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Retention and release of odorants in cotton and polyester fabrics following multiple soil/wash procedures

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Abstract:

Odorous clothing can be an annoying and unpleasant problem particularly when odorants are not effectively removed via laundering. Cotton and polyester knit fabrics were soiled with three selected odorants, representing different polarities and lipophilicities (i.e. octanoic acid, 2-nonenal, dodecane). Fabrics were subjected to 1, 5 and 10 soil/wash cycles using a regular liquid detergent (Tide® Free and Gentle) or a sport liquid detergent (Tide® Plus Febreze Sport). Odorants released into the headspace were collected using solid phase micro-extraction (SPME), and odorants retained within the fabric were collected using solvent extraction. Analysis of odorant peaks was carried out using gas chromatography-flame ionization detection (GC-FID). Prior to laundering, higher amounts of all odorants were released into the headspace above polyester fabrics than above cotton fabrics. Cotton fabrics retained more octanoic acid within the fabric and lower amounts of 2-nonenal than polyester. Laundering was more effective at removing odorants from cotton than from polyester, and the polar octanoic acid was more readily removed than the two nonpolar odorants from both fabrics. Accumulation of odorants occurred as soil/wash cycles increased from 1 to 5 cycles. However, between 5 and 10 soil/wash cycles the amounts of compounds did not significantly increase, with significantly lower amounts of octanoic acid extracted from cotton at 10 cycles compared to 5 cycles. The results from this study indicate that incomplete removal of odorants during washing, especially from oleophilic polyester fabrics, is a cause for odor build-up in clothing.

Keywords: odor, cotton, polyester, laundering, detergents

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Clothing worn next to the skin can pick up odors generated from odiferous parts of the body (e.g. underarms, feet) and can continue to smell even after removal from the body. This can result in consumer dissatisfaction with clothing items and potentially also lead to embarrassment in social situations. The quality and intensity of odor may differ depending on the fiber content of the clothing, with natural fibers (e.g. cotton and wool) typically perceived as being less odorous than clothing made from synthetic fibers (e.g. polyester and nylon) after wear.^{1–5}

Body odors formed through the biotransformation of non-odorous compounds available in sweat by odor-causing bacteria are made up of a diverse array of volatile organic compounds (VOCs).^{6–9} Short-chain to medium-chain fatty acids have been recognized as the most common category of odorous VOCs emanating from high-odor body sites, particularly the axillary and foot regions.¹⁰ Whereas, aldehydes have been identified as a significant source of odor in worn fabrics following laundering.¹¹ These odorants differ in lipophilicity being dependent on the polarity of their functional groups and length of their carbon chains. Such differences in the chemistry of odorous VOCs influence their retention and release from different textile fibers, with polar compounds being more readily adsorbed by cotton than polyester.¹²

Perceiving odor, particularly sweat related body odors, in selected items of clothing following wear can be a common experience among many consumers.¹³ From a consumer standpoint, laundering should remove odor where clothing is made fresh and ready to wear again¹⁴ as a result of the combined action of water, temperature, detergent and agitation (referred to as the Sinner's Circle)¹⁵ to remove soils and malodor. Yet, laundering may not always be effective in completely removing odor, with malodors being more pronounced in synthetic clothing.^{2,11,16} This disparity can also be attributed in part to the chemistries of the soiled fibers and the odorants.¹⁷ Both cotton and polyester were shown to retain and subsequently emit many odorants, including carboxylic acids, after laundering, although polyester initially retained and

then released more.² In one study,¹⁶ polyester and cotton swatches were contaminated with six selected odorants (i.e. ethylbutanoate, (Z)-4-heptenal, (E)-2-nonenal, isovaleric acid, 4-methyloctanoic acid, guaiacol) then laundered to assess the ease of removal. Odorants were less readily removed from polyester by washing than from the hydrophilic cotton fabrics. The authors of the study suggested that odorous compounds may continue to accumulate over several wears and washes.¹⁶ Although, the contamination and washing processes were done only once.

Accessible hydroxyl groups on the cellulose polymer chains may be available for hydrogen bonding of polar odorants in cotton.¹⁸ Non-polar compounds have a greater affinity for polyester, being attracted to the fiber surface. Odor control of odorous VOCs can be achieved through adsorption by highly porous materials exhibiting high surface-area-to-weight ratios (e.g. activated carbon or zeolites).⁵ The sorption capacity of different fibers may also go toward explaining difference in odor control.^{18,19} Wool with its many reactive sites within the amino acid side chains is capable of forming bonds with carboxylic acids.²⁰ Greater retention of the ‘sweat’ odorant isovaleric acid on cotton, wool and polyester fabrics was associated with lower affinity of the odorant to fabrics, where wool retained the greatest amount of the acid, followed by cotton and lastly polyester; whereas, polyester was the most odorous followed by cotton then wool the least.¹⁹ Despite this key work by Hammer et al.,¹⁹ where sensory analysis was correlated with isovaleric acid retention within fabrics, only one odorant was examined.

Previous researchers have approached investigations into textile odor by either extracting or measuring compounds directly from the fibers/fabrics (i.e. what is retained within the fibers)^{11,16} or by monitoring the headspace above the fabrics (i.e. what is released from the fibers).^{2,18,21} Measuring compounds both retained within and released from the fibers has not been examined previously. This is an important part of any study on odor. On the one hand, many odor controlling materials that work on the principal of sorption may trap high amounts of odorants within the fiber, therefore not release them into the headspace to be smelt by the human nose. On the other hand, odorants may not be bound tightly to all fibers so that a fiber that has initially

retained higher quantities of odorants may be perceptibly more odorous as desorption occurs over time. Furthermore, detergents and laundry aids can enhance or inhibit the removal of malodor from clothing fabrics.^{11,16,22} Changes in formulations of detergents for enhancing soil removal from sports clothing, where odor build-up on synthetic textiles is likely, has received little attention in the scholarly literature.

