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## **Persistence of transferred fragrance on fabrics for forensic reconstruction applications**

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**Abstract**

It has recently been established that volatile organic compounds (VOCs) successfully transfer between clothing even with a short contact of 10 s, highlighting the potential to use VOCs in forensic reconstruction scenarios, such as sexual assault cases. The mid and low volatility compounds transferred in greater amounts than high volatility compounds. This study presents empirical data addressing the persistence of transferred VOCs on clothing for the first time. A series of experiments were carried out to determine the persistence of VOCs on clothing for time periods of up to 4 weeks, on natural and synthetic fibres, and at three different environmental temperatures. The data indicate that the highest VOC amounts are generally obtained for shorter persistence times of up to 1 d. Whilst high volatility compounds were not recovered in sufficient amounts to allow quantification, the four other transferred VOCs were successfully quantified for persistence times of up to 4 weeks. The persistence for mid-volatility compounds follows decay curve trends in line with those previously obtained for fibres, glass and pollen. When comparing the persistence of VOCs on a natural and a synthetic fibre, for a persistence time of 1 h, the transferred VOCs were retained on a natural fibre in higher amounts than on a synthetic fibre. However, for longer persistence times the concentration of VOCs was similar between the two fabrics. Lastly, lower environmental temperatures resulted in higher recoveries for most VOCs, especially for short persistence times. These findings demonstrate that optimal recovery of VOCs from clothing occurs when the fabric is kept at cooler temperatures and analysed soon after the fragrance transfer occurred, although VOC recovery was possible at higher temperatures and after longer persistence times. Given the transfer and persistence characteristics of VOCs from fragrance, there is potential for fragrance to be used as a form of trace in forensic reconstruction approaches.

**Keywords:** Forensic reconstruction, Volatile organic compounds (VOCs), Trace evidence, Experimental studies, Persistence

## 1. Introduction

A decade has passed since the National Academy of Science (NAS) has published the pivotal “Strengthening forensic science in the United States: a path forward” report [1] challenging the reliability of forensic science and calling for rigorous research to determine its capabilities and limits. The NAS report has been followed by a number of reports, such as the Law Commission report [2], the Forensic Regulator annual reports [3–6], the Government Chief Scientific Adviser annual report [7], and the House of Lords Inquiry report [8]. One recurrent theme has been the call for research in forensic science that can aid in the effective interpretation of forensic evidence. Concomitantly, it has been argued in the academic published literature that there is a need for a research culture [9] that regains the ‘endeavour’ of forensic science (rather than considering only the exploitation of forensic science in the operational and processing activities at the crime scene [10]). Morgan [11] addresses this by demonstrating the importance of taking a holistic approach to forensic reconstruction that not only considers all the key stakeholders (police, science, law/policy) [12], but also the importance of bringing together expertise and empirical studies that can underpin all steps of the forensic science process (from crime scene to court) for robust forensic reconstructions [11].

A key consideration in forensic reconstruction approaches is providing transparent and robust evaluative interpretation of science evidence. The hierarchy of propositions [13–16] offers a valuable model for evaluating evidence, introducing a consideration of two alternative propositions at the source, activity, and offence level. In cases of sexual assault where biological material has been detected and identified, it is often not the source level consideration of that material that becomes important (unless the complainant is a minor), but the activity and offence level. Issues of consent, the means of transfer and the timing of a transfer (persistence) of the biological material can become key issues for establishing activity level propositions, which inform offence level conclusions which can contribute to a robust and transparent reconstruction of events.

There is a strong focus in forensic science on establishing the source level of recovered trace materials [17] and developing technologies and advances in analytical capabilities to identify, quantify, and classify smaller amounts of trace more accurately and in shorter timescales. Recent studies have identified that 66% of misinterpreted evidence in a sample of upheld cases heard at the Court of Appeal of England and Wales was due to the interpretation of activity level propositions [18]. There is, therefore, a need to address the gaps in the

evidence base in order to tackle activity level propositions. The UK Forensic Science Regulator has stated consistently in all four of her annual reports that empirical research on the transfer and persistence of trace evidence and the factors that affect these processes is one of the highest priorities for forensic science [3–6].

Since the work of Pounds and Smalldon [19–21] who addressed the persistence of fibres, it has been well established that trace materials are dynamic and once transferred there is an initial rapid loss of material followed by a longer period of more gradual loss. Whilst studies concerning the transfer and persistence of traces have been undertaken (DNA [22,23], fibres [24], glass [25,26], paint [27–29], hair [30–32], sediments [33–36]), there is still a long way to go.

Recently, Gherghel et al. [37] highlighted the potential use of volatile organic compounds (VOCs) as a form of trace evidence for sexual assault cases due to the high use of fragrance by both men and women, and the fact that clothing is often recovered in these cases. In a further study focused on the transfer of fragrances [38], traces of VOCs were detected from a secondary piece of fabric even when the fragrance mixture was aged on the primary fabric for 2 d prior to transfer, and even when the contact between fabrics was as short as 10 s. Therefore, this current article builds on that work to provide additional data on the persistence of fragrances once they have been transferred, to contribute to a more complete picture on the evidence dynamics of VOCs and their potential application to forensic reconstruction approaches.

Persistence studies are especially important for sexual assault cases where there is agreement that sexual intercourse took place, but disagreement on the timing of the events [39]. However, there are currently no published studies that have addressed the persistence of transferred VOCs on clothing within a forensic context, so there is a lack of an empirical evidence base which is needed to infer the timing of an event.

It is very important for forensic science research to be predicated on real world challenges [40] to aid the judicial system [10]. As such, this study sought to generate data to demonstrate the persistence of VOCs from fragrance in a way that was informed by relevant casework (as outlined above) and considering relevant published literature [37,38,41]. This study sought to contribute to an empirical evidence base to establish the nature of the persistence of transferred VOCs on clothing and develop an evaluative interpretation of detected fragrance VOCs. The variables addressed were persistence time, fabric type and environmental temperature.

## 2. Material and methods

### 2.1. Chemical and materials

The analytical method used in this study follows the method developed by Gherghel et al. [42]. The reference standards used were: (+)- $\alpha$ -pinene (98.5% purity), (R)-(+)-limonene (97%), linalool (97%), geraniol (98%), eugenol (99%), and ethylene brassylate (97%) were purchased from Sigma Aldrich, Gillingham, UK. The CAS number, molecular weight, boiling point, and vapour pressure values for the six compounds are provided in Table 1. The internal standards were dibromobenzene and methyl nonanoate. Dibromobenzene was used for the quantification of cyclic compounds including  $\alpha$ -pinene, limonene, eugenol, and ethylene brassylate, and methyl nonanoate was used for the quantification of the two linear compounds, linalool and geraniol. Stock solutions of the reference standards and of the internal standards were prepared in methanol on a monthly basis at concentrations between 10 - 25 mM.

