Characterizing the Sorption and Release of Odorous Compounds in Clothing Fabrics

by

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Abstract

Body odour, particularly in the axillary region, consists of a rich bouquet of volatile organic compounds (VOCs) varying in functional groups including carboxylic acids, aldehydes, ketones, esters, etc. Clothing fabrics worn next to the axillae can easily ad/absorb and retain malodours. Odorous compounds also can be transferred to the garment during laundering from old/unclean washing machines. The physical morphology and chemical structures of different fibre types affect the sorption and desorption of odorants. Therefore, the purpose of this study was to characterize the initial sorption of six selected VOCs by apparel fabrics that differed in generic fibre content and measure their subsequent release after 3 h, 8 h and 24 h. Experimental fabrics were all plain weave structures and included cotton (119 ± 0.7 g/m^2), viscose (146 ± 1.6 g/m^2), polyester (134 ± 0.9 g/m^2), and nylon (136 ± 1.3 g/m^2). The selected VOCs were previously detected either in body odour and/or laundry malodour and differed in their functional groups: two carboxylic acids (isovaleric acid and octanoic acid), two aldehydes (nonanal and undecanal), and two ketones (2-heptanone and 6-undecanone). Fabric samples were immersed in an odorant/artificial sweat solution in order for odorants to be selectively adsorbed by fabrics. Immersing fabrics in the aqueous solution provided a more realistic condition of the interaction between clothing garments with body odour during wear or odorants transferred during washing. Following inoculation, fabrics were either extracted immediately in dichloromethane (initial sorption) or deployed in a test chamber where VOCs were able to dissipate from the fabrics for selected time periods (i.e. 3 h, 8 h, 24 h). The compounds extracted from the fabrics were measured using gas chromatography-flame ionization detection.

The findings showed that there was higher initial sorption of the VOCs by the synthetic fibres compared to the two cellulosic fibres. Polyester tended to ab/adsorb higher quantities than nylon, and viscose slightly higher quantities than cotton. In general, the non-polar VOCs were ab/adsorbed by all four fibre types in higher concentrations. VOCs tended to be released from the polyester and cotton fabrics more rapidly than nylon and viscose over the first 3 h. Moreover, the highest amounts of VOCs were retained by nylon fabrics after 24 h. This research has furthered our understanding of why some selected fibre types (i.e. cotton and viscose) are perceptibly less odorous than others (i.e. nylon and polyester) following wear and even laundering. This research has demonstrated that when odorants in an aqueous solution are transferred to fabrics, hydrophilic fibres will have preferential sorption of water molecules and initially adsorb fewer odorants and as a consequence fewer odorants to release to be smelt. Whereas, hydrophobic fibres will preferentially adsorb odorants and therefore retain higher quantities of odorous compounds, to begin with, and subsequently more to release.

Preface

This thesis is an original work by Sara Vaezafshar. No part of this thesis has been previously published.

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List of Abbreviations

ANOVA	analysis of variance
C	Concentration
c.v.	coefficient of variation
CGSB	Canadian General Standards Board
cm	Centimetre
DCM	Dichloromethane
Exp.	Experimental
df	degrees of freedom
F	F statistic
G	Grams
g/m^2	grams per square metre
g/L	grams per litre
GC-FID	Gas chromatography- Flame ionization detection
h	hour
Hz	Hertz
ISO	International Organization for Standardization
Log Kow	n-Octanol/water partition coefficient
L	litre
m^2	metre square
Max	maximum value
mg	milligram
Min	minimum value

min	minutes
mL	millilitre
mm	millimetre
mmHg	millimetre of mercury
MS	mean squares
n.d.	no date
OH	hydroxyl groups
P	p-value
pH	acidity
μg/mL	microgram per millilitre
Pred.	predicted
RH	relative humidity
T	temperature
V	volume
VOCs	volatile organic compounds
$\bar{x}$	mean value
SS	sum of squares
%	per cent
≤	less than or equal to
Ø	diameter
°C	Degrees Celsius
μL	microlitre

List of definitions

Axillary region	Relating to the armpit area (Merriam-webster.com, 2019).
Hydrophilic	“Having an affinity to water” (Daintith, 2008).
Hydrophobic	“Lack of having an affinity to water” (Daintith, 2008).
Inoculate	Introducing solutions to substances. In this study, the solution was an odorous sweat solution, and the substances were the experimental fabrics.
Non-polar compounds	“Any compound either with covalent molecules and lack of permanent dipole moment” (Daintith, 2008).
Odour	Recognizing the volatile chemicals by a sense of the smell through the olfactory organs (International Organization for Standardization, 2008).
Oleophilic	“Having a strong affinity to mix or dissolve in oil” (Merriam-webster.com, 2019).
Polar compounds	“Any compound with either ionic charge or a large permanent dipole moment” (Daintith, 2008)
Volatile organic compounds	VOCs are large groups of chemicals known due to their ability to evaporate easily from different substances, low vapour pressure (≥0.01 KPa at 20 ºC), and low solubility in water (Herrmann, 2010).
Adsorption	Adsorption is defined as a surface phenomenon occurring through the physical binding of chemical molecules on the surface of the sorbent (Bajpai & Rajpoot, 1999).
Absorption	Absorption phenomena involving the permeation of molecules in the phase of gas or liquid through the sorbent substances several nanometers (Weber, McGinley, & Katz, 1991).
Sorption	Sorption is a general term that can be referred to both adsorption and absorption. Sorption process, including the capture of chemical molecules by a substance (i.e. sorbent) (Crini & Badot, 2011).

Chapter 1

Introduction

1.1 Background

Odour is a feature of some volatile organic compounds (VOCs) that can elicit an olfactory sensory response and may be described as either pleasant (e.g. plant scent, fresh food, spices) or unpleasant (e.g. bodily fluids, decaying food) (Brewer & Cadwallader, 2004). Olfaction can have a significant influence on our judgment about the quality of foods, the environment, and people's health state (Synnott, 1992). From a cultural perspective, a pleasant odour can often be perceived as being healthy and hygienic (Waskul & Vannini, 2008). Whereas, pungent body odour emanating from a person can cause embarrassment and loss of self-confidence (Kanlayavattanakul, & Lourith, 2011). Studies on life activity patterns have revealed that people spend much more time in the indoor environment than outdoors (Brasche & Bischof, 2005; Khajehzadeh, & Vale, 2017; Leech, Nelson, Burnett, Aaron, & Raizenne, 2002). For example, Canadian people spend 88.6% of 24 hours/day in indoor environments (Leech et al., 2002). In the indoor environment, body odours may become more noticeable and be considered unacceptable, especially in workplaces (Riach & Warren, 2015). In fact, odour intensity and quality can be significantly increased by clothing fabrics due to its ability to uptake and hold odorous compounds (McQueen et al., 2014).

Since clothing is usually worn in close proximity to the skin, any odours produced on the skin can easily be picked up, retained, and further intensified within the fabric even after it is no longer worn. Odour arising from the axilla (underarm) has been described as being the most distinctive and strongest among human body odours (Takeuchi, Yabuki, & Hasegawa, 2013). Axillary odour is created through the biotransformation of apocrine sweat by certain strains of bacteria living in this site (Dravnieks & Krotoszynski, 1968; Leyden, McGinley, Hölzle, Labows, & Kligman, 1981; Shelley, Hurley, & Nichols, 1953). Furthermore, eccrine sweat generates a moist microclimate further facilitating bacterial growth as well as helping volatilization of formed VOCs through bacterial activities (Shelley et al., 1953). This is due to the high density and strains of resident bacteria (Jackman & Noble, 1983), along with the great number of sweat glands in the armpit area (Groscurth, 2002).

Because odour is so important in human interaction and social life, managing body odours and controlling distinctive odours within the home, workplace, and automobiles have been well established and improved (Waskul & Vannini, 2008). Such odour management techniques can include using soaps for bathing to remove unpleasant odours from the body itself or using laundry detergents to remove body odours from clothing. The global market size of personal care and perfume products highlights the importance of body odour management with making 72.7 billion US dollars in 2018 (Statista, 2019). However, a possible involvement between exposure to xenoestrogenic chemicals (i.e. chemicals that mimic estrogen) in personal care products in the underarm region and breast cancer has been postulated due to endocrine disruption (Darbre, 2009; Konduracka, Krzemieniecki, & Gajos, 2014). Underarm cosmetic products can also contain several chemicals, including alcohols, aldehydes, esters, and ketones, which can result in environmental contamination (Vance, 1999). Triclosan, for instance, is a chemical used in deodorant products that are reported to be a source of wastewater contamination in the US which cannot be filtered through wastewater treatment methods (Bloch, 2009).

Another source of odour is through the contamination of garments from malodours formed by biofilms in unclean or old washing machines (Stapleton, Hill, Day, Perry, & Dean, 2013). Despite the role microorganisms play in odour formation, odour retention within different textiles can greatly depend on the selective sorption and desorption of malodours by clothing rather than survival of bacterial populations (Klepp, Buck, Laitala, & Kjeldsberg, 2016; McQueen, Laing, Brooks, & Niven, 2007). These two specified sources of malodours in clothing fabrics (i.e. axillae and washing machine) could result in wearers' embarrassment as well as providing an unpleasant situation for others in close proximity to them. Characterizing the sorption and release of body odour compounds by different fibres, for example, can be a useful approach for modifying or generating a new type of fibres with better performances.

Fabrics composed of different fibre types exhibit distinct odour generation/retention profiles. While natural fibres (e.g. cotton, wool) or regenerated cellulosic fibres (e.g. viscose) tend to uptake polar VOCs, the non-polar chemicals are sorbed easily by synthetic fibres (e.g. polyester) (Prada, Curran, & Furton, 2011). One study reported high relative adsorption of VOCs for both polyester and wool compared to cotton fibres when VOCs were exposed to fibres in a gaseous form, followed by differing rates of release (Richter, Bremer, Silcock, & Laing, 2018). In human wear trials, worn wool fabrics have been found to emit lower odour after removal from the body, while VOCs were still detected in the headspace of polyester fabrics even seven days after they had been worn (McQueen, Laing, Delahunty, Brooks, & Niven, 2008). In social research, people have described polyester to be their smelly clothing (Stanes & Gibson, 2017) and clothing made from natural fibres tend to be less problematic for building up odour, even requiring less frequent laundering

There have been minimal studies focusing on the sorption and release of odorous VOCs by fabrics differing by generic fibre type. Among the studies that have assessed the sorption and desorption behaviours of chemicals by different fabrics, such as semi-volatile organic compounds (SVOCs) in the indoor environment (Saini, Okeme, Parnis, McQueen, & Diamond, 2017) or VOCs related to body odour (Richter et al., 2018), the compounds have been exposed to fabrics in the gaseous phase. However, in the case of the transfer of axillary odour onto clothing fabrics or through laundering systems, sorption occurs in an aqueous media (i.e. liquid sweat or laundry water). Desorption of odorous compounds in a controlled temperature and humidity environment is also of interest to better understand the release of odorants from fabrics varying by fibre content. Thus, in the current study, fabrics were inoculated with a mixture of odorous VOCs in a sweat solution to better simulate the transfer of odorants from axillary sweat or unclean washing machines via laundry water. Moreover, chamber tests were conducted to control of environmental factors (i.e. temperature, humidity, and air-flow) during the release phase of the experiment.

1.2 Statement of problem and purpose

1.2.1 Statement of problem

Clothing fabrics are worn near the wearer’s skin and can contribute to the intensity of body odour, especially odours generated in the axillary region. Human body odour, as well as odour from old or unclean washing machines (Stapleton et al., 2013), have been found to be responsible for malodours emitted from clothing fabrics. The amount of sorption and intensity of odorous VOCs emitted from different fabrics vary according to the fibres’ inherent chemical properties. In addition to the sorption of VOCs by fabrics in the gaseous phase, many odorants can be transferred to the garments through either sorption of liquid sweat secreted from the axillary region or through laundry water. Therefore, measuring the concentration of VOCs after fabrics were inoculated with a mixture of odorous VOCs in an aqueous sweat solution better simulates the transfer of odours to clothing fabrics. The rate of release of compounds can also differ depending on fibre type, and this can influence the odour in the headspace above fabrics where it may be detected by the sense of smell. Measuring the concentrations of VOCs at predetermined periods following deployment in a test chamber allows a better understanding of the release of compounds by fabrics. A better understanding of the mechanisms involved in the sorption and release of odorous VOCs is necessary toward improving our selection of fabrics for low-odour apparel.

1.2.2 Objectives

The objectives of this study are to:

1. compare the sorption of six selected odorous VOCs (i.e. isovaleric acid, 2-heptanone, nonanal, octanoic acid, 6-undecanone, and undecanal) present in an aqueous sweat solution by fabrics composed of different textile fibres (i.e. cotton, nylon, polyester and viscose); and

2. determine the rates of release of selected odorous VOCs from fabrics composed of different textile fibres at discrete time periods (i.e. 3 h, 8 h and 24 h).

Chapter 2

Review of Literature

2.1 Odour and clothing

The organoleptic attribute of some volatile organic compounds (VOCs) is defined as odour with two integrated physiological and moral aspects (International Organization for Standardization, 2008; Synnott, 1992). As a physiological phenomenon, odour detection is through an olfactory system which has been described as a powerful sense (Synnott, 1992). Evaluating an odour in descriptive terms is due to its moral dimension, which is instinctively employed to judge our surroundings, including qualities of food and drink, environment, and other people (Synnott, 1992).

Human body odour can provide essential information about a person's emotional, health, and mental conditions. For instance, changing emotional states and some diseases result in the emissions of different types of odours (Chen & Haviland-Jones, 2000; Shirasu & Touhara, 2011). Furthermore, odour in the axillary and breast regions of mothers have been found to be recognizable by infants (Cernoch & Porter, 2017). Sociologists have examined the social meanings of odours, describing how smells can have cultural meanings and can dictate social order (Largey & Watson, 1972; Waskul, & Vannini, 2008). Smelling good or like a "rose" is symbolic of attraction and represents good hygiene and health. In contrast, avoiding a "skunk" and undesirable smells like strong body odour has been widely accepted (Largey & Watson, 1972). Therefore, when a person emanates unpleasant body odour it can be interpreted as unhygienic and can cause embarrassment; as well, people may be discredited in both their personal and social lives (Waskul & Vannini, 2008). Although body odour arises from the body, clothing can intensify natural body odours due to the proximate location between garments and the wearer's skin, particularly in the axillary and foot regions (McQueen et al., 2014; Shelley et al., 1953). Thus, identifying the sources of malodours and finding a suitable controlling strategy in order to manage odours within clothing can be considered an essential research area.

2.1.1 Sources of odour associated with clothing malodour

Clothing by nature covers much of the human body, and as such is worn close to the odour-producing parts of the body, including the armpits, feet, scalp and sex organs (Havlíček, Fialová, & Roberts, 2017). The generation of body odour, mostly in the axillae and feet, results from the biodegradation of compounds in sweat and sebum by microorganisms (Kanlayavattanakul & Lourith, 2011).

Three types of sweat glands, namely eccrine, apocrine and apoeccrine, are present on the skin and all vary in structure and function. Apocrine, eccrine and sebaceous glands provide the initial compounds for producing body odour (Inaba & Inaba, 1992). The secreted substances are initially odourless but are converted to odorous VOCs in the presence of certain microorganisms, especially gram-positive bacteria, such as staphylococci (i.e. *Staphylococcus epidermidis, Staphylococcus haemolyticus*), aerobic coryneforms (i.e. *Corynebacterium tuberculostearicum, Corynebacterium minutissimum*) and micrococcae (Troccaz, Starkenmann, Niclass, van de Waal, & Clark, 2004; Taylor et al., 2003). The watery secretion of eccrine sweat glands can enhance bacterial growth by creating a moist environment (Inaba & Inaba, 1992). The human axilla (underarm) has been reported as one of the most odorous parts of the body (Takeuchi et al., 2012). This is due to a large number of apocrine sweat glands in this area (i.e. 1:1 ratio to the number of eccrine glands) and the high numbers of resident corynebacteria and other odour-causing microorganisms on this site (Montagna & Parakkal, 1974; Taylor et al., 2003). Microorganisms consume the milky odourless apocrine secretions constituting of proteins, lipids, electrolytes, vitamins, and steroids as a source of nutrition (Fredrich, Barzantny, Brune, & Tauch, 2013; Wilke, Martin, Terstegen, & Biel, 2007) converting them to odorous VOCs. The intensity of the odour generated can be further increased within clothing fabrics. Axillary odour can transfer and develop within fabrics through two main processes. First, odorous compounds are primarily formed on the skin and then picked up by the clothing fabrics; and second, further production of malodour occurs through the biotransformation of sorbed sweat within the fabric (Dravnieks & Krotoszynski, 1968).

Odour in garments can also arise during the laundering process. This may occur due to the bacteria and odorous chemicals transferred from the washing machine and/or wash water (Munk, Johansen, Stahnke, & Adler-Nissen, 2001; Stapleton et al., 2013). Due to the key role microorganisms play in the development of odour within clothing, the effectiveness of laundering with the aim of removing bacteria and malodours have been investigated (Munk et al., 2001; Takeuchi et al., 2012; Wiksell, Pickett, & Hartman, 1973). Some types of bacteria not only survive the washing process but can also be transferred between different laundry items (Munk et al., 2001; Wiksell et al., 1973). Analyzing odorants in fabric swatches contaminated with either axillary sweat or selected odorous chemicals after laundering revealed differences in how effective the washing process was and depended on the chemical composition of the odorant and fibre content (Munk, Münch, Stahnke, Adler-Nissen, & Schieberle, 2000; Abdul-Bari, 2018). Additionally, bacteria build-up in old and/or unclean washing machines may also result in the generation of further odour that can then be taken up by clothing fabrics during laundering (Stapleton et al., 2013).

2.1.2 Overview of odorous compounds emitted from the skin and laundry

2.1.2.1 Odours from the skin

A rich bouquet of volatiles are emitted from the human skin. In a review of previous works on VOCs found in body odour, 532 VOCs from skin secretions were identified exhibiting wide variation in functional groups and chemical classes (see Table 2.1) (de Lacy Costello et al. 2014). The odorous chemicals related to skin secretions differ among body sites, such as the axillae (Zeng et al., 1991), feet (Ara, et al., 2006), hands (Bernier, Booth, & Yost, 1999), forearms, and upper back (Gallagher et al., 2008). These differences can be due to the variations in sweat glands as well as the resident bacteria throughout the different parts of the body. For example, while there are both eccrine and apocrine sweat glands in the axillary region, the palms of hands and soles of feet only have eccrine glands (Groscurth, 2002). Characterizing the samples extracted from socks

Table 2.1

VOCs detected in skin secretions

Functional group	Chemical classes	Number of identified compounds
Halogen-containing	X = Cl, Br, and I	
	A mix of halogen and another hetero	
Hydrocarbon	Benzyls and phenyls	20
	Branched-chain alkanes	6
	Non-aromatic cyclics	3
	Non-cyclic alkanes	32
	Straight chain alkanes	20
	Others	6
Nitrogen-containing	Different chemical classes like amines, amides, imides, nitriles, etc.	69
Oxygen-containing	Alcohols	75
	Aldehydes	2
	Carboxylic acids	88
	Esters	91
	Ethers	36
	Ketones	41
Sulfur-containing	Different chemical classes like disulfides, sulfides, sulfones, etc.	24

Adapted from de Lacy Costello et al., (2014).

and feet of participants with different intensities of foot odour showed greater amounts of short-chain carboxylic acids in samples from participants with a stronger odour (Kanda et al., 1990). Also, isovaleric acid, which is known as responsible for distinctive foot odour, was only found in samples from individuals who were assessed as being more odorous (Kanda et al., 1990).

Despite there being 100s of compounds making up the overall axillary bouquet, there have been three main groups of compounds that have been identified in the literature as being primarily responsible for typical or characteristic axillary odour. These are 1) steroidal fragments (16-androstene steroids); 2) volatile sulfur compounds (VSCs); and 3) volatile fatty acids (VFAs) (Kanlayavattanakul & Lourith, 2011).

The VSCs have been described as having the most considerable influence on axillary odour intensity compared to the other two groups mentioned (Hasegawa, Yabuki, & Matsukane, 2004; Natsch, Schmid, & Flachsmann, 2004; Troccaz et al., 2004). The identification of these compounds and relevance to human axillary odour began to be reported in the early 21st century. Incubation of odourless sweat (collected from 30 male participants) with a specific bacterial strain of *Staphylococcus haemolyticus* was carried out. The resultant odours were characterised by gas chromatography-olfactometry (GC-O) and gas chromatography-mass spectroscopy (GC-MS) and resulted in the identification of (R)- and (S)-3-methyl-3-sulfanylhexan-1-ol (Troccaz et al., 2004). Through GC-O analysis (S)-3-methyl-3-sulfanylhexan-1-o1 was described as “sweat, onion and animal” whereas the (R)-3-methyl-3-sulfanylhexan-1-ol was described as “fruity, grapefruit and sulfury” (Troccaz et al., 2004). Other members of the VSCs group, namely 2-methyl-3-sulfanylbutan-1-ol, 3-sulfanylpentan-1-ol, and 3-methyl-3-sulfanylhexan-1-ol, were found by analyzing the NaOH-treated and reacidified axillary sweat samples with GC-O and further GC-MS (Natsch et al., 2006). In a later study by Hasegawa et al., (2004) fresh axillary samples were collected from 50 individuals by using sorptive stir bars, then VOCs were desorbed using a thermal desorption system (TDS) followed by analysis with GC-MS. Through this process, the authors demonstrated that the S-enantiomer of 3-methyl-3-sulfanylhexan-1-ol was a contributor to axillary odour (Hasegawa et al., 2004). Yet, despite the importance of the VSCs in overall axillary odour, as they are present in extremely low concentrations, they can be difficult to detect through instruments such as GC, particularly in the headspace. Therefore, VSCs have not been reported as being present in clothing-related malodour (Munk et al., 2000; Prada, Curran, & Furton, 2011; Rathinamoorthy & Thilagavathi, 2016).

The steroidal compounds such as androstenone and androstenol in axillary sweat have been described as providing the acrid and musky body odours (Amoore, Pelosi, & Forrester, 1977; Labows, McGinley, & Kligman, 1982). This class of chemical was of particular interest in the 1980s and 1990s due to their pheromonal property responsible for olfactory communication (Labows et al., 1982). The GC analysis of participants' axillary samples (12 young men) showed the presence of 5α-androst-16-en-3α-ol but no 5α-androst-16-en-3-one (Brooksbank, Brown, & Gustafsson, 1974). Later, four main detectable odorous 16-androstene steroids were 5α-androst-16-en-3-one, 5α-androst-16-en-3α-ol, androsta-4,16-dien-3-one, and androsta-4,16-dien-3α-ol (Gower, Nixon, & Mallet, 1988). However, it is estimated that 40% of the normal population cannot detect androstenone (and 12% for musky androstenol), which means many people are anosmic or odour-blind to key 16-androstene steroids (Labows et al., 1982).

The other compounds responsible for distinctive axillary odour are volatile fatty acids (VFAs). As well as VFAs, analysis of the headspace of the axillae of eight participants (4 males and 4 females) by solid phase microextraction gas chromatography-mass spectroscopy (SPME GC-MS) indicated the existence of other chemicals in addition to VFAs varying in functional groups including ketones, aldehydes, esters and alcohols (Curran, Rabin, Prada, & Furton, 2005). The characterization of VFAs and two other selected chemical groups for this research, ketones and aldehydes, are explained in further detail in Section 2.2. However, not all of these odorants have high odour thresholds or are deemed to be unpleasant or pungent. For example, the odour of esters can be described as fruity, and the odour of 4-methoxybenzaldehyde as having a flowery scent (Munk et al., 2000).

2.1.2.2 Malodours arising from laundry

Odorous compounds arising from washed clothes can also be a common experience and is troublesome and unpleasant (Takeuchi, Hasegawa, Ishida, & Kashiwagi, 2012). Malodour detected in clothing after it has been laundered has been related to microorganisms surviving the wash cycle coupled with the incomplete removal of sweat, sebum and other soils (Denawaka, Fowlis, & Dean, 2016; Kubota et al., 2012; Munk et al., 2001). Bacteria and fungi may come from the skin of the person who wore the clothing (Callewaert, Van Nevel, Kerckhof, Granitsiotis, & Boon, 2015), inflow of wash water (Callewaert et al., 2015), and biofilms present in the washing machines (Callewaert et al., 2015; Gattlen, Amberg, Zinn, & Mauclaire, 2010). Therefore, these malodorous compounds emitted from laundered clothing may result from the transfer of odorous compounds generated in old and/or unclean washing machines (Stapleton et al., 2013).

Study on the oily soils on clothing showed a strong dependency between the compound's polarity and efficiency of the laundry process (Chi & Obendorf, 1998) which can be extended to the elimination of malodours from clothing fabrics. The polarity of soils can influence how they adhere to different fibres, how they interact with detergent, and the water/soil interfacial energy (Chi & Obendorf, 1998). While polar components such as fatty acids have been found to be easily removed from garments during wash cycles, non-polar compounds containing aldehydes and ketones remain in fabrics on account of their low solubility in water (Munk et al., 2000).

2.2 Selected compounds

2.2.1 Monocarboxylic acids

Carboxylic acids are hydrocarbon chains, including the carboxyl group (-COOH) with the general formula of R-COOH. Presence of this functional group results in carboxylic acids being highly soluble in polar solvents, like water, due to the formation of hydrogen bonds. Carboxylic acids are commonly named as fatty acids (FAs). There is a great number of carboxylic acids and their derivatives in nature on account of their stable chemical structure to any oxidation such as lactic acid, citric acid, capric acid, etc. The short-chained VFAs which have lower numbers of carbon atoms emit sharp, pungent and strong odours; whereas, VFAs with longer hydrocarbon chains are rancid or even odourless (Schönfeld, & Wojtczak, 2016).