The main purpose of the current study was to examine the retention and release of odorants selected to represent different polarities and lipophilicities, in two apparel fabrics that represent different fiber chemistry and properties (cotton and polyester) during multiple soil/wash cycles. A comparison of two commercial detergents was also included as part of the study design, in order to evaluate the effect on odor removal by a detergent specifically marketed as being effective on sports clothing.

Materials and methods

Experimental fabrics

Experimental fabrics were 100% cotton and 100% polyester interlock knit fabrics and were manufactured to be matched as closely as possible in physical properties (see Table 1). Fabrics were supplied by Cotton Incorporated (Cary, NC, USA). Prior to experimental work, fabrics were laundered five times continuously with a fragrance-free detergent (Tide® Free & Gentle, Proctor & Gamble, Toronto, ON) followed by one machine dry cycle. Specimens with a diameter of 50 mm were cut using a circular die from the pre-laundered fabrics.

Table 1. Experimental fabrics

| | 100% Cotton | 100% Polyester |
|---------------------------|-------------------------|-------------------------|
| Fabric structure | Interlock knit | Interlock knit |
| Mass ^a | 234 g/m ² | 224 g/m ² |
| Thickness ^b | 1.28 mm | 1.31 mm |
| Wales | 18 stiches/cm | 16 stiches/cm |
| Courses | 14 stiches/cm | 14 stiches/cm |
| Moisture regain | 7.3% | 0.3% |
| Surface area ^c | 0.712 m ² /g | 0.313 m ² /g |

^a. CAN/CGSB-4.2 No.5.1-M90 (Canadian General Standards Board, 2013)

^b. CAN/CGSB 4.2 No.37-M 87 (CGSB, 2002)

^c. Brenauer-Emmett-Teller (BET) adsorption method (Kryton Gas Physisorption) as per method described in Saini et al.,³⁰

Odorants and preparation of stock solution

Odorants used in the study were octanoic acid (Sigma Aldrich, Oakville, ON, Canada), trans-2-nonenal (2-nonenal) (Sigma Aldrich) and dodecane (Eastman Organic Chemicals, NY, USA).

The selected properties of each odorant are shown in Table 2. Octanoic acid was selected to represent a more polar odorant and has been found in the headspace of fabrics following contact with human skin.^{2,21} The aldehyde, 2-nonenal was selected to represent a less polar odorant and has been recognized as a common body odorant;^{23,24} as well it has been identified in fabrics following contact with the skin.^{11,16,21} Dodecane is a hydrocarbon that has been reported to be released from human skin and present in body odor.²³ Although it is unlikely to be a significant source of malodor, it was included because it represented a more strongly nonpolar compound (see Table 2).

Table 2. Selected properties of odorants

| | Octanoic acid | 2-Nonenal | Dodecane |
|---------------------------------|---------------------|---------------------|---|
| Molecular weight | 144.2 | 140.2 | 170.3 |
| LogP ^{a,b} | 2.735±0.184 | 3.319±0.282 | 6.821±0.166 |
| Water solubility ^a | 2.2 g/L | 0.91 g/L | Sparingly soluble (2.0×10 ⁻⁶ g/L) |
| Polar surface area ^a | 37.3 Å ² | 17.1 Å ² | 0 Å ² |

^a. Values predicted by Advanced Chemistry Development (ACD/Labs) Software V11.02; ^b. LogP = partition coefficient of a molecule between the aqueous and lipophilic phases (usually water and octanol);

A stock solution was prepared by dissolving odorants in dichloromethane (40-50 ppm amylene, ACS reagent, 99.5%; Sigma-Aldrich). The resultant stock solution had a concentration of 10,000 ppm for octanoic acid and for 2-nonenal and 20,000 ppm for dodecane. The stock solution was stored in a fridge (4 °C) throughout the experiment. When needed it was taken out of the fridge, shaken for 30 seconds and allowed to sit for at least 1 minute before use.

Procedure

A volume of 10 µL of odorant solution, which equated to 100 µg of odorant (200 µg of dodecane), was pipetted onto fabric specimens using a syringe. The fabric specimens (placed in Petri dishes) were covered with the Petri dish lid immediately after odorant application. Dichloromethane (10 µL) without odorants was applied to fabric specimens as a control. Fabric specimens were allowed to stand for 24 h in a fume hood after which the specimens were assigned to be washed or extracted (i.e. headspace extraction and then solvent extraction).

The experimental set-up involved three odorants (octanoic acid, 2-nonenal and dodecane), two fiber types (cotton and polyester), three levels of soil/wash cycles (soiled and washed 1, 5 and 10 times) and two detergents (regular and sport – for a list of ingredients see Table S1 in supplementary materials). Cotton and polyester fabric specimens were also exposed to odorants without a subsequent wash procedure to evaluate the initial retention of the odorants. Three replicates for each soil/wash cycle were performed.