Table 1 The chemical properties of the six VOCs of interest

Compound	CAS number	Molecular weight (g/mol)	Boiling point (°C) <sup>*</sup>	Vapour pressure (mm Hg)
$\alpha$ -pinene	80-56-8	136.24	156	5.098 at 23.5 °C <sup>a</sup>
Limonene	5989-27-5	136.24	176	2.129 at 23.5 °C <sup>b</sup>
Linalool	78-70-6	154.25	198	0.159 at 23.5 °C <sup>a</sup>
Geraniol	106-24-1	154.25	230	0.042 at 23.5 °C <sup>a</sup>
Eugenol	97-53-0	164.20	254	0.026 at 23.5 °C <sup>a</sup>
Ethylene brassylate	105-95-3	270.37	332	4.38E-07 at 25 °C <sup>c</sup>

\* Boiling point values at 760 mm Hg

<sup>a</sup> Based on calculation using Antoine Coefficients from Yaws' Handbook of Antoine Coefficients for Vapor Pressure [43]

<sup>b</sup> Based on Li et al. [44]

<sup>c</sup> Based on Belsito et al. [45]

50/30  $\mu\text{m}$  StableFlex divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS), 23 gauge SPME fibres (Supelco) were used to extract the VOCs from the headspace of 20 mL vials containing the fabric samples. Prior to first use and daily when used, the fibre was conditioned according to the manufacturer recommendations for 1 h at 270  $^{\circ}\text{C}$ , followed by a fibre blank analysis to confirm the effectiveness of conditioning.

The fabrics selected for this study were a white 100% cotton T-shirt and a blue 100% polyester T-shirt. The fabrics were previously washed in a conventional washing machine without adding any detergent, and once dried they were stored in a sealed plastic bag at ambient temperature. Blank fabric samples were analysed to account for any contamination.

## 2.2. Instrumentation

In this study, the previously validated chromatography-mass spectrometry (GC-MS) method [42] was used for the VOCs extraction and instrumental analysis of the samples. The GC-MS analyses were carried on a Scion GC system equipped with a Scion QqQ-MS/MS detector (Bruker Corporation, Fremont, CA, USA) and coupled to a Combi Pal autosampler (CTC Analytics, Switzerland). The chromatographic column was a VF-5ms capillary column (30 m  $\times$  0.25 mm, 0.25  $\mu\text{m}$  film thickness) from Varian (Palo Alto, CA, USA). The chromatographic gradient was programmed as follows: initial GC oven temperature of 35  $^{\circ}\text{C}$  (held for 1 min) increased to 180  $^{\circ}\text{C}$  (held for 1 min) at 5  $^{\circ}\text{C}/\text{min}$  rate, and then to 300  $^{\circ}\text{C}$  at 25  $^{\circ}\text{C}/\text{min}$  rate. The final temperature was held for 2 min. Mass spectra was generated in Electron Ionisation (EI) mode at -70 eV. As presented in Gherghel et al. [42], for the SPME extraction of VOCs from fabrics, an incubation time of 5 min, an extraction time of 60 min, and an extraction temperature of 58  $^{\circ}\text{C}$  were used.

The temperature and the humidity of the storage conditions were monitored using a portable thermometer-hygrometer (model 82021, VWR Scientific). Throughout this study, the laboratory ambient temperature where the samples were prepared ranged from 19 to 24  $^{\circ}\text{C}$ , and the humidity ranged from 25 to 51%.

A Stainingtester crockmeter (Komputekst, Hungary) was used to simulate fabric contact in a reproducible way as carried out in Gherghel et al. [38]. The donor cotton swatch spiked with the VOCs mixture was mounted onto the crockmeter finger and then rubbed against a blank recipient sample fabric under a fixed load of 9 N.

## 2.3. Preparation of solutions and experiments

A mixture of the six VOCs was prepared in methanol at a concentration of 2 mM. The two internal standards were prepared into an internal standard solution at 20  $\mu$ M in methanol. The VOCs mixture was spiked onto the primary piece of fabrics, whilst the internal standard solution was added to the secondary piece of fabric (the recipient) immediately prior to adding it to the vial and adding the 10 mL water, as carried out in Gherghel et al. [38]. In this way, the internal standards were not submitted to the transfer process and they were only used for the GC-MS calibration step.

For all persistence experiments, following the spiking of the donor cotton swatch with the VOCs mixture, an immediate transfer of the VOCs onto the secondary piece of fabric was carried out using the crockmeter for 1 min. Therefore, for all experiments, an ageing time of 0 s, and a contact time of 1 min was employed. The secondary piece of fabric onto which the VOCs were transferred and then left to persist was cotton, with the exception of the room temperature experiment, where cotton and polyester were investigated. This secondary piece of fabric with transferred VOCs was placed on a time-stamped clean Petri dish and left to dry in specific environmental conditions (room temperature, cool temperature (fridge) and very cold (freezer) temperature) until the appropriate analysis time. These three different temperature regimes were chosen to replicate the environments of indoor crime event locations and subsequent storage environments of seized items of clothing in either a fridge or freezer. All samples were prepared in triplicates. A breakdown of the number of samples and the variables evaluated is given in Table 2.



Table 2 The number of samples analysed and the values for the variables examined for the persistence studies

Donor fabric		Cotton			
Perfume ageing time (min)		0			
Contact time (min)		1			
Environmental temperature		Room temperature		Fridge	Freezer
Recipient fabric		Cotton	Polyester	Cotton	Cotton
Persistence time (d)	0.04	3	3	3	3
	0.33	3	3	-	-
	1	-	-	3	3
	3	3	3	-	-
	4	-	-	3	-
	5	3	3	-	-
	7	3	3	-	-
	10	3	3	3	3
	14	3	3	-	-
	15	-	-	3	-
	17	3	3	-	-
	21	3	3	-	-
	24	3	3	-	-
28	3	3	-	-	

### 2.3.1 Room temperature

For the room temperature experiment, two different fabrics, cotton and polyester, were used as recipient fabric. The time-stamped samples were left to dry in a laboratory storage room at temperatures between 20 and 24 °C, and humidity between 27 and 51 % to replicate temperate climate conditions. The persistence times ranged from 1 h (0.04 d) up to 28 d (Table 2).

### 2.3.2. Fridge

For the fridge experiment, the samples were left in a designated shelf in laboratory fridge at temperatures between 2 and 4 °C. The samples used were cotton fabrics, and the persistence time ranged from 1 h to 15 d (Table 2).

### 2.3.3. Freezer

For the freezer experiment, the samples were kept in a laboratory freezer at temperatures between -28.3 and -27.5 °C. The samples used were cotton fabrics, and the persistence time ranged from 1 h to 10 d (Table 2).

### 2.4. Data analysis

For each of the VOCs of interest and the two internal standards, three characterising ions were chosen for calculation of the peak areas. The resulting raw data was exported to an Excel (Microsoft Inc.) file for further processing. Within Excel relative peak area ratios of analytes were calculated against the internal standards, which were further used to determine the concentration of analytes in fabric by using the calibration curves.