In many studies investigating axillary odour, the presence of short- (C_2-C_5) and medium-chain (C_6-C_{11}) fatty acids have been identified (Curran, Rabin, Prada, & Furton, 2005; Hasegawa et al., 2004; Zeng et al., 1991). There are several routes in the production of carboxylic acids in body odour. Biotransformation of long-chained carboxylic acids with unusual chemical structure secreted from sebum and apocrine glands can result in shorter chained fatty acids (Nicolaides, 1974). Also, amino acids can be converted to odorous carboxylic acids through bacterial activities. For example, the production of isovaleric acid, which has been found to be produced by the biotransformation of L-leucine (Thierry, Maillard, & Yvon, 2002). The short-chained fatty acids, particularly isovaleric acid, have been postulated as being key compounds in distinct foot odour (Kanda et al., 1990). However, they have also been detected in axillary odour (Hartungen et al., 2004). Carboxylic acids identified from different sites and present in body odour, as well as those related to laundry malodour, are listed in Table 2.2. Also, the chemical and physical properties of carboxylic acids detected in axillary odours are presented in Table 2.3.

The key role acidic compounds play in axillary odour was demonstrated by Zeng et al., (1991). The GC-O analysis of axillary samples collected from 25 healthy male participants (25-40 years) identified short-chained carboxylic acids (C_2-C_5) that exhibited the pungent acidic smells of isovaleric acid and butyric acid (Zeng et al., 1991). Among the medium-chain carboxylic acids (C_6-C_{11}) (saturated, unsaturated, and branched), the unsaturated (E)-3-methyl-2-hexenoic acid (3M2H) was identified as the compound primarily responsible for typical body odour (analyzed by gas chromatography-Fourier transform infrared spectroscopy (GC-FTIR)) (Zeng et al., 1991). Despite the low concentrations, other VFAs including 2-methyl C_6 to C_{10}, 4-ethyl C_5 to C_{11} along with terminally unsaturated acids were reported as also contributing to overall body odour (Zeng et al., 1991). Analysis of axillary samples collected from 50 healthy Japanese participants showed

Table 2.2

Carboxylic acids, aldehydes, and ketones related to body odour and laundry malodour

Source a. Body site	Reference	Collection method	Analysis method	Detected compounds		
				Carboxylic acids	Aldehydes	Ketones
All body	Ellin et al. (1974)	Detection of ketones emitted from 16 human participants through conducting tests using a man-sized chamber.	GC-MS			• Acetone • 2-butanone • 3-pentanone • 4-methyl-2-pentanone • 4-heptanone • Allyal-acetone • Cyclohexanone • 2-octanone • Mesityl oxide
Axillae	Hartungen et al. (2004)	Detection of volatiles in the headspace of axillae from 5 individuals by using an axilla-sampling device made of glass. The temperature of the sampling device was kept at 40 ºC.	PTR-MS	• n-C_2 to C_6 acids • Isobutyric acid • Isovaleric acid	–	
	McQueen et al. (2008)	Collection of odorants via polyester, cotton, and wool specimens placed in the underarm regions of cotton t-shirts. Worn by male participants (n=4) who wore t-shirts/fabrics for two 8-hour days.	PTR-MS		• Acetaldehyde	

Table 2.2 (continued)

Source	**Reference**	**Collection method**	**Analysis method**	**Detected compounds**		
a. Body site				**Carboxylic acids**	**Aldehydes**	**Ketones**
Axillae	Hasegawa et al. (2007)	Collection of odorants from 50 healthy Japanese male participants on cotton swatches attached in armpit areas of T-shirts. Participants wore the t-shirts for 24 h without using any deodorant in axillary regions.	GC-MS	• 3-hydroxy-3-methylhexanoic acid	–	
	Zeng et al. (1991)	Sampling the axillary sweat of 6 male individuals (ages 26- 40) on cotton pads.	GC-MS GC-FTIR	• 2-methyl-C_6 to C_9 • 4-ethyl-C_5 to C_{11} • Terminally unsaturated acids	–	
	Curran et al. (2005)	Collection of underarm odours of 8 volunteers (4 females, 4 males) on cotton gauzes. The underarm regions were wiped with 2x2 cotton gauze after workout 30 min work out sessions.	SPME-GC-MS	• Dodecanoic acid • Tetradecanioc acid	• 2-Furancarboxaldehyde • C_7 to C_{11} aldehyde • E-2-nonenal • Tetradecanal • Benzaldehyde	• 6,10-Dimethyl-5,9-Undecadien-2-one • 6-Methyl-5-hepten-2-one
	Rathinamoorthy et al. (2016)	Collection of odorants using fabric swatches stitched into the armpit areas of vests worn by 10 male participants. Half of the volunteers involved in a sedentary job and rest 5 participants did non-sedentary jobs.	GC-MS	• 1,2-Benzenedicarboxylic acid • Fumaric acid	• [2.2]Metacyclophane-4,12-Dialdehyde	

Table 2.2 (continued)

Source	Reference	Collection method	Analysis method	Detected compounds		
a. Body site				**Carboxylic acids**	**Aldehydes**	**Ketones**
Axillae	Labows et al. (1982)	In vitro analysis of incubation of apocrine sweat with bacteria.	GC	- Isovaleric acid	–	–
	Natsch et al. (2006)	Collection of axillary odour samples from five male participants during exercise onto cotton pads.	GC-MS	- (E)-3-methyl-2-hexenoic acid - (Z)-3-methyl-2-hexenoic acid - 4-ethyloctanoic acid	–	–
Feet	Ara et al. (2006)	Collection of foot odour samples from plantae of 30 participants.	GC-MS	- n-C_2 t C_6 acids - Isobutyric acid - Isovaleric acid - Caprylic acid - Capric acid	–	
Back	Gallagher et al. (2008)	Collection of VOCs of the headspace of 25 participants (12 female, 13 male) back area by placing glass funnels on their skins. The funnels were narrow enough to hold SPME fibres.	SPME-GC-MS	- n-C2 to C4 acids - n-C11 to C17 acid - Isovaleric acid - Hexanoic acid - Octanoic acid - Lactic acid - Benzoic acid - 2-ethyl hexanoic acid - 9-hexadecanoic acid	- Octanal - Nonanal - Decanal - Benzaldehyde - Dodecanal	- Acetone - 6-methyl-5-hepten-2-one - 2,5-hexanedione - Camphor - 6-hydroxy-hexan-2-one - Isophorone - Acetophenone - Geranylacetone

Table 2.2 (continued)

Source	Reference	Collection method	Analysis method	Detected compounds		
a. Body site				**Carboxylic acids**	**Aldehydes**	**Ketones**
Back	Haze et al. (2001)	Collection of samples of 22 participants (9 female, 13 male) on t-shirts. Pieces with dimensions of 20 cm x30 cm were cut from the back of t-shirts which were worn for 3 days.	GC-MS	• Acetic acid • Butyric acid	• n-C_6 to C_{10} aldehyde • 2-Nonenal	• 4-Methyl-2-pentanone • 6-Methyl-5-heptanone
Hands	Prada et al. (2011)	Sampling the VOCs emanating from participants' hands by non-contact and contact methods for 4 days. 12 samples were collected from each participant in total. The experimental fabrics were on bleached and desized mercerized cotton, viscose rayon, polyester, and wool.	SPME-GC-MS	• n-C_4 to C_{10} acids • Dodecanoic acid • 2-Ethyl- hexanoic acid	• n-C_7 to C_{12} aldehyde • Benzaldehyde • 2-E-Octanal • 2-E-Nonenal • 2-E-Decanal • Tetradecanal • Lilial	• 5-Hepten-2-one, 6-methyl • 2-Decanone • 5,9-Undcadien-2-one,6,10-dimethyl-(E)
	Curran et al. (2007)	Sampling hand odour of 60 individuals (30 males, 30 females) with the age range of 17-28 years by pre-treated pads.	SPME-GC-MS	• Isovaleric acid	• n-C_6 to C_{13} aldehydes • Benzaldehyde • 2-E-Octenal • 2-E-Decenal • 2-E-Nonenal • 2-Furancarboxaldehyde	

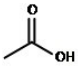
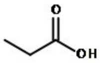
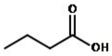
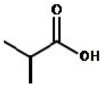
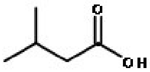
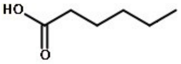
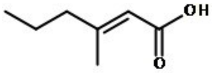
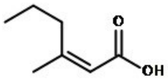
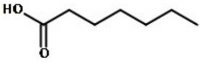
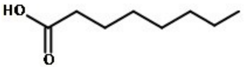
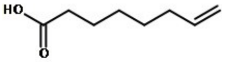
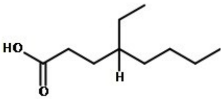
Table 2.2 (continued)

Source	Reference	Collection method	Analysis method	Detected compounds		
a. Body site				**Carboxylic acids**	**Aldehydes**	**Ketones**
	Bernier et al. (2000)	Using glass beads to collect the VOCs arising from four male individuals' hands with the ages of 26, 49, 52, and 61yarses.	GC-MS	• 1,2-Benzenedicarboxylic acid • Fumaric acid	• n-C_7 to C_{10} aldehydes • Propanal • 2-methylpropanal • 2-methyl-2-butenal • 2-methylbutenal • 3-methylpentenal • 2,2-dimethylhexanal • 2,4-nonadienal • 3,7- dimethyl-2,6-octadienal • 2-methlhexadecanal • Benzaldehyde • 3-hydroxy-4-methyl benzaldehyde • 4-phenylmethoxybenzaldehyde	• Butanone • 2-pentanone • 3-pentanone • 2-hexanone • 6-methyl-3,5-heptadien-2-one • 6-methyl-5-hepten-2-one • 2-nonen-4-one • 2-decanone • 2-methoxy-2-octen-4-one • 6,10-dimethyl-5.9-undecadien-2-one • 3-hydroxyandrostan-11,17-dione
b. Washing machine						
Axilla and sebum	Munk et al. (2000)	Sampling human sebum and axillary odours of 8 male runners on attached 100% cotton or 100% polyester interlock knitted specimens in the underarm region of long sleeve shirts.	HRGC-MS	• 3-Methylbutanoic acid • 4-Methyloctanoic acid • 4-Ethyloctanic acid	• Octanal • E-2-Octanal • Z-2-Nonenal • E-2-Nonenal • E,E-2,4-Nonadienal • E,Z-2,4-Decadienal	• 1-hexen-3-one • 1-octen-3-one
Washing machine	Stapleton et al. (2013)	Analyzing four washing machines as well as washing terry and fleece fabrics by the same washing machines and identifying the transferred odorants to the fabrics.	HS-SPME-GC-MS DHS*-GC-O-MS	• Isovaleric acid • Isobutyric acid • Propionic acid • Acetic acid	• n-C_8 to C_{10} aldehyde • Benzaldehyde	• 2-undecanone • 6-methyl-5-hepten-2-one

* Dynamic headspace

Table 2.3

Properties of selected carboxylic acids found in axillary and laundry odour

IUPAC name	Common name	CAS number	Chemical structure[a]	Vapour pressure (mmHg at 25 °C)	Odour[b]
Ethanoic acid	Acetic acid	64-19-7		15.7[a]	Vinegar-like
Propanoic acid	Propionic acid	79-09-4		3.53[a]	Pungent-rancid
Butanoic acid	Butyric acid	107-92-6		1.65[a]	Rancid
2-Methylpropanoic acid	Isobutyric acid	79-31-2		1.81[a]	Rancid butter
3-Methylbutanoic acid	Isovaleric acid	503-74-2		0.44[a]	Rancid cheese
n-Hexanoic acid	Caproic acid	142-62-1		0.044[a]	Goat-like
3-Methylhexanoic acid	-	3780-58-3		0.058[b]	Goat-like
Trans-3-methyl-2-hexenoic acid	-	2796-21-0		-	Goat-like
Cis-3-methyl-2-hexenoic acid	-	18951-40-1		-	Goat-like
n-Heptanoic acid	Enanthoic Acid	111-14-8		0.010[a]	Rancid
n-Octanoic acid	Caprylic Acid	124-07-2		0.037[a]	Mild fruity acidic
7-Octenoic acid	-	18719-24-9		0.027[b]	Mild fruity acidic
4-Ethyloctanoic acid	-	16493-80-4		0.020[b]	Goat-like

[a] "National Center for Biotechnology Information" (2017); [b] "The Good Scents Company Information System," (2018).

20% of all participants had “normal body odour,” whereas, 80% had a “sour and acidic odour” (Hasegawa, Yabuki, & Matsukane, 2007). In the same study, the S-isomer of 3-hydroxy-3-methylhexanoic acid, which was described as having a spicy odour has been found as a key compound in typical axillary odour (Hasegawa et al., 2007).

The retention and release of VFAs from worn fabrics depend on the chemical structure of the generic fibre from which the fabric is made. Headspace analysis of VFAs that accumulated on fabrics from three different fibre contents (cotton, wool, and polyester) following wear next to the axillary region suggested that desorption rates may vary according to the fibre type (McQueen, Laing, Delahunty, Brooks, & Niven, 2008). The polar short-chain fatty acids may bind to the natural fibres on account of the availability of reactive sites such as hydroxyl groups in cotton fibres and side chains in the amino acids in wool fibres (McQueen et al., 2008). Polyester lacks these kinds of bonding sites, which may result in polyester exhibiting lower overall sorption of VFAs, resulting in higher odour intensity (McQueen et al., 2008). Munk et al., (2000) stated that despite the importance of these organic acids in axillary odour that they can be easily removed from clothing fabrics by laundering (Munk, Münch, Stahnke, Adler-Nissen, & Schieberle, 2000). The polar structure and the possibility of reaction with alkalies are the reasons for dissolving and dispensation of fatty acids in water (Chi & Obendorf, 1998). However, in research on malodours arising from the washing machine, isovaleric and butyric acids have still been identified in VOCs based on microbiological isolates (Stapleton et al., 2013).

2.2.2 Aldehydes

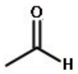
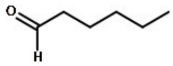
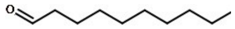
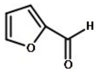
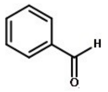
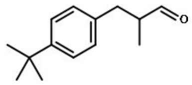
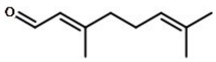
Aldehydes are a class of chemicals with a carbon double bonded to an oxygen atom (carbonyl group), a single bond with a hydrogen atom and another single bond with a hydrocarbon group. The partial negative and positive charges on oxygen and carbon atoms, respectively form a dipole imparting a slight polarity to the aldehydes (Ball, Hill, & Scott, 2011). Aldehyde chains with 4 and 5 carbon atoms have an odour like butter, while chains with a greater number of carbons (C_8 to C_{12}) such as nonanal and undecanal emit floral odours and are butter-like (Choi & Han, 2015). There are several aldehydes present in nature, such as vanillin (4-hydroxy-3-methoxybenzaldehyde) in vanilla bean extract or 12-methyltridecanal in beef fat (Rowe, 2005). Furthermore, the reduction of carboxylic acids is a route to synthesizing aldehydes (Cha, 1989). In the case of body odour, for instance, degradation of mono-saturated fatty acids like palmitoleic or vaccenic acids (Curran et al., 2005) and human sebum triglycerides (Munk et al., 2000) are considered as mechanisms for aldehyde formation in body odour.

Although aldehydes have not been implicated as being as important in axillary odour as the carboxylic acids and VSCs, they are still present in body odours emitted from human skin. A review of the research on body odour reported about 42 different aldehydes might be detected in skin odour (de Lacy Costello et al., 2014). Curran, Prada & Furton (2010) found using GC-MS that 32% of all compounds released from the hands of 10 individuals (5 males and 5 females, age range 17-28 years) were aldehydes (Curran, Prada, & Furton, 2010). A considerable number of studies on body odour, as well as malodours detected in washed fabrics and washing machines, have identified a significant number of aldehydes (see Table 2.3). The properties of some selected aldehydes related to axillary and laundry odour are presented in Table 2.4.

A few C_9-C_{10} saturated and unsaturated aldehydes have been identified as being important contributors to human body odour by increasing age (Haze et al., 2001). Haze et al. (2001) examined the headspaces of body odours collected on cotton t-shirts and found an age-dependent relationship with 2-nonenal.

Table 2.4

Properties of selected aldehydes found in axillary and laundry odour

IUPAC name	Common name	CAS number	Chemical structure[a]	Vapour pressure (mmHg at 25 C)	Odour[b]
Ethanal	Acetaldehyde	75-07-0		902[a]	Fruity
Hexanal	Caproic aldehyde	66-25-1		11.3[a]	Fruity-green grass
Heptanal	Heptyl aldehyde	111-71-7		6.52[a]	Strong fruity
Octanal	Caprylic aldehyde	124-13-0		1.18[a]	Strong fruity
Nonanal	pelargonaldehyde	124-19-6		0.37[a]	Orange-rose
Trans-2-Nonenal	-	18829-56-6		0.25[b]	Cucumber
Decanal	caprinaldehyde	121-31-2		0.103[a]	Floral-fatty
Undecanal	undecyl aldehyde	112-44-7		0.083[b]	Floral-citrus
Tetradecanal	-	124-25-4		0.060[b]	Citrus peel
Tridecanal	Tridecyl aldehyde	10486-19-8		0.015[b]	Citrus
Furan-2-carbaldehyde	2-furaldehyde	98-01-1		2.21[a]	Almond
Benzaldehyde	-	100-52-7		1.27[a]	Bitter almond
3-(4-tert-Butylphenyl)-2-methylpropanal	Lilial	80-54-6		0.0913[a]	Lemon
3,7-dimethyl-2,6-octadienal	Geranial	5392-40-5		0.005[b]	Floral

[a] "National Center for Biotechnology Information" (2017); b "The Good Scents Company Information System," (2018).

The data from GC-MS analysis indicated the presence of 2-nonenal with distinct "greasy" and "grassy" scents in participants who were 40 years or older (Haze et al., 2001). In a later study, body odour samples collected from subjects with different ages (13 males, 12 females; young 19-40 years, old 41-79 years), also resulted in the identification of another saturated aldehyde, nonanal (Gallagher et al., 2008). The existence of nonanal, along with undecanal, was investigated through the headspace characterization of axillary sweat samples of 8 participants (4 males and 4 females) on sterile gauze. Both nonanal and decanal not only were found in the axillae but also have been reported as the most frequently detected type of aldehydes in skin odour (Dormont, Bessière, & Cohuet, 2013).

Similar to other odorous compounds, the sorption by fabrics depends on the inherent fibre content of the fabrics and the properties of the compounds. The hydrophobic nature of aldehydes resulted in better adsorption to fabrics composed of synthetic fibres, such as polyester than natural fibres such as cotton (Munk et al., 2001). Furthermore, the removal of aldehydes was less effective from polyester than cotton (Munk et al., 2001). Munk et al., (2000) reported that the aldehydes contributed the most to axillary odour extracts after laundering as carboxylic acids (although more prevalent in axillary malodour) would dissolve in water and be released in the laundering process (Munk et al., 2000). The relationship between fibre content and sorption of aldehydes has been less clear. Comparison of the sorption capacity of polyester and synthetic nylon fabrics showed higher sorption of 2-nonenal (representative of a key aldehyde body odour compound) by nylon than polyester (Abdul-Bari, McQueen, Nguyen, Wismer, de la Mata, & Harynuk, 2018). However, the results of a study on hand odour by Prada et al., (2011) demonstrated cotton fabric takes up much more aldehydes than polyester whereas wool and rayon have better sorption capacities than polyester fabric but less than cotton fibres (Prada et al., 2011).

2.2.3 Ketones

Ketones are another class of organic compounds that can be present in body odour and include only carbonyl functional groups attached to hydrocarbon groups within the chemical structure. Similar to aldehydes, the dipole-dipole interactions in the carbonyl group causes less volatility compared with alkanes and ethers, but their volatility is higher than alcohols (Ball et al., 2011). In contrast to aldehydes, the ketones with lower molecular weight are reported as compounds that have pleasant odours, and those of higher carbon numbers emit weaker scents (Ball et al., 2011). Like the aldehydes and carboxylic acids, some ketones can be extracted from available materials in nature. For example, the flowery odours of irises and jasmine are due to the presence of α-ionone and jasmone (Roberts & Caserio, 1977).

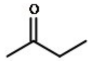
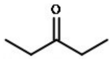
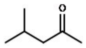
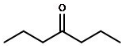
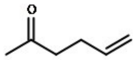
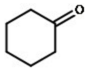
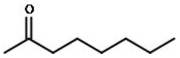
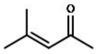
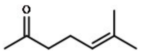
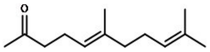
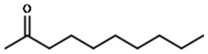
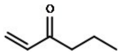
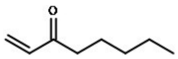
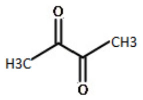
In one of the earliest studies using a man-size chamber experiment to collect volatiles released from the human body, a significant number of ketones were reported (Ellin et al., 1974). However, despite this earlier work, ketones have not generally been considered as important in human body malodour, which is likely due to the pleasant aroma of ketones (Table 2.5). Nonetheless, there are still several ketones that have been identified in both body and laundry odours in different research studies which are presented in Table 2.2. Also, the properties of ketones related to axillary and laundry odour are shown in Table 2.5.

Gallagher et al., (2008) observed that C_8-C_{12} aldehydes, ketones, 6-methyl-5-heptene-2-one and geranylacetone were consistently identified in all male and female participants following sampling of the upper back. Hara, Kyuka & Shimizu (2015) noted that the inclusion of butane-2,3-dione positively correlated with increasing odour intensity of axillary odorants (Hara et al., 2015).

Among the three major groups of compounds contributing to body odour, considerable research has been focused on odorous ketones derived from steroids (Brooksbank, Brown, & Gustafsson, 1974; Gower, Nixon, & Mallet, 1988; Gower, Holland, Mallet, Rennie, & Watkins, 1994). The 16-unsaturated androstenes (e.g. 5α-androstenone) are known to represent a urine-like or pungent odour (Gower, Nixon, & Mallet, 1988).

Table 2.5

Properties of selected ketones found in axillary and laundry odour

IUPAC name	Common name	CAS number	Chemical structure[a]	Vapour pressure (mmHg at 25 C)	Odour[b]
Propanone	Acetone	75-07-0		231[a]	Sweet
2-Butanone	Methyl Ethyl keton	78-93-3		90.6[a]	Acetone-like
3-Pentanone	Diethyl ketone	96-22-0		37.7[a]	Acetone-like
4-Methyl-2-Pentanone	Isopropylacetone	180-10-1		19.9[b]	Fruity
4-Heptanone	Butyrone	123-19-3		5.2[a]	Pleasant
5-Hexe-2-one	Allyl-acetone	109-49-9		21.3[b]	Floral
Cyclohexanone	Pimelic ketone	108-94-1		5.2[b]	Acetone-like
2-Octanone	-	111-13-17		1.35[a]	Fruity-floral
4-Methyl-Pent-3-en-2-one	Mesityl oxide	141-79-7		8.21[a]	Pungent
6-Methyl-5-Hepten-2-one	-	110-93-0		1.27[b]	Cirtrus
6,10-Dimethyl-5,9-Undecadien-2-one	-	689-67-8		0.016[b]	Floral
2-Decanone	Methyl octyl ketone	693-54-9		0.25[b]	Floral
1-Hexen-3-one	-	2497-21-4		9.91[b]	Cocked vegetable
1-Octen-3-one	-	4312-99-6		1.06[b]	Mettalic
Butanedione	Diacetyl	431-03-8		56.8[a]	Pungent butter-like

[a] "National Center for Biotechnology Information" (2017); [b] "The Good Scents Company Information System," (2018).

Two detected 16-unsaturated androstene; 5α-androst-16-en-3-one (5α-A) and 4,16-androstadien-3-one (androstadienone) have been studied widely because they emit a pungent odour, and also due to the formation of odorous 3α- and 3β-androstenols due to the steroidal compounds biotransformation (Gower et al., 1994). However, as previously mentioned, there can be a high proportion of specific anosmia (odour blindness) to many of the androstene steroids (Labows et al., 1982).

A few studies have examined the retention or development of ketones (as well as other compounds) in fabrics during wear or following inoculation with artificial sweat and bacteria. Chung and Seok (2012) inoculated cotton fabrics with triolein as the representative sebum-like soil and *Staphylococcus epidermidis* as the representative organism. They detected an increase in volatiles such as alcohols and one ketone (2-heptanone) after 168 h of incubation, which indicated some metabolism of the triolein soil by *S. epidermidis*. Compared to other VOCs, the volatile ketones had a lower tendency to be adsorbed by fabrics (Prada et al., 2011). The relative adsorption of odorous ketones by different fibre types demonstrated highest sorption capacity for wool which was followed by rayon, cotton and polyester (Yao et al., 2015; Prada et al., 2011). Evaluation of cotton and polyester fabrics that had axillary secretions previously sorbed onto them indicated that ketones could remain in samples after a mild washing process (Munk et al., 2000). The compounds androstenone, 1-hexen-3-one, and 1-octen-3-one were all determined as being contributors to odour in the laundered samples (Munk et al., 2001). Moreover, 2-undecanone was observed in the chromatograms of VOCs in unclean and old washing machines (Stapleton et al., 2013), which might be transferred to items of clothing during laundering.

2.3 VOCs sorption/desorption

Volatile organic compounds (VOCs) are chemicals that have high vapour pressure (lower boiling point from 50 to 260 °C) and able to evaporate easily under normal environmental temperature and pressure (United States Environmental Protection Agency [EPA], 2017). There are also two other groups of volatile compounds: 1) very volatile organic compounds (VVOCs) with higher vapour pressure than VOCs (i.e. boiling point <0 to 50-100 °C); and 2) semi-volatile organic compounds (SVOCs) with boiling point from 240 to 400 °C have a lower vapour pressure (EPA, 2017). Evaluating the amount of VOCs (Jørgensen, Bjørseth,& Malvik, 1999) and SVOCs (Weschler & Nazaroff, 2008) adsorbed and desorbed from materials has been an important area of research in many fields, but particularly in the indoor environment where there can be public health implications and transfer of indoor toxins to the outdoor environment (Koszowski, Goniewicz, Czogala, & Zymelka, 2009; Rauert et al., 2014; Schick et al., 2014). Accordingly, most of the information about the VOCs adsorption/desorption mechanisms, effective factors on adsorption amount, and methods to prevent adsorption and release have been studied in the indoor environment field (Farajollahi, Chen, & Haghighat, 2009; Zhang, Zhang, & Chen, 2014). These findings may also be expanded to other research areas like the adsorption/desorption of odour within apparel textiles.