Laundering procedure

Fabric specimens were washed in a Launder-Ometer (Atlas Electric Devices Co., Chicago, IL, USA) following a modified method of a test method for colorfastness.²⁵ Two separate wash liquors were prepared in a 10 L flask with either Tide® Free and Gentle Liquid detergent (regular) or Tide® Plus Febreze Sport Liquid detergent (sport) using tap water and the temperature raised to 30 °C. The concentration of each wash liquor was 5 mL of detergent to 1 L of water as specified in the test standard.²⁵ A volume of 450 mL of wash liquor was filled into each canister, then 10 steel balls and one test fabric specimen were added to each canister. The water bath temperature of the Launder-Ometer was set to 30 °C. Washing was carried out for 10 min in the canisters were rotated through the bath at 40 ± 2 rotations/min. At the end of the wash cycle the canisters were removed from the apparatus and fabric and steel balls were emptied into a sieve to allow the washing liquor to be poured away. While in the sieve, fabric specimens were rinsed under running tap water for 30 seconds on each side of the fabric. Using tweezers, the fabric was removed from the sieve and rinsed again in three different flasks full of fresh water which were shaken by hand for 30 s each. A clean paper towel was used to remove some of the excess water from the fabric specimen. The specimen was then hung on a line in a fume hood to air dry for 22 h. Control fabric specimens were also washed in the same manner and dried on the same line as the test specimens. The soil/wash procedure was carried out 1, 5 and 10 times (cycles).

Odorant extraction and analysis

After the designated treatment was completed a fabric specimen was folded once and placed into a 20 mL crimp-top clear headspace vial (Chromatographic Specialties Inc., Brockville, ON, Canada) and capped. The headspace extraction was performed by solid phase micro-extraction (SPME) using divinylbenzene/carboxen/polydimethylsiloxane coated fibers (SUPELCO, Bellefonte, PA, USA). Before performing an extraction, the fiber was thermally cleaned for 3 min at 250 °C. Extractions were conducted for 22 h at 30 °C with sample vials immersed in a

temperature-controlled, stirred oil bath. Odorants were desorbed from the SPME fiber in the gas chromatograph injector for 3 min.

Solvent extraction was conducted to quantify odorants still remaining in the fabrics and conducted immediately after headspace extraction on the same fabric specimen. When the SPME fiber was inside the GC inlet, the vial was uncapped, and 18 mL of dichloromethane was added with the fabric specimen inside and the vial capped again. The vial was left to sit for at least 30 min with periods of 2 min shaking (by hand) for the first 2 min, after 10 min and for the final 2 min. Afterwards, the fabric was squeezed using tweezers against the inside of the vial and removed. The extract was dried over anhydrous sodium sulfate (Millipore Sigma Canada), then concentrated on a Kuderna-Danish column evaporator (500 mL reservoir, 15 mL conical receptor, and 3-ball Snyder column, 24/45 joint). The bottom of the concentrator was immersed halfway inside a water bath set at 60 °C and wrapped with aluminum foil. When the remaining solution reached 1 mL the column was raised to sit outside of the water bath and then concentrated more slowly to 200 µL. 1 µL was injected into the GC for analysis of odorants extracted from the fabric specimen.

The analysis was performed using gas chromatography-flame ionization detector (GC-FID) with a 6890GC (Agilent Technologies, Santa Clara, CA, USA). The column used was a 30 m x 0.53 mm, 1 µm film thickness Restek Rxi-5MS (Chromatographic Specialties). Helium (5.0 grade; Praxair, Edmonton, AB, Canada) was used as the carrier gas with flow controlled at 3.3 mL/min. The analytes for both headspace (volatiles) and solvent extraction (liquid) were desorbed or injected respectively, in the split/splitless injection port of the GC-FID using an inlet temperature set at 250 °C, operating in splitless mode. The primary oven temperature program was 50 °C – 240 °C (held for 10 min) at 10 °C/min.

Data analysis

The independent variables were fiber content, number of soil/wash cycles and detergent. The dependent variables were the total peak area per mass for each odorant, i) released from the fabrics determined via headspace extraction and ii) retained within the fabric determined via solvent extraction. All data was \log_{10} transformed in order to meet assumptions of normality and equal variance. One three-way analysis of variance (ANOVA) was conducted for \log_{10} -transformed headspace data for octanoic acid with fiber content, soil/wash cycle and detergent as the factors. For all other data sets a bimodal distribution of the \log_{10} -transformed data was apparent as polyester peak areas were distinctively higher than cotton peak areas. Therefore, polyester and cotton were analyzed separately and a series of two-way ANOVAs were conducted with soil/wash cycle and detergent as the factors for each odorant and fiber type. Where significant differences were found, Tukey's honestly significant difference (HSD) tests were carried out to establish which differed significantly at the $p < 0.05$ level. All statistical analyses were completed using IBM SPSS.²⁶

Results and discussion

Initial sorption of odorants in fabrics

The peak areas of octanoic acid, 2-nonenal and dodecane released into the headspace above cotton and polyester fabrics, normalized by fabric mass (g/dm^2) and also surface area (m^2) are shown in Table 3. Peak areas of volatiles released into the headspace per mass were much greater for polyester than for cotton. Since cotton had a surface area that was approximately twice as large as that of the polyester fabric, then the difference between the fiber types were increased even more after normalizing by surface area. Peak areas of octanoic acid and 2-nonenal retained within the fabric, determined by solvent extraction and normalized by fabric mass and surface area are also presented in Table 3. The amounts obtained for dodecane retained within the fabric were not included as peak areas were initially very low and for some specimens following laundering no detectable peaks were observed. Slightly higher amounts of octanoic

acid were extracted from cotton fabrics than from polyester when normalized by fabric mass. However, since cotton had a larger surface area the amount of octanoic acid extracted per surface area was lower than that obtained from polyester. For the less polar 2-nonenal, greater amounts of the compound were extracted from polyester than from cotton fabrics when normalized by both fabric mass and surface area. The higher retention of octanoic acid by cotton was in agreement with earlier findings,^{16,19} where 20-24 hours following application cotton fabrics retained greater quantities of the polar acidic compounds, such as isovaleric acid and 4-methyloctanoic acid, than polyester.