## 3. Results

In a similar manner to the transfer experiments presented in Gherghel et al. [38], the chromatographic peak area data from this work (SI-Table 1) were quantified using the calibration curves presented in that study. The calibration curves were built in methanol at six levels with three replicates by level, ranging from 0.2 to 200 µM. The calibration curves are also provided in the SI of this article with the permission of authors (SI-Table 2). The resulting concentration (µM) (SI-Table 3) was further divided by the fabric weight, which varied between 0.19 and 0.28 g for all samples (average weight was 0.24 g). The specific fabric weights can be found in SI-Table 4. The resulting data with the concentration of the VOCs determined in the fabrics is provided in Table 3. As such, for all trendline graphs presented in this article, the x axis represents the persistence time (d) and the y axis is represented by the detected concentration of the analyte in the fabric divided by the fabric weight (µM/g). Nine, five and three different persistence times were sampled in triplicate for each of the three temperature experiments (as outlined in Table 2).

For the room temperature and fridge experiment, the recoveries of pinene and limonene were below the linear range of the calibration, which did not allow for reliable quantification of these two compounds. However, for the other four VOCs (linalool, geraniol, eugenol and ethylene brassylate), all recoveries were within the calibration ranges reported in SI-Table 2, unless otherwise specified in Table 3.

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2 4	11.2	15.6	7.8	165.	9.4	9.4	10.1	52.6	-	-	-	-	-	-	-	-	-
	±	±	±	1 ±	±	±	±	± 6.8	-	-	-	-	-	-	-	-	-
2 8	1.3	3.8	2.2	22.6	2.8	2.9	0.5 <sup>a</sup>										
	8.0	18.1	15.1	350.	4.8	7.0	9.0	36.4	-	-	-	-	-	-	-	-	-
	±	±	±	5 ±	±	±	±	± 3.7	-	-	-	-	-	-	-	-	-
	2.4	7.0	5.3	104. 1	1.7	1.0	2.4 <sup>a</sup>										

<sup>a</sup> Concentrations estimated as values were below limit of quantitation

<sup>b</sup> Concentration estimated as value was above calibration range

### 3.1. Room temperature

For the room temperature experiments two fabrics were tested to assess persistence on both natural (cotton) and synthetic (polyester) fibres.

When the VOCs were transferred from cotton to cotton and the secondary fabric was left to dry at room temperature, it was observed that geraniol and eugenol followed a typical decay curve (Figure 1, orange), with the highest recoveries obtained for the shortest time studied of 1 h (0.04 d) persistence time; at 8 h (0.33 d) their recoveries diminished by a factor of 4 and 5 respectively, followed by a steady, but slower decay. For linalool and ethylene brassylate, the trends were not as clear. Ethylene brassylate exhibited an initial decrease in concentration from 1 h to 3 d persistence time, followed by a spike at 5 d, and then a more regular decay curve of slower loss.

For the polyester samples left to dry at room temperature, the results were very similar to the cotton samples, with linalool displaying a rather undefined pattern and geraniol and eugenol following a trend similar to a decay curve (Figure 1, dark grey). However, geraniol and eugenol were released at a faster rate from cotton than from polyester. For polyester, the initial concentration at 1 h was only about two times higher than at 8 h (49.5  $\mu\text{M/g}$  in comparison to 33.1  $\mu\text{M/g}$  for geraniol, and 58.6  $\mu\text{M/g}$  in comparison to 29.8  $\mu\text{M/g}$  for eugenol). On the other hand, for cotton, the initial concentration at 1 h for these two compounds was about 4-5 times higher than at 8 h (181.7  $\mu\text{M/g}$  in comparison to 45.8  $\mu\text{M/g}$  for geraniol, and 261.3  $\mu\text{M/g}$  in comparison to 53.5  $\mu\text{M/g}$  for eugenol). Lastly, ethylene brassylate at 1 h persistence time was recovered in the highest amounts, unlike in the cotton samples, where the recovery was high at 1 h, but also after 5 d (Figure 1, dark grey).

When compared alongside the results for cotton and polyester at room temperature (Figure 1), it can be observed that with the exception of linalool, higher amounts of VOCs were obtained generally from cotton, especially for geraniol (181.7  $\mu\text{M/g}$  in comparison with

49.5  $\mu\text{M/g}$ ) and eugenol (261.3  $\mu\text{M/g}$  in comparison with 58.6  $\mu\text{M/g}$ ) at persistence of 1 h, and for ethylene brassylate at all persistence times (Table 3). Linalool, despite not displaying a clear trend for each material, when compared together the trends were similar, with a peak at 1 h, at 7 d, and at 24 d (Figure 1).

