and quantify the VOCs present in a range of regular and green household cleaning products. While the composition of each product formulation was unique, it was found that both regular and green cleaners contained VOCs pertaining to the broad chemical classes of monoterpenes, monoterpenoids, sesquiterpenes, alcohols, esters, carbonyls and other hydrocarbons. Monoterpenes and monoterpenoids were the most common compounds identified in the formulations of fragranced cleaners.

Targeted quantitative analysis of each formulation showed that there was large variety in the concentrations of VOCs in the product formulations. A comparison of the compounds detected *versus* those disclosed by manufacturers on the product labels supported evidence of ambiguity regarding cleaning product compositional information, highlighted in previous studies.[24,25] Alcohols (ethanol and methanol) were measured in high concentrations from some regular and green cleaners, while lactic acid was observed in predominantly green cleaners. These observations highlight potential compositional differences in the formulations of regular and green cleaners, for which there is currently very little information on in the available literature.

The implications of reactive monoterpene emissions from each cleaner on the indoor air chemistry was investigated using a detailed chemical model. The results of the model simulations highlighted the significance of both the quantity and the chemical reactivity of monoterpene emissions on the concentrations of oxidants, radicals and secondary pollutants indoors. In the present study, green cleaners were generally larger sources of monoterpene emissions compared to regular cleaners, resulting in larger increases in harmful secondary pollutants such as HCHO and PAN species. However, emissions of highly reactive monoterpenes such as α-terpinene,

terpinolene and α-phellandrene were observed from more regular cleaners than green cleaners, resulting in a disproportionately large impact on the concentrations of radical species and the production of HCHO.

The production of secondary pollutants from cleaning emissions reported in this study are unlikely to cause detrimental health effects to occupants. However, it is important to note that there is large variability in product formulations and occupant/environmental factors that would influence the VOC emissions from cleaning and subsequent chemical processing. Therefore, it is necessary to investigate a broader range of products and study VOC emissions from cleaning on a more realistic scale, to get a better understanding of how cleaning can contribute to indoor air pollution.

As sales of green cleaning products are increasing there exists a greater need for better regulation of these products. More transparent disclosure of cleaning product formulation ingredients is required to better inform consumers about potential exposure risks. Also, more careful consideration is required for the potential exposure to secondary pollutants resulting from chemical processing of the mixtures of reactive primary VOC emissions from cleaning. The quantity and chemical reactivity of monoterpene compounds used to provide fragrance for cleaning products should be carefully considered in the formulation development stage of product manufacture, and the potential implications on indoor air pollution assessed. These findings are also applicable to other fragranced household products, such as personal care products and laundry products.

Author contributions

E. H. S. conceptualisation, methodology, data curation, formal analysis, validation, visualisation, writing – original draft, writing – review & editing. D. S. formal analysis, methodology, writing – review & editing. M. S. methodology, data curation, writing – review & editing. T. D. conceptualisation, writing – review & editing, supervision. N. C. conceptualisation, writing – review & editing, supervision, funding acquisition.

Conflicts of interest

There are no conflicts to declare.

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