Table 3. Peak areas of odorants released from and retained within fabrics after soiling (no wash) in a. above the headspace of the textile, and b. within the textile substrate (mean \pm s.d.)

| | Fabric mass (g/dm ²) | | Surface area (m ²) | |
|------------------------|----------------------------------|------------------|--------------------------------|---------------------|
| | Cotton | Polyester | Cotton | Polyester |
| a. In headspace | | | | |
| Octanoic acid | 5281 \pm 1633 | 26455 \pm 7731 | 37778 \pm 11681 | 430468 \pm 125787 |
| 2-Nonenal | 1337 \pm 679 | 3086 \pm 700 | 9565 \pm 4856 | 50211 \pm 11395 |
| Dodecane | 220 \pm 104 | 549 \pm 173 | 1573 \pm 747 | 8938 \pm 2819 |
| b. In textile | | | | |
| Octanoic acid | 169 \pm 57 | 95 \pm 26 | 1206 \pm 410 | 1548 \pm 417 |
| 2-Nonenal | 5.2 \pm 1.0 | 7.2 \pm 0.8 | 37 \pm 7 | 117 \pm 14 |

Munk and colleagues¹⁶ inoculated six different odorants, including two carboxylic acids (isovaleric acid, 4-methyloctanoic acid) and two aldehydes (4-heptenal, 2-nonenal) onto cotton and polyester fabrics. After immediate extraction of compounds from the textile substrate, higher amounts were obtained from polyester fabric for all six odorants. This was also the case when compounds were extracted 24 hours after inoculation, except for 4-methyloctanoic acid where higher amounts remained on the cotton fabric. In the current study headspace analysis did not occur until 22 hours after inoculation, and extraction of fabrics a further 22 hours later. Therefore, it appears that cotton does not release the polar octanoic acid as rapidly as the

nonpolar 2-nonenal, likely due to the ability to form hydrogen bonds with octanoic acid within the fiber structure. The retention of octanoic acid within the cotton fiber corresponds to less of this volatile in the headspace above the fabric, and therefore would likely correspond with a lower acid odor if smelled. Conversely, as 2-nonenal is less polar and oily in nature, it has a stronger affinity to the oleophilic, less polar polyester fiber.^{27,28} However, despite the stronger attraction between 2-nonenal and polyester, more 2-nonenal was released from the polyester fabric than cotton fabric, which indicates distinctively different mechanisms are responsible.

Hammer et al.,¹⁹ found when isovaleric acid was applied to cotton, wool and polyester fabrics there was a negative association between the acid retention within the fabric and odor intensity. Polyester fabric retained less isovaleric acid than cotton, but was more odorous after 3 h and 20 h, indicating that when fibers retain more compound, less is in the headspace to be perceived by the human nose. Although, our findings agree with the findings of Hammer and colleagues¹⁹ with respect to the odorant octanoic acid, our results differ for 2-nonenal where we found greater amounts of 2-nonenal remained within the polyester fabric yet, higher amounts were released into the headspace and adsorbed on the SPME fiber. The opposite was true for cotton, that is, cotton emitted lower amounts of 2-nonenal as well as retained less of the odorant.

In one study after 20 wears against the axillae (and 19 washes), a higher proportion of carboxylic acids was released from unwashed polyester fabrics than unwashed cotton fabrics.² The more nonpolar aldehydes or hydrocarbons were not examined. In an earlier study,²¹ examining fabrics in contact with participants' (three males and three females) hands, 2-nonenal was detected in the headspace above cotton fabrics worn by four of the six individuals and above rayon fabrics worn by three of the six individuals and not detected above polyester fabrics at all. Polyester represented a much smaller and cotton a higher percentage of aldehyde mass in general. Conversely, octanoic acid was present in the headspace analysis of polyester fabrics for five of the six individuals, but was not detected for the cotton fabrics. In fact, carboxylic acids represented the highest relative percentage mass emitted from polyester fabrics, which was far

greater than that emitted from the other fabrics. This appears contradictory to the findings of our study, however, one explanation is that in the work by Prada et al.,²¹ the concentrations of the compounds emitted from the hands during the hand-fabric contact period were so low that the compounds exhibiting a higher affinity for one type of fabric (e.g. aldehydes to polyester, acids to cotton) may not have been sufficiently high to be detected in the headspace. The human hand is not a strong source of human odor when compared with the human axilla, so the quantities of odorants applied and later extracted from the fabrics in the current study would be much higher than those taken up by the fabrics in the study by Prada et al.²¹

Reduction in odorants following one wash

Table 4 shows the percent reduction of odorants in a) the headspace above the fabrics and b) retained within the fabrics following one wash cycle using regular and sport detergents. Washing was more effective at removing odorants from cotton fabrics than it was at removing odorants from the polyester fabrics. For example, when washed using the regular detergent 99.6% of octanoic acid and 94.2% of 2-nonenal was removed from cotton whereas, only 86.2% of octanoic acid and 59.0% of 2-nonenal was removed from polyester (Table 4). Similarly, a much greater reduction in volatiles emitted into the headspace was apparent from cotton compared with polyester in general (although percent removal of octanoic acid was similar at >98% from both cotton and polyester). This less effective removal of odorants from polyester compared to cotton was expected as in other studies laundering has been shown to be more effective in removing carboxylic acids, aldehydes, one ester and one phenol from cotton compared with polyester fabrics.¹⁶ Oily soil removal from hydrophilic fibers, such as cotton, is more effective because water with detergent can wet the fabric, facilitating the action of the detergent to release soils into the wash water. Whereas, with hydrophobic fibers, oily soils are more difficult to remove because of the attraction of the oil to the fiber over the attraction of the oil to the detergent required for its removal.²⁹