VOCs adsorption is conditional to the chemical and physical properties of VOCs and sorbents, respectively (Zhang, Zhang, Chen, & Yang, 2002). Environmental factors, including temperature, relative humidity, and air flow rates can affect the rates of adsorption and desorption (Zhang et al., 2002). For instance, evaluating the sorption of VOCs that varied in functional groups under different levels of RH, temperature, and airflow revealed inconsistencies among three substances (i.e. drywall, carpet, and ceiling) (Zhang et al., 2002).

2.3.1 Sorption/desorption measurement methods

As adsorption capacity and selectivity of sorbent (e.g. fibres) to different liquids and gases within a mixture are known to affect the release of odorants from fabrics (Richter et al., 2018). Various set-ups and apparatus have been developed to measure the adsorption and subsequent release of

VOCs and SVOCs by materials. Furthermore, as part of the experimental process, the transfer of VOCs or SVOCs to fibres/fabrics can occur through directly inoculating compounds to the materials, or indirectly when VOCs in the gas phase are adsorbed by materials.

The experimental set-ups for measuring adsorption and subsequent desorption depend on the research questions and the specific context of the research problem. Several studies have been conducted where fabrics that may be present in a home or office environment are deployed in a real-life context (Van Loy, Riley, Daisey, & Nazaroff, 2001; Ongwandee & Sawanyapanich, 2012). For example, Saini, Okeme, Parnis, McQueen, & Diamond (2017) placed swatches of rayon and cotton fabrics in real-life environments (20 homes and 5 offices) to determine the uptake kinetics of SVOCs (i.e. phthalates) that would be present in indoor environments over a 56-day period. In another study, the sorption kinetics and equilibria of nicotine (a SVOC) were investigated under different RHs through chamber tests (Ongwandee et al., 2012). The examined materials were stainless steel, cotton/polyester curtain, and polypropylene carpet (Ongwandee et al., 2012). Although these methods provide insight into real-life issues, it is not always possible to control variables that may influence rates of adsorption and desorption (e.g. temperature, humidity, air-flow). Controlling these parametres on a smaller-scale may be done by large-scale chamber tests or small scale chamber tests.

Another approach is to deploy fabrics in chambers or containers that have been exposed to compounds introduced to the containers. For example, in one study, two 1 L glass bottles, A and B, were used for determining the adsorption of body odour compounds by bundles of three different yarns (i.e. polyester, cotton, and wool) (Yao et al., 2015). Firstly, a prepared liquid mixture of body odour compounds was injected into bottle A for 2 hours at 33 °C. Then 15 mL of vapour was removed and transferred to bottle B that contained the yarns, and the yarns and vapours were left to equilibrate for 24 h (Yao et al., 2015). Volatiles were measured using proton transfer reaction-mass spectroscopy (PTR-MS), and the amount adsorbed by the fibres were compared with a control (i.e. no yarns in bottle B). This example and a follow-up study by Richter et al. (2018) exposed fabrics to VOCs as a vapour. However, during wear, although odorants could pass to fabrics via the air, the greatest transfer of odorants is likely to occur through compounds present in liquid sweat.

2.4 Textile fibres

Properties of fabrics strongly depend upon the inherent properties of the textile fibres from which they are made. A textile fibre is defined as a “type of matter that forms the basic elements of a textile, and that is characterised by having a length at least 100 times its diameter” (American Society for Testing and Materials [ASTM], 2015). Textile fibres can be further classified as natural and manufactured (ASTM, 2015). Natural fibres originate from either plants or animals (e.g. cotton, wool, and silk). Manufactured fibres are produced by regenerating natural sources like rayon (regenerated cellulose) or have synthetic origins, such as nylon and polyester fibres. As different types of fibres differ from one another in specific chemistry and physical structure, they ultimately behave differently in chemical and physical properties. The fibre properties can have an influence on end performance of the final textile such as wearer comfort, quality and care procedures. Therefore, in most countries, there are consumer protection laws in place that many textile products must specify the generic textile fibre from which it is made (in content 5% or greater) (Textile Labelling Act, 2011). Inherent properties can be altered by fibre/fabric finishing treatments which may impact a property that an unfinished fabric would not have (e.g. washable wool finishes that prevent wool from felting during laundering, durable-press finishes to cotton that prevent cotton from wrinkling) (Kadolph & Marcketti, 2016).

Although finishing treatments applied to fibres/fabrics could reduce or control odour, there has been some evidence that odour control finishes applied to fabrics that tend to be perceived as more odorous following exercise or wear (i.e. polyester) are less effective than generic fibre content (i.e. wool and cotton) (Klepp et al., 2016). Therefore, differences in odour intensity can strongly depend on the fibre chemical properties which may include their propensity to absorb moisture (e.g. hydrophilic, hygroscopic) or oily soils (e.g. oleophilic). For example, an inverse relationship between the level of odour intensity and fibre hygroscopicity was reported in the literature (McQueen et al., 2008). Because of these differences in odour intensity by generic fibre type the research in this field examining odour intensity following wear using sensory panels, or analytical chemistry techniques such as GC-TOFMS or PTR-MS above the headspace or via direct extraction of the compounds have been conducted (see Table 2.6).

Most of the inherent chemical and physical properties of fibres strongly depends on the smallest building blocks of a fibre; molecules with chain-like structures (Cumberbirch, 1970). Fibre molecules consist of long-chain molecules (i.e. polymers) which are created by joining of very short molecular units known as monomers (Cumberbirch, 1970). Thus, determining characteristics of fibre forming polymers such as flexibility, strength, and chemical reactivity lead to a better understanding of the properties of different fibre types (Cumberbirch, 1970). One of the influential features on the fibre strength is the orientation of the molecular polymers within the fibre structure. The orientation of the fibre molecule is defined as “a tendency for the majority of the molecules to lie in one direction” (Cook, 2001, p. X). Due to the orientations of the polymer chains, two possible regions can be created; crystalline and amorphous regions. The proportion of the crystalline degree to the amorphous order in a fibre structure indicates the level of the strength (i.e. crystalline > amorphous) or flexibility (i.e. amorphous > crystalline) (Cook, 2001). Although the molecular orientation within natural fibres is an inherent characteristic, the degree of crystallinity in synthetic fibres are affected by the production method (Burkinshaw, 2016). When long molecular chains align closely together through a strong attraction force, a regular and periodic structure is created, knowing as a crystalline region (Cook, 2001). In contrast, the random arrangement of the molecular chains result in the amorphous region. Figure 2.1 shows the crystlline and amorphous structure in nylon 6.

Table 2.6

Chemical analysis of odorants and interactions among fabrics varying in fibre content

Reference	Collection method of odorants	Results	Analysis method	Experimental fabrics
McQueen et al. (2008)	Axillary odours collected by sewing fabrics specimens in the underarm region of 100% cotton t-shirts. T-shirts were worn for two 8 h days by male participants (n=5).	An increase of three short-chained carboxylic acids detected in the headspace above polyester fabrics after 7 days. This increase was not detected in cotton and wool fabrics.	PTR-MS	100% **cotton**, 100% **polyester** and 100% wool interlock knit fabrics.
Richter et al. (2018)	Six selected odorants identified as being present in body odour were applied in a gaseous form on yarns. The initial adsorption, as well as releasing behaviour, was measured.	Cotton showed low relative adsorption and low overall release while high relative adsorption and continuously desorption.	PTR-MS	100% **cotton**, 100% **polyester** and 100% wool. Fabrics were dissected to the yarns to remove effects associated with fabric structure.
Yao, Lei et al. (2015)	Six selected odorants present in body odour were applied in a gaseous form on yarns. Their initial adsorption behaviour was measured.	Weaker sorption observed by cotton yarns compared with polyester for both polar and non-polar chemicals.	PTR-MS	100% **cotton**, 100% **polyester** and 100% wool. Fabrics were dissected to the yarns to remove effects associated with fabric structure.
Rathinamoorthy et al. (2014)	Body odour was collected on fabric swatches stitched into armpit area of vests worn by 10 male participants.	There was the highest odour intensity for polyester, followed by nylon. Cotton had the lowest odour intensity, and viscose indicated higher odour intensity that viscose.	FTIR*	Single jersey knitted 100% **cotton** fabric

Table 2.6 (continued)

Reference	Collection method of odorants	Results	Analysis method	Experimental fabrics
McQueen et al. (2014)	Body odours of eight participants (5 males, 5 females) were collected through wear trial during 20 exercise sessions on bi-symmetrical cotton/polyester t-shirts. The washed and unwashed samples were compared by evaluating the odour intensity by the sensory panel. Also, the bacteria population was count and selected VOCs were analytically measured for washed and unwashed samples.	The odour intensity was highest by polyester than cotton before and after the washing process. Short-chain carboxylic acids (C_4-C_8) were detected in both cotton and polyester samples but more frequent in polyester.	Sensory analysis GC x GC –TOFMS	100% **cotton,** 100% **polyester** single jersey knit fabrics.
Abdul Bari et al. (2018)	Odour reduction rates (ORR) of isovaleric acid and 2-nonenal were measured using the ISO 17299-3 method as well as collecting body odour through the wear trials (4 males, 4 females) worn during 12 h day and at least 1 h of exercise. Wear trial fabrics were frozen (then thawed) or stored at room temperature for 7 days before	Higher amounts of the odorant were adsorbed by nylon fibres as indicated by a higher ORR. Sensory evaluation of fabrics did not show significant differences in the odour intensities between polyester and nylon.	GC-FID Sensory analysis	Texturized 100% **nylon**and 100% **polyester**, double knit 100% **nylon** and 100% **polyester** (type 54) spun yarn, plain weave
Hammer et al., 2013	Sorption capacities of fabrics were assessed through conducting ^{14}C-radiolabelled isovaleric acid dissolved in artificial sweat to fabrics.	Higher sorption of the isovaleric acid by polyester fibres along with faster releasing it than cotton fibres.	Liquid scintillation	100% **cotton**, 100% **polyester** and 100% wool

* Fourier Transform Infrared Spectroscopy

**Two-dimensional gas chromatography and time-of-flight mass spectrometry detection.

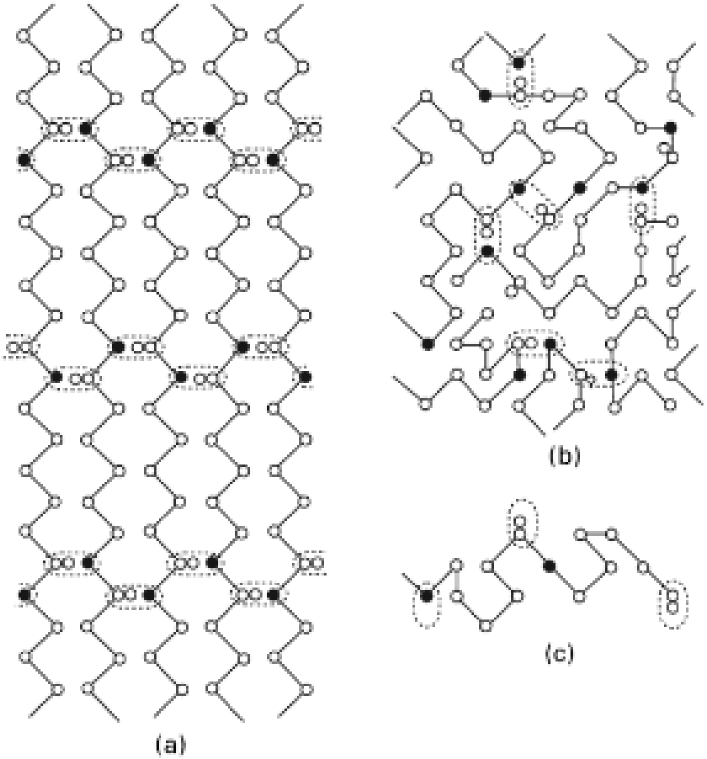


Figure 2.1

Nylon 6: a) Schematic structure of a crystalline area; b) amorphous region; c) cross-links intersections

(Morton & Hearle, 2008, p. 60)

2.4.1 Cotton

Cotton fibres, known as “white gold” (Basra & Malik, 1984, p. 65), have been used for textiles since 900 BC on account of their excellent properties including softness, excellent absorbency, breathability, and strength (Hosseini Ravandi & Valizadeh, 2011). Cotton is a natural seed hair fibre obtained from the boll of the cotton plant. Cotton fibres consist primarily of cellulose (88-96%) (Figure 2.2) but also a minor proportion of noncellulosic substances such as pectins (0.7-1.2%), protein (1.1-1.9%), ash (0.7-1.6%), waxes (0.4-1%), and other organic components (0.5-1%) (Kozłowski, 2012; Wakelyn et al., 2007). In cotton clothing, the cellulose content is closer to 99% cellulose, as removal of the noncellulosic materials occurs through textile processes such as scouring (Wakelyn et al., 2007). Single cotton fibre is a single cell having a multilayer helical structure consisting of the cuticle (as the outer layer), primary cell wall and secondary cell wall along with the inside layer known as the lumen (Dochia, Sirghie, Kozlowski, & Roskwitalski, 2012). The structure of cotton is shown in Figure 2.3 and microscopic images of cotton fibres in Figure 2.4 (Dochia et al., 2012). Cellulose is a linear polymer chain of β-D-glucopyranose. Glucose monomers are linked together through the loss of one water molecule (linked via the number 1 and 4 carbon atoms on the glucose) (Wakelyn et al., 2007). The cotton fibre is a formation of microfibrils which are bundled in tight, ordered crystalline structures that are created through the close packing of glucose monomers along the polymer chain. There are both amorphous and crystalline areas in the fibre structure, and intermolecular bonding occurs via van der Waals forces, and with the involvement of hydroxyl groups, hydrogen bonds (Abidi & Gordon, 2017). Regarding the intermolecular bonds, the hydrogen bonds can easily form between polymer chains in each layer within the fibre structure due to the hydroxyl groups along the cellulosic polymer chains (Wakelyn et al., 2007). This strong intermolecular force (i.e. hydrogen bonds) results in a highly crystalline and strong structure in cotton fibres such as observed in the fibre’s secondary wall (Dochia et al., 2012). Cellulosic layers are stabilized parallelly through the van der Waals forces and hydrogen bonding.

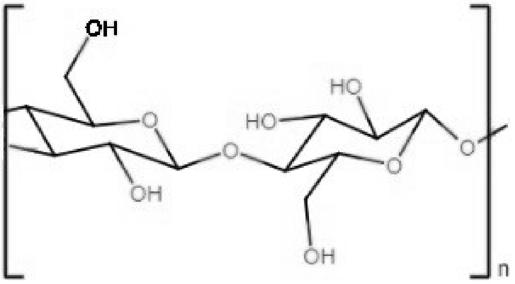


Figure 2.2

Molecular structure of cellulose (repeating monomer units)

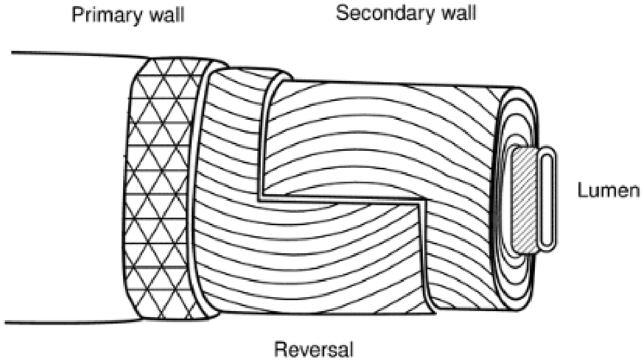


Figure 2.3

Schematic diagram of cotton fibre structure

(Dochia et al., 2012, p.14)

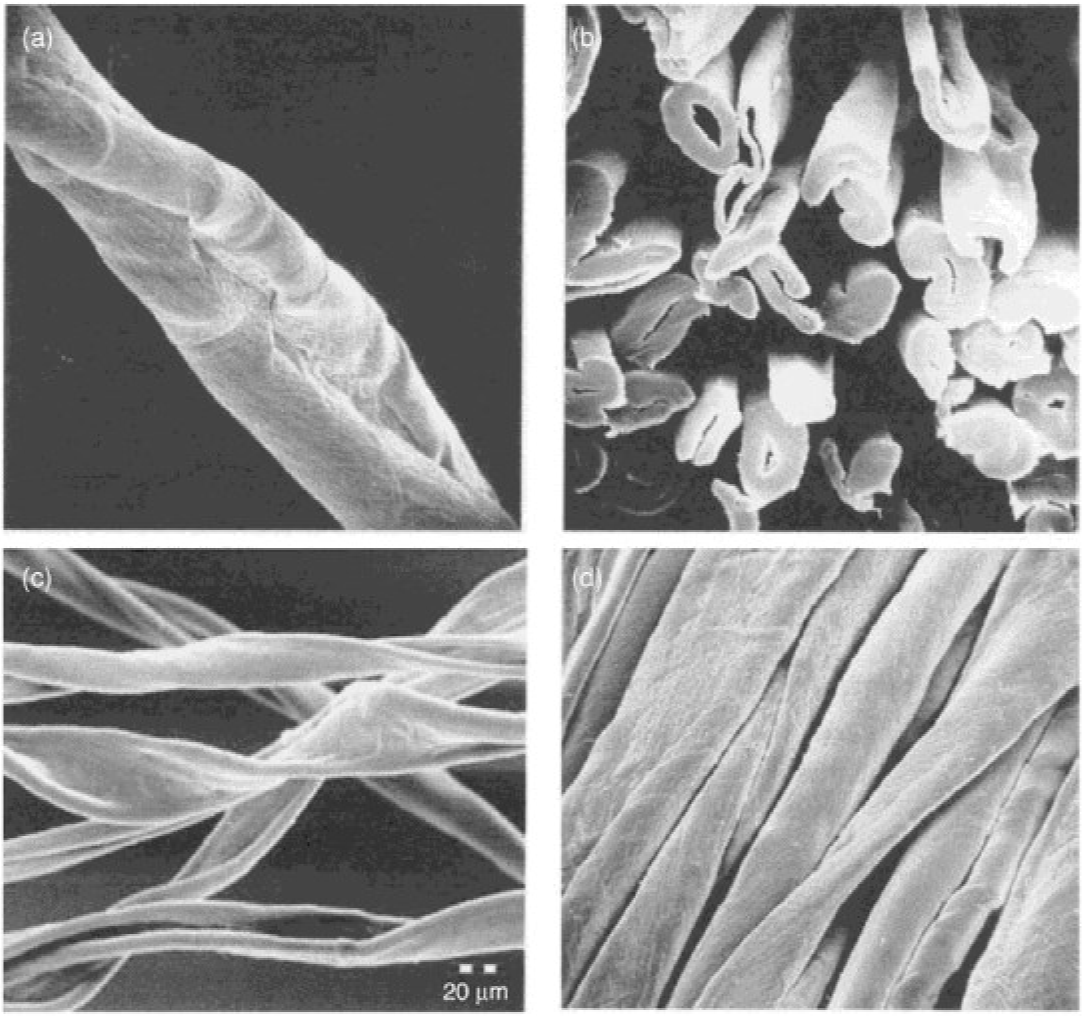


Figure 2.4

Microscopic images of cotton fibres: a) twisted cotton fibre; b) cross-sectional image showing the lumens; c) collapsed and twisted cotton fibres; d) bundle of cotton fibres

(Dochia et al., 2012, p.16)

Natural fibres have high moisture sorption capacity because of their ability to form hydrogen bonds with water molecules and are therefore characterised as being hydrophilic (i.e. water-loving). Also, the pore structure of the cotton fibre results in better penetration of molecules such as dyes and chemicals used as finishing agents (Rowland, 1977). In comparison, most synthetic fibres repel moisture and are considered hydrophobic or oleophilic, such as polyester and nylon. Moisture regain for cotton at standard textile testing conditions (i.e. 20°C and 65% R.H.) is 7-8% (Canadian General Standardsneral Board, 2001b), which is the lowest value among all natural fibres but is still much higher than moisture regain of synthetic fibres (Mather & Wardman, 2015). As a result, clothes made of cotton fibres are capable of absorbing body sweat (Hosseini Ravandi & Valizadeh, 2011). In addition to water molecules, the hydroxyl functional groups in cotton fibres provide reactive sites for forming hydrogen bonds with polar VOCs (McQueen et al., 2008).

Due to the high demand for cotton in the apparel industry (Textiles Intelligence, 2017), the interaction between different kinds of odorants, such as, malodours generated on the body (McQueen et al., 2008; Yao et al., 2015), fragrances in detergents (Liu, Obendorf, Leonard, Young, & Incorvia, 2005), and SVOCs present in indoor environments (Saini, Rauert, Simpson, Harrad, & Diamond, 2016) by cotton fibres/fabrics have been investigated more than fabrics composed of other generic fibres (although, in many of the studies, polyester has also often been compared). In one study, a comparison of adsorption and desorption of VOCs present in body odour by three generic fibres (i.e. wool, cotton, and polyester) was conducted by allowing yarns to adsorb VOCs in the gaseous phase (Richter at al., 2018). The number of compounds adsorbed and subsequently released was monitored through PTR-MS. The authors reported that there was both low relative adsorption and a low rate of release of VOCs by cotton fibres, compared with the other two types of fibres (Richter at al., 2018). Also, the effectiveness of the laundry process for removing odorous chemicals and bacterial strains have been studied (Munk et al., 2001; Wiksell et al., 1973). Removal of odorants from cotton fabrics by laundering has been shown to be more effective when compared to polyester (Abdul-Bari, 2018; Munk et al., 2001).

2.4.2 Viscose

Viscose is a regenerated cellulosic fibre that can be referred to as rayon, viscose rayon or viscose on textile labels. Although, rayon can be used for any regenerated or precipitated cellulosic fibres (e.g. modal, lyocell), viscose can only be used for regenerated cellulosic fibres that have been manufactured by the viscose process (Textile Labelling Act, 2011). Viscose rayon was developed in the late 19th century, where the chemical modification of cellulose contributed to a new generation of fibres, manufactured regenerated fibres (Mather & Wardman, 2015). Viscose is formed by first steeping wood pulp in sodium hydroxide solution to produce alkali cellulose; then aged under controlled conditions and reacted with carbon disulfide to form sodium cellulose xanthate that can then be dissolved in a dilute sodium hydroxide solution. Following filtering of the sodium cellulose xanthate, it is then wet spun (by extruding liquid through fine holes in the spinneret) in an acidic bath, where the fibres coagulate into cellulose filaments. Following stretching and drawing to increase fibre strength, these fibres may be used as filaments or cut into staple fibres to eventually be turned into useable textile products with particular desirable textile properties (e.g. softness, adequate strength, absorbency, flexibility) (Kotek, 2007; Mather & Wardman, 2015). Although viscose is made up of cellulose, as is cotton, it has a distinctively different fine structure (i.e. level of crystallinity, degree of polymerization, level of orientation) and therefore differs in physical and mechanical properties, and to some degree chemical properties (Hatch, 1993). In the case of the microscopic appearance of viscose, the surface is smooth with striations in longitudinal directions along with nearly oval or circular cross sections (see Figure 2.5) (Chen, 2014).

Compared with cotton there are almost no fibrils (i.e. small fine fibres) in viscose, as well due to the process of dissolving cellulose, viscose has a lower degree of polymerization (i.e. length of the repeating monomers) (Clark, 2011).

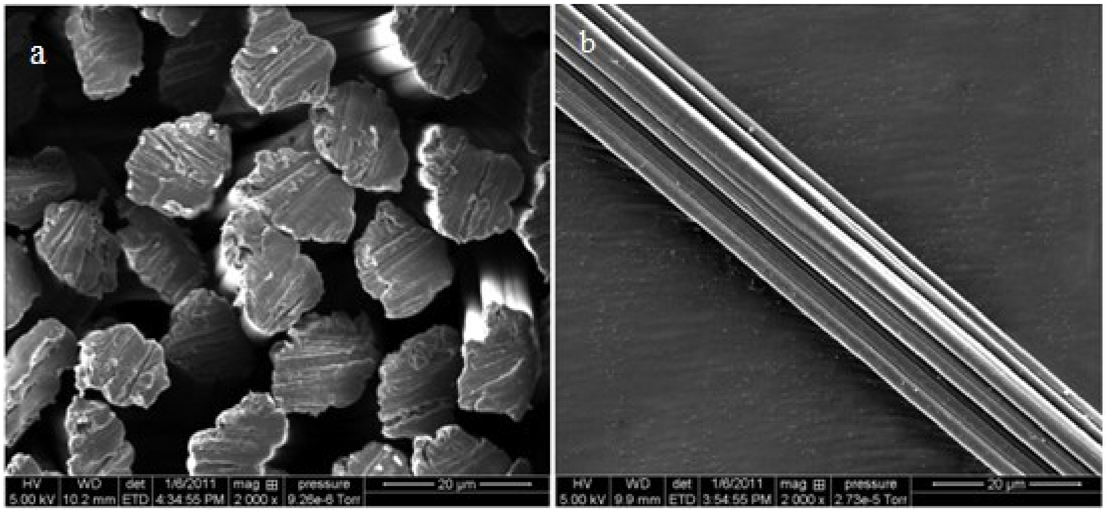


Figure 2.5

Viscose fibre microscopic images a) cross-sectional; b) longitudinal view

(Chen, 2014, p. 84)

Many of the cellulosic chains are not aligned parallel to the fibre axis resulting in a less crystalline fibre structure, and less intermolecular hydrogen bonding capability, than that which are present in the more crystalline natural cellulosic fibres such as cotton (Mather & Wardman, 2015). However, due to the lower levels of crystallinity, there are more free spaces for water molecules to be absorbed within the fibre structure resulting in moisture regain values of 11-13% (under standard conditions, 20 °C and 65% RH) (Fan, 2005).

There have been minimal studies carried out investigating the adsorption/desorption of VOCs by viscose fibres/fabrics. However, one study of contact and non-contact sampling of hand odour indicated the existence of a variety of chemicals in viscose fabrics based on their functional groups (Prada et al., 2011). Moreover, the highest recovery amount of VOCs represented in body odour have been reported by viscose fabric in a comparison among fabrics composed of other fibre types (i.e. cotton, wool, polyester, viscose) (Prada, Curran, & Furton, 2014). In another study involving a wear trial followed by sensory evaluation, Rathinamoorthy et al., (2014) found viscose to emit lower odour intensity than synthetic fibres but higher odour than cotton. Regarding the appropriate characteristics such as high absorbency and desirable strength, especially for use in the apparel industry, investigating the VOCs adsorption/desorption behaviour of viscose fibres with odorous compounds is an essential research case.

