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Unexpectedly high concentrations of monoterpenes in a study of UK homes†

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The abundance of volatile organic compounds (VOCs) found in homes depends on many factors such as emissions, ventilation and the oxidative environment and these are evolving over time, reflecting changes in chemical use, behaviour and building design/materials. The concentrations of VOCs in 25 UK homes of varying ages, design and occupancy were quantified using continuous indoor air sampling over five days. Air was collected through low flow (1 mL min^{-1}) constant flow restrictors into evacuated 6 L internally silica-treated canisters until the canisters reached atmospheric pressure. This was followed by thermal desorption-gas chromatography and high mass accuracy time-of-flight mass spectrometry (TD-GC-TOF/MS). A fully quantitative analysis was performed on the eight most abundant hydrocarbon-based VOCs found. Despite differences in building characteristics and occupant numbers 94% of the homes had D-limonene or α-pinene as the most abundant VOCs. The variability seen across the 25 homes in concentrations of monoterpenes indoors was considerably greater than that of species such as isoprene, benzene, toluene and xylenes. The variance in VOCs indoors appeared to be strongly influenced by occupant activities such as cleaning with 5-day average concentrations of D-limonene ranging from 18 μg m^{-3} to over 1400 μg m^{-3}, a peak domestic value that is possibly the highest yet reported in the literature.

Environmental impact

This analysis focuses on 8 volatile organic compounds with variable indoor and outdoor sources found in UK homes. The home environment is the major setting for human exposure to indoor air pollutants as people spend most of their time indoors. Substantial variability was observed in VOCs between similarly designed homes, highlighting the difficulty in inferring exposure based on simple indirect metrics such as the building age or occupancy. We observe that monoterpenes dominated the composition in most homes and that variability in their concentrations was driven primarily by occupant behaviour. Using this information, individuals can potentially play an active role in reducing their exposure to these chemicals and their secondary products by either minimising their usage or by ensuring adequate home ventilation.

1. Practical implications

This analysis identifies volatile organic compounds found in private homes in the UK. It was observed that monoterpenes were the most individually abundant VOCs in the majority homes and that variability in their concentrations was driven primarily by occupant behaviour, specifically the frequency of use of cleaning products and fragranced materials. Using this information individuals can potentially then play an active role in controlling exposure to VOCs, and their secondary products, by either moderating their usage or ensuring adequate home ventilation. The substantial variability observed in VOCs found inside similarly designed homes highlights how difficult it may be to infer indoor chemical exposure based only on simple indirect metrics such as the building location, type, age or occupancy.

2. Introduction

Indoor air quality plays an important role in the well-being of occupants and greatly affects their behaviour and health quality.[1] People in Europe spend at least 90% of their time indoors[2] making this on a time weighted basis the dominant environment for exposure. Two thirds of the time indoors is spent at home, rendering the home environment a key setting for potential human exposure to air pollution.[3] Indoor pollutants include volatile organic compounds (VOCs), some of which

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have both short- and long-term adverse health effects and are directly classified as toxic or carcinogenic.[4–7] Many VOCs can also be oxidised to form more functionalised and sometimes harmful secondary products, particularly if they contain reactive carbon double bonds.[8–10] Monoterpenes are one class of VOCs found indoors that have high reactivity with hydroxyl (OH) radicals, ozone and nitrate (NO_3) radicals. Many hundreds of different structures are possible in nature and they are released from a very wide range of sources including cooking, foodstuffs, plants and multiple kinds of fragranced products. In practice only a small number of monoterpenes are found in high abundance reflecting the common use of certain individual chemicals (such as D-limonene and α-pinene) in multiple products. In terms of atmospheric chemistry, D-limonene and α-pinene are unsaturated monoterpenes which are susceptible to ozonolysis by the electrophilic attack of ozone on the $C{=}C$ double bonds, forming an unstable ozonide intermediate which breaks down into two possible combinations of a carbonyl and a Criegee biradical.[11,12] Intermediate reactive radicals, such as OH, are formed in this reaction[11,12] which could further react with indoor VOCs and contribute to the further formation of indoor oxidised VOC products.[13,14] Oxidation products of D-limonene include formaldehyde and 4-acetyl-1-methylcyclohexene, and those of α-pinene include formaldehyde, acetone and pinonaldehyde.[15]

Within any built environment VOCs are ubiquitous but there is considerable variation in their speciation and abundance. Sources of indoor VOCs include ingress of outdoor pollution from traffic and industries, outgassing from building materials, flooring, electronic equipment and furnishings, and emissions from food, cooking, cleaning products, personal care products, and from people and pets.[2,16,17] The concentrations and speciation of VOCs in indoor environments can also be influenced by seasonality, duration of occupancy, personal activities such as smoking and showering, and even the education levels of the occupants.[18–20]

Compared to half a century ago, there have been significant changes in the use of consumer products and building materials with impacts on both the concentrations and diversity of VOCs found indoors. In parallel there has been a move towards energy-efficient buildings with improved insulation and reduced air leakage and ventilation.[21,22] Sick or tight building syndrome is a term that has been used to describe circumstances whereby occupants within a building experience health-related effects or discomfort that seem to be related to the duration spent in a building. In such cases no specific cause can be found and relief from the symptoms, *i.e.* eye, nose and throat irritation and headaches, is typically experienced upon exiting or moving away from the building.[23–26] These building related symptoms have been reported to have increased discomfort and negative health effects, and result in reduced productivity at work and in schools.[23,27]