Table 4. Per cent reduction^a of odorants following one soil/wash cycle, a. above the headspace of the textile, and b. within the textile substrate (%)

| Fiber | Detergent | Octanoic acid | 2-Nonenal | Dodecane |
|------------------------|-----------|---------------|-----------|----------|
| a. In headspace | | | | |
| Cotton | Regular | 98.7 | 97.8 | 78.3 |
| | Sport | 98.2 | 97.0 | 84.3 |
| Polyester | Regular | 99.5 | 44.7 | 27.3 |
| | Sport | 99.6 | 66.5 | 51.1 |
| b. In textile | | | | |
| Cotton | Regular | 99.6 | 94.2 | - |
| | Sport | 98.6 | 92.1 | - |
| Polyester | Regular | 86.2 | 59.0 | - |
| | Sport | 76.2 | 59.8 | - |

^a. Per cent reduction was calculated by $100(A-B)/A$ where A is the mean of three replicates for samples exposed to one soiling and no wash and B is the mean of three replicates for one soil/wash cycle

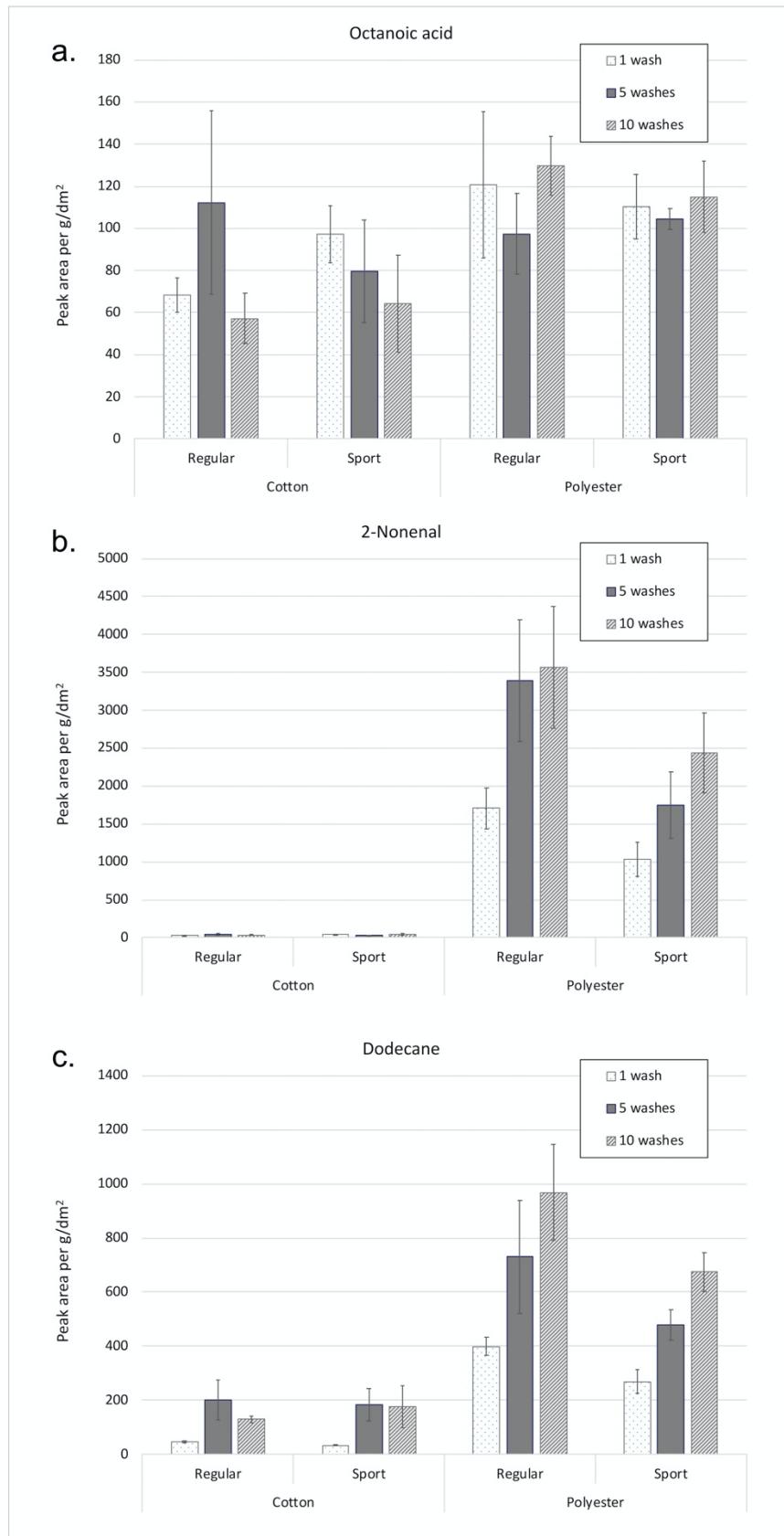
Octanoic acid was removed more effectively than 2-nonenal in both fabrics with 86.2% and 76.2% of octanoic acid removed from polyester for regular and sport detergents respectively, and only 59.0% (regular) and 59.8% (sport) of 2-nonenal removed from polyester. Octanoic acid with a LogP value of 2.735 and polar surface area of 37.3 \AA^2 is more polar and soluble in water than 2-nonenal with a LogP value of 3.319 and polar surface area of 17.1 \AA^2 (see Table 2), which accounts for the more effective removal of octanoic acid via laundering in our study.