2.4.3 Polyester

In the 1930s the creation of a "second generation" of textile fibres, i.e. synthetic fibres, by chemists occurred which was the consequence of their attempts to create the same chemical structures as natural fibres (Hongu & Phillips, 1997). Among all different types of synthetic fibres, polyester which was develped in 1945, has commercially had the highest demand ascribed to desirable physical properties such as being light-weight, strong, wrinkle-resistance, and durable (East, 2005). Also, the variety in length of fibres (i.e. staple or filament) provided the possibility to use polyester individually or to blend it with other fibres, mostly cotton (Clark, 2011).

Polyester fibre is a synthetic fibre and is defined as "a long-chain synthetic polymer that is composed of 85 per cent or more by mass of an ester of dihydric alcohol or dial (i.e. HO-R-OH) and terephthalic acid" (Textile Labelling Act, 2011). Although there are many polyesters, the most common polyester in apparel clothing is polyethylene terephthalate (PET) (Figure 2.6) (East, 2005). In all types of polyester, there are polymer chains with at least one ester functional group (i.e. –C(O)O-) (East, 2005). PET is synthesized through the condensation reaction between terephthalic acid and ethylene glycol (Clark, 2011). Also, the reaction between ethylene glycol and dimethyl terephthalate can result in PET production (Resse, 2005). PET has a benzene ring in the main chain, which gives it structural stability. The main forces of attraction between polymer chains are van der Waals' forces, and although these are not as strong as hydrogen bonds (as with nylon fibres), they can be effective due to the close packing of the benzene ring which allows high crystallization within the polymer (Figure 2.7) (Morton & Hearle, 2008). In polyesters, the electeronic interation between neighbouring benzene rings results in an intermolecular binding similar to hydrogen bonds (Morton & Hearle, 2008). Polyester is therefore non-polar, and the chemical structure of the polymer has no available sites for forming hydrogen bonds. Polyester is, therefore, hydrophobic and so repels rather than absorbs water. The moisture regain of polyester fibre is 0.4% under conditions of 65% RH and 20 °C (Mather & Wardman, 2015). Due to its non-polar nature of the polyester fibre, fabrics can have problems with building up static electrical charges, attracting oily soils (such as long-chained fatty acids) and difficulty in removing soils through laundering (Bishop, 1995; East, 2005).

The shape of polyester fibres are uniform, and due to the method of manufacture (i.e. melt spun), it can be difficult to distinguish synthetic fibres from each other through microscopy. The shapes of cross-sections vary (e.g. round or triangular) and only depend on the spinneret shape (Markova, 2019) (Figure 2.7).

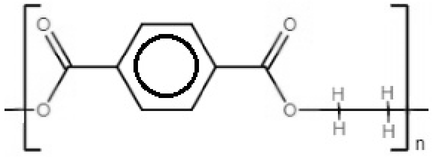


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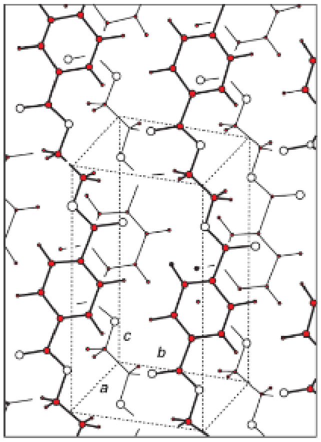
Figure 2.6

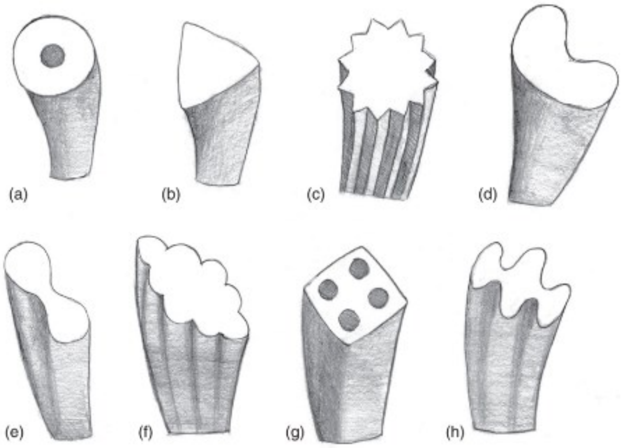
Polyester fibre chemical structure (polyethylene terephthalate)



(Morton & Hearle, 2008, p. 62)

Figure 2.7

The crystalline structure of the polyester fibre



(Markova, 2019, p. 126)

Figure 2.8

Synthetic fibres cross-section shapes: a) hollow round; b) triangular; c) serrated; d) kidney bean; e) dog bone; f) wavy flat; g) square with voids; h) hexachannel

Polyester is a popular fibre due to its excellent wicking and fast drying capabilities, particularly in sportswear, but also in other apparel products as well as home interiors. Also, as it is durable and relatively low cost, this adds to its dominance on the textile market (East, 2005). However, people wearing clothing made of polyester fibres may tend to wash them more frequently due to the ability of the fibre to retain "bodily smell" (Stanes & Gibson, 2017, p.33). Research comparing polyester with natural fibres such as cotton has been carried out by several researchers (Klepp et al., 2016; McQueen et al., 2007; McQueen et al., 2014; Munk et al., 2001), with polyester consistently being perceived as more odorous following wear by a panel of human assessors (Klepp et al., 2016; McQueen et al., 2007; McQueen et al., 2014; Rathinamoorthy et al., 2014). As well, when analyzing the volatile compounds released in the headspace of polyester fibres exposed to axillary odour through wear trials (McQueen et al., 2008) or after application of selected VOCs representative of body odours (Richter et al., 2018) polyester has been found to continue to desorb odorants.

2.4.4 Nylon

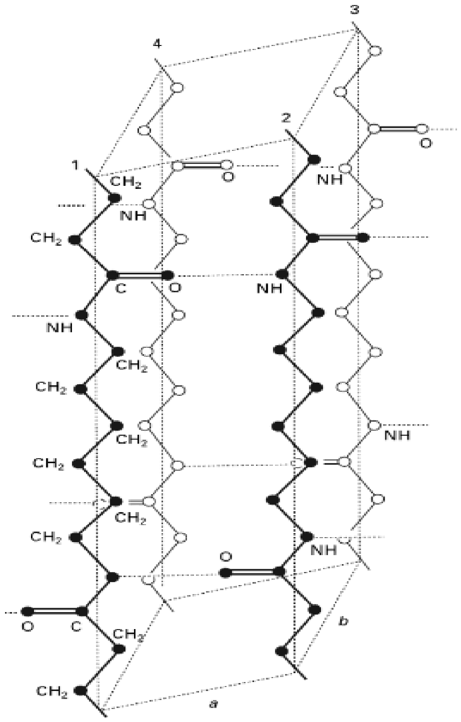
Nylon was the first synthetic fibre produced in 1935 and was developed in an endeavour to produce a fibre "finer than spider thread, stronger than steel and more elegant than silk" (Honngu, Phillips, 1997, p. 1). The appeal of nylon grew rapidly among consumers with nylon fibre production growing from 69000 tonnes in 1950 to 4.8 million tonnes over 20 years (Richards, 2005). Nylon, also known as polyamide, is "a long-chain synthetic polyamide that has recurring amide groups as an integral part of the main polymer chain in which at least 85 per cent by mass of the amide linkages are attached to aliphatic or cycloaliphatic groups" (Textile Labelling Act, 2011). The linear polyamide polymers are linked together by amide functional groups (i.e. –C(O)NH-) (Figure 2.9

Nylon fibres, like all fibres, have a semi-crystalline structure, with a general estimate of nylon being about 50% crystalline, although this can vary depending on the conditions of drawing during fibre manufacture (Richards, 2005). However, the physical structure of different types of nylons concerning the level of crystalline and amorphous regions depends on the conditions of production

(Mather & Wardman, 2015). For instance, nylon 6,6 is more crystalline, whereas nylon 6 has a slightly more open structure (Mather & Wardman, 2015). Nylon 6 and nylon 6,6 together cover the highest percentage of polyamides in the market, and each has different arrangements within their molecular chains (Figure 2.9

Nylon fibres compared with other synthetic fibres have far higher moisture regain values ranging from 3.5% to 4.5% for nylon 6 and nylon 6,6 respectively at standard textile testing conditions (i.e. 20 °C, 65% RH). When the air is saturated (100% R.H.), nylon fibres can contain about 10% of moisture relative to their dry weight (Richards, 2005). This is due to the ability of nylon to form hydrogen bonds with water molecules due to the NH and CO groups. Thus, the absorption capacity of fabrics made of nylon fibres is significantly greater than other synthetic fibres. In addition to involved groups in hydrogen bonds (i.e. NH and CO), there are also CH_2 chains in nylon fibres structure which are flexible at room temperature and show weak attraction with other groups in their neighbours (Morton & Hearle, 2008).

Like viscose, there have been fewer studies characterizing the sorption and desorption of VOCs represented in body odour by nylon fibres. However, some are beginning to emerge, particularly due to its presence in sportswear applications nylon as another synthetic fibre was of interest to compare with against high odour polyester (Abdul-Bari et al., 2018) . Rathinamoorthy et al. (2014) found nylon fabrics to be slightly less odorous than polyester fabrics after wear next to the axillary region. However, nylon was perceptibly more odorous than cotton, viscose and linen. Whereas in the study by Abdul-Bari et al., (2018) comparing two different polyester fabrics with two different nylon fabrics, they found there to be no significant differences in odour intensity between polyester and nylon fabrics (Abdul-Bari et al., 2018). Despite, the odour reduction rate (ORR) nylon fabrics exhibiting a greater sorption capacity with isovaleric acid and 2-nonenal than polyester fabrics (Abdul-Bari et al., 2018).

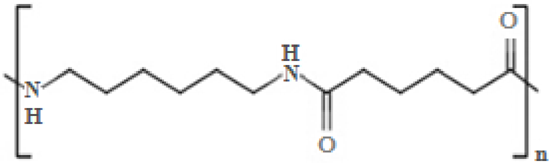


(Morton & Hearle, 2008, P.59)

Figure 2.9

Crystalline region in nylon 6.6

a) Nylon 6,6



b) Nylon 6

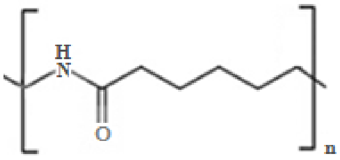


Figure 2.10

Nylon fibres chemical structures

Chapter 3

Methodology

3.1 Experimental fabrics

Four experimental fabrics were purchased from TestFabrics Inc. (West Pittson, PA, USA). All fabrics were plain weave and composed of 100% cotton, 100% viscose, 100% nylon, and 100% polyester. A description of the fabrics is provided in Table 3.1. Fabric specimens were cut 10 cm x 10 cm and placed in standard textile testing conditions (i.e. 65% ± 2% relative humidity [RH] and 20 ± 2% °C) for at least 24 hours according to CAN/CGSB-4.2 No.2-M88 (CGSB, 2001). Following conditioning, the fabric specimens were then weighed in the standard environment. Yarns were removed from the edges of the fabric specimens to avoid losing yarns during the experiment. The removal of yarns from each side of the fabric specimens was also carried out in order to reach a weight that was approximately equivalent to 0.75 g of the fabric's dry weight. This calculation was based on the moisture regain (i.e. the ratio between consitioned fabric weight to the weight of the oven-dried fabric) percentages of conditioned fabrics (see Table 3.2). Therefore, based on the conditioned mass, the dry mass could be calculated (Table 3.2). The fringes were approximately 2 cm in length for viscose, nylon, and polyester specimens, and 1.5 cm for cotton specimens. An example of one fabric specimen (cotton) after yarns were removed is shown in .

Fabric specimens were then rinsed three times in methanol (≥99.8 %, Sigma-Aldrich, ON) in order to remove any residue finishes that may be present following fabric manufacture. Solvent cleaned and air-dried fabrics specimens were stored in aluminum foil to reduce the likelihood of further contamination.

Table 3.1

Description of experimental fabric properties

Fabric	ISO code	Mass per unit area (g/m^2)[a]	Thickness (mm)[b]	Fabric count (warp/cm x weft/cm)[c]
Cotton	105-F02[d]	119.0 ± 0.7	0.34 ± 0.03	21 x 21
Nylon	105-F04[e]	134.0 ± 0.9	0.45 ± 0.01	11 x 10
Polyester	105-F03[f]	136.0 ± 1.3	0.54 ± 0.01	8 x 8
Viscose	105-F02[d]	146.0 ± 1.6	0.37 ± 0.02	16 x 16

a. CAN/CGSB- 4.2 NO.5.1-M90 (Canadian General Standard Board [CGSB], 2004); b. CAN/CGSB- 4.2 NO. 37-M 87 (CGSB, 2002); c. CAN/CGSB 4.2 NO. 6-M89 (CGSB, 2013); d. International Organization for Standardization (2009); e. International Organization for Standardization (2001); f. International Organization for Standardization (2001).

Table 3.2

Calculation of fabrics specimens final mass

Fabric	Length of fringe (cm)	Moisture regain (%)	Conditioned weight (g) * = assigned weight /(1- moisture regain %)
Cotton	1.5	6.0	0.797
Nylon	2.0	4.0	0.781
Polyester	2.0	0.4	0.753
Viscose	2.0	13.0	0.862

* Assigned weight is equal to 0.75 g

Figure 3.1

Cotton specimen with the fringe lengths of 1.5 cm from each side

The specific surface area (SSA) was also measured (Table 3.3). Total surface area of a solid sobstance per unit of mass is defined as SSA (Gregg, Sing, & Salzberg, 1967). For extending the kinetic model related to monolayer adsorption to multilayer, the Brunauer–Emmett–Teller (BET) model was developed (Gregg, Sing, & Salzberg, 1967). The SSA values calculation based on the results of BET tests on experimental fabrics are presented in Table 3.3 following a method described in Saini et al., (2017). These results were available at the end of the research; thus, the statistical analysis was done without normalizing the data based on the SSA values.

Table 3.3

Experimetnal fabrics specific surface area

Fabric	**SSA (m^2/g)**
Cotton	0.967
Viscose	0.493
Polyester	0.302
Nylon	0.239

3.2 Experimental chemicals

3.2.1 Artificial sweat

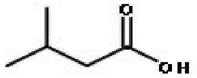
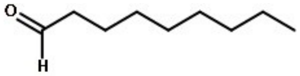
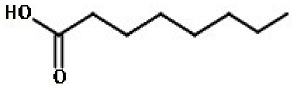
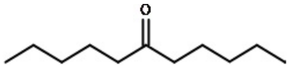
Odorous VOCs were applied to experimental fabric specimens in an aqueous solution. The fabric specimens were inoculated in an artificial acidic sweat solution. The artificial sweat was synthesized according to the AATCC Test Method 15 (American Association of Textile Chemists and Colorists, 2002). One litre of sweat solution was prepared by dissolving L-histidine (0.25 g) (Matheson Coleman & Bell, OH, U.S), sodium chloride (10 g) (Sigma-Aldrich, ON, Canada), L-(+)-lactic acid (1g) (≥ 98%, Sigma-Aldrich, ON, Canada), and sodium phosphate dibasic dodecahydrate (2.5 g) (Acros-Organic, Geel, Belgium) in distilled water. The pH of the sweat solution was checked with pH paper (HYDRION, Micro Essential Laboratory, Ins.) in the range of 4 to 4.5 (American Association of Textile Chemists and Colorists, 2002). A fresh sweat solution was prepared every three days.

3.2.2 Selected VOCs

Odorous VOCs were selected based on their presence in either axillary odour and/or laundry malodour. Initially, nine odorants were selected. Since the odorants were applied in a mixture to experimental fabrics, it was necessary to screen the selected odorants to ensure no overlapping of the peaks occurred during gas chromatography-flame ionization detection (GC-FID) (see Appendix A). Therefore, six odorous VOCs were selected to make up the final odorous solution (Table 3.4). The retention time which is the time take for compounds to pass through the chrimatography column is also presented in Table 3.4 (Moldoveanu & David, 2002). It is important to note that the retention time is dependent o n the properties of the compounds, GC column type, and the gas flow (Moldoveanu & David, 2002). Therefore the information presented in Table 3.4 is dependant pn the parameters described in Section 3.4.2.

Table 3.4

Properties of experimental VOCs

VOCs	Chemical structure	Retention time (min)	Vapour pressure (mmHg at 25°C)	Log Kow[a] (Exp.)	Log P [c] (Pred.)	Water solubility (g/L) [c]
Isovaleric acid[i,j]		3.56	0.44 [a]	1.16	1.26	64.9
2-Heptanone[i]		4.05	3.85 [a]	1.98	1.92	2.26
Nonanal[i]		8.08	0.37	3.27	3.81	0.06
Octanoic acid[i]		9.44	0.037 [a]	3.05	2.92	0.91
6-Undecanone[j]		10.61	0.05 [a]	-	4.07	0.029
Undecanal[i]		11.13	0.083[b]	-	4.98	0.002

[a] "National Center for Biotechnology Information" (2017) ; [b] "The Good Scents Company Information System," (2018); [c] "fooDB," (n.d.); [d] Labows (1988); [e] Stapleton et al., (2013); [f] Denawaka, Fowlis & Dean (2016); [g] Curran et al., (2005); [h] Zeng et al., (1991); [i] Axillary odour; [j] washing machine

The odorants used in this study were two carboxylic acids (isovaleric acid and octanoic acid), two aldehydes (nonanal and undecanal), and two ketones (2-heptanone, and 6-undecanone). All VOCs were from Sigma-Aldrich (ON, Canada), except 6-undecanone with an unknown supplier. Selected VOCs varied by their sources namely from human body odour (mostly axillary odour) and/or old/unclean washing machines (Curran et al., 2005; Denawaka et al., 2016; Labows et al., 1982; Stapleton et al., 2013; Zeng et al., 1991). In this study, 6-undecanone was used instead of 2-undecanone.

3.3 Experimental procedure

The experimental procedure was conducted in two distinct parts (see Figure 3.2). The objective of the first part was to quantify the concentrations of VOCs initially adsorbed from the sweat solution by the fabrics during the inoculation process. The objective of the second part was to quantify the concentrations of VOCs remaining in fabrics after they had been placed in test chambers and volatiles were allowed to dissipate. The concentration of each VOC after the chamber tests was measured at three discrete time intervals (3 h, 8 h, 24 h).

3.3.1 Inoculation of fabrics with VOCs in sweat solution

To account for any potential variation in sweat solution, two fabric specimens for each fibre type were matched. One fabric specimen was assigned for measuring the initial sorption (also known as at 0 h), and the other fabric specimen was assigned for measuring the number of compounds remaining following a specific time interval which was related to release (i.e., 3 h, 8 h, 24 h).

On the day of an experiment, eight clean 100 mL reusable glass media bottles (Fishebrand®) were filled with 20 mL of the odorous sweat solution. Four bottles were used for the initial sorption tests (0 h) and the remaining four bottles for release experiments (3 h, 8 h or 24 h). A fabric specimen was placed in a bottle and shaken by hand for 2 min. After 2 min of shaking the fabric and excess sweat, the solution was poured into a Buchner funnel, and the excess liquid was removed from the fabric specimen through vacuum suction. This was to ensure that the solution did not drip off the

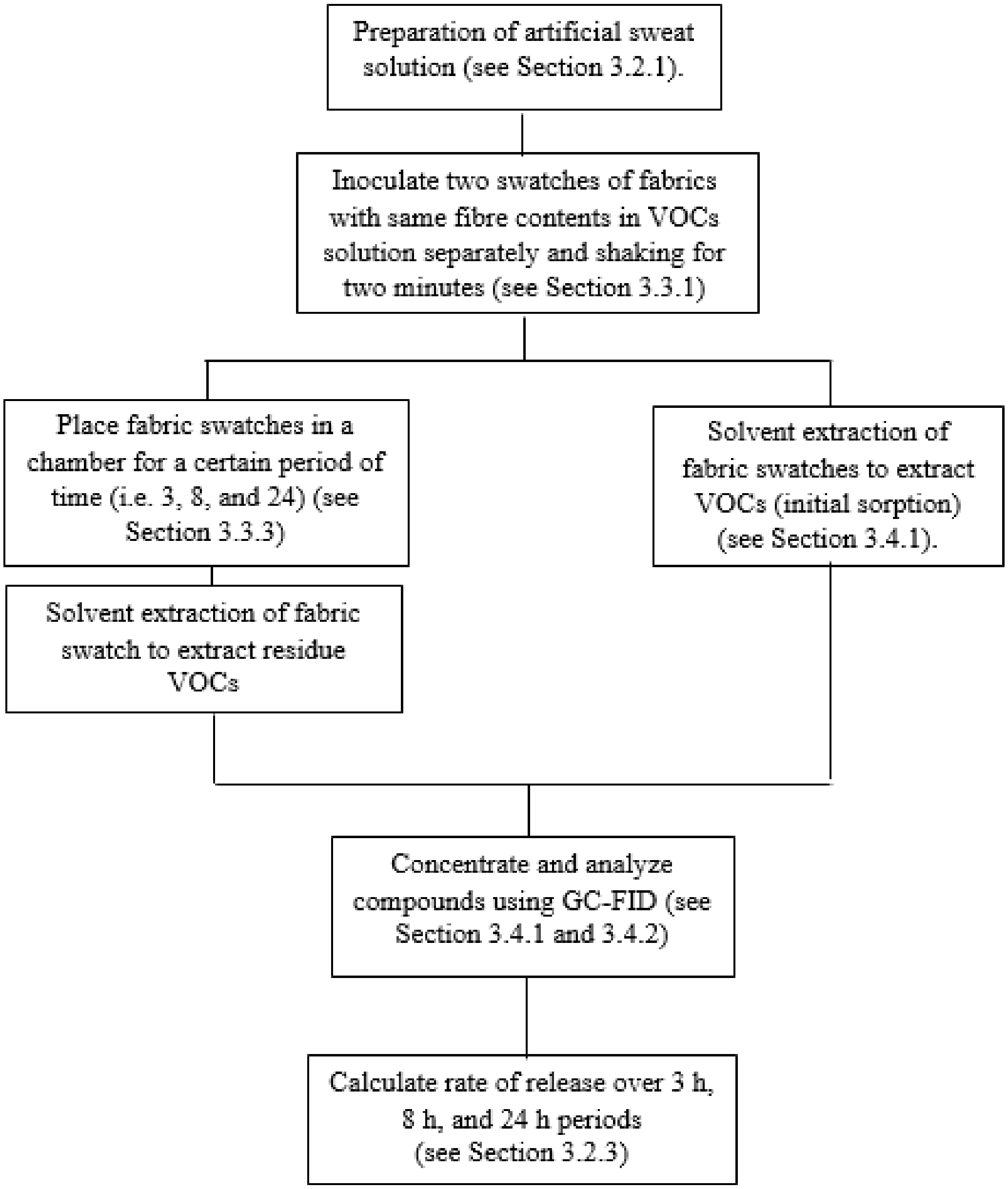


Figure 3.2

Flow chart of the experimental procedure

fabrics during the chamber experiments. A filter paper (Fishebrand®) was also placed inside the Buchner funnel to facilitate the suction process. The fabric specimen was then removed from the sweat solution and was flattened on the filter paper for 30 seconds using two tweezers. Between each filtration, the filter paper was changed.

3.3.2 Initial sorption

The initial sorption of odorants after inoculating fabrics in the sweat solution was measured by extracting the VOCs immediately after the suctioning step described in Section 3.3.1. Each 0 h fabric specimen was transferred to a 20 mL vial containing 10 mL dichloromethane (DCM). The vial was immediately capped, labelled, and kept under the fume hood until extraction could begin. The extraction process began after deploying all the other fabric specimens in the chambers (see Section 3.3.3). The minimum time a 0 h fabric specimen remained in DCM before extraction was 34 min, and the maximum time was 58 min.

3.3.3 Release of odorous VOCs

Release rates of odorous VOCs by fabrics were assessed after 3 h, 8 h, and 24 h. Fabric specimens assigned to desorption experiments for a specific period of time were exposed to the odorous sweat solution, as described in Section 3.3.1. Following inoculation and suctioning the fabric specimen was hung on the frame and placed inside the chamber (described in Section 3.3.3.1). The chamber was then closed tightly, and the air flow was checked to ensure it was within the defined range (75 ± 2 mL/min). Once the defined time interval was reached, the fabric specimen was removed and transferred to a 20 mL vial containing 10 mL of DCM and capped in preparation for extraction.

3.3.3.1 Test chambers

Four identical stainless steel chambers were constructed based on the design by Rauert & Harrad (2015) (Figure 3.3). The dimensions of each chamber were 9.7 cm in inner diameter, 11.2 cm in outer diameter, and 20 cm in height. The lid of each chamber had four ports. One port was an inlet port for clean air to pass into the chamber.