This paper provides an estimate of the current concentrations, speciation and variability of VOCs in UK homes in 2015, providing an updated set of estimates of the predominant indoor air composition at that time. The study used whole air sampling, the default method for high precision sampling outdoors and applied this indoors alongside a universal GC-TOF/MS analysis. By using whole air samples and GC-TOF, rather than adsorption tubes (which are the more commonly used indoor method), skewing of sampling based on compound volatility is largely eliminated and this allows a quantification of volatiles such as isoprene. The data reported in this work combined two different studies conducted in London and York in 2015. In total 25 homes were sampled on multiple occasions, 19 in London representing homes of diverse property types, ages and occupant densities. The remaining 6 homes were located in York and were of a very similar age (~2000) and building design. The samples collected from the 19 London homes were used to improve the understanding of the current distribution across a property mix in a major city, and the repeated sampling of 6 similar modern-build homes in York to understand how the current variability in VOC concentrations and speciation can be driven by occupant behaviour.

3. Experimental

Sampling in London and York was carried out in homes which were located in residential urban areas. In both cities information on the air exchange rate of the homes was not collected; there was no available information about the heating, ventilation and air-conditioning (HVAC) systems in the homes, nor the occupants' frequency and duration of opening windows. Whilst details were not collected domestic air conditioning systems are exceptionally rare in UK homes.

3.1. VOC sampling and analysis

The most common method reported in the literature for VOC sampling indoors is to either passively sample (*via* diffusion) or pump sample air onto chemical adsorption tubes, often packed with Tenax polymer, and various ISO methods exist. For outdoor air sampling such methods are only infrequently used since the sampling is skewed to the collection of VOCs that have moderate to low volatility whilst more volatile species, for example ethane, propane, butane, pentane and isoprene, pass through the adsorbent bed with poor adsorption.[28–30] Instead we apply the preferred World Meteorological Organisation (WMO) method for measurement of ambient VOCs based on sampling air into initially evacuated whole air canisters. Such an approach collects all VOCs that are present without discrimination and the method allows for multiple repeat analysis of the same sample. The method does not require electricity, uses no chemicals and is intrinsically safe and suitable for untrained users. A further advantage of stainless canisters is that the effects of ozone on the sample are much reduced, with co-sampled ozone destroyed on contact with the stainless steel inlet and walls through autoxidation. No chemical scrubbers are needed.[31,32]

To collect the samples in both London and York 6 liter internal volume canisters (SilcoCan, Thames Restek U.K. Ltd) were used followed by analysis using gas chromatography and time-of-flight mass spectrometry (GC-Q-TOF/MS). Using this approach there was no discrimination in the sampling towards

VOCs of intermediate volatility. Since we are working only with preserved gaseous samples we then extend this to the calibration using picomole per mole gas standards and with no reliance on the liquid spiking of test materials onto adsorption tubes.

Prior to sampling, the canisters were evacuated with a dry scroll vacuum pump to around 3×10^{-3} atm, following the WMO methodology. Each of the canisters was fixed with a constant flow inlet system (Thames Restek U.K. Ltd). This is a critical orifice made from machined 316 stainless steel that allows a constant gas flow through the orifice into the canister, irrespective of the internal vacuum of the canister until the canister reaches ambient atmospheric pressure. The critical orifice inlets allowed a flow rate of $\sim$1 mL min^{-1} until the canister pressure reached ambient pressure after approximately 5 days. Using this method a true 5-day average concentration is determined.

Prior to chemical analysis the canisters containing sample air at ambient pressure were pressurised from atmospheric pressure to 3 atmospheres with helium (BOC Gases, 6.0 ultra-high purity grade), resulting in a dilution factor later corrected for during quantification. The large sample of gas in each canister allowed for repeated analyses if required, an advantage over sorption tubes. All canisters were analysed within two weeks after completion of sampling to minimise any losses due to physical adsorption, reactions with reactive compounds and degradation.[33] This time period was largely a result of the time needed to effect the collection of samples from participants' homes and the shipping of those samples to York. Blanks were run with canisters containing pressurised helium.

A difference between the method used here and the more traditional methods used for VOC measurement using adsorption tubes is the use of direct gas phase standards rather than liquid surrogates spiked onto tubes. We use multi-component high pressure VOC gas standards at the parts per billion mixing ratio with a balance gas of N_2 from the UK National Physical Laboratory. These standards contain ozone precursor hydrocarbon VOCs typically at 4 ppb with a gravimetric preparation uncertainty of 5%. A range of monoterpenes in a gas phase standard from NPL were also available for calibration, the choice of these species taken from the current target list of the WMO Global Atmospheric Watch. The analytical method included a routine calibration of the whole system response to VOCs, achieved through flowing gas calibrant mixtures through water removal, thermal desorption and the GC-MS procedure. VOC gas standards and zero samples using high purity helium bracketed the analysis of individual sample canisters.