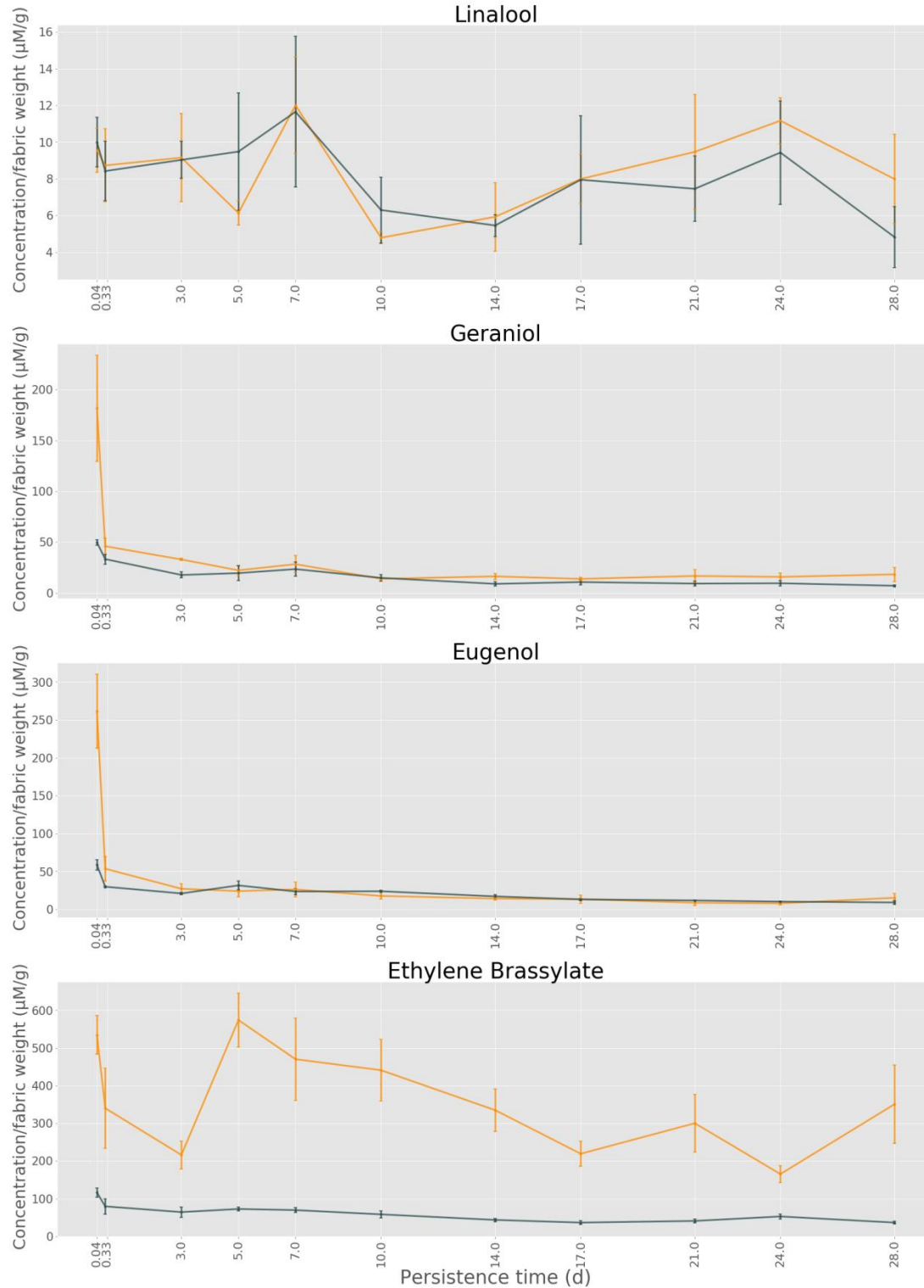


Figure 1 Persistence of four transferred VOCs of interest on cotton (orange) and polyester (dark grey) at room temperature for periods between 1 h and 28 d. The error bars are standard deviations (n = 3). The persistence trend for linalool is similar

between the two materials, and the persistence of geraniol, eugenol and ethylene brassylate is generally higher on cotton than on polyester

### 3.2. Fridge temperature

For the cotton samples with transferred VOCs left in a fridge, due to time constrictions, the experiment was carried out for a shorter time frame, from 1 h to 15 d. The results (Table 3) showed that for linalool, the most volatile compound out of the 4 VOCs, there was a considerably higher amount determined at 1 h (65.7  $\mu\text{M/g}$ ) compared to the other persistence times ( $>5.9 \mu\text{M/g}$ ). However, for 10 and 15 d persistence time, the limonene concentration reported is estimated as it was below the lower limit of quantification (Table 3). Geraniol exhibited a decay curve too, albeit with a more gradual decrease (Figure 2, blue). Eugenol displayed an initial increase in concentration from 1 h to 1 d persistence time (from 219.6  $\mu\text{M/g}$  to 384  $\mu\text{M/g}$ ), after which the concentration steadily decreases up to 15 d (104.7  $\mu\text{M/g}$ ) (Table 3). For ethylene brassylate, the trend was not very clear (Figure 2, blue).

When comparing the room and fridge conditions, higher amounts of linalool, geraniol, and eugenol were generally recovered for the samples kept in the fridge (blue) compared to the samples left at room temperature (orange) (Figure 2). This was especially true for shorter persistence times for linalool (at 1 h, 65.7  $\mu\text{M/g}$  in comparison with 9.6  $\mu\text{M/g}$ ) and geraniol (at 1 h, 428.6  $\mu\text{M/g}$  in comparison with 181.7  $\mu\text{M/g}$ ), and for all persistence times studied for eugenol with the exception of the shortest time of 1 h (Table 3). The concentrations determined for ethylene brassylate were consistent between the two temperatures (Figure 2).

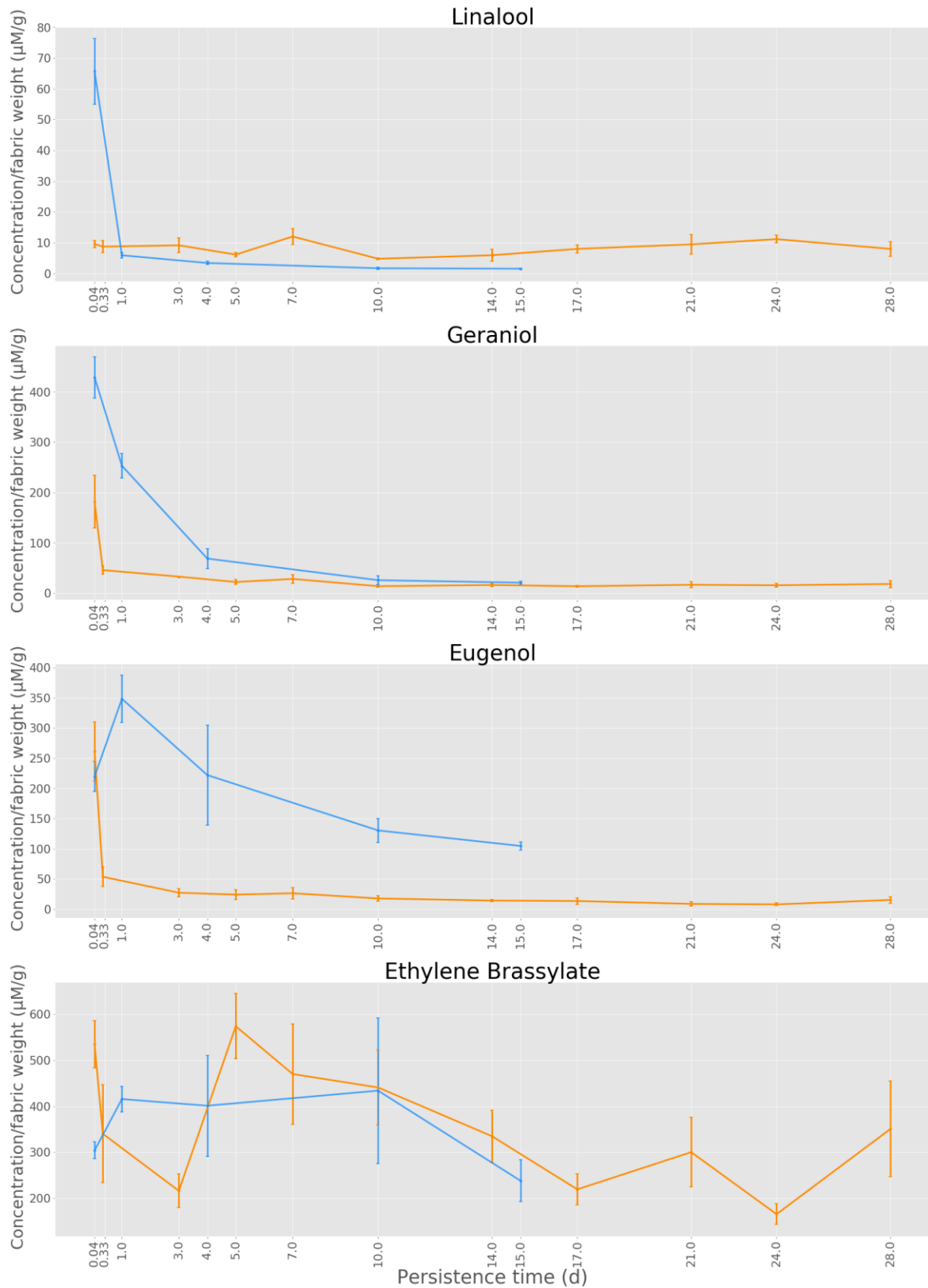


Figure 2 Persistence of four transferred VOCs of interest on cotton at room temperature (orange) and fridge temperature (blue) for periods between 1 h and 28 d. The error bars are standard deviations ( $n = 3$ ). Generally higher amounts of VOCs were obtained from the samples kept in the fridge compared to the samples kept at room temperature. The determined concentrations for ethylene brassylate are similar between the two temperatures.