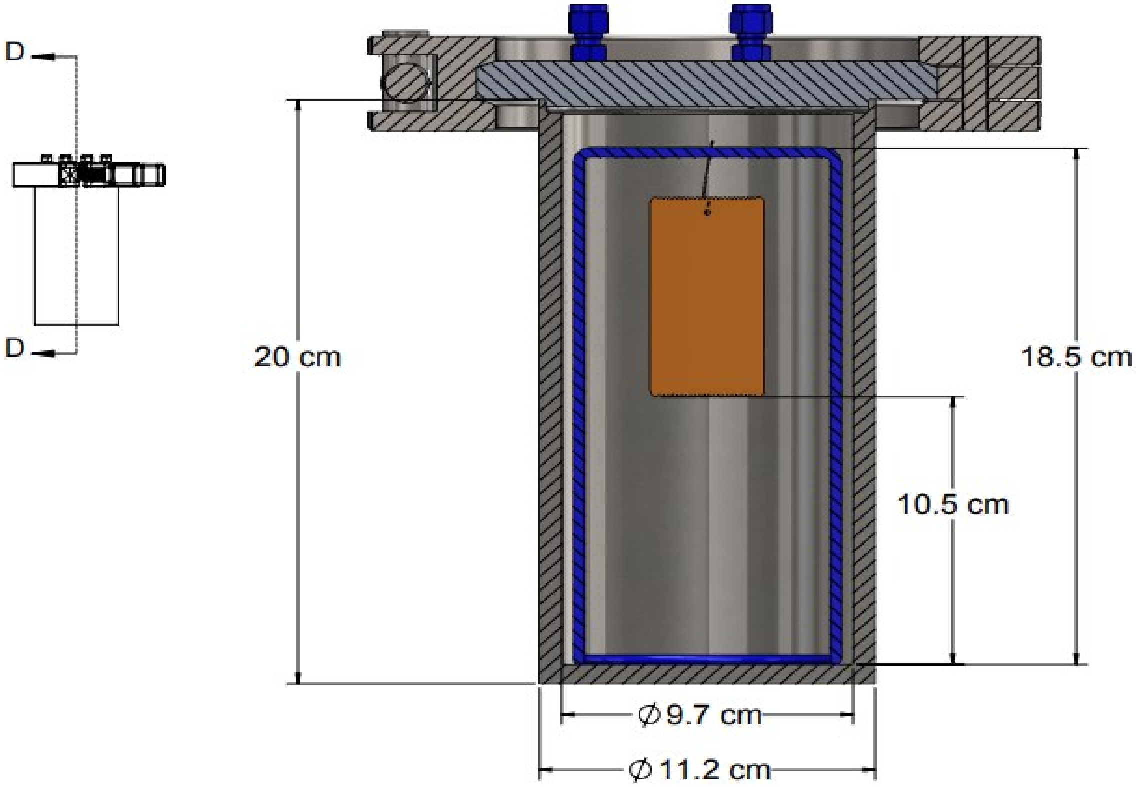


Figure 3.3

Designed chamber dimensions

A stainless-steel tube (16.7 cm in length, 0.5 cm in diameter) was soldered to the inlet port so that the air entered 1.8 cm from the bottom of the chamber. A second port was the outlet port for air to leave the chamber. The third port was used to insert a sensor with the aim of monitoring the relative humidity and temperature (RH/T) of the inside of the chamber with digital RH/T sensors (Sensirion, Switzerland). For this experiment, only three of the four ports were used. Therefore, the fourth port was plugged. Split ring hangers closed the chambers with the dimension of 10.7 cm in inner diameter and 12.3 cm in outer diameter.

The fabrics specimens were deployed in the chamber by hanging them on a stainless-steel standing frame that was 18.5 cm in height (Figure 3.3). They were hung by safety pins approximately 10.5 cm above the bottom of the chambers. The experimental set-up is illustrated in Figure 3.4.

All four chambers were placed in a water bath with a controlled temperature of ~33 °C. The internal RH and temperature of inside the chambers were 61 ± 30% RH and 29 ± 6 °C respectively. While the recorded data for the internal temperature demonstrated approximately constant situation, high variabilities were observed for RH (i.e. 30%). To increase the RH inside the chamber, the air was led into a container filled with water with the dimension of 21.6 cm in diameter and 43.2 cm. After passing the water container, humidified air passed through a gas manifold connecting to four individual valves (Figure 3.5). The valves were responsible for controlling the flow of air entering the chamber. Airflow was maintained at 75 mL/min by measuring the air flow in outlet tubes with the Agilent Flowmeter ADM2000. The inside walls and the lids of the chambers, as well as the standing frames, were washed by acetone three times after finishing each test.

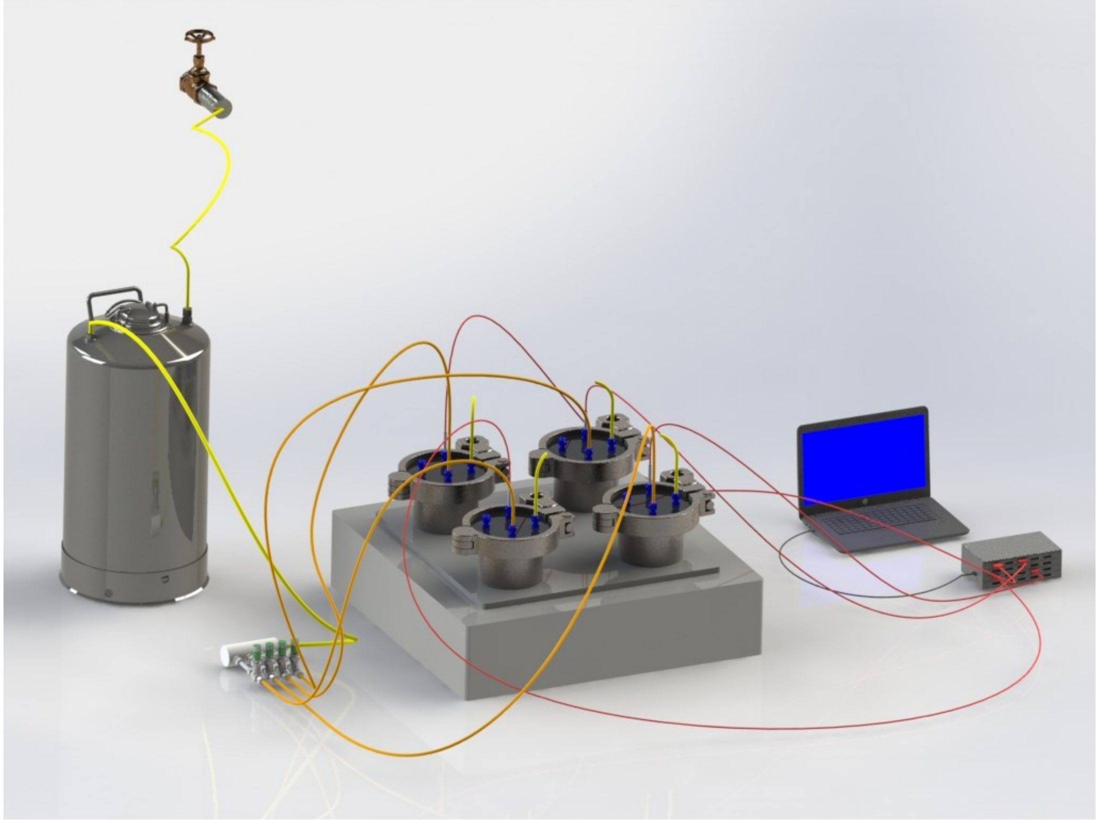


Figure 3.4

Experimental set-up

Figure 3.5

Designed valves for controlling air-flow

3.4 Chemical analysis

3.4.1 Extraction and concentration

The amounts of VOCs retained within the fabric specimens were quantified by solvent extraction with GC-FID. DCM was used as the solvent as it was capable of extracting both polar and non-polar chemicals and has been used for a mixture of compounds previously (Munk et al., 2001; Takeuchi, Hasegawa, Ishida, & Kashiwagi, 2012). A fabric specimen was placed in a 20 mL vial and filled with 10 mL of DCM. The vial was sonicated for 5 min. Following sonication, the solvent including the extracted odorants, was poured into another vial, then an additional 5 mL of DCM was added to the vial containing the fabric specimen. The vial was sonicated again for another 5 min. The fabric was then squeezed to the wall of the vial to remove as much of the DCM and odorant as possible. To dry the solution, 2 g of anhydrous sodium sulfate (Na_2SO_4) was added. The vial was shaken for 2 min, and then another 2 g of Na_2SO_4 was added to remove any remaining water molecules. Approximately 10 mL of dried solution was collected to be concentrated using a Kuderna-Danish column evaporator.

A Kuderna-Danish evaporative concentrator that consisted of a 500 mL reservoir, 15 mL conical receptor, and 3-ball Snyder column, 24/45 joint was used to concentrate the materials dissolved in volatile solvents. A beaker with 2 L volume was filled with water and put on a hot plate set at 45 °C. The conical receptor and bottom of the reservoir were placed in the water. The mouth of the beaker along with the bottom of the reservoir was wrapped by aluminum foil to keep the temperature constant (Figure 3.6). After reaching the required temperature, 10 mL of dried DCM/odorant solution was poured into the Snyder column. When the volume of the solvent reached 2 mL, the Snyder column was opened, and the reservoir and conical receptor were taken out of the water. When the solution stopped boiling, the reservoir and conical receptor were then placed in the water, and the Snyder column was assembled again to monitor the solution volume better. Once the volume reached 1 mL, the solution was transferred to a 2 mL GC vial, capped and labelled in preparation for analysis.

Figure 3.6

Set up of Kuderna-Danish evaporator during the concentration step

3.4.2 Gas chromatography with flame ionization detection (GC-FID)

Following concentration, the samples were analyzed using GC-FID, with 30.0 m x 250 µm x 0.25 µm Restek Rxt®-5MS (Crossbond® 5% phenyl/ 95% dimethyl polysiloxane) Rxt®-5MS (Chromatographic Specialtie Inc., ON, Canada). Helium gas (5.0 grade; Praxair, Edmonton, AB) was used as the carrier gas with a constant flow rate (3.1 mL/min). The analytes were injected into the split/splitless injection port of the GC in a split mode using an inlet temperature set at 250 ºC. The setpoint of the oven temperature was 50 °C and increased by a ramp-up to 10 °C/min to 170 °C. The total run was 15 min. The detector data rate was set at 200 Hz/0.001 min. The injection volume was 1 µL, and the approximate retention times for each VOC are shown in Table 3.4.

Peak areas of each of the six odorants were recorded after each run. The peak areas related to the carboxylic acids were overloaded in the initial sorption tests as the VOCs had much higher concentrations than after release in the chambers. Thus, manual integration was applied to both isovaleric acid and octanoic acid peaks to derive more accurate recorded areas. Examples of chromatograms related to odorants, which were extracted from the experimental fabrics after 3 h are presented in Appendix B.

3.4.3 Calculation of concentration

Calibration curves were calculated for all six VOCs in order to establish the relationship between the odorants' recorded peak areas to their concentrations in mg/g of fabric. A mixture of odorants with a concentration of 20,000 µg/mL was prepared and diluted to lower concentrations. The calculations related to the calibration curves and the recorded peak areas of injecting 1 µL of diluted solutions to the GC-FID are presented in Table 3.5 and

Table 3.6. Three injections for each concentration were done. Peak areas and concentertations were $\log_{10}$ transformed and calibration curves were plotted on the log transformed data. This was because of the regresson analysis on the non-transformed data resulted in negative concenterations in lower values. The regression lines and related equations of $\log_{10}$ transformed data are shown in (see Figure 3.7).

Table 3.5

Calculation of VOCs calibration curves

Conc	C1V1 = C2V2				
	C_1 (µg/mL)	V_1 (mL)	C_2 (µg/mL)	V_2 (mL)	V methanol (mL)
5000	20000	2.5	5000	10	7.5
4000	5000	8	4000	10	2
3000	4000	7.5	3000	10	2.5
2000	3000	6.67	2000	10	3.33
1000	2000	5	1000	10	5
500	1000	5	500	10	5
250	500	5	250	10	5
100	250	4	100	10	6
50	100	5	50	10	5
25	50	5	25	10	5
10	25	4	10	10	6

Table 3.6

VOCs peak area related to calibration curve calculation

Conc	Peak area					
	Isovaleric acid	2-heptanone	Nonanal	Octanoic acid	6-undecanone	Undecanal
5000	630.32	759.27	858.47	638.41	1635.73	693.53
4000	496.78	627.20	732.23	552.79	1281.20	510.40
3000	366.54	461.26	510.47	411.41	1006.67	428.33
2000	233.16	296.10	331.67	260.47	668.97	265.67
1000	102.79	128.57	151.50	118.51	298.83	129.00
500	56.94	69.57	83.63	66.38	170.07	70.90
250	27.43	34.20	43.03	35.57	80.51	35.27
100	12.43	15.77	19.43	13.36	37.93	14.40
50	4.76	6.65	7.67	5.73	15.40	6.97
25	3.20	3.20	4.03	3.01	7.77	3.78
10	1.14	1.39	1.69	1.94	3.40	1.90

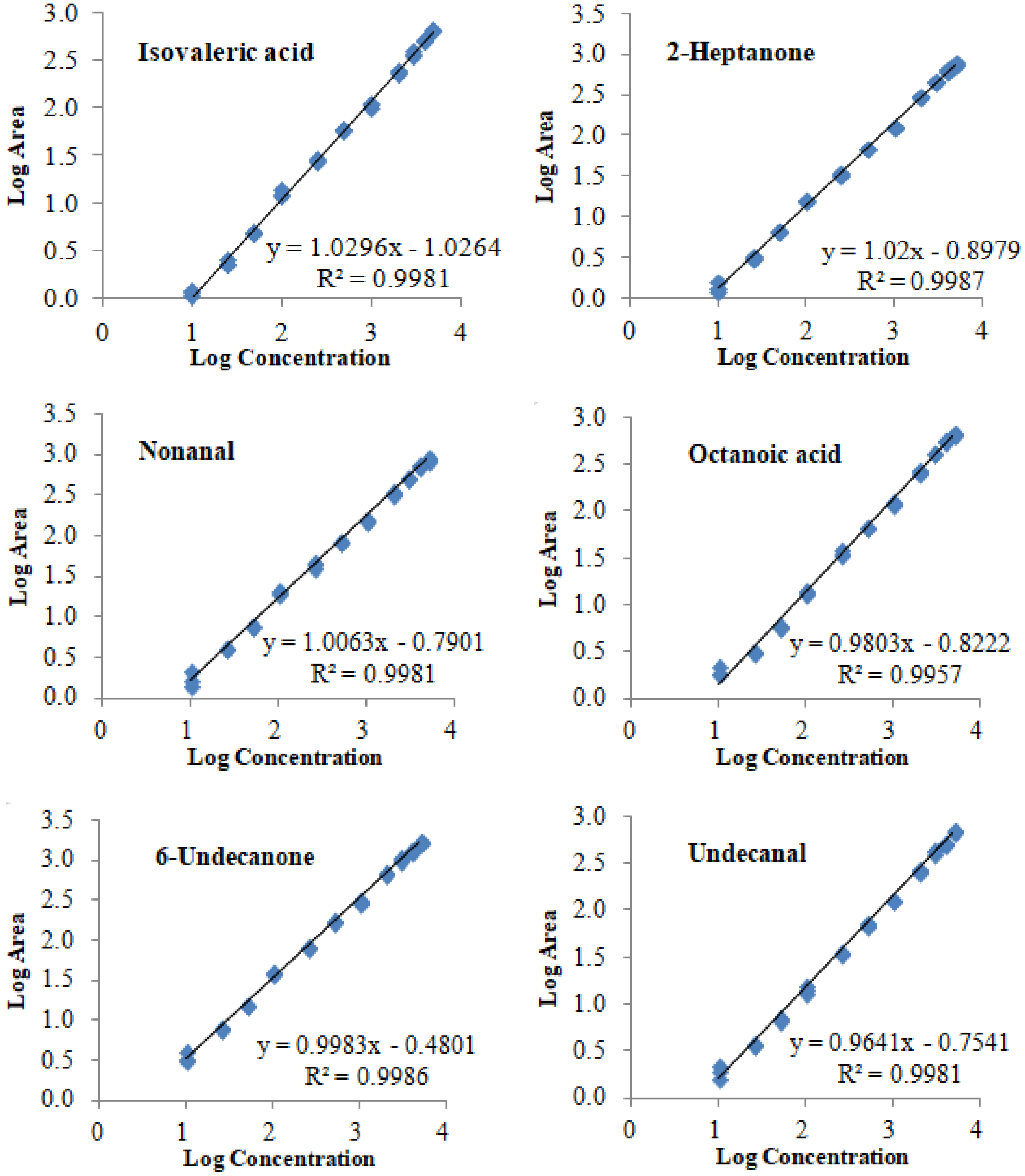


Figure 3.7

Calibration curves and related equations of six selected VOCs

The peak areas of the initial sorption (0 h) and the amounts of odorants remaining within the experimental fabrics after 3 h, 8 h, and 24 h were converted to relative concentrations in µg/mL using the equations derived from the calibration curves. Although there were minimal variations among the fabrics' weight, the odorants concentrations were normalized based on the dry weights of fabrics specimens to eliminate the effect of weight on the amount of sorbed compounds by experimental fabrics. Concentrations in µg/mL were transformed into mg. The final dependent values (mg/g) were corrected based on the recovery percentages for each fibre type (described in Section 3.4.4).

3.4.4 Percent recovery

The recovery capacity of DCM used for extracting the odorants can vary based on the properties of the fibres. As well, some loss of VOCs may occur during the extraction and concentration steps. To determine the percent recovery for each fibre type, swatches were placed in separate 20 mL vials. A 20,000 µg/mL solution of VOCs was prepared in methanol from which 0.2 mL of the solution was directly spiked onto the fabrics (equivalent to 4,000 µg/mL). An additional 0.5 mL of non-odorous sweat solution was also added to the fabrics. The odorants were extracted and concentrated following the same procedure described in Section 3.4.1.

One microliter (1 µL) of the concentrated solution was injected to the GC-FID, and the peak areas related to the six selected chemicals were recorded. An aliquot of 1 µL of 4,000 µg/mL solution was also injected into the GC-FID to determine the maximum expected concentrations. The peak areas were then converted to concentrations mg/g using the calculation obtained from the calibration curves. The percent recovery was calculated for each fibre using Equation 3.1.

$$\boldsymbol{Percent\ Recovery} = \left(\frac{\boldsymbol{Amount\ of\ VOCs\ extracted}}{\boldsymbol{Expected\ amount\ of\ VOCs}}\right)\mathbf{100} \qquad (3.1)$$

The percent recoveries calculated used to correct the results of the experiments are shown in Appendix C.

3.5 Statistical analysis

Descriptive statistics (mean [$\bar{x}$], standard deviation [s.d.] and coefficient of variation [c.v.%]) were calculated for all data at each time period (0 h, 3h, 8 h and 24 h). Moreover, the rate of change was calculated after 3 h, 8 h and 24 h relative to the matched 0 h results.

Concentrations of VOCs initially adsorbed by the fabrics (0 h) and VOCs that remained within the fabrics after 3 h, 8 h and 24 h were $\log_{10}$ transformed in order to meet the assumptions of normality and equal variance. As the selected VOCs showed substantial variations from each other, the differences among fibres for each odorant were assessed for each VOC separately. One-way analysis of variances (ANOVAs) was carried out for each compound. Where significant F-ratio values were found, Tukey's Honestly Significant Difference (HSD) post-hoc analysis was carried out to determine which fabrics differed from one another. Fibre content was deemed to be significantly different at $p<0.05$.

For release rates of the VOCs over 3 h, 8 h and 24 h periods, the data were compared with the matched 0 h results and divided by the time period. Data were $\log_{10}$ transformed, and a two-way ANOVA test was carried out with fibre types and VOCs as factors. Where there were any significant F-ratio values, Tukey's HSD post-hoc analyses for interactions were conducted. All the statistical analysis was performed by using IBM SPSS 25 software.

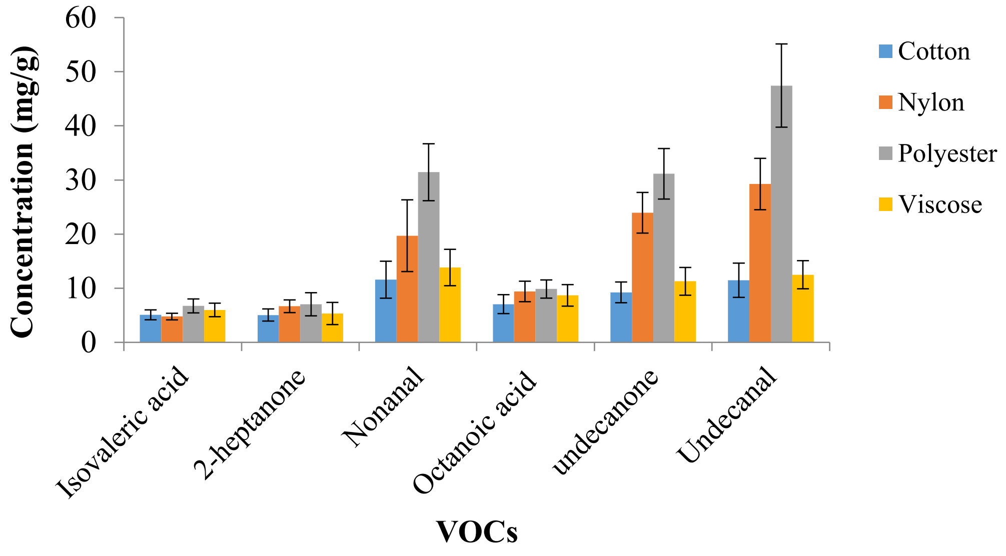
Chapter 4

Results and Discussion

4.1 Initial sorption of odorants by experimental fabrics

Concentrations (mg/g) of odorants initially ad/absorbed (adsorbed will be used from this point) by experimental fabrics are shown in Figure 4.1a (by VOCs) and Figure 4.1b (by the fibre content of fabric). A summary of concentrations of VOCs initially adsorbed by the four experimental fabrics is shown in Table 4.1. Among the six selected VOCs, isovaleric acid had the lowest amount initially adsorbed by the fabrics overall, ranging from 4.76 ± 0.61 mg/g for nylon to 6.73 ± 1.29 mg/g for polyester. This was closely followed by 2-heptanone (ranging from 5.05 ± 1.12 mg/g to 7.03 ± 2.14 mg/g for cotton and polyester respectively) and then octanoic acid (ranging from 7.06 ± 1.75 mg/g to 9.85 ± 1.68 mg/g for cotton and polyester respectively) (Table 4.1). There appeared to be only small differences among the four fibre types in the average amounts adsorbed for the two carboxylic acids as well as 2-heptanone. Mean differences between the fibre type that adsorbed the highest amount to the fibre that adsorbed the lowest amount being 1.97 mg/g, 1.98 mg/g and 2.84 mg/g for isovaleric acid, 2-heptanone and octanoic acid respectively. Whereas, for the other three compounds (i.e. nonanal, 6-undecanone, and undecanal) the synthetic fabrics (polyester and nylon) adsorbed substantially more than cotton and viscose fabrics. These differences among fibre types are clearly evident in Figure 4.1a. For example, nonanal retained amounts of 19.70 ± 6.63 mg/g and 31.43 ± 3.41 mg/g for nylon and polyester respectively, while this was lower at 11.57 ± 3.41 mg/g and 13.82 ± 3.36 mg/g for cotton and viscose respectively. Although cotton and viscose tended to adsorb approximately the same amount of odorants, typically cotton retained the lowest concentrations of compounds overall (except for isovaleric acid). Conversely, polyester consistently adsorbed the highest amounts of compounds after initial exposure to the odorous sweat solution.

a.



b.

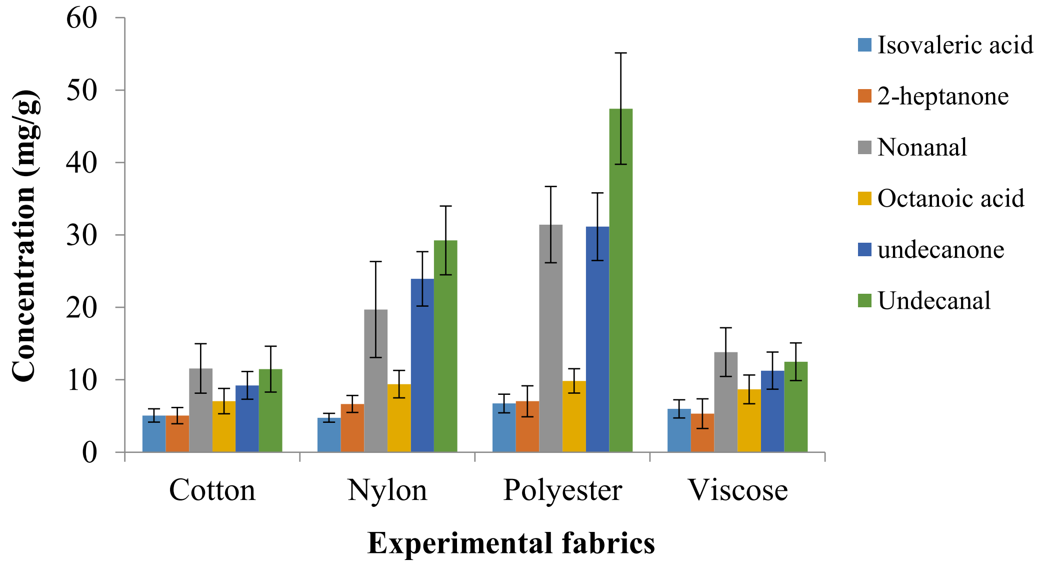


Figure 4.1

Initial sorption of odorants by experimental fabrics, a) by VOCs; and b) by fibre content of fabrics

Table 4.1

Normalized peak areas of initial sorption of odorants by experimental fabrics (mg/g) (n=9)

VOCs	Fibre	$\bar{x}$	s.d.	c.v.%	Min	Max
Isovaleric acid	Cotton	5.08	0.92	18.1	4.19	7.15
	Nylon	4.76	0.61	12.8	3.90	6.00
	Polyester	6.73	1.29	19.1	4.43	8.66
	Viscose	5.99	1.25	20.9	4.80	7.94
2-heptanone	Cotton	5.05	1.12	22.1	2.78	6.58
	Nylon	6.67	1.17	17.5	4.87	8.75
	Polyester	7.03	2.14	30.4	4.33	11.32
	Viscose	5.33	2.05	38.4	2.70	9.00
Nonanal	Cotton	11.57	3.41	29.5	5.98	17.4
	Nylon	19.70	6.63	33.6	8.83	28.20
	Polyester	31.43	5.26	16.7	20.73	38.55
	Viscose	13.82	3.36	24.3	10.87	20.95
Octanoic acid	Cotton	7.06	1.75	24.7	5.62	11.13
	Nylon	9.40	1.89	20.1	7.07	12.56
	Polyester	9.85	1.68	17.1	7.07	12.20
	Viscose	8.68	1.99	22.8	6.53	12.05
6- undecanone	Cotton	9.23	1.91	20.7	6.00	11.20
	Nylon	23.94	3.76	15.6	19.61	30.85
	Polyester	31.14	4.67	14.9	25.63	38.52
	Viscose	11.27	2.56	22.7	7.59	14.94
Undecanal	Cotton	11.47	3.17	27.5	7.62	15.42
	Nylon	29.24	4.75	16.2	23.14	38.67
	Polyester	47.44	7.69	16.2	38.06	57.77
	Viscose	12.49	2.60	20.8	7.80	15.70

The results of one-way Analysis of Variances (ANOVAs) showing the significance of variables affecting the initial sorption of odorants by experimental fabrics are presented in Table 4.2. Significant differences for each chemical by fibre content was evident at $p<0.05$ (isovaleric acid: $F_{3,32} = 6.721$, $p = 0.001$; 2-heptanone: $F_{3,32} = 3.205$, $p = 0.036$; nonanal: $F_{3,32} = 21.456$, $p = 0.000$; octanoic acid: $F_{3,32} = 4.895$, $p = 0.007$; 6-undecanone: $F_{3,32} = 82.384$, $p = 0.000$; and undecanal: $F_{3,32} = 92.720$, $p = 0.000$). Tukey's HSD post-hoc tests indicating which fibres differed significantly from one another for each VOC is shown in Table 4.3. For each of the six VOCs, the initial amount adsorbed by cotton and viscose fabrics did not significantly differ. Polyester was significantly different from cotton for all VOCs except for 2-heptanone, where none of the fibre types differed significantly from one another at $p<0.05$. Significant differences in the initial amount adsorbed by polyester compared with viscose were also found for nonanal, 6-undecanone, and undecanal, but not for the other three compounds. No significant differences were found between polyester and nylon at $p<0.05$ for 2-heptanone and octanoic acid, whereas for the other four VOCs polyester and nylon did differ significantly. Nylon also differed significantly from cotton as well as from viscose in initial sorption of VOCs with the exception of isovaleric acid and 2-heptanone (and additionally octanoic acid for viscose).