3.2. Analytical method

The pressurised air sample was introduced into a thermal desorption unit (Markes Unity Series 2 Thermal Desorption Unit) prior to separation on a gas chromatography (GC) column. A metered flow of the sample gas was first passed through a glass cold-finger assembly maintained at a temperature of about −35 °C. This served to remove moisture from the gas before it entered the thermal desorption unit, to prevent icing in the adsorbent trap and to reduce the amount of water ultimately entering the mass spectrometer. 1000 mL of gas was sampled at 100 mL min^{-1} onto a refocusing adsorption trap packed with a Tenax sorbent. The choice of Tenax as the adsorbent was to specifically support the sampling of monoterpenes, since this material provides the most stable matrix for avoiding molecular rearrangements. The relatively low temperature of the Tenax trap was necessary to allow for the quantitative collection of volatile VOCs, for example isoprene, that were in the sample gas. Once the VOCs were focused on the Tenax trap, it was then purged for 1 minute at 100 mL min^{-1} with helium to remove permanent gases. After this, the trap was ballistically heated from −30 °C to 300 °C at the maximum heating rate of the system and held for 3 minutes, with the VOCs transferred to the GC column in splitless mode at a flow rate of around 1.5 mL min^{-1}.

High purity helium (BIP Air Products, Keumiee, Belgium) was used as the carrier gas for GC. Separation was performed on a BPX5 column (50 m × 0.32 mm × 1.0 μm, length × internal diameter × film thickness) with two split outlets, one going to the Agilent time-of-flight/mass spectrometer (TOF/MS) and the other going directly into an olfactory port, used either for human assessment or as a mounting for a secondary photoionisation detector (PID). The GC column was programmed to run at 40 °C for 3 min; then ramp at 15 °C min^{-1} to 125 °C; then at 20 °C min^{-1} to 250 °C; and held for 2 minutes.

The time-of-flight mass spectrometer collected all masses between 45 and 500 amu simultaneously, with data binning to an accuracy of 1 part per million. For subsequent data analysis a mass accuracy of 10 ppm was typically used, providing a good balance between the exact molecular elemental composition and sensitivity. The sensitivity of the method is largely defined by the sample volume pre-concentrated on the thermal desorption, any blank or artefact value and the sensitivity of the mass spectrometer to each VOC. The last of these factors varies considerably depending on the fragmentation patterns of VOCs. For hydrocarbon-based VOCs the blank values are typically not significant in an indoor context and a limit of detection (LOD) of around 2 ppt is typically achieved, using 3 × standard deviation definition. The limit of quantification is typically 10 ppt for hydrocarbon based VOCs in this system (10 × std dev definition), but this is largely irrelevant given that the most abundant VOCs are in the parts per billion range. For species such as cyclic volatile methyl siloxanes (cVMSs), their detection limit is below 1 part per trillion because their fragmentation pattern are highly advantageous and unique. However their LOQ is then very significantly affected by blank and background values and this prevents a quantitative analysis here, even though many cVMSs are present in the parts per billion range.

An expanded uncertainty in measurement for hydrocarbon-based VOCs can be derived based on the canister to canister sampling reproducibility, canister stability, and analytical run to run reproducibility, combined with uncertainty introduced by the gaseous gravimetric standards. The canister stability is the hardest value to assess since it is potentially unique to each environment tested. The storage of samples in the canisters used here show no statistically significant (that is outside of the

Table 1 The detected compounds

VOCs quantitatively analysed	VOCs detected qualitatively
Isoprene	Hexamethylcyclotrisiloxane
Benzene	Octamethylcyclotetrasiloxane
Toluene	Decamethylcyclopentasiloxane
Ethylbenzene	Dodecamethylcyclohexasiloxane
m + *p*-Xylenes	Butan-2-one
o-Xylene	1,2-Dichloroethane
α-Pinene	Tetrachloroethylene
D-Limonene	Dichloromethane
	Allylmethylsulfide
	Diallylsulfide
	Naphthalene
	3-Carene
	p-Cymene
	Trimethylbenzenes
	Acetone
	Hexanal

measurement uncertainty) changes over periods of two weeks. The expanded uncertainty when the measurand is in the 1–1000 parts per billion mixing ratio range is typically 10%, with the gravimetric standards introducing the largest single source of error.

The analysis of formaldehyde was carried out on a high performance liquid chromatography (HPLC) apparatus with an elution gradient and ultra-violet (UV) detection. Separation was performed on a reverse phase C_{18} HPLC column (150 mm length, 4.6 mm diameter, and 5 μm packing particle size). The detector was set to a wavelength of 365 nm. The flow rate was set at 1.9 mL min^{-1}, and isocratic elution was carried out with acetonitrile/water 38 : 62 v/v in 10 minutes, and reverse gradient to acetonitrile/water 38 : 62 v/v in 5 minutes.

The list of the most abundant (as a mass concentration) detectable VOC compounds in the study is shown in Table 1 and these are the eight most abundant hydrocarbon-based species that are then subject to a fully quantitative analysis in this paper. Fig. 1 shows a total ion GC-MS chromatogram obtained from the analysis of one of the homes in London with major peaks identified, and Fig. 2 shows the extracted ion chromatograms of the selected VOCs at their exact masses (except D_4) to confirm their identities using the high mass accuracy of the Agilent GC-QTOF mass spectrometer.