Furthermore, the reduction of compounds released into the headspace after one wash cycle was even less effective for the hydrophobic nonpolar dodecane (LogP: 6.821; polar surface area: 0 \AA^2 ; water solubility: $2 \times 10^{-6} \text{ g/L}$). For example, reduction in headspace peaks for polyester with regular detergent was 99.5% for octanoic acid, 44.7% for 2-nonenal and 27.3% for dodecane.

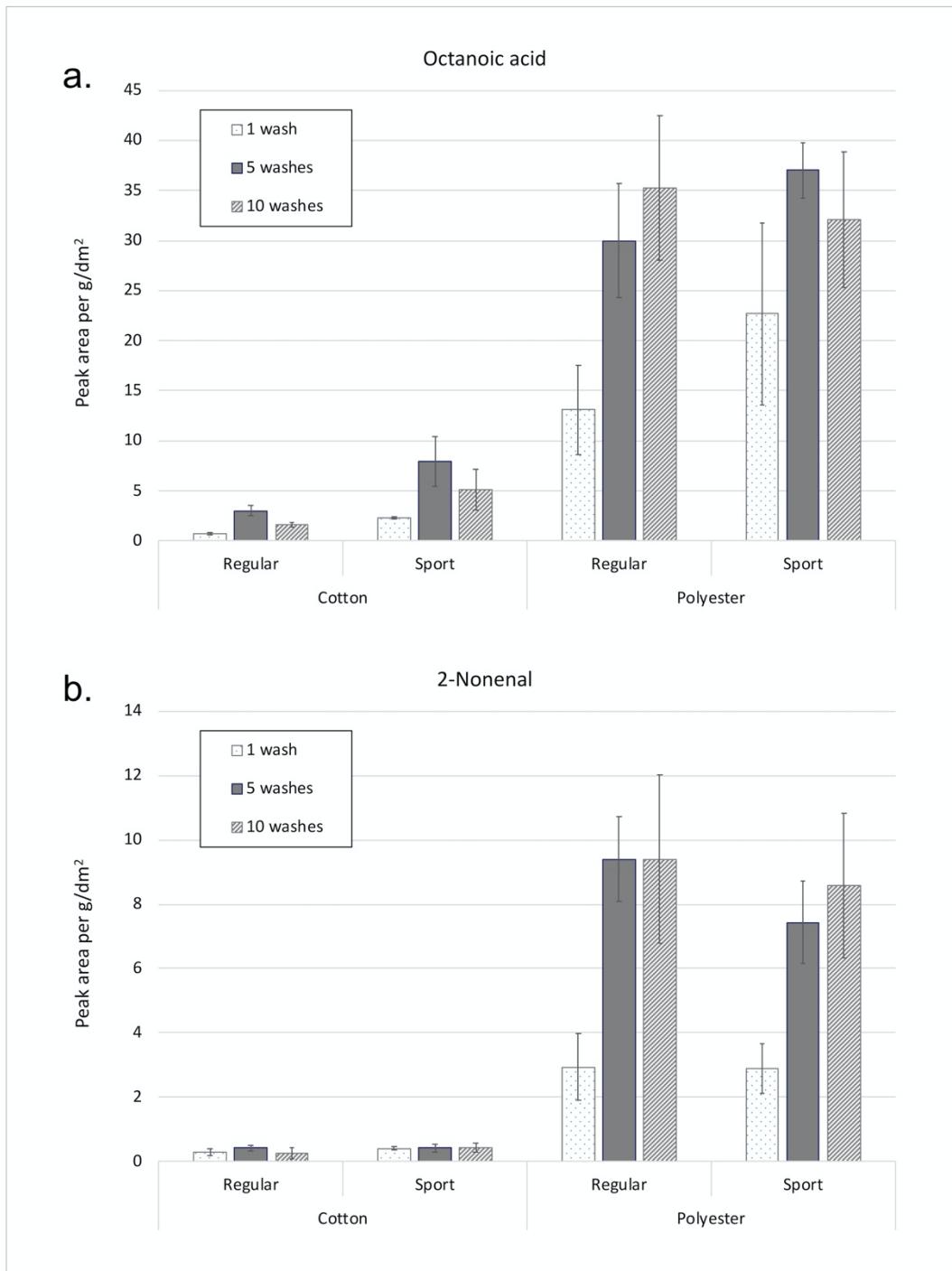
The relationship between polarity of the compound and hydrophilicity of the fabric is described in the work by Saini and colleagues.³⁰ They found that polar semi-volatile organic compounds (SVOCs) present in an indoor office environment that had adsorbed onto fabrics more readily released from hydrophilic cotton as well as hydrophobic polyester fabrics during laundering than nonpolar SVOCs. The nonpolar SVOCs remained sorbed on both polar (cotton) and nonpolar (polyester) fabrics.

Repeated soil and wash cycles

Figures 1 and 2 show the peak areas of compounds released into the headspace above fabrics and extracted from the fabrics respectively, after 1, 5 and 10 soil/wash cycles. In both figures the results are normalized by fabric mass.