These results indicating that cotton and viscose were not significantly different in their initial sorption of odorous VOCs present in a sweat solution is not entirely unexpected. While the physical morphology, the orientation of fibres, and the level of crystallinity vary between cotton and viscose (Mather & Wardman, 2015), both fibres are hydrophilic due to the presence of hydroxyl groups in the cellulose structure (Wakelyn et al., 2007). This likely resulted in the cellulosic fibres exhibiting preferential selectivity for sorption of water in the sweat solution rather than the VOCs. It was observed that both cotton and viscose tended to adsorb greater quantities of the non-polar and hydrophobic compounds (i.e. nonanal, 6-undecanone, undecanal) than the more polar and water-soluble compounds. This can be explained through the partitioning process of the odorants in an aqueous solution.

Table 4.2

Significance of variables affecting initial sorption of VOCs by experimental fabrics

One-way ANOVA (log 10 transform)

Source	**d.f.**	**SS**	**MS**	**F**	**p**
a. Isovaleric acid					
Between groups	3	0.119	0.040	6.721	0.001
Within groups	32	0.188	0.006		
Total	35	0.307			
b. 2-heptanone					
Between groups	3	0.149	0.050	3.205	0.036
Within groups	32	0.496	0.015		
Total	35	0.645			
c. Nonanal					
Between groups	3	1.022	0.341	21.456	0.000
Within groups	32	0.508	0.016		
Total	35	1.531			
d. Octanoic acid					
Between groups	3	0.116	0.039	4.895	0.007
Within groups	32	0.253	0.008		
Total	35	0.369			
e. 6-undecanone					
Between groups	3	1.779	0.593	82.384	0.000
Within groups	32	0.230	0.007		
Total	35	2.009			
f. Undecanal					
Between groups	3	2.246	0.821	97.720	0.000
Within groups	32	0.283	0.009		
Total	35	2.745			

Table 4.3

Significance of differences in initial sorption of six VOCs by four experimental fabrics - Tukey range tests ($\log_{10}$ transform)

Source	$\bar{x}$	n	Tukey groupings**	
a. Isovaleric acid				
Nylon	0.67	9	│	
Cotton	0.70	9	│	
Viscose	0.77	9	│	│
Polyester	0.82	9		│
b. 2-heptanone				
Cotton	0.69	9	│	
Viscose	0.70	9	│	
Nylon	0.82	9	│	
Polyester	0.83	9	│	
c. Nonanal				
Cotton	1.05	9	│	
Viscose	1.13	9	│	
Nylon	1.27	9		
Polyester	1.49	9		
d. Octanoic acid				
Cotton	0.84	9	│	
Viscose	0.93	9	│	│
Nylon	0.97	9		│
Polyester	0.99	9		│
e. 6- undecanone				
Cotton	0.96	9	│	
Viscose	1.04	9	│	
Nylon	1.37	9		
Polyester	1.49	9		
f. Undecanal				
Cotton	1.04	9	│	
Viscose	1.09	9	│	
Nylon	1.46	9		
Polyester	1.67	9		

** Means grouped by vertical lines are not significantly different at $p \leq 0.05$

Liu, Obendorf, Leonard, Young & Incorvia (2005) found that the chemicals with high log K_{OW} which are more hydrophobic, partitioned onto the cotton fibres in higher amounts from aqueous solutions (Liu et al., 2005). The same interpretation can be considered for viscose fibres due to the similarity between viscose and cotton in chemical structure. Although differences were not significant, there still was a trend of higher amounts of VOCs being retained within the viscose than by cotton. Due to the higher moisture sorption capacity of viscose compared with cotton (moisture regain for viscose is 13% and cotton 6%) then more compounds existing in the aqueous solution can be adsorbed by viscose. Rathinamoorthy et al., (2014) found that following a wear trial viscose was slightly more odorous than cotton. They suggested that due to axial swelling that occurs in viscose, as a result of its high water sorption, that this facilitates the penetration of oily compounds present in sweat into the fibre structure (Rathinamoorthy et al., 2014). This could explain the slightly higher sorption of VOCs by viscose compared to cotton in the current study. In the indoor environment, Saini et al., (2017) reported that a lower amount of non-polar SVOCs were adsorbed by cotton fabrics compared to rayon (viscose) when normalized by surface area (Saini et al., 2017). However, the method of adsorption was not via an aqueous solution, so Saini and colleagues (2017) results may not be readily comparable to those in the current study.

Unlike the two cellulosic fibres, polyester and nylon are examples of synthetic fibres and are hydrophobic in nature (Deopura, Alagirusamy, Joshi, & Gupta, 2008). Although nylon fibres can also be characterised as slightly hydrophilic due to the existence of the NH and CO groups in its chemical structure, leading to the formation of hydrogen bonds with water molecules. No available binding site in the chemical structure of polyester fibres exists (Richards, 2005). The inherent fibre properties in relation to water are reflected in the moisture regain values of 4.0% for nylon and 0.4% for polyester. Therefore, the findings that nylon adsorbed less odorous VOCs than polyester from the sweat solution may relate to these differences in moisture sorption. As more aqueous solution could adsorb and potentially enter the nylon fibre structure, similarly to the cellulosic fibres, there may be preferential selection of water than VOCs to nylon. Conversely, the attraction of the non-polar VOCs from the aqueous solution toward the non-polar, oleophilic polyester fibre was likely occurring. This process of odorous compounds in liquid sweat media is in some ways similar to the process of dispersing dyeing. Disperse dyes in water form an aqueous dispersion, and as they are insoluble in water, they are attracted to the synthetic fibre and therefore move out of the aqueous dye solution to be adsorbed to the fibre (Shang, 2013). Heating the dye liquor to more than 90°C increases the movement energy of dye molecules and facilitates their diffusion into the amorphous regions of the polyester fibres (Mahapatra, 2016). At the lower temperatures of fabrics worn on the body (~35°C) diffusion into the fibre, structure is less likely. Due to the high crystallinity of the polyester fibres, the adsorbed VOCs on the surface of fibres can not easily diffuse into the inside of the structure. Nylon does tend to have a higher sorption capacity than polyester which has been shown in other studies. Using the ISO 17299-3 method which involves fabric samples adsorbing volatiles from the air, Abdul-Bari et al. (2018) found nylon adsorbed greater quantities of isovaleric acid and 2-nonenal than polyester. In the Abdul-Bari et al., study the sorption capacities of polyester and nylon were assessed with the odorants in the gas phase, whereas, immersing fabrics in an odorous sweat solution, as was done in the current study, was quite different.

The greatest differences among the four fibre types were evident in the initial sorption of VOCs between the cellulosic fibres (cotton and viscose) compared to the synthetic fibres (nylon and polyester). Although the differences in initial sorption of carboxylic acids and 2-heptanone by the fabrics were not as considerable as the adsorbed amounts of aldehydes and the higher molecular weight ketone, 6-undecanone. Immediate extraction of the odorants from the fabrics resulted in higher concentrations adsorbed by polyester and nylon compared with cotton and viscose for all compounds (except adsorption of isovaleric acid by nylon which was lower). The following order was observed in initial sorption by fabrics: polyester > nylon > viscose > cotton. It has been stated that the acidic environment (pH ~ 4.5) can facilitate the sorption of dyes molecules by fibres in the disperse dying process, which is usually used for synthetic fibres (Shang, 2013). The pH of the sweat solution in the current study was 4 to 4.5, which may have facilitated higher adsorption of the VOCs by the synthetic fibres.

Differences in sorption of odorous compounds between cotton and polyester fabrics have been reported elsewhere. For example, extraction following application of carboxylic acids (i.e. isovaleric acid and 4-methyl octanoic acid) and aldehydes (i.e. Z-4-heptanal and E-2-nonenal) dissolved in DCM to cotton and polyester fabrics resulted in higher quantities retained by polyester (Munk et al., 2001). This was consistent with the findings from the current study, despite entirely different methods of the odorant application being used. In another investigation, the adsorption of VOCs by cotton, wool and polyester yarns resulted in more non-polar aldehydes and ketones being sorbed by polyester fibres (Yao et al., 2015). Again, different methods of odorant application occurred as the odorants were dispersed as gas in the air to be picked up the by fibres (Yao et al., 2015).

Due to the solubility of the selected VOCs, it was hypothesized that 2-heptanone, nonanal, 6-undecanone and undecanal would be initially sorbed in higher amounts by polyester and nylon than cotton and viscose. Significant differences in the masses of nonanal, 6-undecanone and undecanal were found between the synthetic and cellulosic fibres which supported this hypothesis (see Table 3.4). However, there were no significant differences monitored for 2-heptanone which was unexpected. It is likely that the greater amounts of hydrophobic compounds extracted from the experimental fabrics compared with the more polar carboxylic acids related to the partitioning of non-polar odorants from the aqueous sweat solution onto the fibres (Liu et al., 2005). In addition to isovaleric acid and octanoic acid which are soluble in water, 2-heptanone can also dissolve in aqueous solutions evident by their water solubility values (see Table 3.3). Furthermore, as well as high solubility of the carboxylic acids in water carboxylic acids disassociate in an aqueous media, particularly if the pH is high. Therefore, despite the importance of the acids in axillary odour, Munk et al., (2000) stated that the predominate odorants in clothing fabrics after laundering were considered the hydrophobic VOCs such as ketones but especially aldehydes in case of polyester fibres (Munk et al., 2000).

4.2 Release of odorous VOCs from experimental fabrics over 24 hours

The desorption or release of selected VOCs from experimental fabrics was evaluated over 24 hours (measured at discrete time intervals) by conducting chamber tests. Table 4.4 presents the amounts of compounds that remained within the fabrics after 3 h, 8 h and 24 h expressed as mg/g. Figure 4.2, Figure 4.3, and Figure 4.4 show the mean concentration of compounds extracted from fabrics at all time intervals (including 0 h) for the carboxylic acids, ketones and aldehydes respectively. As time progressed there was a general reduction in VOCs retained within the fabrics, with higher quantities of compounds at 3 h compared with 8 h and 24 h. Generally, the most notable decrease in VOCs occurred between 0 h and 3 h (see Figures 4.2-4.4). This indicated that during the chamber tests the compounds were being released from the fabrics into the air, and generally the most rapid release occurred within the first 3 hours.

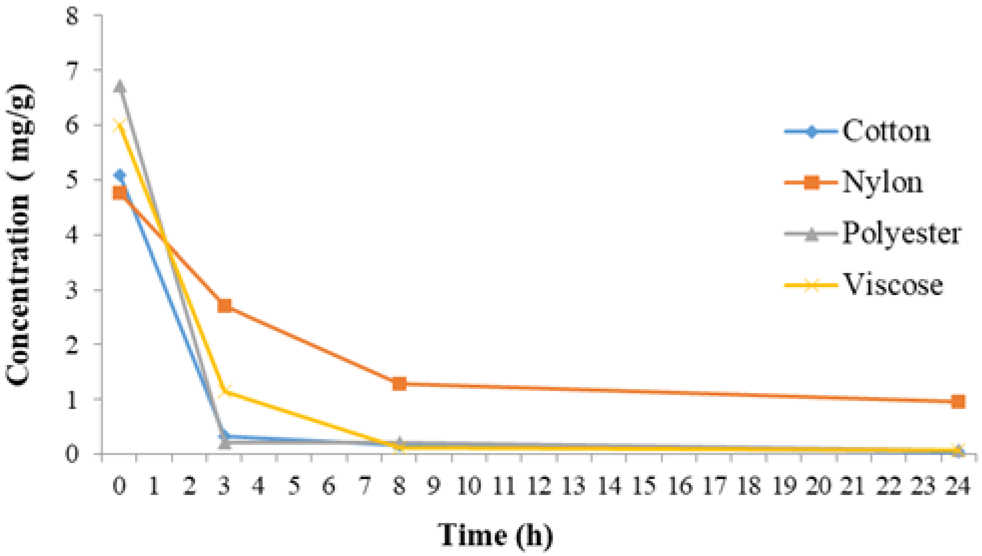
Cotton retained the smallest quantity of compounds after 3 h in the test chambers, with the exception of isovaleric acid and 2-heptanone that overall had low amounts remaining on all fabrics. For example, for undecanal, the amounts remaining on cotton were 3.30 ± 0.63 mg/g which was less than viscose at 11.53 ± 2.86 mg/g, nylon at 32.13 ± 6.26 mg/g and polyester at 40.12 ± 3.25 mg/g. This trend continued after 8 h, although there were some exceptions including isovaleric acid and octanoic acid with the lowest retained amount in viscose at 0.13 ± 0.01 mg/g and 0.44 mg/g respectively after 8 h, and for 2-heptanone where cotton retained the highest amount (0.08 ± 0.01 mg/g) after 8 h. After 24 h in the test chamber, the lowest amounts of compounds were extracted from cotton fabrics except for octanoic acid and 6-undecanone where mean values were comparable to viscose, and also 2-heptanone where the mean values for all fabrics were 0.02 mg/g.

Table 4.4

Initial sorption of odorants by experimental fabrics after 3 h, 8 h, and 24 h (mg/g) (n=3)

		3 h					8 h					24 h				
VOCs	**Fibres**	**x̄**	**s.d.**	**c.v. %**	**Min**	**Max**	**x̄**	**s.d.**	**c.v. %**	**Min**	**Max**	**x̄**	**s.d.**	**c.v. %**	**Min**	**Max**
a. Isovaleric acid																
	Cotton	0.34	0.04	11.7	0.31	0.39	0.17	0.04	23.5	0.14	0.21	0.04	0.01	25.0	0.03	0.05
	Nylon	2.70	0.35	12.9	2.35	3.04	1.29	0.35	27.1	0.90	1.55	0.96	0.20	20.8	0.81	1.19
	Polyester	0.20	0.02	10.0	0.19	0.23	0.21	0.05	23.8	0.15	0.25	0.06	0.03	50.1	0.04	0.09
	Viscose	1.14	0.26	22.8	0.94	1.43	0.13	0.01	7.6	0.11	0.14	0.07	0.06	85.7	0.00	0.12
b. 2-Heptanone																
	Cotton	0.08	0.02	25.0	0.06	0.10	0.08	0.01	12.5	0.07	0.10	0.02	0.04	200.0	0.00	0.07
	Nylon	0.07	0.01	14.2	0.05	0.07	0.04	0.01	25.0	0.04	0.05	0.02	0.01	50.1	0.01	0.03
	Polyester	0.04	0.00	0	0.03	0.04	0.03	0.01	33.3	0.02	0.04	0.02	0.01	40.1	0.01	0.03
	Viscose	0.01	0.01	98.4	0.00	0.02	0.04	0.02	50.1	0.03	0.06	0.02	0.02	88.1	0.00	0.04
c. Nonanal																
	Cotton	1.18	0.16	13.5	1.01	1.33	0.76	0.09	11.8	0.67	0.84	0.43	0.11	25.5	0.32	0.54
	Nylon	9.91	1.58	15.9	8.64	11.68	4.73	0.85	17.9	3.67	5.34	2.84	0.82	28.8	2.14	3.74
	Polyester	11.63	3.20	27.5	9.52	15.32	6.86	1.57	22.8	5.06	7.97	1.64	0.40	24.3	1.27	2.07
	Viscose	3.24	0.70	21.6	2.66	4.02	1.08	0.19	17.5	0.93	1.29	0.86	0.29	33.7	0.57	1.16
d. Octanoic acid																
	Cotton	2.51	0.32	12.7	2.14	2.71	0.46	0.08	17.3	0.40	0.55	0.37	0.06	16.2	0.31	0.44
	Nylon	7.91	1.48	18.7	6.64	9.53	4.22	1.03	24.4	3.28	5.31	2.87	0.72	25.1	2.29	3.67
	Polyester	9.33	2.10	22.5	7.44	11.58	5.19	1.29	24.8	3.71	6.12	0.85	0.15	17.6	0.68	0.95
	Viscose	6.51	1.11	17.0	5.46	7.67	0.44	0.07	15.9	0.39	0.52	0.31	0.32	103.2	0.10	0.68
e. 6-Undecanone																
	Cotton	0.68	0.08	11.7	0.60	0.75	0.20	0.04	20.0	0.18	0.25	0.15	0.06	40.0	0.10	0.22
	Nylon	15.32	2.41	15.7	12.89	17.72	2.57	0.59	22.9	2.13	3.24	1.55	0.38	24.5	1.31	1.99
	Polyester	4.62	0.90	19.4	3.84	5.60	5.74	2.82	49.1	3.04	8.67	0.46	0.08	17.3	0.40	0.55
	Viscose	2.45	0.40	16.3	2.08	2.88	0.20	0.02	10.1	0.19	0.23	0.15	0.17	113.3	0.02	0.34
f. Undecanal																
	Cotton	3.30	0.63	19.1	2.66	3.92	1.85	0.37	20.0	1.63	2.28	1.31	0.15	11.4	1.14	1.41
	Nylon	32.13	6.26	19.4	27.07	39.12	9.49	0.88	9.2	8.56	10.31	8.09	2.33	28.8	5.50	10.02
	Polyester	40.12	3.25	8.1	36.37	42.01	26.48	6.25	23.6	19.98	32.46	8.93	1.53	17.1	7.93	10.70
	Viscose	11.53	2.86	24.8	9.23	14.73	3.32	1.02	30.7	2.34	4.38	2.86	0.45	15.7	2.36	3.20

a. Isovaleric acid



b. Octanoic acid

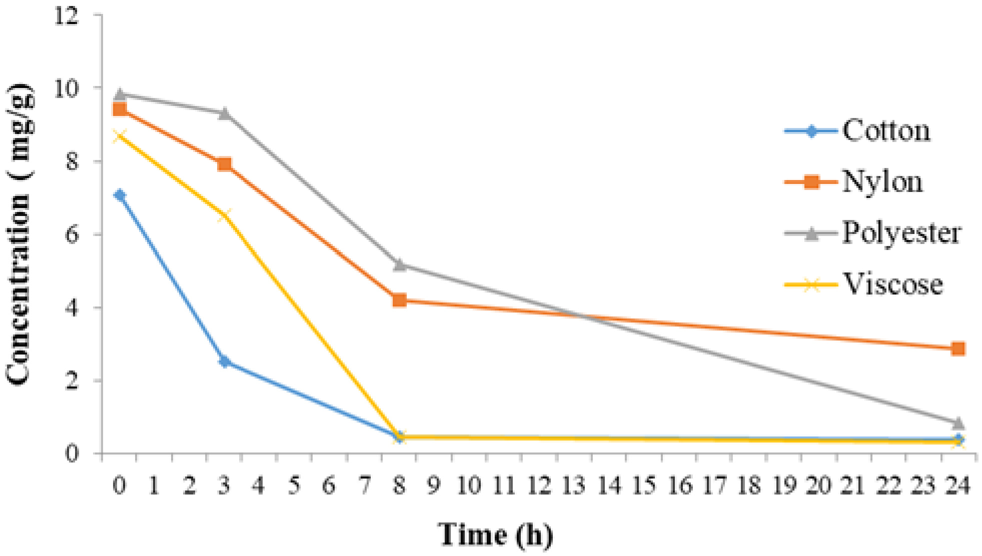
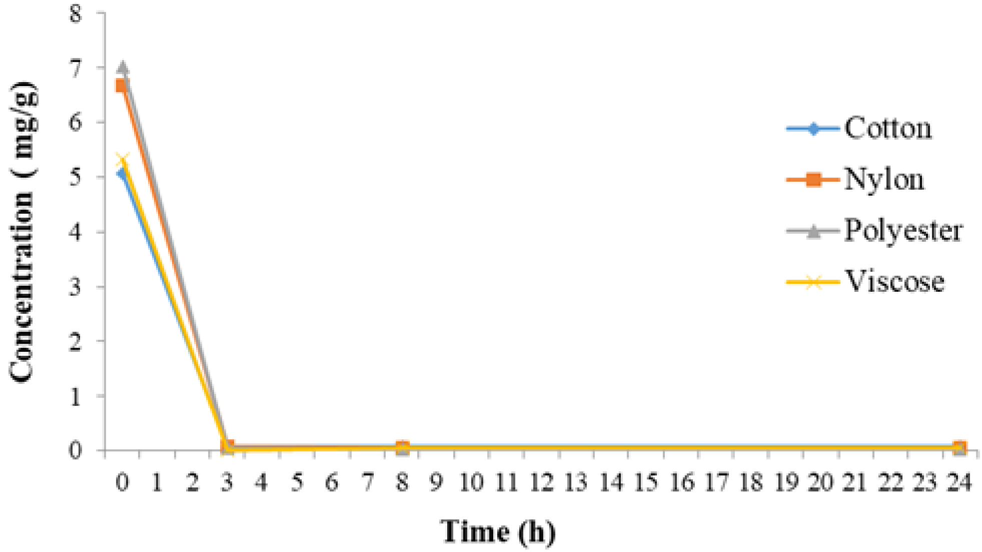


Figure 4.2

Mean values representing the concentrations of carboxylic acids extracted from four experimental fabrics (standard deviation values are reported in Table 4.1 and Table 4.4)

a. 2-heptanone



b. 6-undecanone

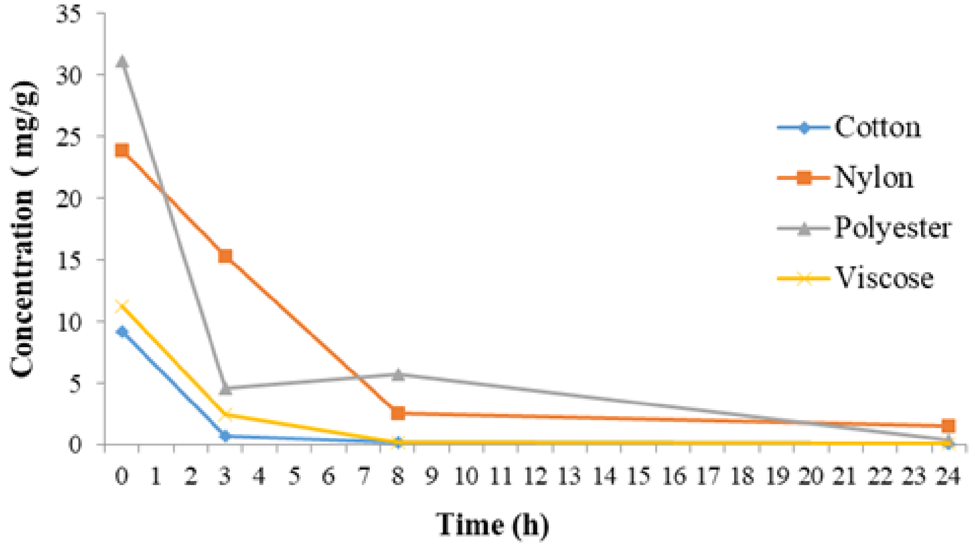
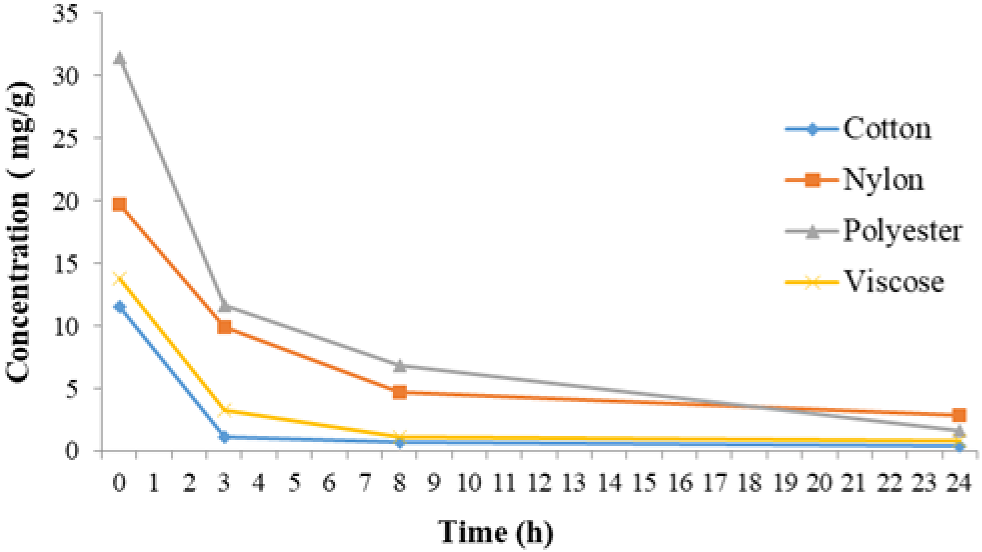


Figure 4.3

Mean values representing the concentrations of ketones extracted from four experimental fabrics (standard deviation values are reported in Table 4.1 and Table 4.4)

a. Nonanal



b. Undecanal

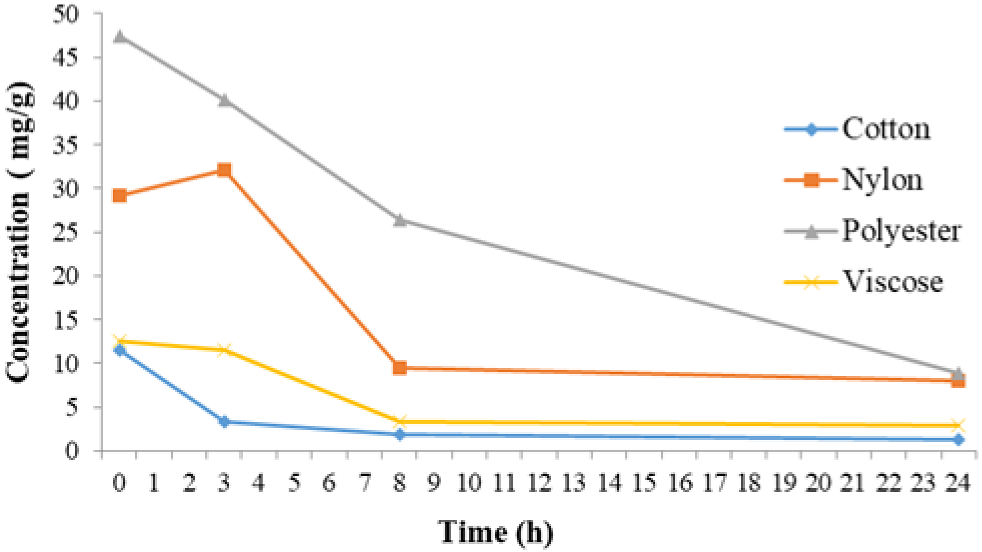


Figure 4.4

Mean values representing the concentrations of aldehydes extracted from four experimental fabrics (standard deviation values are reported in Table 4.1 and Table 4.4)

In genera, polyester retained the highest amounts of VOCs after 3 h in the test chambers, with the exception of isovaleric acid and 6-undecanone where higher quantities were retained in nylon, and 2-heptanone where more was extracted from cotton. Except for isovaleric acid and 2-heptanone, polyester continued to retain the highest quantities ofVOCs after a period of 8 h. For example, the amount of undecanal extracted after 8 h from polyester was 26.48 ± 6.25 mg/g compared to nylon at 9.49 ± 0.88 mg/g, viscose at 3.32 ± 1.02 mg/g and cotton at 1.85 ± 0.37 mg/g. However, this changed by 24 h where the highest amount of compounds were then extracted from nylon (with the exception of undecanal which was higher in polyester at 8.93 ± 1.53 mg/g compared to 8.09 ± 2.33 for nylon).