3.3. 19-home study in London

As part of an exposure assessment during a pregnancy study in London, static sampling units were installed in participants' homes with sensors to account for a number of environmental stressors (including VOCs *via* canister sampling) shown to impact pregnancy outcomes.[34] The sampling occurred in the spring of 2015.

A questionnaire survey was conducted to collect further information about the homes sampled. In summary, the occupancy density ranged from 2–5 people in each home; 74% of the homes were double-glazed; 50% of the homes had gas cooking; the mean temperature values ranged from 19 °C to 26 °C and the humidity from 30% to 54%. Indoor sampling took place in the living rooms of all the homes, with 32% of the homes featuring an open-plan living room and kitchen. Household characteristics recorded for the London houses mainly captured factors that can influence the concentration of VOCs generated indoors such as the building age, square footage of the homes, flat/house types, glazing of windows, and occupancy densities, as well as the type of stoves installed in the kitchen.

VOC samples were collected in evacuated canisters as described in Section 3.1. The canisters were packaged with passive air sampling inlet kits at ambient temperature and shipped from York to London. After sampling, the canisters from London were sent back to York at ambient temperature and analysed within 14 days.

Temperature and relative humidity measurements were conducted using an integral unit developed by the University of Cambridge Department of Chemistry, 'SNAQ Wireless sensor

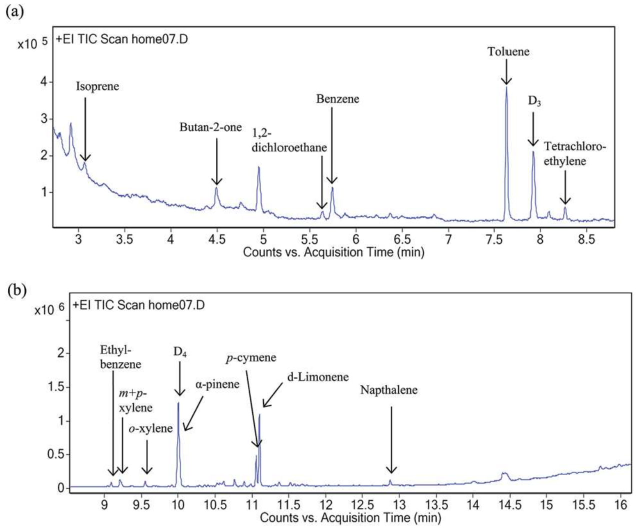

Fig. 1 Total ion chromatogram of one of the homes in London. Detection by using the TOF/MS detector. Retention time period: (a) 2.5–8.5 min and (b) 8.5–16 min.

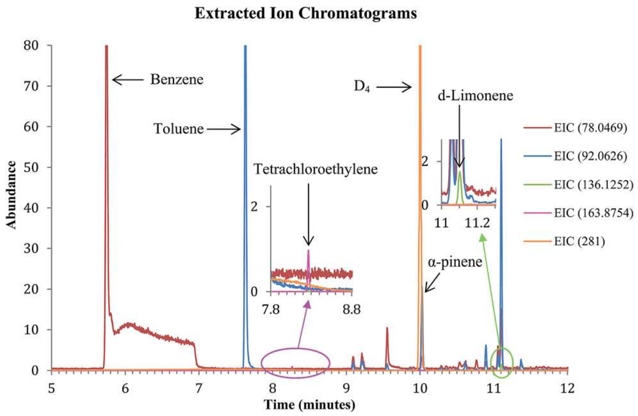

Fig. 2 Extracted ion chromatograms of the selected VOCs at their exact masses (except for D4) for one of the homes in London.

unit'.[35] The unit incorporated temperature and RH probes with a logging interval set to 2 seconds. A GPRS transmitter stored and uploaded data to a server for post-processing and off-line analysis.

3.4. 6-homes study in York

Six homes in York were chosen at random by BBC researchers as part of the programme "Trust me I'm a Doctor" broadcast in January 2016. Sampling was conducted in the autumn of 2015. The selected homes were of 3 and 4 bedroom-size, built around 15 years ago. Three samples were taken in each home, and the time span between each sampling period was approximately two weeks. In a similar fashion to the London measurements VOC samples were collected into evacuated 6 litre silica-treated steel passivated canisters integrated over a week using constant flow critical orifice restricted inlets. The sampling canisters were placed in living rooms. In addition to canister sampling, formaldehyde sampling was performed at three of the homes, using a carbonyl derivatisation method with a stainless steel net cartridge filled with 2,4-dinitrophenylhydrazine (2,4-DNPH) coated Florisil®[36] (Radiello code 165, Supelco Analytical, USA) followed by HPLC analysis.

Information such as the types and frequency of consumer/cleaning products used was collected from each of the homes studied in York. In the homes studied, between six to ten different products were used in each home per week. The frequency of usage of each item ranged between one to ten times per week. It was noted that the types and frequency of product usage varied significantly from household to household; the types of products used included general room fragrances, plug-in air fresheners, cleaning sprays and polishes, scented candles, and washing liquids as well as numerous different personal care products. None of the selected residences had attached garages and no indoor smoking activity was reported.