### 3.3. Freezer temperature

For the freezer temperature, three persistence times were studied: 1 h, 1 d and 10 d. Whilst for the room temperature and fridge experiments, the two most volatile compounds, pinene and limonene were recovered in quantities below the lower limit of the calibration range, for the freezer experiment limonene was successfully recovered, and pinene was above the limit of detection. Figure 3 displays the gas chromatograms for pinene and for limonene at 1 h, 1 d and 10 d persistence time at the three different experimental temperatures. It can be observed how the chromatographic peaks for the freezer sample (green) are considerably higher than for the other two environmental conditions. Moreover, when looking at the y axis, representing the peak height, for pinene this value is expressed in kCps (kilo Counts per second) or MCps (Mega Counts per second) and for limonene in GCps (Giga Counts per second). What is even more interesting, is that for both analytes, the amount recovered increased with persistence time, for example the peak height for limonene at 1 h was c. 1.25 GCps and at 10 d c. 2.5 GCps.

This observed effect, where considerably higher amounts of VOCs are recovered for the samples kept at freezer temperature in comparison to the sample kept at fridge or room temperature, was not encountered for any of the other VOCs. For ethylene brassylate, the recoveries did not considerably differ between the three temperatures sampled at 1 h, 1 d or 10 d persistence time (Table 3). For linalool, geraniol and eugenol, the lowest amounts of VOCs were generally recovered for the samples with transferred perfume kept at room temperature (Table 3).

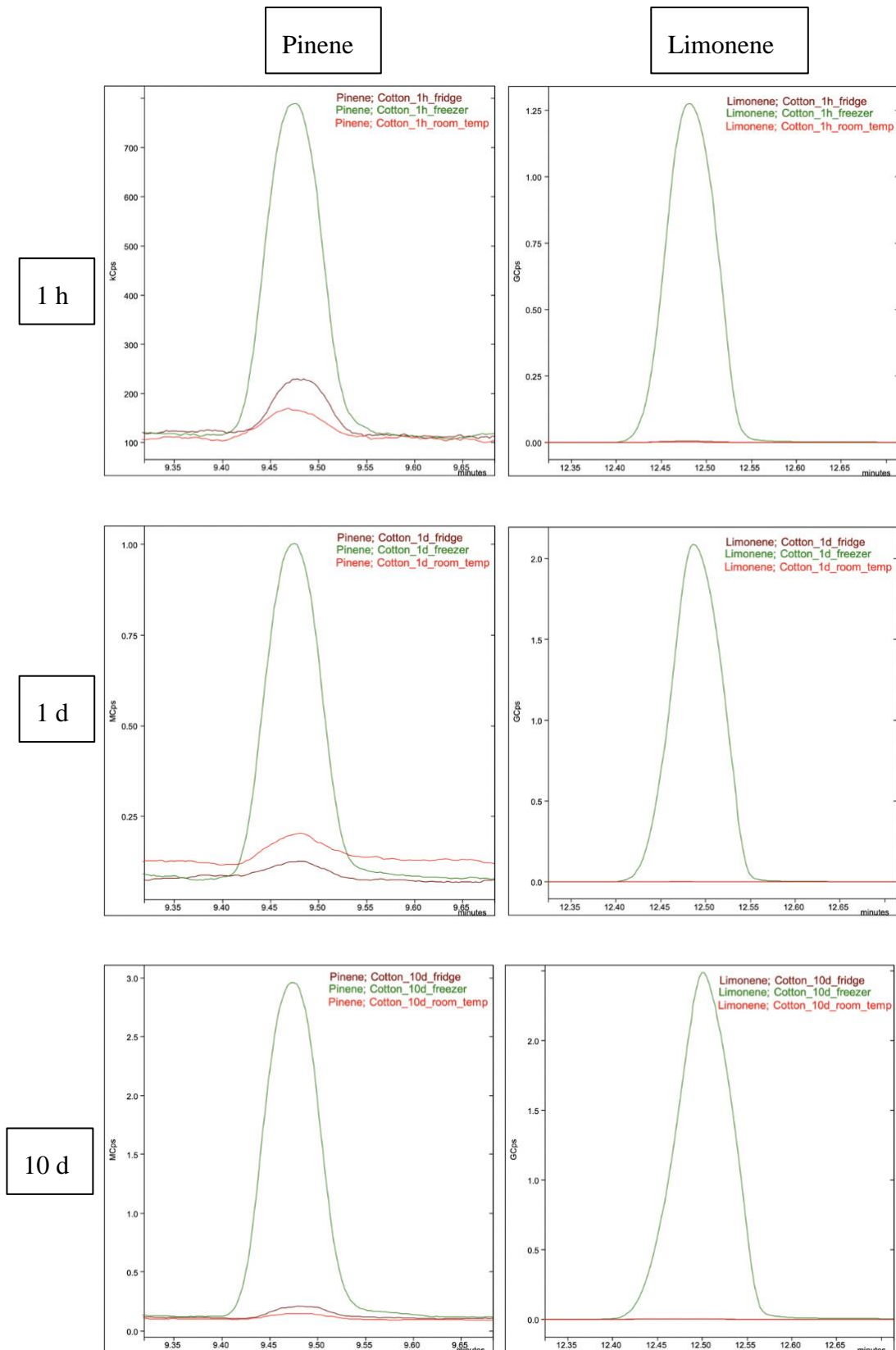


Figure 3 Gas chromatograms of pinene (left side) and limonene (right) at 1 h (top), 1 d (middle) and 10 d (bottom) persistence time for three environmental conditions: freezer (green), fridge (brown) and room temperature (red). Pinene and linalool were recovered in considerably higher amounts from the samples left in the freezer compared to the samples kept in the fridge and at room temperature

## 4. Discussion

This is the first empirical study addressing the persistence of transferred fragrance VOCs on clothing for forensic applications. With casework application in mind, and based on previous research addressing the persistence of VOCs and other forms of trace material transferred to clothing [20,33,41], as well as work from Gherghel et al. [38] looking at the transfer of VOCs between clothing, three variables were investigated to assess the persistence of transferred fragrance VOCs: environmental temperature (room, fridge and freezer temperature), fabric type (cotton and polyester) and persistence time (1 h to 28 d).