The results of the one-way ANOVAs showing the significance of variables affecting the release of odorous VOCs by experimental fabrics after 3, 8, and 24 h are Table 4.5, Table 4.6, and Table 4.7 respectively. Significant differences for each compound by fibre content was evident at $p<0.05$ after 3 h (isovaleric acid: $F_{3,8} = 182.485$, $p = 0.000$; 2-heptanone: $F_{3,8} = 7.728$, $p = 0.010$; nonanal: $F_{3,8} = 87.993$, $p = 0.000$; octanoic acid: $F_{3,8} = 31.640$, $p = 0.000$; 6-undecanone: $F_{3,8} = 197.833$, $p = 0.000$; undecanal: $F_{3,8} = 113.657$, $p = 0.000$). Significant differences for all compounds by fibre content was apparent after 8 h (isovaleric acid: $F_{3,8} = 61.652$, $p = 0.000$; 2-heptanone: $F_{3,8} = 7.185$, $p = 0.012$; nonanal: $F_{3,8} = 99.657$, $p = 0.000$; octanoic acid: $F_{3,8} = 118.446$, $p = 0.000$; 6-undecanone: $F_{3,8} = 93.526$, $p = 0.000$; undecanal: $F_{3,8} = 81.847$, $p = 0.000$). After 24 h significant differences were detected for all compounds except for 2-heptanone at $p<0.05$ level (isovaleric acid: $F_{3,8} = 4.432$, $p = 0.041$; nonanal: $F_{3,8} = 24.259$, $p = 0.000$; octanoic acid: $F_{3,8} = 12.939$, $p = 0.002$; 6-undecanone: $F_{3,8} = 9.548$, $p = 0.005$; undecanal: $F_{3,8} = 58.922$, $p = 0.000$).

Tukey's HSD post-hoc tests indicating which fibres differed significantly from one another for each compound is shown in Table 4.8. In general after 3 h of deployment of fabrics in the chambers polyester significantly differed from what remained within cotton (except for 2-heptanone). After 3 h, polyester also differed significantly from viscose fabrics (except for 2-heptanone and octanoic acid).

Table 4.5

Significance of variables affecting concentrations of VOCs extracted from experimental fabrics after 3 h

One-way ANOVA ($\log_{10}$ transform)

Source	d.f.	SS	MS	F	P
a. Isovaleric acid					
Between groups	3	2.319	0.773	182.485	0.000
Within groups	8	0.034	0.00		
Total	11	2.353			
b. 2-heptanone					
Between groups	3	2.521	0.840	7.728	0.010
Within groups	8	0.870	0.109		
Total	11	3.391			
c. Nonanal					
Between groups	3	1.925	0.642	87.993	0.000
Within groups	8	0.058	0.007		
Total	11	1.983			
d. Octanoic acid					
Between groups	3	0.579	0.193	31.640	0.000
Within groups	8	0.049	0.006		
Total	11	0.628			
e. 6-undecanone					
Between groups	3	2.851	0.950	197.833	0.000
Within groups	8	0.038	0.005		
Total	11	2.889			
f. Undecanal					
Between groups	3	2.226	0.742	113.657	0.000
Within groups	8	0.052	0.007		
Total	11	2.287			

Table 4.6

Significance of variables affecting concentrations of VOCs extracted from experimental fabrics after 8 h

One-way ANOVA ($\log_{10}$ transform)

Source	d.f.	SS	MS	F	P
a. Isovaleric acid					
Between groups	3	1.833	0.611	61.652	0.000
Within groups	8	0.079	0.010		
Total	11	1.912			
b. 2-heptanone					
Between groups	3	0.389	0.130	7.185	0.012
Within groups	8	0.145	0.018		
Total	11	0.534			
c. Nonanal					
Between groups	3	1.964	0.655	99.657	0.000
Within groups	8	0.053	0.007		
Total	11	2.017			
d. Octanoic acid					
Between groups	3	3.083	1.028	118.446	0.000
Within groups	8	0.069	0.009		
Total	11	3.152			
e. 6-undecanone					
Between groups	3	4.874	1.625	93.526	0.000
Within groups	8	0.139	0.017		
Total	11	5.013			
f. Undecanal					
Between groups	3	2.353	0.784	81.847	0.000
Within groups	8	0.077	0.010		
Total	11	2.429			

Table 4.7

Significance of variables affecting concentrations of VOCs extracted from experimental fabrics after 24 h

One-way ANOVA ($\log_{10}$ transform)

Source	d.f.	SS	MS	F	P
a. Isovaleric acid					
Between groups	3	4.756	1.585	4.432	0.041
Within groups	8	2.862	0.358		
Total	11	7.617			
b. 2-heptanone					
Between groups	3	0.992	0.331	0.658	0.600
Within groups	8	4.021	0.503		
Total	11	5.013			
c. Nonanal					
Between groups	3	1.136	0.379	24.259	0.000
Within groups	8	0.125	0.016		
Total	11	1.261			
d. Octanoic acid					
Between groups	3	2.145	.0715	12.939	0.002
Within groups	8	0.442	0.055		
Total	11	2.587			
e. 6-undecanone					
Between groups	3	2.672	.0891	9.548	0.005
Within groups	8	0.746	0.093		
Total	11	3.419			
f. Undecanal					
Between groups	3	.1388	0.463	58.922	0.000
Within groups	8	0.063	0.008		
Total	11	1.451			

Table 4.8

Significance of differences in concentrations of extracted six VOCs from four experimental fabrics after 3, 8, and 24 h - Tukey range tests ($\log_{10}$ transform) *

		3 h				8 h				24 h		
VOCs	**Fibres**	**$\bar{x}$**	**n**	**Tukey's grouping**	**Fabrics**	**$\bar{x}$**	**n**	**Tukey's grouping**	**Fabrics**	**$\bar{x}$**	**n**	**Tukey's grouping**
a. Isovaleric acid												
	Polyester	-0.69	3		Viscose	-0.90	3	│	Viscose	-1.64	3	│
	Cotton	-0.48	3		Cotton	-0.77	3	│	Cotton	-1.43	3	│ │
	Viscose	0.05	3		Polyester	-0.69	3	│	Polyester	-1.24	3	│ │
	Nylon	0.43	3		Nylon	0.10	3		Nylon	-0.02	3	│
b. 2-heptanone												
	Viscose	-2.28	3	│	Polyester	-1.58	3	│	Cotton	-2.39	3	│
	Polyester	-1.42	3	│ │	Viscose	-1.44	3	│ │	Viscose	-1.97	3	│
	Nylon	-1.19	3	│	Nylon	-1.35	3	│ │	Nylon	-1.72	3	│
	Cotton	-1.14	3	│	Cotton	-1.09	3	│	Polyester	-1.66	3	│
c. Nonanal												
	Cotton	0.07	3		Cotton	-0.12	3	│	Cotton	-0.38	3	│
	Viscose	0.50	3		Viscose	0.03	3	│	Viscose	-0.09	3	│ │
	Nylon	0.99	3	│	Nylon	0.67	3	│	Polyester	0.21	3	│ │
	Polyester	1.06	3	│	Polyester	0.83	3	│	Nylon	0.44	3	│
d. Octanoic acid												
	Cotton	0.40	3		Viscose	-0.36	3	│	Viscose	-0.67	3	│
	Viscose	0.81	3	│	Cotton	-0.35	3	│	Cotton	-0.44	3	│
	Nylon	0.89	3	│	Nylon	0.62	3	│	Polyester	-0.07	3	│ │
	Polyester	0.96	3	│	Polyester	0.71	3	│	Nylon	0.45	3	│
e. 6- undecanone												
	Cotton	-0.17	3		Viscose	-0.70	3	│	Viscose	-1.03	3	│
	Viscose	0.39	3		Cotton	-0.69	3	│	Cotton	-0.85	3	│
	Polyester	0.66	3		Nylon	0.40	3	│	Polyester	-0.34	3	│
	Nylon	1.18	3		Polyester	0.72	3	│	Nylon	-0.18	3	│
f. Undecanal												
	Cotton	0.51	3		Cotton	0.26	3	│	Cotton	0.12	3	
	Viscose	1.05	3		Viscose	0.51	3	│	Viscose	0.45	3	
	Nylon	1.50	3	│	Nylon	0.98	3		Nylon	0.89	3	│
	Polyester	1.60	3	│	Polyester	1.41	3		Polyester	0.95	3	│

* means grouped by vertical lines are not significantly different at $p \leq 0.05$

A similar trend was also apparent for nylon with cotton and viscose, as differences were significant for all compounds at 3 h except for 2-heptanone and octanoic acid respectively. The Tukey's HSD post-hoc tests demonstrated a different trend in the amount of the odorous VOCs held by fabrics after placing them in chambers for 8 h. No significant differences in extracted amounts of all odorants from cotton were observed compared to viscose at $p<0.05$. Polyester was significantly different from cotton for all compounds except for isovaleric acid and viscose with the exception of isovaleric acid and 2-heptanone. Polyester also differed significantly from nylon for isovaleric acid and undecanal only. Amounts remaining in nylon at 8 h was significantly different from cotton and viscose (except for 2-heptanone). After deploying the fabrics in the chambers for 24 h, the Tukey's HSD post-hoc tests showed that there were no significant differences between cotton and viscose in the amounts retained for all odorants except for undecanal. There were no significant differences in the amount remaining in polyester compared with the two cellulosic fibres, with the exception of undecanal and nonanal (cotton only). Also, polyester did not significantly differ from nylon in the amounts retained for all odorants.

In the current study, the amount of compounds remaining within four selected fabrics varying by fibre content were measured at discrete time intervals. It is important to note that the relative differences among the fibre contents at 3 h, 8 h and 24 h were in some part dependent on the mass of compounds initially adsorbed by the fabrics during the inoculation in the odorous sweat solution. For example, the mean of 6-undecanone initially sorbed by cotton was 9.23 mg/g while it was 31.14 mg/g for polyester (see Table 4.1). The low amounts of VOCs initially adsorbed by cellulosic fibres resulted in a lower amount retained by these fibres compared with the synthetic fibres, particularly after only 3 h. Therefore, after 3 h of release, it was not unexpected that lower mean amounts of 6-undecanone would be extracted from cotton (0.68 mg/g) in comparison to polyester (4.62 mg/g). Despite non-significant differences in initial adsorption of compounds to cotton and viscose, after 3 h there were significantly lower amounts of VOCs retained within cotton compared to viscose. However, after 8 h of release VOCs retained within cotton and viscose were generally not significantly different. An observation made during the experimental process was that when the fabrics were removed from the chambers after 3 h, they did not appear to be as dry as when they were removed from the chambers after 8 h. Therefore, due to the differences in moisture regain values for viscose and cotton (13% and 6% respectively) it is likely that viscose took longer to dry than cotton. The presence of water molecules in the fibre structure may slow down the release of VOCs by the fabrics. By 24 h, when fabrics would have been dry for a number of hours, no significant differences in the amounts of VOCs retained within the viscose and cotton fabrics were found (with the exception of undecanal).

A few studies have investigated the proportion of odorous VOCs remaining in fabrics that vary by fibre type (Abdul-Bari, 2018; Hammer, Berner-Dannenmann, & Hoefer, 2013; Munk et al., 2001; Richter et al., 2018). Hammer et al. (2013) applied diluted ^{14}C-radiolabelled isovaleric acid in artificial sweat to cotton, polyester and wool fabrics and extracted the compounds 1 h, 3 h and 20 h after inoculation. After 1 h they found that 100%, 79% and 97% of isovaleric acid remained on wool, cotton and polyester fabrics respectively compared with the initial amount inoculated (Hammer et al., 2013). Whereas, 3 h after inoculation 98% of the acid remained on wool, 50% on cotton and 3% on polyester. This was similar to the findings in the current study for polyester, as much of isovaleric acid was released during that first 3 h of the chamber tests. However, for cotton, there were lower amounts remaining after 3 h.

In another study sorption of octanoic acid and 2-nonenal by cotton and polyester fabrics was made (inoculation of compounds using DCM), greater quantities of polar octanoic acid remained in cotton and a higher amount of non-polar nonenal remained in polyester after the compounds were allowed to dissipate for 24 h in air before extraction (Abdul-Bari, 2018). However, in the current study polyester exhibited higher sorption of octanoic acid initially, and continued to retain higher amounts at 3 h and 8 h (although by 24 h there was no significant difference between cotton and polyester). The findings of Abdul-Bari (2018) were similar for the non-polar compounds where polyester retained higher amounts after 24 hours than cotton but dissimilar in that cotton retained more octanoic acid after the 24 h period than polyester. The differences may be interpreted due to the dissimilarity in experimental procedures and the differences in initial sorption of odorants by cotton and polyester fabrics. In Abdul-Bari's (2018) study the compounds were dissolved in DCM and then a specific volume was inoculated onto the fabrics which resulted in applying the same quantity of chemicals on both fabrics initially. Whereas, the initial amount adsorbed by the cotton fabric was less than polyester in the current study.

In Munk et al., (2001), the extractions of the odorants spiked onto cotton and polyester fabrics after 24 h indicated that the non-polar aldehydes (i.e. Z-4-heptanal and E-2-nonenal) were retained within polyester in higher concentrations that in cotton. Moreover, greater quantities of carboxylic acids (i.e. 3-methyl butanoic acid and 4-methyl octanoic acid) were retained by cotton. However, the extracted amounts of all VOCs from the polyester in the current study were higher after 24 h compared to cotton. This may also relate to differences in experimental procedures where fabrics were spiked with specific quantities of odorants in a DCM solvent by Munk et al., (2001) as opposed to being immersed in an aqueous sweat solution.

Sensory analysis of body odours collected on different fabrics during a wear trial found the highest odour intensity was released from polyester followed by nylon, viscose, and cotton (Rathinamoorthy et al., 2014). Although the methods between a wear study and the current study differ considerably the lower quantities of compounds remaining in polyester (a fibre type that initially exhibited high adsorption) indicates that higher quantities of compounds were released into the headspace during the 24 h period where the volatiles could potentially be perceived by the human nose. Nylon, on the other, had sorbed slightly fewer compounds initially and then released less of them over time (indicated by higher quantities after 24 h). As a result, nylon may be perceived as being less odorous than polyester, as the nylon fibres trap odorants within the fibre structure. Therefore, these findings support the outcome of the research by Rathinamoorthy et al., (2014).

However, in another study comparing polyester and nylon fabrics for odour intensity following wear next to the axillae the results were less conclusive and neither polyester nor nylon could be confirmed as more odorous than the other (Abdul-Bari et al., 2018). Interestingly, when differences between the fibre contents were perceived it appeared for one type of nylon fabric that had been stored at room temperature for 7 days (as compared to polyester and nylon fabrics stored in the freezer) was perceptibly more odorous. In the current stud, only a 24 h period was examined. If the greater release of compounds occurs from polyester than nylon during a 24 h period, then after 7 days nylon may still have some compounds remaining to slowly release, whereas, those remaining on polyester could be so minimal that they are less perceptible. Despite this speculation as to why nylon may be more odorous in the study by Abdul-Bari et al. (2018), the results from a wear trial where bacteria, skin cells, lipidous sweat compounds can be transferred to a fabric during wear is far more complex than the retention and release of odorous compounds as conducted in the current study. For example, in the headspace analysis of polyester, cotton, and wool samples exposed to human body odour 7 days following the wear trial an increase in quantities of some short-chain carboxylic acids were detected from polyester but not on cotton or wool fabrics (McQueen et al., 2008). The authors suggested this was due to bacterial metabolism of lipidous compounds retained in higher amounts on the polyester than on wool and cotton that may have occurred (McQueen et al., 2008).

There is inconsistency in the desorption behaviour of viscose fabric. While viscose was noted as less odorous than polyester, nylon, and cotton in research by Rathinamoorthy et al., (2014), the maximum amount of compounds were detected for viscose through analysis by SPME-GC/MS compared with cotton, polyester, wool fabrics (Prada et al., 2014). This disagreement may result from the dissimilar methods and the mixture of odorants. A limited number of VOCs were spiked onto fabric specimens in the study by Prada et al., (2014) while human body odour consists of a complex mixture of 100s of odorants (de Lacy Costello et al., 2014). What was detected in the current research was a lower amount of compounds remaining in viscose than that remaining in the two synthetic fibres, albeit still slightly higher than that remaining in cotton. Although the limited number of VOCs were involved in the current study as well, the method of immersing fabrics in an aqueous sweat solution to apply odorants on the fabrics may have also accounted for differences in the results.

There were considerable differences in the quantities of compounds remaining on fabrics depending on the physical and chemical properties of the odorants. As Figure 4.2a and Figure 4.3a demonstrated, rapid loss of isovaleric acid and 2-heptanone were clearly evident by all fabrics during the first 3 h. These two odorants as well as octanoic acid are more soluble in water (Table 3.3). Thus initial sorption of these compounds by the fibres was far lower than the other VOCs. Furthermore, the fast releasing of 2-heptanone and isovaleric acid, particulary during the first 3 h, was likely due to the higher levels of volatility. High vapour pressures have been reported for 2-heptanone and isovaleric acid which result in lower level of the volatility (Table 3.3). The chemicals with low level of the volatility can be easily evaporated and released from substances (EPA, 2017).

4.3 Rates of release of VOCs from fabrics over time

The rate at which fabrics released odorous VOCs was calculated by comparing each replicate to its matched zero time then divided by the number of hours the fabric was placed in the test chamber. The rates of release were expressed as mg/g/h and calculated for each discrete period (i.e. 3 h, 8 h, 24 h) and are presented in Table 4.9. Among the four experimental fabrics, polyester had the highest rates of release during the first 3 hours of the experiments for three of the six compounds (i.e. isovaleric acid at 2.00 ± 0.17 mg/g/h; nonanal at 7.43 ± 0.32 mg/g/h; and 6-undecanone at 8.93 ± 2.16 mg/g/h). After 8 h, polyester exhibited the highest rate of release for isovaleric acid (tied with viscose) (0.78 ± 0.22 mg/g/h), nonanal (2.92 ± 0.85 mg/g/h), 6-undecanone (3.02 ± 0.42 mg/g/h), and undecanal (2.74 ± 0.44 mg/g/h). After 24 h, polyester had the highest rate of release for all compounds except for octanoic acid. The continuously high rates of release by polyester may be supported by the findings that polyester tends to be more odorous in sensory analysis following wear trials compared to natural fibres (McQueen et al., 2014; Klepp, Buck, Laitala, & Kjeldsberg, 2016; McQueen et al., 2008; Rathinamoorthy et al., 2016). There appeared to be no consistent trend in the rate of release for the other fabrics/VOCs, with nylon exhibiting the lowest rate of release for isovaleric acid (0.62 ± 0.07 mg/g/h), nonanal (1.79 ± 0.18 mg/g/h) and octanoic acid (0.38 ± 0.48 mg/g/h) during the first 3 hours, but the highest release rate for 2-heptanone (2.20 ± 0.53 mg/g/h). Nylon tended to retain the VOCs more than polyester. Due to the hydrophobic nature of nylon, oily compounds can be adsorbed more readily by the fibres. But, nylon fibres are also slightly hydrophilic due to the available sites (i.e. NH and CO) for forming hydrogen bonds. Therefore, this hydrogen bonding capability may account for greater adhesion of polar compounds to the fibres and even within the fibre structure, while the adsorption of odorants by polyester, especially non-polar compounds, most likely occurs only on the surface of fibres (Obendorf & Webb, 1987). Thus, this may explain the higher rate of release from polyester fibres.

Whereas, cotton exhibited the lowest release for 2-heptanone (1.32 ± 0.35 mg/g/h) and 6-undecanone (2.34 ± 0.43 mg/g/h), but the highest rate of release for octanoic acid (1.77 ± 0.18 mg/g/h) and undecanal (2.63 ± 0.52 mg/g/h) during the first 3 hours. When examining the rate of release by fabrics during the entire 24 hour period of testing, the odorants were emitted from the experimental fabrics with the approximately similar rates (with the exception of nonanal, octanoic acid, and undecanal desorptions from the polyester swatches).

Results from the two-way ANOVA of release rates of VOCs from the experimental fabrics with fibre and compounds as factors for each period are shown in Table 4.10. Significant differences were noted for fibre content (3 h: $F_{3, 72} = 8.579$ p = 0.000; 8 h: $F_{3, 72} = 10.504$, p = 0.000; 24 h: $F_{3, 72} = 18.026$, p = 0.000) as well as for VOCs (3 h: $F_{5, 72} = 9.098$, p = 0.000; 8 h: $F_{5, 72} = 73.636$, p = 0.000; 24 h: $F_{5, 72} = 34.795$, p = 0.000). In addition, there were small but significant interactions in the rates of release by fibre content and VOCs (3 h: $F_{15, 72} = 1.958$, p = 0.040; 8 h: $F_{15, 72} = 7.557$, p = 0.000; 24 h: $F_{15, 72} = 2.327$, p = 0.014). Furthermore, Tukey's HSD post hoc tests showing which fibre types and compounds were significantly different from one another is shown in Table 4.11.