4. Results and analysis

4.1. 19-homes study in London

The most abundant and frequently detected VOCs in almost all UK homes were α-pinene and D-limonene. These originate from a combination of natural sources, including plants and foods, and from fragranced consumer products, a class that we define as including personal care and more general cleaning materials.[37] Compounds including toluene, ethylbenzene and xylenes which are constituents of household products *i.e.* paints, adhesives[38,39] *etc.* were also ubiquitous. In a study by Liu *et al.*, the concentration and source characteristics of carbonyls, benzene, toluene, ethylbenzene and xylenes in Beijing homes were studied with higher concentrations of some compounds (*i.e.* formaldehyde, acetaldehyde, benzene and toluene) attributed to the recent renovation of the homes.[40] In a separate study by Xu *et al.*, the measured VOC (including alkanes, benzene, toluene, xylenes and terpenes) concentrations in indoor environments were generally higher than those of outdoor environments, with the exception of carbon tetrachloride.[41]

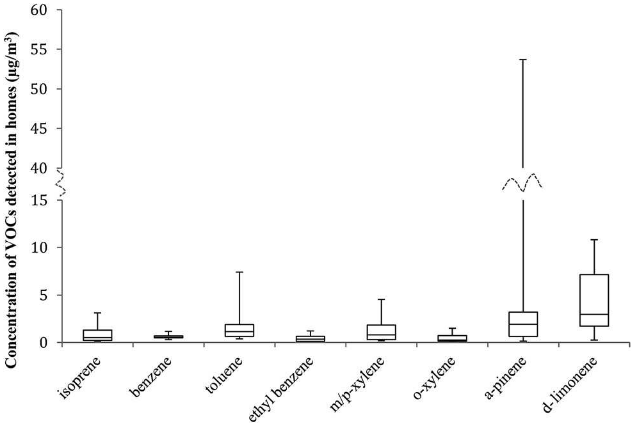

Fig. 3 Variability in the selected indoor VOCs for 19 homes in London, showing the median, interquartile range and the maximum and the minimum amount detected.

Additionally, it was inferred that while compounds such as benzene and short-chain alkanes were likely to be from outdoor sources, compounds such as monoterpenes and naphthalene were likely to have originated from indoor sources.[41] In some of the London homes naphthalene was observed, although its origins could be from many different sources including cigarette smoke, pesticides and insecticides, or diesel fuel.[42–44] Known halogenated compounds such as 1,2-dichloroethane and tetrachloroethylene were observed in several homes. Cyclic volatile methyl siloxanes (cVMSs) such as hexamethylcyclotrisiloxane (D_3), octamethylcyclotetrasiloxane (D_4) and decamethylcyclopentasiloxane (D_5) were also detected frequently. These compounds are ubiquitous and can easily be found as background contamination in blank or control samples[45] resulting in persistently high background concentrations of cVMSs found in our analyses. Although the concentrations of these cVMSs were not quantifiable, their apparent high concentrations and wide occurrence indoors are highlighted here as a significant feature of UK homes.

The variability in the concentration of the selected indoor VOCs for the 19 homes is shown in Fig. 3. Fig. 3 illustrates that certain VOCs within the London homes vary considerably, and no significant relationship was found to be associated with the building age, size or occupancy. Whilst most VOCs show considerable variability between homes the most abundant species observed are typically the monoterpenes, *i.e.* D-limonene and α-pinene. These compounds were observed in concentrations ranging from below the detection limit ($0.01\ \mu g\ m^{-3}$) to as high as $54\ \mu g\ m^{-3}$. This is a 5-day average concentration and hence the short-term peak concentrations are likely to have been higher. It was inferred that the greater variability seen in monoterpenes, compared to other VOCs, likely reflects the heterogeneous daily habits of the inhabitants in their use of cleaning and personal care products. Given that there are sources of D-limonene from food, plants and flowers it would be reasonable to consider that there is a 'natural' component to the observed variability and an anthropogenic component, although of course the definition is somewhat arbitrary. In the

Table 2 Ratios of concentrations of VOC/benzene

	VOC/benzene ratio						
	Isoprene	Toluene	Ethyl-benzene	*m* + *p*-Xylenes	*o*-Xylene	α-Pinene	D-Limonene
Mean	1.35	2.71	0.73	2.03	0.75	5.88	7.64
Median	1.20	1.99	0.54	1.25	0.46	2.55	5.16
Q_1[a]	0.36	1.40	0.28	0.69	0.27	1.30	3.60
Q_3[b]	1.65	2.97	1.01	2.55	0.88	5.28	12.11

[a] Q_1 is the middle value in the first half of the data set (first quartile). [b] Q_3 is the middle value in the second half of the data set (third quartile).

UK under wintertime conditions an outdoor natural source of monoterpenes from trees and plants can be considered negligible. Order-of-magnitude differences were seen in the average concentration of compounds such as toluene (factor of 19) and xylenes (factor of 26 for *o*-xylene) between homes in the study, with the least variability, a factor of 4, shown for benzene.

The indoor concentration of benzene is known to be well correlated with its outdoor concentrations, with the indoor/outdoor (I/O) ratio being close to 1.[46–49] Hence, the variability in benzene concentrations observed in this study was taken to be a proxy for variation in outdoor concentrations and ventilation influences on the concentrations of the other compounds observed in each of the homes. The ratios of the concentrations of each of the compounds to the respective concentrations of benzene for each sampling point were calculated and averaged as shown in Table 2. The ratios obtained for D-limonene (mean: 8; median: 5) and α-pinene (mean: 6; median: 3) were of a greater magnitude when compared to the other VOCs which had mean and median ratios of about 1 to 3. This indicated that the most likely source of the high concentrations of, and variability in, D-limonene and α-pinene was from indoor sources.