### 4.1. Room temperature

Generally, with longer persistence times, lower amounts of VOCs were recovered from the fabric samples left at room temperature, as the compounds volatilise and evaporate from the fabrics. Geraniol and eugenol displayed typical exponential decay curves, with a high initial recovery followed by a rapid loss in recovery and then a steadier loss. This behaviour is consistent with the published literature for the persistence of forensic traces, such as fibres [20], pollen and flint [33] on fabrics.

In terms of persistence of different VOCs on fabrics, Obendorf et al. [41] showed that compounds with lower vapour pressure resulted in increased retention on the two fabrics studied, cotton and polyester. This observation is consistent with the results in this current study, as it can be noted for example in Figure 1, as well as in the inability to quantify the two compounds with the highest vapour pressure. Obendorf et al. [41] also found that the recoveries of the VOCs at 70 min did not differ as much between cotton and polyester as they did at 480 min. At the extended time, the VOCs were released at a faster rate from polyester than from cotton [41]. However, in this present study, for the shortest time of 1 h, higher amounts of VOCs were consistently recovered from cotton compared to polyester, with the exception of linalool, where the recoveries were similar between the two fabrics (Figure 1). This behaviour has been previously observed for the persistence on fabrics of other traces, such as hair, pollen, and fibres [33,46,47]. For example, in a study focused on the persistence of human scalp hair on fabrics for times as long as 8 h, it was demonstrated that with the exception of wool, the greatest persistence of hair was observed on a cotton t-shirt (maximum of around 5 h) and the shortest persistence on a polyester top (maximum 1 h) [46].

#### 4.2. Fridge temperature

There are currently no published studies comparing the persistence of VOCs on fabrics at various temperatures for forensic science applications. The findings from this study showed that generally, the VOCs from the fabric samples were preserved better at fridge temperature than at room temperature, so that higher recoveries were obtained for the extracted VOCs (Figure 2). The approximately 20 °C cooler temperatures between the fridge and room conditions helped reduce the evaporation of VOCs, especially the VOCs with higher volatility such as linalool and geraniol, at shorter persistence times. These lower boiling point compounds are more sensitive to environmental conditions. For ethylene brassylate, the least volatile compound, there were no major differences in the obtained recovery for the two temperatures. These findings demonstrate the value of storing garments that have been seized in suspected assault cases in fridge conditions. The lower temperature can help preserve the samples until instrumental analysis.

#### 4.3. Freezer temperature

Pinene and limonene are the compounds with the lowest boiling point from this study, and in turn with the highest volatility. The freezer temperature was the only temperature that allowed the recovery of limonene for all three persistence times tested at amounts above the lower range of the calibration curve and of pinene above the limit of detection (Figure 3). Moreover, longer persistence times led to higher recoveries for both analytes.

Whilst the fridge temperature experiment demonstrated that cooler temperatures of 2 - 4 °C help increase the recovery of compounds such as linalool and geraniol, the freezer experiment showed that temperatures as low -28 °C led to the recovery of the compounds with even higher volatility. It might be assumed that compounds with vapour pressure in the range of the compounds from this study ( $4.4E^{-7}$  - 2.1 mm Hg at 23.5°C) will have similar behaviour under the studied storage conditions. These findings demonstrate the utility of storing garments that have been seized in suspected assault cases in freezer conditions over fridge conditions where possible. The lower temperature can help preserve the samples until instrumental analysis.

## 5. Conclusions

The persistence behaviour of six VOCs on a secondary fabric was examined. All the factors studied, persistence time, fabric type, and environmental temperature, affected how the volatile compounds persisted on a secondary piece of fabric after transfer.

The persistence time of transferred VOCs on fabrics is a crucial factor in the potential to recover these compounds. In a sexual assault case, there is often a period of time from the crime taking place until an exhibit is recovered and the laboratory analysis is undertaken. The findings from this study showed that the highest recoveries are generally obtained for shorter persistence times of up to 1 d. It was found that it was possible to successfully recover four of the six transferred VOCs from fabrics even after as long as 28 d since the initial fragrance transfer. Therefore, these results show the applicability of this technique for forensic cases such as sexual assault, even when the crime is reported weeks after it has been committed. This is especially important as a Home Office report from 2007 [48] found that 46% of rapes were reported on the same day on which they occurred, 23% between 1 d to 1 week, 17% between 1 week to 6 months, and only 14% after more than 6 months. However, in line with other forms of trace materials, the length of persistence also raises questions on how to discern materials transferred pre-, syn- and post- forensic event and provide evaluative interpretations regarding activity level propositions.

The fabric medium onto which the perfumes were transferred and then persisted, led to differences in VOCs recovery especially for shorter timeframes. At 1 h persistence time, considerably higher amounts of VOCs were generally recovered from cotton compared to polyester. This trend where cotton enables higher recoveries compared to polyester has been previously reported in the published forensic science literature for the persistence of multiple traces such as hair, pollen, and fibres [33,46,47]. After 1 h, similar quantities of VOCs were recovered from both fabrics.

Temperature had a greater effect in recoverability especially for the VOCs with lower boiling points. For temperatures between 4 and 22 °C, the recovered quantity of the two most volatile compounds was below the lower limit of the calibration range, whilst for the other four VOCs, the shorter the time frame the higher the recovery of VOCs from fabrics. For temperatures of approximately -28 °C, an additional fifth VOC, limonene, was also successfully recovered.

In conclusion, the findings from this study have confirmed that transferred VOCs can persist on different fabrics at different environmental temperatures for times as long as 28 d. For fragranced fabrics kept at temperatures between 2 and 22 °C, medium and low volatility

compounds are most likely to be recovered and to be of value in forensic investigations. For samples kept at freezing temperatures of approximately  $-28\text{ }^{\circ}\text{C}$ , high volatility compounds may also be recoverable. These data provide additional support for the potential of being able to use fragrance analysis in the investigation and detection of sexual assault cases, especially for the cases where the clothing is available for analysis even up to a month after the assault took place.

**Declarations of interest:** none

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Figure 1 Persistence of four transferred VOCs of interest on cotton (orange) and polyester (dark grey) at room temperature for periods between 1 h and 28 d. The error bars are standard deviations ( $n = 3$ ). The persistence trend for linalool is similar between the two materials, and the persistence of geraniol, eugenol and ethylene brassylate is generally higher on cotton than on polyester.

Figure 2 Persistence of four transferred VOCs of interest on cotton at room temperature (orange) and fridge temperature (blue) for periods between 1 h and 28 d. The error bars are standard deviations ( $n = 3$ ). Generally higher amounts of VOCs were obtained from the samples kept in the fridge compared to the samples kept at room temperature. The determined concentrations for ethylene brassylate are similar between the two temperatures.