[Insert "Figure 1. Headspace extraction of odorants released from fabrics normalized by fabric mass, a. octanoic acid, b. 2-nonenal, and c. dodecane (mean \pm s.d.)" about here]



[Insert “Figure 2. Solvent extraction of odorants released from fabrics normalized by fabric mass, a. octanoic acid, b. 2-nonenal (mean \pm s.d.)” about here]

When normalized by fabric mass far greater quantities of 2-nonenal and dodecane were released into the headspace from polyester fabrics than from cotton (Figure 1), where the lowest total mean peak areas for polyester (after 1 wash) were larger than the highest mean peak area values for cotton (even after 5 or 10 washes). Peak areas ranged from approximately 4 to 8.5 times higher from polyester than cotton for dodecane and from 26 to 104 times higher from polyester for 2-nonenal. These differences between polyester and cotton were further increased when results were normalized by surface area (data not shown) due to the higher surface area of cotton. Polyester also released greater quantities of octanoic acid than did cotton ($F_{1,35}=25.04$, $p<0.001$) although the difference was not as large as for the nonpolar compounds. Considerably lower amounts of both octanoic acid and 2-nonenal were retained (determined by solvent extraction) within the cotton fabrics (see Figure 2) following washing. The overall mean peak areas of octanoic acid extracted from cotton following washing was 3.4 ± 2.7 peak area per g/dm² and from polyester 28.4 ± 2.7 peak area per g/dm². Mean peak areas (per g/dm²) of 2-nonenal extracted from cotton after washing was 0.4 ± 0.1 and from polyester 6.6 ± 3.2 . As mentioned earlier, laundering is more effective at removing soils and odorants from hydrophilic cotton fabrics than hydrophobic polyester fabrics. This was evident in the results from the repeated soil/wash cycles conducted in the current study. Cotton fabrics retained significantly lower amounts of odorants within the fabrics, as well as emitted lower amounts into the headspace. It is important to note that due to the experimental procedure there were three periods where odorants were allowed to release from the fabrics. These occurred after application of odorant and before washing (24 h), after washing while the fabrics dried (22 h), during headspace extraction and before solvent extraction (22 h). At each of these stages volatiles would have released from the fabrics and the rate of release would have differed depending on fiber content. In other work on sorption and release of selected odorants in the gas phase, cotton was found to have a low

relative adsorption capacity, and an initial relatively fast rate of release during the first 6 h, followed by slow release; whereas, polyester had a high relative adsorption followed by continuous release of odorants.³¹ Therefore, by allowing odorants to release from the fabric prior to extraction does mean that the initial quantity of odorants at the time of washing would not be the same. This is supported from the initial sorption results presented in Table 3. Nonetheless, this process of ‘airing’ does reflect what would occur in real use circumstances as few people will wash their clothes immediately after removing them.

The results showed that an accumulation of odorants as a result of multiple soiling and wash cycles can occur, particularly within polyester. This confirms previous claims that accumulation of odor can result from multiple use.^{2,16} However, there appears to be a limit to this cumulative effect. For most of the odorant-fiber interactions, there was either no difference in the amounts retained within or released from the fabrics between 5 and 10 soil/wash cycles; and in the case of cotton and octanoic acid there was a decrease after 5 cycles. Greater quantities of both octanoic acid and 2-nonenal were extracted from polyester fabrics following 5 and 10 cycles, than after only 1 cycle, showing this accumulative effect; yet between 5 and 10 soil/wash cycles there were no significant differences in amounts extracted. A similar finding was apparent for the two nonpolar odorants (2-nonenal, dodecane) released from polyester. Less was emitted after only 1 soil/wash cycle than after 5 and 10 cycles (which again were not significantly different from one another). A slightly different effect was observed with cotton, as a significant increase in the amount of octanoic acid extracted between 1 and 5 cycles occurred, but a significantly lower amount of the acid was extracted after 10 cycles compared to 5 cycles. For 2-nonenal remaining within cotton following washing there were no significant differences among any of the three soil/wash cycles ($F_{2,17} = 0.851$, NS). In terms of the effect of soil/wash cycles on the release of odorants into the headspace, the number of wash cycles did not influence the release of octanoic acid from polyester, but there was a small significant decrease in the quantity released from cotton after 10 cycles compared to 5.

The finding that the odorants retained within or released from the fabrics of the two fiber types did not continue to increase with application and laundering was unexpected. Even more unexpected, was the decrease in octanoic acid after 10 soil/wash cycles on cotton. One possible explanation for this observed decrease after more than 5 soil/wash cycles may be due to fiber degradation occurring during the laundering process. Under electron microscopic examination of machine laundered cotton fibers signs of damage was seen by Bishop³² after only six washes and after eleven washes fiber fibrillation was quite noticeable. Both fabrics in the current study had been machine laundered five times prior to the experimental work, therefore, by the first soil/wash cycle the fabrics had been washed 6 times, then 10 and 15 times for 5 soil/wash and 10 soil/wash cycles respectively. Fibrillation during laundering may have opened up the structure of cotton fibers allowing wash liquor to readily enter the cotton fibers resulting in more effective removal of accumulated and newly sorbed odorants in 10 soil/wash cycles than in 1 and 5, and subsequently lead to a reduction in residual octanoic acid noted after the 10 soil/wash cycles. It is not clear why a similar decrease did not occur for 2-nonenal, but it may be related to the ease with which the polar octanoic acid can be removed in laundering. Polyester fibers do not experience the same damage during laundering although a “slow surface hydrolysis” from alkaline detergents can occur resulting in polyester fibers becoming more hydrophilic with repeated laundering and therefore less susceptible to retaining oily soils.³² However, this type of hydrolysis would not likely have occurred during the course of this experiment. If an accumulation of detergent residue resulted after multiple wash cycles³³ then some change in surface properties of the polyester fibers rendering them more hydrophilic may have occurred. During laundering surfactants attach themselves to oily soils, facilitating their removal and emulsification within the wash water. Reportedly, soil-release additives in detergent formulations can build-up over multiple washes making polyester more hydrophilic increasing the surface energy of the fabric.³⁴ Water contact angles on unfinished polyester woven fabrics were shown to progressively decrease following multiple laundering cycles using detergent formulations with soil-release additives.³⁵ If polyester becomes more hydrophilic with washing, this may impact

the retention of odorants following contamination and affect their release during washing. Further work to better understand the interaction between odorants and textile substrates under repeated soiling and laundering processes and how this may translate to clothing during use is needed. This can include examining the role that detergent may have on increasing the hydrophilicity of polyester fabrics and would therefore require such measurements of contact angles of wash liquor on polyester and cotton fabrics, as well as examination of changes to surface characteristics by such means as scanning electron microscopy (SEM).