A comparison was made between the concentrations of various VOCs in homes with single glazed windows *versus* those with double glazed windows. In the absence of ventilation measurements from each house this was considered to be a proxy for air exchange. Previous analysis of the ventilation effects of changing single pane to double glazed windows in UK homes showed large effects on air infiltration. Average impacts in the study by Ridley *et al.* showed a reduction from 0.9 ach (air change per hour) to 0.64 ach when window types were swapped.[50] However, as seen from Fig. 4, it was difficult to draw a relationship between the types of windows and the concentrations of VOCs observed. *T*-Tests were conducted for all the compounds listed in the figure, and the results showed that there was no statistically significant difference ($\alpha = 0.05$) between the concentrations of the compounds in homes with single and double glazed windows, *i.e.* for benzene: $t = 0.59$ and $p = 0.58$; for ethylbenzene: $t = -2.05$ and $p = 0.057$ (most significant); for D-limonene: $t = -0.299$ and $p = 0.772$ (least significant). Although the type of glazing may give a general idea about the ventilation in a home, further tests would have to be conducted utilising larger sample sizes for a more conclusive relationship to be inferred between the types of glazing in homes, ventilation rates (or tightness) of the buildings and concentrations of compounds found in the indoor environment. In addition no information was available on the frequency of window opening and the impact of outdoor sources of traffic-related VOCs could not be assessed, since no immediate outdoor data were available in the current study.

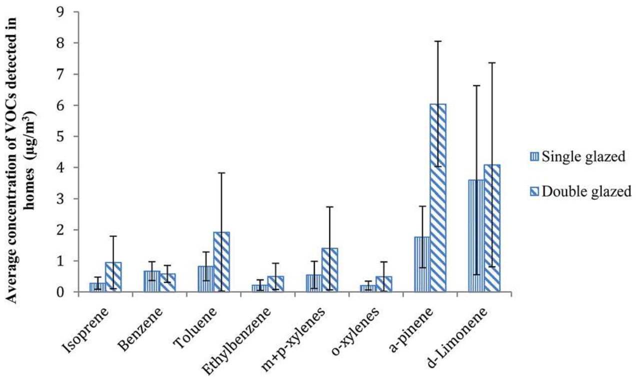

Fig. 4 Comparison between homes with single-glazed windows and double-glazed windows.

4.2. 6-homes study in York

The London results provided a single 5-day average sample snapshot across a range of houses. The York study was designed to examine the house-to-house variability for similar building types, albeit for a small sample size and period. This aimed to remove some of the variability induced by building construction and leave the predominant source of variability as occupant behaviour. Quantitative analysis was conducted for the same eight most abundant VOCs found in all homes. Similar to the results in London, the concentrations of α-pinene and D-limonene showed a much greater variability and range compared to those of other VOCs (see Fig. 5). The 5-day average concentrations of α-pinene and D-limonene ranged from 2 to 229 μg m^{-3} and 18 to 1439 μg m^{-3} respectively, whereas the concentrations of isoprene and benzene were within much narrower ranges of 11 to 22 μg m^{-3} and 7 to 19 μg m^{-3} respectively. An activity log (Table 3) kept by occupants in the 6 homes showed that the highest concentration of D-limonene found in home 4, with a mean D-limonene concentration of 807 μg m^{-3}, was associated with occupants who used 9 different cleaning and fragrance products, each used on more than 10 occasions over the week. For other homes, 6–10 different products were used 1–5 times per week during the

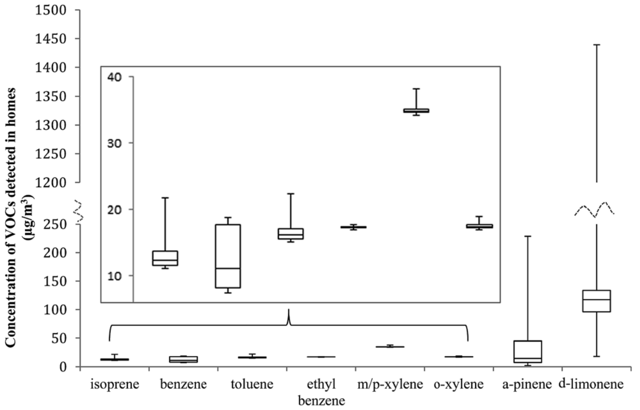

Fig. 5 Averaged concentration of the most abundant indoor VOCs from six similarly built homes in York showing the median, interquartile range and the maximum and minimum values.

sampling period. Another interesting observation was that aside from home 4 which had exceptional D-limonene concentrations, there were two more homes which exceeded mean D-limonene concentrations of 100 µg m^{-3} (home 3 with a mean of 157 µg m^{-3} and home 6 with a mean of 111 µg m^{-3}). Although both homes used a variety of fragrances and cleaning products with different and lower frequencies of usage, they also burnt scented candles five times during the sampling period.