Figure 3 Gas chromatograms of pinene (left side) and limonene (right) at 1 h (top), 1 d (middle) and 10 d (bottom) persistence time for three environmental conditions: freezer (green), fridge (brown) and room temperature (red). Pinene and linalool were recovered in considerably higher amounts from the samples left in the freezer compared to the samples kept in the fridge and at room temperature.

## Highlights

- Transferred fragrance can persist on clothing for as long as 4 weeks
- Highest VOC amounts were obtained for shorter persistence times of up to 1 day
- Similar amounts of VOCs were recovered from a natural and a synthetic fibre
- Storage in a freezer offered greater levels of VOC recovery
- Fragrance as a form of trace evidence shows potential for forensic reconstructions

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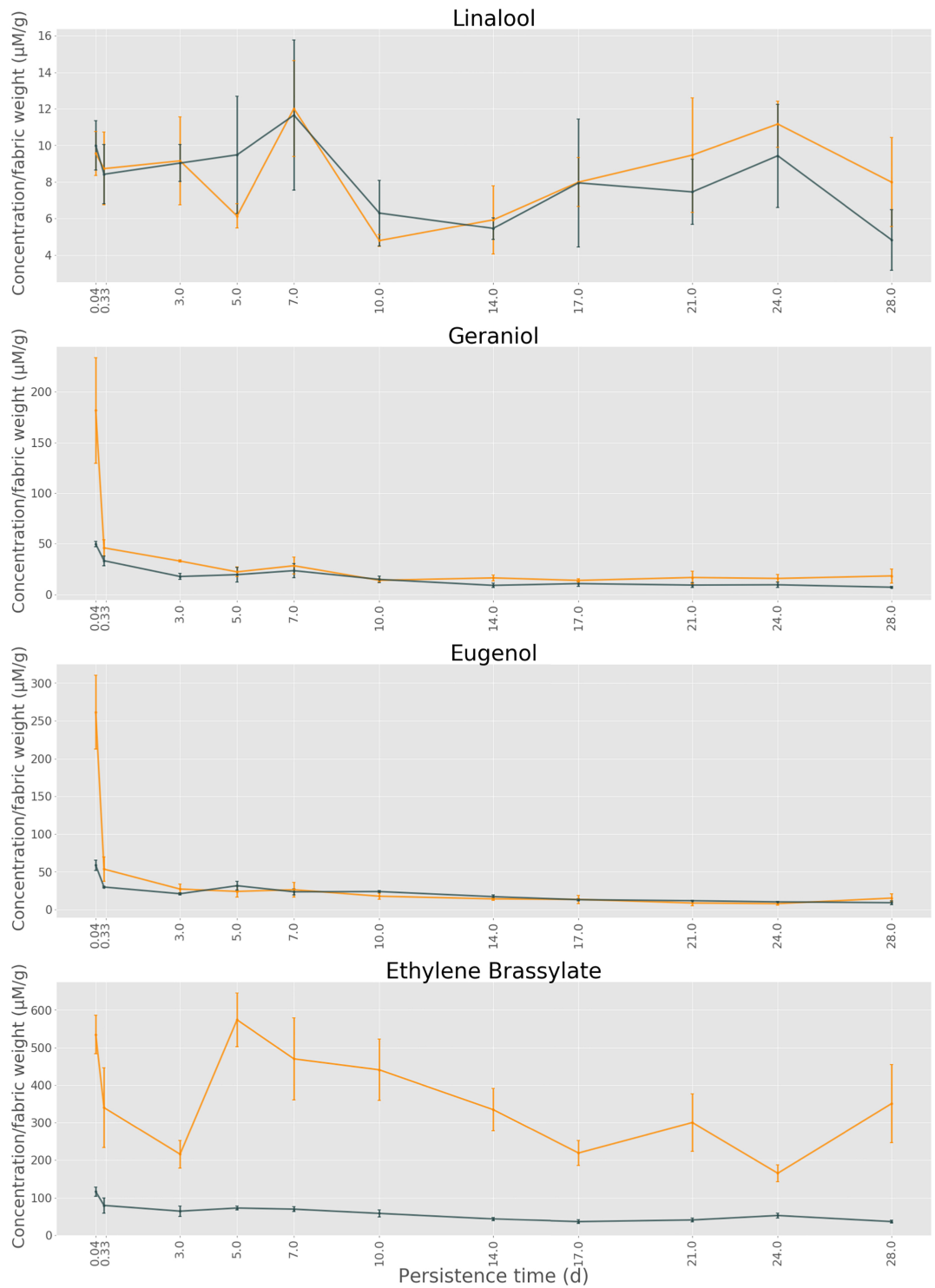