The laundering procedure used in the current study was likely more efficient than laundering procedures carried out at home by consumers. For example, the detergent concentration specified by the test standard²⁵ was higher than that generally recommended by the manufacturer (e.g. 0.5% compared with ~ 0.05% - 0.13%). Furthermore, the liquor to fabric ratio was 900:1, which far exceeds a typical load of laundry ranging from 15:1 – 30:1.³⁶ At 30 °C, the wash temperature was lower than the 40 °C or greater that has been found to be more common wash temperature reported in the literature based on consumer surveys for laundering cotton T-shirts^{37–39} and athletic clothing.³⁸ The Launder-Ometer was used because multiple samples could be washed simultaneously while preventing carry over of compounds from one fabric sample to another. However, one author of an earlier study⁴⁰ concluded that the Launder-Ometer was not reflective of results obtained through household washing machines, and called for further development of laboratory devices in consumer laundry testing. With this in mind, future studies should select parameters that better represent consumer laundering habits.

Effect of detergent on removal of odorants over multiple soil/wash cycles

Any effect due to the detergent was minimal compared with other factors such as fiber content and repeated soil/wash cycles. The regular detergent was more effective at removing octanoic acid from cotton ($F_{1,17}=76.4$, $p < 0.001$), as lower quantities of the acid remained within the fabric following washing. However, this did not translate into lower amounts of the acid released into the headspace above cotton ($F_{1,17}=3.8$, NS). Detergent had no effect on octanoic acid

retained within ($F_{1,17}=3.7$, NS) or released from polyester ($F_{1,17}=0.2$, NS). Lower amounts of 2-nonenal were released into the headspace above polyester fabrics ($F_{1,17}=25.6$, $p < 0.001$) following washing with the sport detergent. A similar trend was apparent for dodecane ($F_{1,17}=32.2$, $p < 0.001$). However, detergent did not influence the amount of 2-nonenal retained within either fabric or for 2-nonenal and dodecane above the headspace of cotton.

The sport detergent is marketed as being designed to “fight sports odors and stains”⁴¹ and includes Febreze technology which in fabric sprays and air fresheners works on controlling odor through entrapment of malodors by cyclodextrins.⁴² The presence of cyclodextrins and their entrapment of malodors could account for differences in the amount of nonpolar compounds detected in the headspace above polyester washed with sport detergent versus regular detergent, but not that retained within the fabric; although, the ingredients list for the detergent does not state cyclodextrins to be present in the sport detergent used in this study.⁴³ Similar ionic and nonionic surfactants are present in both detergent formulas, with some differences in the combination of surfactants. Builders which are used to soften the water are also present in both detergents.^{43,44} The main difference between them is the addition of fragrance and additives to preserve fragrance in the sport detergent. The results of our study showed that the detergent designed to reduce odors on sports clothing (typically polyester) had some benefit for controlling odors in the polyester fabric, but less effect for the cotton fabric. As the two detergents used in our study were both commercially produced by the same manufacturer, and subsequently had similar formulations, future work could examine other detergents formulations. This could also include standard textile reference detergents (e.g. ISO or AATCC standard reference detergents), and/or the use of specific laundry auxiliaries that may enhance the removal of lipophilic soils.

Conclusions and recommendations

Differences in the retention and release of three selected odorants, that varied in polarity and lipophilicity, from cotton and polyester fabrics were found. Prior to laundering, but after an

airing period of 24 hours, higher amounts of all odorants were released into the headspace above polyester fabrics than cotton fabrics. However, cotton fabrics retained more octanoic acid than did polyester fabrics initially; while retaining less 2-nonenal than polyester. This highlights the importance of examining both sorption and release of compounds in textile odor research.

Laundering was more effective at removing the polar octanoic acid than the two nonpolar odorants, and hydrophilic cotton was more effectively cleaned than oleophilic polyester, regardless of odorant chemistry. An accumulation of odorants because of multiple soil/wash cycles was evident, but only to a point. Between 5 and 10 soil/wash cycles further accumulation of odorants above the headspace or within the fabric did not occur and with a decrease in the amount of octanoic acid extracted from cotton was found. This lack of an increase may be a result of fiber degradation which facilitates laundering efficacy in cotton. For polyester, changes in the surface chemistry from the retention of detergent may result in increased hydrophilicity and also facilitate laundering efficiency. A small but significant difference in laundering efficacy in relation to the removal of nonpolar odorant in the headspace of polyester fabrics when using the sport detergent was noted. This may reflect an improvement in odor control due to using a detergent specifically designed for sporting odors and polyester athletic apparel.

Recommendations for future work have included investigating the changes to surface properties and degradative effects of multiple laundering cycles that may facilitate odor removal over time. Selection of laundering procedures that better reflect those used by consumers in household laundering is also another factor that should be considered in future research on this topic. The role of bacteria in textile malodor was not addressed in the current study. However, during real use, further bacterial metabolism of non-odorous sweat compounds may cause further odor to develop within unlauded clothing, as earlier research on body odor within fabrics has suggested.¹⁸ So, even though odorants may dissipate with airing more odor could be produced over time through bacterial metabolism. Therefore, the adherence of non-odorous sweat

compounds that may become odorous due to microbial action should also be investigated in future research.

Supplementary materials

Table S1 can be accessed through the following link: [Note a permanent link to Table S1 will be provided through the university's library Education and Research Archive website]

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