This large variability in the concentrations of α-pinene and D-limonene within similar building-types highlighted the significant impact of inhabitant behaviour and indoor sources in each of the homes. It showed that whilst the average estimated concentrations of species such as benzene are broadly representative of general exposure, more individualised measurements are vital for monoterpenes and mean values across a population study are not informative for individual exposure estimates.

Although both α-pinene and D-limonene are generally considered to have low toxicity,[6,51] they can form secondary pollutants by reaction with ozone and hydroxyl radicals, including compounds such as limonene oxide and formaldehyde.[7,52] When the concentrations of limonene are in the range of 100–1000 µg m^{-3}, the secondary yields of products such as formaldehyde have the potential to become significant, relative to the expected indoor ambient concentrations of formaldehyde. The formaldehyde yield from the oxidation of D-limonene is around 10–19% (ref. 53) under typical outdoor atmospheric conditions, and so there exists at least the chemical potential for the formation of tens of micrograms per cubic meter of formaldehyde in the steady state. This can be compared with the values of formaldehyde observed here which are of the same order of magnitude. The exact oxidative environment indoors is of course different to that outdoors, but we would highlight that even relatively low yield reactions from monoterpenes would have the potential to make notable contributions to indoor formaldehyde when the primary VOC was in such high abundance.

Table 3 Activity log for the York homes

	Type of consumer product	Quantity	Frequency used over the sampling period
Home 1	Cleaning products	4	4 products used once
	Fragrance/freshener	2	2 products used 5 times
Home 2	Cleaning products	6	2 products used once 4 products used twice
	Fragrance/freshener	1	1 product used 3 times
Home 3	Cleaning products	4	1 product used twice 1 product used 3 times 2 products used 5 times
	Fragrance/freshener	2	2 products used once
	Scented candle	1	1 product used 5 times
Home 4	Cleaning products	8	8 products used 10 times
	Fragrance/freshener	1	1 product used 10 times
Home 5	Cleaning products	8	4 products used once 4 products used 5 times
	Fragrance/freshener	2	2 products used 5 times
Home 6	Cleaning products	5	5 products used 5 times
	Fragrance/freshener	1	1 product used 5 times
	Scented candle	1	1 product used 5 times

Formaldehyde was also measured in parallel in three homes (homes 3, 4 and 5) in this study, taking the average measurement from pairs of co-deployed 72-hour average diffusion tubes. These three homes were chosen since they spanned the lowest to the highest D-limonene concentrations. Average formaldehyde in home 4, which reported the highest VOC concentrations, was 66 µg m^{-3}, in home 3 it was 47 µg m^{-3}, and in home 5 which reported the lowest VOC concentrations, it was 33 µg m^{-3}.

Fig. 6 shows the data obtained for each home. The tabulated data for the analysis of the homes in York is in the ESI (Table S1†).

Similar to the data analysis for the London homes the indoor/outdoor benzene concentrations were assumed to be ~1. The ratios of the concentration of each of the compounds to the respective concentrations of benzene observed in each of the homes in York were calculated and are shown in Table 4. The ratios obtained for D-limonene were much higher, with a mean of 21 and median of 10, compared to those of the other compounds which had mean and median ratios of about 1 to 3. Again, this pointed to predominant indoor sources of the monoterpene species.

4.3. Comparison with other studies

The median concentrations of D-limonene in the homes observed in the York study ranged from 79 µg m^{-3} to as high as 814 µg m^{-3}. While there was week-to-week variability within each of the homes sampled, the measured D-limonene concentrations were higher than any previously reported for homes in other studies. A previous national large survey conducted in 875 homes in England found that D-limonene values ranged from 0.1 µg m^{-3} to 308 µg m^{-3}, with a geometric mean of 6.2 µg m^{-3}.[54] In the AIRMEX (European Indoor Air Monitoring and Exposure assessment) study involving VOC measurements in public buildings, schools and homes in eleven European cities, D-limonene was identified as being predominantly derived from indoor sources, with mean concentrations of 9.4 µg m^{-3} and 29.2 µg m^{-3} and maximum concentrations of 176 µg m^{-3} and 493 µg m^{-3} observed in schools and homes respectively.[55] Studies in Detroit, Michigan, USA observed D-limonene with median and maximum concentrations of 16 µg m^{-3} and 173 µg m^{-3},[17] and 14 µg m^{-3} and 135 µg m^{-3}.[56]