Figure 1

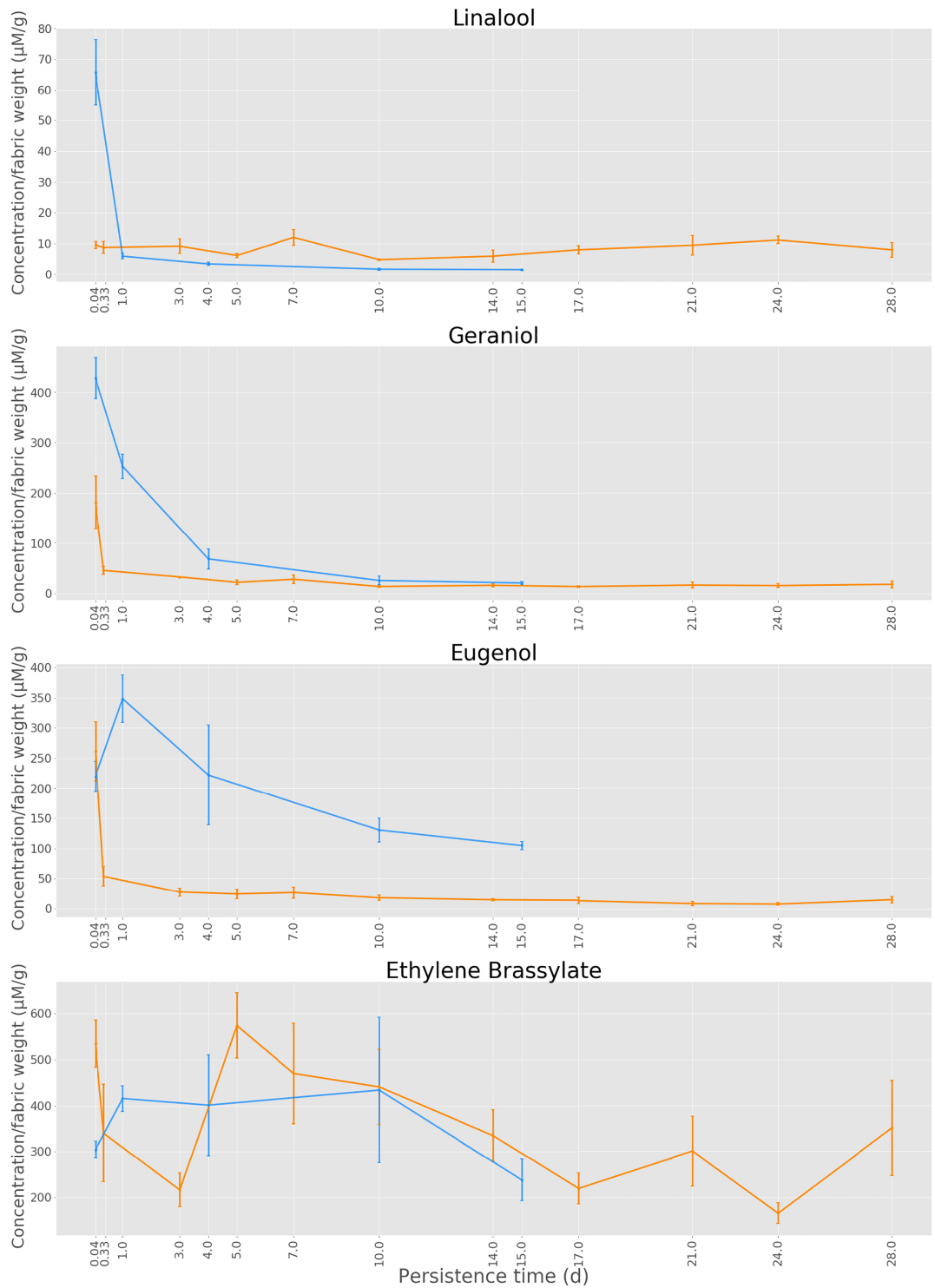
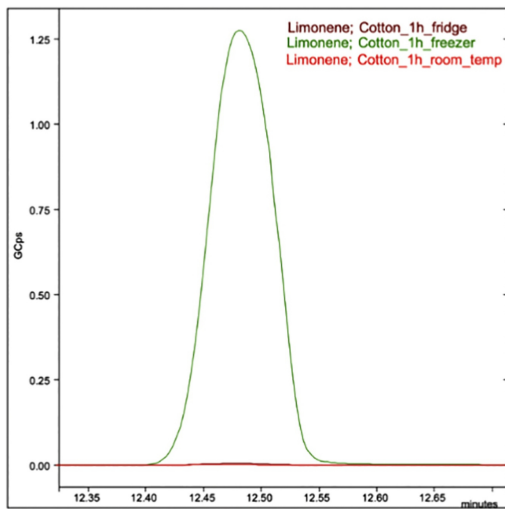
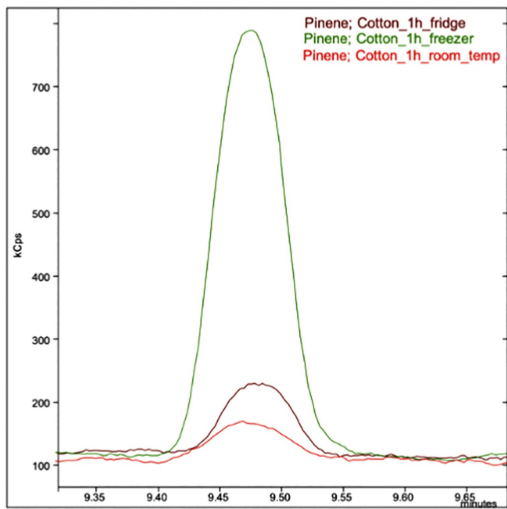


Figure 2

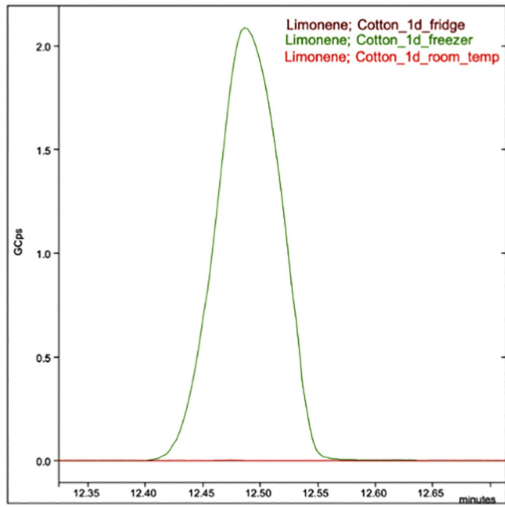
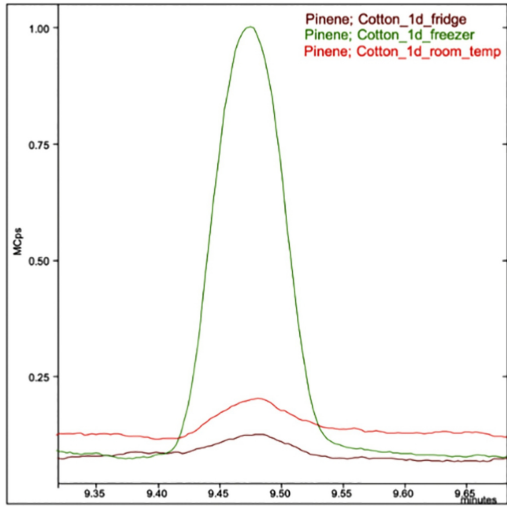
# Pinene

# Limonene

1 h



1 d



10 d

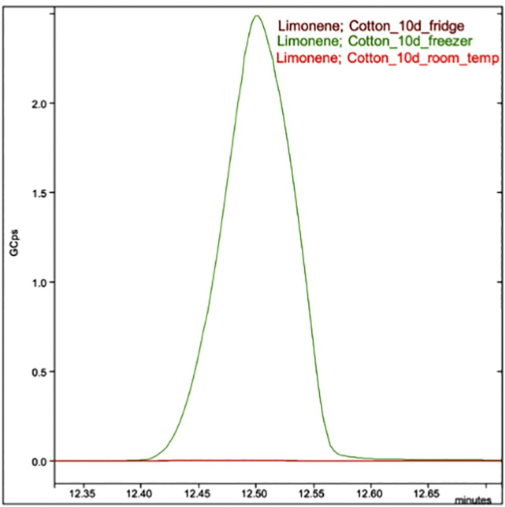
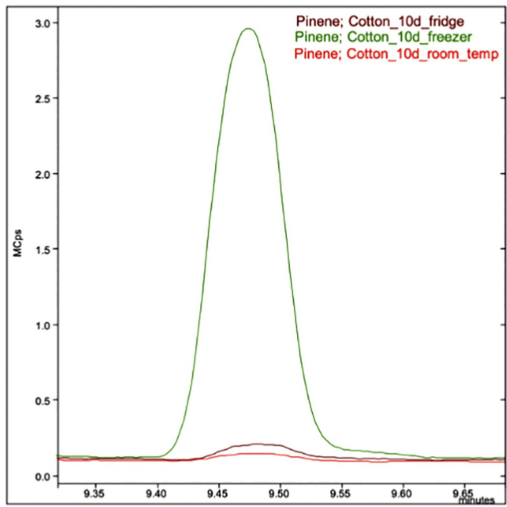


Figure 3