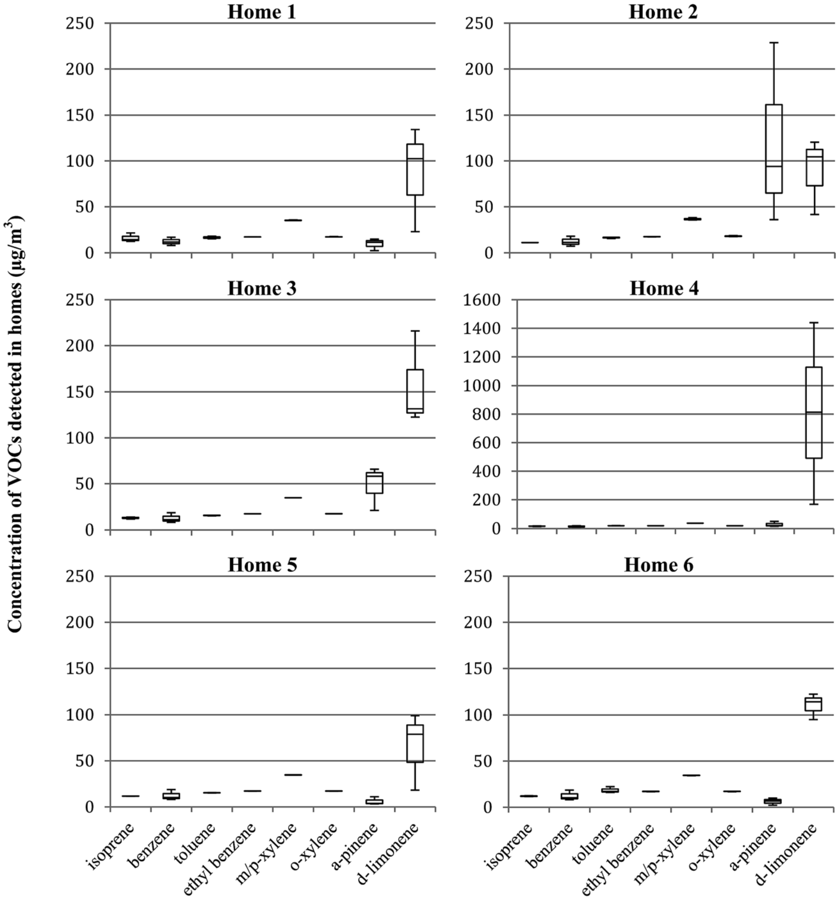

Fig. 6 Variability in the selected indoor VOCs for each of the homes in York, showing the median, interquartile and the maximum and minimum values.

Table 4 Ratios of concentrations of VOCs/benzene[a,b]

	Compounds/benzene ratios						
	Isoprene	Toluene	Ethyl-benzene	$m + p$-Xylenes	o-Xylene	α-Pinene	D-Limonene
Mean	1.17	1.50	1.57	3.17	1.58	3.28	20.75
Median	1.20	1.51	1.57	3.19	1.59	1.18	10.35
Q_1	0.79	0.94	0.98	2.06	1.02	0.47	7.26
Q_3	1.47	1.91	2.12	4.26	2.12	3.02	15.09

[a] Q_1 is the middle value in the first half of the data set (first quartile). [b] Q_3 is the middle value in the second half of the data set (third quartile).

Similarly, 53 indoor environments in Ypsilanti, Michigan, USA showed D-limonene with median and maximum concentrations of 17 μg m^{-3} and 259 μg m^{-3}.[57] Another study of 22 homes in Puertollano, Spain observed D-limonene with median and maximum concentrations of 13 μg m^{-3} and 87 μg m^{-3},[58] while a study in Germany observed D-limonene with median and maximum concentrations of 16 μg m^{-3} and 65 μg m^{-3}.[59]

5. Conclusions

This study identifies a common set of the most abundant VOCs found in 25 homes including benzene, toluene, xylenes, D-limonene and α-pinene, all classified in the European Commission INDEX strategy report as priority pollutants to be regulated.[7] Although substantial variability in the concentrations of all the top eight VOCs was recorded across the 25 homes, monoterpenes were clearly the most abundant and variable. In the London homes 68% had D-limonene as the most abundant VOC, and 26% had α-pinene as the most abundant VOC. In the more modern energy efficient homes studied in York, the concentrations of D-limonene were as high as 1000 μg m^{-3}, associated with occupant behaviours of frequent use of cleaning and fragranced products. In at least one home the number of plug-in air fresheners used was likely beyond manufacturer's guidelines for use, although we do not have the original packaging information to confirm the advice given. It was observed that occupant behavioural patterns strongly influenced the indoor concentration of monoterpenes to a much greater degree than that of any other class of VOCs. This was consistent with other studies.[7]

The five-day averages recorded here would indicate that the short-term transient concentrations of some VOCs may well regularly exceed parts-per-million mixing ratios. At the highest concentrations, and in the small number of homes where consumer products are used apparently in large quantities, there is at least the potential for ozone and hydroxyl reactions to generate secondary products including formaldehyde and aerosols under conditions with essentially unlimited feedstock of reactive carbon as monoterpenes.[8] The actual yields indoors remain very uncertain, and are not predicted here, but would be controlled by ozone ingress and interior photochemical and surface reactions. Although canister sampling is very commonly used for outdoor regulatory VOC measurements,[60] it is rarely used indoors. The study found the sampling methods to be compatible with a moderate size cohort study, straightforward for volunteer participants and compatible with their homes. The analytical method was characterised by low detection values in the parts per trillion range, but the method sensitivity was rarely a limiting factor. In addition to some abundant hydrocarbon-based VOCs, a number of cyclic volatile siloxanes were seen in high amounts in all homes, but they could not be reported quantitatively due to high blank values in the analytical system.

Domestic indoor air cannot be easily regulated through public policies and the health impacts of exposure to monoterpenes may well not be significant in the vast majority of homes. However a precautionary case could be made that better public information on fragranced product use would be worthwhile, with the objective to discourage behaviours that may in a small number of cases lead to unnecessarily excessive emissions in low ventilation domestic settings. This might be achieved relatively simply through improved product labelling alongside more explicit advice on ventilation.

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