Table 4.9

Normalized peak areas of concentration change rates of extracted odorants from experimental fabrics (mg/g/h)

(n=3)

		3 h					8 h					24 h				
VOCs	**Fibre**	**x̄**	**s.d.**	**c.v. %**	**Min**	**Max**	**x̄**	**s.d.**	**c.v. %**	**Min**	**Max**	**x̄**	**s.d.**	**c.v. %**	**Min**	**Max**
a. Isovaleric acid																
	Cotton	1.46	0.08	5.3	1.38	1.53	0.69	0.16	22.4	0.57	0.87	0.21	0.03	14.9	0.17	0.23
	Nylon	0.62	0.07	10.6	0.55	0.68	0.39	0.09	22.3	0.29	0.45	0.18	0.02	9.7	0.17	0.20
	Polyester	2.00	0.17	8.6	1.87	2.20	0.78	0.22	28.0	0.53	0.96	0.31	0.05	16.8	0.26	0.36
	Viscose	1.27	0.16	12.6	1.12	1.44	0.78	0.18	23.0	0.61	0.97	0.27	0.05	18.9	0.22	0.33
b. 2-Heptanone																
	Cotton	1.32	0.35	26.2	0.92	1.53	0.67	0.11	16.0	0.56	0.78	0.24	0.03	12.4	0.22	0.27
	Nylon	2.20	0.53	24.2	1.60	2.62	0.91	0.16	17.4	0.79	1.09	0.25	0.02	6.2	0.23	0.27
	Polyester	1.93	0.62	31.9	1.43	2.62	0.80	0.19	24.2	0.62	1.01	0.37	0.09	24.9	0.30	0.47
	Viscose	1.63	0.44	27.1	1.23	2.10	0.57	0.10	18.3	0.50	0.69	0.27	0.14	51.8	0.11	0.38
c. Nonanal																
	Cotton	3.45	0.06	1.9	3.40	3.53	1.32	0.28	21.5	1.00	1.53	0.52	0.25	47.9	0.24	0.70
	Nylon	3.00	0.72	24.2	2.24	3.69	2.12	0.41	19.4	1.81	2.59	0.80	0.37	45.5	0.38	1.02
	Polyester	7.43	0.32	4.3	7.10	7.74	2.92	0.85	29.2	1.96	3.58	1.19	0.12	10.4	1.09	1.33
	Viscose	3.33	0.92	27.6	2.61	4.36	1.44	0.09	5.9	1.34	1.49	0.62	0.22	35.1	0.41	0.84
d. Octanoic acid																
	Cotton	1.77	0.18	10.1	1.57	1.90	0.82	0.15	17.7	0.66	0.94	0.32	0.12	36.5	0.22	0.45
	Nylon	0.38	0.48	125.7	0.06	0.93	0.51	0.09	17.3	0.41	0.58	0.33	0.08	25.1	0.24	0.39
	Polyester	0.59	0.34	57.9	0.20	0.86	0.51	0.09	18.1	0.42	0.60	0.35	0.08	22.4	0.27	0.42
	Viscose	0.71	0.54	76.3	0.20	1.28	0.96	0.13	13.5	0.81	1.06	0.37	0.10	27.8	0.27	0.47
e. 6-Undecanone																
	Cotton	2.34	0.43	18.5	1.97	2.82	1.21	0.20	16.2	0.99	1.36	0.44	0.02	4.7	0.43	0.46
	Nylon	2.98	1.92	64.6	1.54	5.16	2.86	0.14	5.1	2.73	3.02	0.86	0.14	16.7	0.75	1.02
	Polyester	8.93	2.16	24.2	7.26	11.37	3.02	0.42	14.1	2.56	3.41	1.32	0.15	11.0	1.22	1.49
	Viscose	2.76	0.40	14.4	2.41	3.19	1.37	0.36	26.2	0.99	1.71	0.49	0.16	32.0	0.31	0.61
f. Undecanal																
	Cotton	2.63	0.52	19.9	2.27	3.22	1.30	0.48	37.0	0.75	1.60	0.50	0.07	14.0	0.46	0.58
	Nylon	0.95	1.63	171.4	0.01	2.83	2.55	0.27	10.5	2.24	2.75	0.84	0.15	17.4	0.68	0.97
	Polyester	2.24	1.56	69.9	1.03	4.01	2.74	0.44	16.0	2.26	3.12	1.59	0.43	26.7	1.25	2.07
	Viscose	0.30	0.32	106.9	0.01	0.64	1.26	0.45	35.5	0.78	1.67	0.40	0.15	37.4	0.23	0.50

Table 4.10

Significance of variables affecting the rates of release of VOCs from four experimental fabrics over 3 h, 8 h and 24 h

Two-way ANOVA ($\log_{10}$ transform)

Source	d.f.	SS	MS	F	p
a. Time = 3 h					
Fibre	3	3.777	1.259	8.579	0.000
VOC	5	6.676	1.335	9.098	0.000
Fibre/VOC	15	4.312	0.287	1.958	0.040
Error	48	7.045	0.147		
Total	72	23.176			
b. Time = 8 h					
Fibre	3	0.301	0.100	10.504	0.000
VOC	5	3.521	0.704	73.636	0.000
Fibre/VOC	15	1.084	0.072	7.557	0.000
Error	48	0.459	0.010		
Total	72	5.514			
c. Time = 24 h					
Fibre	3	0.955	0.318	18.026	0.000
VOC	5	3.071	0.614	34.795	0.000
Fibre/VOC	15	0.616	0.041	2.327	0.014
Error	48	0.847	0.018		
Total	72	14.722			

Table 4.11

Significance of differences in rates of release of VOCs from four experimental fabrics by main effect (fibre and VOCs) over 3 h, 8 h and 24 h

Tukey range tests ($\log_{10}$ transform)

3 h						8 h						24 h					
Interaction	$\bar{x}$	**n**	**Turkey's grouping**			**Interaction**	$\bar{x}$	**n**	**Turkey's grouping**			**Interaction**	$\bar{x}$	**n**	**Turkey's grouping**		
Fibres																	
Nylon	-0.19	18	│			Cotton	-0.02	18	│			Cotton	0.47	18	│		
Viscose	0.04	18	│	│		Viscose	0.00	18	│	│		Viscose	0.43	18	│		
Cotton	0.31	18		│	│	Nylon	0.07	18		│	│	Nylon	0.36	18	│		
Polyester	0.39	18			│	Polyester	0.14	18			│	Polyester	0.17	18			
VOCs																	
Octanoic acid	-0.25	12	│			Isovaleric acid	-0.20	12	│			Isovaleric acid	0.63	12	│		
Undecanal	-0.23	12	│	│		Octanoic acid	-0.18	12	│			2-Heptanone	0.57	12	│		
Isovaleric acid	0.09	12	│	│	│	2-Heptanone	-0.14	12	│			Octanoic acid	0.48	12	│		
2-Heptanone	0.23	12		│	│	6-Undecanone	0.25	12		│		6-Undecanone	0.16	12		│	
Nonanal	0.45	12			│	Nonanal	0.26	12		│		Nonanal	0.16	12		│	
6-Undecanone	0.54	12			│	Undecanal	0.28	12		│		Undecanal	0.15	12		│	

When all VOCs were combine, there were no significant differences observed in release rates by cotton and viscose in the first 3 h and 8 h at $p < 0.05$, but over 24 h viscose had a significantly higher rate of release than cotton. The rate of release from polyester did not significantly differ from cotton over 3 h, but was significantly different when evaluated over an 8 h and 24 h period. Polyester did differ significantly from viscose over all time periods. The rate of release for polyester and nylon differed significantly over 3 h as polyester released greater quantities of compounds during that first 3 h. Polyester and nylon also differed over 24 h, but not over 8 h. This was because nylon tended to have higher quantities of compounds remaining after 24 h but did not adsorb as much as polyester initially (see Tables 4.4 and 4.1 respectively).

For VOCs, there were significant differences for rates of release over all time periods. During the first 3 h, the lowest rates of release were apparent for isovaleric acid, octanoic acid and undecanal, which did not differ significantly from one another (see Table 4.11). Whereas, over the 8 h and 24 h periods isovaleric acid, 2-heptanone and octanoic acids exhibited the lowest rates of release and were not significantly different from one another. The lower rates of release for these three compounds were partly associated with the lower uptake of compounds initially (see Table 4.1 and Figure 4.1a). However, over the 3 h period, it was interesting that undecanal which had higher initial adsorption was much slower. Undecanal has a lower vapour pressure than all the other compounds except for 6-undecanone (see Table 3.3). Therefore, volatiles may not have dissipated as readily during that first 3 hours.

The results of the Tukey's HSD post-hoc tests indicating which fibre significantly differed from one another in release rates for each VOC is presented in Table 4.12. However, as previously mentioned the interaction effect between fibre type and VOCs were less significant than the main effects of fibre or VOC alone (Table 4.10). No significant differences were observed between cotton and viscose fabrics in the release rates of all VOCs over any of the periods at $p<0.05$, even at 3 h when cotton typically had faster rates of release than viscose. Over the entire 24 h period, there were few differences in rates of release of VOCs that were statistically significant among the fibre types.

Table 4.12

Significance of differences in rates release of six VOCs from experimental fabrics over 3 h, 8 h and 24 h

Tukey range tests ($\log_{10}$ transform)

		3 h						8 h					24 h				
VOCs	Fibres	$\bar{x}$	n	Tukey's grouping			Fabrics	$\bar{x}$	n	Tukey's grouping		Fabrics	$\bar{x}$	n	Tukey's grouping		
a. Isovaleric acid																	
	Nylon	-0.21	3				Nylon	-0.41	3	│		Nylon	-0.75	3	│		
	Viscose	0.10	3	│			Cotton	-0.17	3	│	│	Cotton	-0.69	3	│	│	
	Cotton	0.16	3	│			Polyester	-0.12	3		│	Viscose	-0.57	3	│	│	
	Polyester	0.30	3				Viscose	-0.11	3		│	Polyester	-0.51	3		│	
b. 2-Heptanone																	
	Cotton	0.11	3	│			Viscose	-0.25	3	│		Cotton	-0.63	3	│		
	Viscose	0.20	3	│			Cotton	-0.18	3	│		Viscose	-0.62	3	│		
	Polyester	0.27	3	│			Polyester	-0.11	3	│		Nylon	-0.60	3	│		
	Nylon	0.33	3	│			Nylon	-0.05	3	│		Polyester	-0.44	3	│		
c. Nonanal																	
	Nylon	0.47	3	│			Cotton	0.11	3	│		Cotton	-0.33	3	│		
	Viscose	0.51	3	│			Viscose	0.16	3	│		Viscose	-0.23	3	│		
	Cotton	0.54	3	│			Nylon	0.32	3	│	│	Nylon	-0.13	3	│		
	Polyester	0.87	3				Polyester	0.45	3		│	Polyester	0.07	3	│		
d. Octanoic acid																	
	Cotton	-0.52	3	│			Polyester	-0.30	3	│		Cotton	-0.52	3	│		
	Nylon	-0.49	3	│			Nylon	-0.29	3	│		Nylon	-0.49	3	│		
	Polyester	-0.47	3	│			Cotton	-0.09	3		│	Polyester	-0.47	3	│		
	Viscose	-0.44	3	│			Viscose	-0.02	3		│	Viscose	-0.44	3	│		
e. 6-Undecanone																	
	Cotton	0.36	3	│			Cotton	0.08	3	│		Cotton	-0.36	3	│		
	Nylon	0.42	3	│			Viscose	0.13	3	│		Viscose	-0.33	3	│		
	Viscose	0.44	3	│			Nylon	0.45	3		│	Nylon	-0.07	3		│	
	Polyester	0.94	3				Polyester	0.48	3		│	Polyester	0.12	3		│	
f. Undecanal																	
	Viscose	-0.43	3	│			Viscose	0.08	3	│		Viscose	-0.42	3	│		
	Cotton	-0.30	3	│	│		Cotton	0.09	3	│	│	Cotton	-0.30	3	│	│	
	Nylon	-0.07	3		│	│	Nylon	0.40	3	│	│	Nylon	-0.08	3		│	│
	Polyester	0.19	3			│	Polyester	0.43	3		│	Polyester	0.19	3			│

* means grouped by vertical lines are not significantly different at $p \leq 0.05$

There have been minimal investigations into rates of release or desorption of odorants from different textiles carried out. One of the only studies that have investigated this was a recent study by (Richter et al., 2018). They investigated the relative adsorption along with the desorption of six VOCs identified in body odour by cotton, polyester, and wool yarns using PTR-MS. The outcomes of their research indicated the low overall release of odorants by cotton whereas steady desorption from polyester yarns (Richter et al., 2018).

A similar trend was also observed in the current study. This can be explained due to the intermolecular forces related to the chemical structure of the fibres. In the case of low adsorption and low desorption of odorants by cotton, the available sites for hydrogen bonds likely resulted in binding the water molecules to the cotton fibres rather than sorptions of odorants, even when the compounds were more polar. The polar VOCs such as the carboxylic acids likely tended to remain in the water instead of being adsorbed by the different fibres. In addition, the chemical and physical properties of polyester fibres including hydrophobic nature and low swelling found to be not only the reason of the better sorption but also can be count as the reason of weak releasing of odorants even after washing (Hammer et al., 2013; Munk et al., 2000).

Chapter 5

Summary, conclusions, and recommendations

5.1 Summary

The purpose of this study was to determine the initial adsorption and desorption of six selected odorous VOCs by apparel fabrics composed of different generic fibres (cotton, nylon, polyester, viscose). As well, as to determine the amounts remaining in the fabrics following specific time periods (3 h, 8 h, 24 h) in order to indicate the rate of release or desorption of the VOCs from the fabrics. The selected VOCs were compounds that have been identified as being present in human body odour and/or unclean or old washing machines. Selected odorants varied in their functional groups and included two carboxylic acids (isovaleric acid and octanoic acid), two aldehydes (nonanal and undecanal), and two ketones (2-heptanone and 6-undecanone). The selected VOCs were added to an artificial sweat solution, and experimental fabrics were immersed in the odorous aqueous solution in order for odorants to be selectively adsorbed by fabrics. Following inoculation, fabrics were either extracted immediately in dichloromethane (initial adsorption) or deployed in a test chamber where VOCs were able to dissipate from the fabrics for selected time periods. The mixtures of extracted VOCs and DCM were concentrated to 1 mL and analyzed through the injections of 1μl into the GC-FID instrument. Recorded peak areas for both initial adsorption and chamber tests were normalized based on the weights of the fabrics. These values were converted to the relevant concentrations of compounds per weight of fabric (mg/g). The rate of release for each specific time period (3 h, 8 h, 24 h) was calculated and expressed as mg/g/h.

In general, cotton adsorbed the lowest amount of compounds from the sweat solution, and polyester adsorbed the greatest amounts. Viscose did not differ significantly from cotton fabrics in the initial adsorption of VOCs. Nylon tended to adsorb greater amounts of VOCs from the sweat solution than cotton and viscose (except for isovaleric acid) but less than polyester. For many of the fabrics/VOCs, the largest reduction in VOCs occurred during the first 3 h of deployment in the test chambers. Whereas, between 3 h and 8 h there was a slower rate of release exhibited. Nylon tended to exhibit the lowest overall release of VOCs during the 24 h period, with the greatest amounts of VOCs retained within nylon after 24 hours (with the exception of undecanal).

5.2 Conclusions

When odorants applied to fabrics in an aqueous synthetic sweat solution, synthetic fibres such as polyester and nylon typically adsorbed higher quantities of VOCs than cellulosic fibres such as cotton and viscose. This was particularly notable for the non-polar odorants with higher log K_{OW} including nonanal, 6-undecanone, and undecanal. Of the two synthetic fibres, polyester which is more hydrophobic, adsorbed higher quantities of odorants than nylon, particularly for the aldehydes. Although amounts of VOCs initially adsorbed by viscose and cotton were not significantly different, viscose consistently adsorbed slightly higher quantities of VOCs than cotton.

Rates of the release of VOCs from fabrics can vary depending on the fibre content of the fabric. Despite having very different fibre chemistries cotton and polyester fabrics released VOCs more rapidly than nylon and viscose during the first 3 h. Whereas, after 8 h, amounts of VOCs remaining in cotton and viscose were not significantly different. That cotton initially released VOCs quickly compared with viscose may be due to the higher moisture absorbency of viscose resulting in slower drying time. The release rates of VOCs by fibres with similar fibre chemistries may be affected by the drying process. Moreover, polyester generally exhibited the fastest rate of release of odorants over the 8 h and 24 h periods, with some exceptions. A generally low rate of release was exhibited by nylon which suggests more VOCs are trapped within the fibre. Nylon retained greater quantities of both carboxylic acids (isovaleric acid and octanoic acid) than polyester after 24 h which may be due to its ability to form hydrogen bonds with the polar compounds.

This research has furthered our understanding of why some selected fibre types (i.e. cotton and viscose) are perceptibly less odorous than others (i.e. nylon and polyester) following wear and even laundering. This research has demonstrated that when odorants in an aqueous solution are transferred to fabrics, hydrophilic fibres will have preferential sorption of water molecules and initially adsorb fewer odorants. Whereas, hydrophobic fibres will preferentially adsorb odorants and therefore retain higher quantities of odorous compounds, to begin with. All compounds including water-soluble compounds adhered less to cotton and viscose than the synthetic fibres (with the exception of isovaleric acid for nylon). Due to the hydrophilic nature of the cellulosic fibres, there is a higher tendency for forming hydrogen bonds between fibres and water molecules than the odorants. For all fibres, higher amounts of the non-polar odorants adsorbed to fibres through the partitioning process in an aqueous solution, which suggests that the non-polar compounds are more important in overall textile malodour than polar compounds.

5.3 Limitations and recommendations

This study will serve as a base for future study in the area of textile science due to the advantages of the experimental method. More realistic conditions from which interactions between VOCs existing in body odour and/or unclean washing machines with clothing fabrics in the aqueous liquid phase were provided. Furthermore, the release of VOCs was conducted in test chambers which enables the ability to control the environmental conditions of release. This method imparted notable differences in findings compared to previous research studies. However, there were limitations in the current study which should be addressed in future research:

1. There were some challenges in selecting the VOCs using in the current study. A limited number of compounds were available and overlaps between peak areas of certain chemicals were detected in preliminary tests. As a result, only six VOCs were selected from three functional groups (i.e. carboxylic acid, aldehyde, and ketone)
2. The dissolved solution of the compounds in the synthesized sweat solution resulted in a cloudy mixture. This indicated creation of heterogenous mixture which may have caused some inconsistency in the sorption of compounds by fabrics.
3. The fabric tests were all ISO test fabrics with taking no finishing and dyeing process which is different from available and usually used fabrics in the apparel industry. Furthermore, there was no sample consisted of blending different fibre contents.

4. The collected samples were concenterated through conducting K-D evaporator. The solutions started boiling after transffering to the column. For better monitoring the volume of the solution, the K-D evaporator was removed from the water bath. In this research, the 3 ball scynder column was removed for a short time (less than 30 second) and then attached to the flask again. This can result in loss of some compounds during taking this steps.

Based on some of these limitations but also on the need to progress the research in odour within textiles, the following recommendations are made:

1. The sorptions and releasing of only six selected odorants were investigated in a mixture due to the limitation in the availability of the compounds with no overlap. However, body odour consists of vast numbers of VOCs with other functional groups rather than only carboxylic acids, aldehydes, and ketones. Thus, considering other chemical groups along with increasing the numbers of compounds is important for further research.
2. The solutions of odorants were dissolved in methanol then added into the aqueous synthetic sweat solution. Some of the VOCs such as undecanal and 6-undecanone are insoluble in water. These chemicals in association with methanol/water solution formed a heterogeneous mixture with detectable oily parts. Finding a better alternative as a carrier compound in order to produce a homogenous mixture of both polar and non-polar compounds in the aqueous solution is essential.
3. All the fabrics were undyed ISO standard fabrics that did not have any additional finishing processes beyond bleaching. Therefore, they differed from what is available in the apparel industry and worn as clothing. Thus, determining the influence of dying or specific finishing treatments as well as examining blends of different fibres may demonstrate variations in sorptions and release rates trends of odorants.
4. Humidity and temperature in the test chambers were 60.99 ± 30.16% RH and 28.63 ± 6.22% °C respectively. However, these conditions do not reflect the humidity and temperature that would generally be experienced in a home environment. Therefore,

conducting these desorption tests at lower temperatures and humidities that may better reflect room temperature which is when volatiles could release is important.

5. There was possibility of lossing chemicals through concenterating process by using K-D evaporator due to the removing the 3 ball synder column. To avoid this error, taking the whole K-D evaporator set-up from the water bath witthout deattaching any part is recmmended.

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Appendix A

Screening of selected VOCs

Several odorants were screened in order to select six final VOCs. The purpose of screening the VOCs was to determine that it was possible to include all compounds in the odorant/sweat solution. Some of the odorants screened could not be used in the mixture with other VOCs due to overlaps observed between two or more peak areas within the GC chromatograms. One of the selected odorants was nonanal due to the frequency that it is mentioned in the literature (Bernier et al., 1999; Curran et al., 2007; Haze et al., 2001; Stapleton et al., 2013). While the retention time of the benzaldehyde when it was injected into the GC-FID as a single compound was 4.06 min, adding it in the mixture containing nonanal (with the retention time of 8.08 min) benzaldehyde showed another peak with the retention time of 8.13 min. Thus, there was the risk of overlap of benzaldehyde with nonanal due to their close retention times (Figure A.1).

Another VOC that was originally screened was hexanoic acid. The detected retention time for this compound was 7.06 min. However, when preparing a mixture of VOCs including hexanoic acid and 6-undecanone (with the retention time of 10.61 min) indicated an overloaded peak with the retention time of 10.81 min. There was a risk of later overlap between hexanoic acid and 6-undecanone due to the changed of the retention time of an overloaded peak in lower concentration (Figure A.2). The ketone 6-undecanone was one of the VOCs detected in unclean washing machines and was therefore chosen instead of hexanoic acid for this study, so that there were two VOCs from each chemical group.

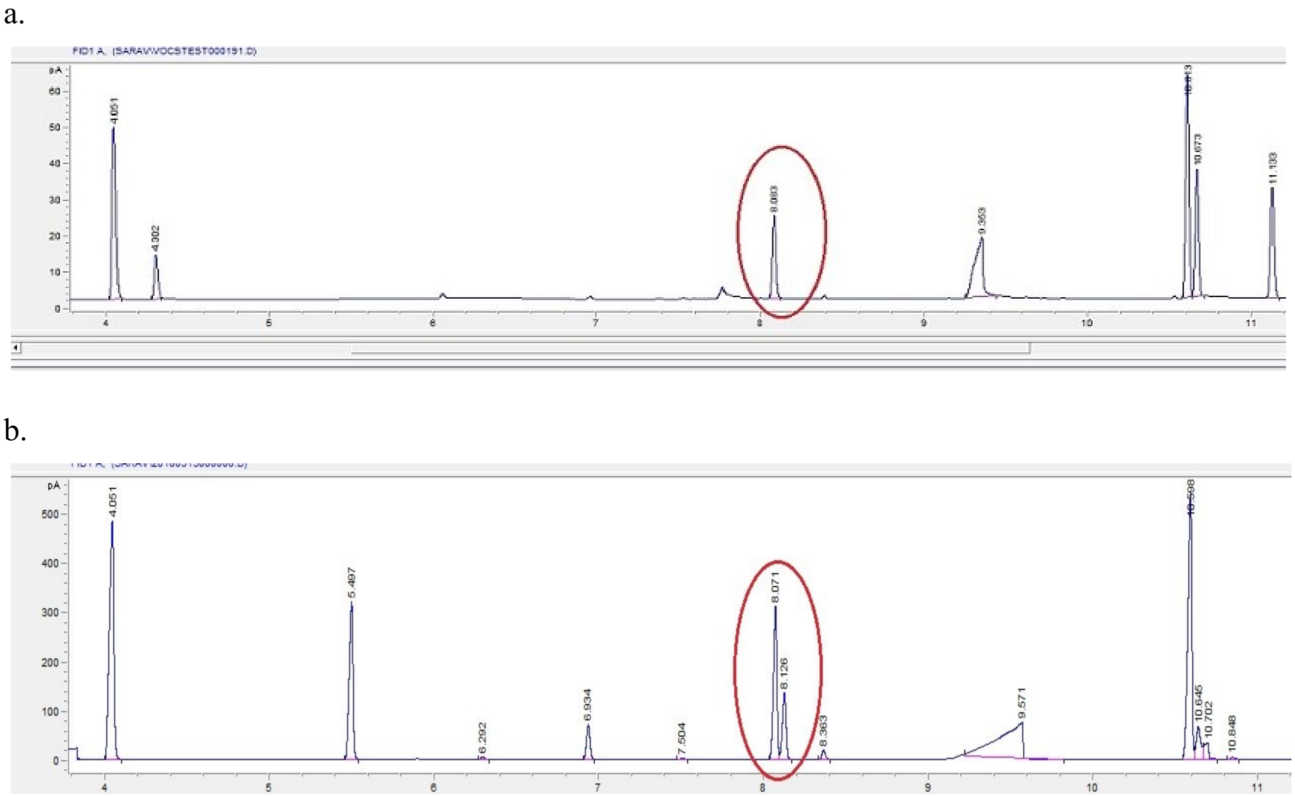

Figure A.1

Chromatograms of selected VOCs a) without benzaldehyde, b) with benzaldehyde

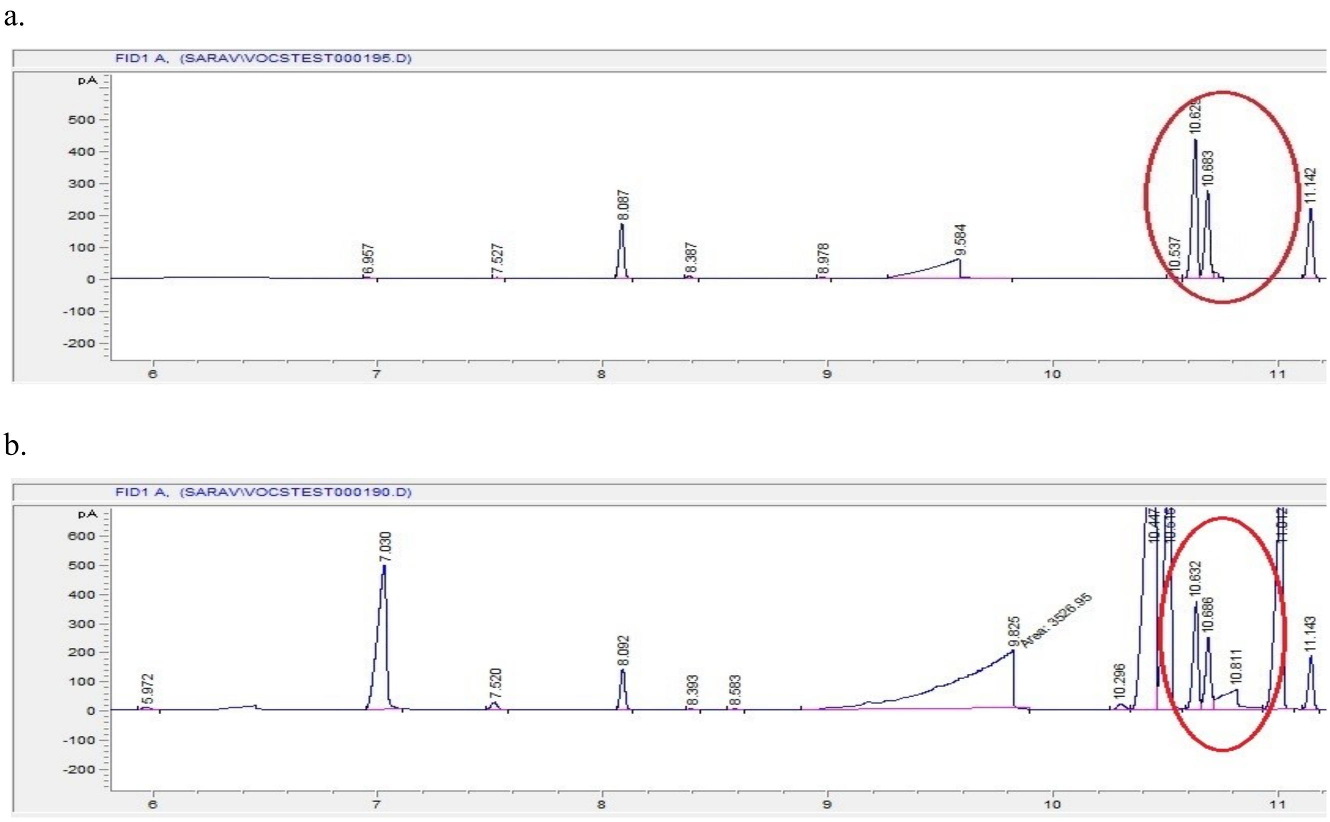

Figure A.2

Chromatogram of selected VOCs a) without hexanoic acid, b) with hexanoic acid

Appendix B

Examples of the chromatograms of test fabrics

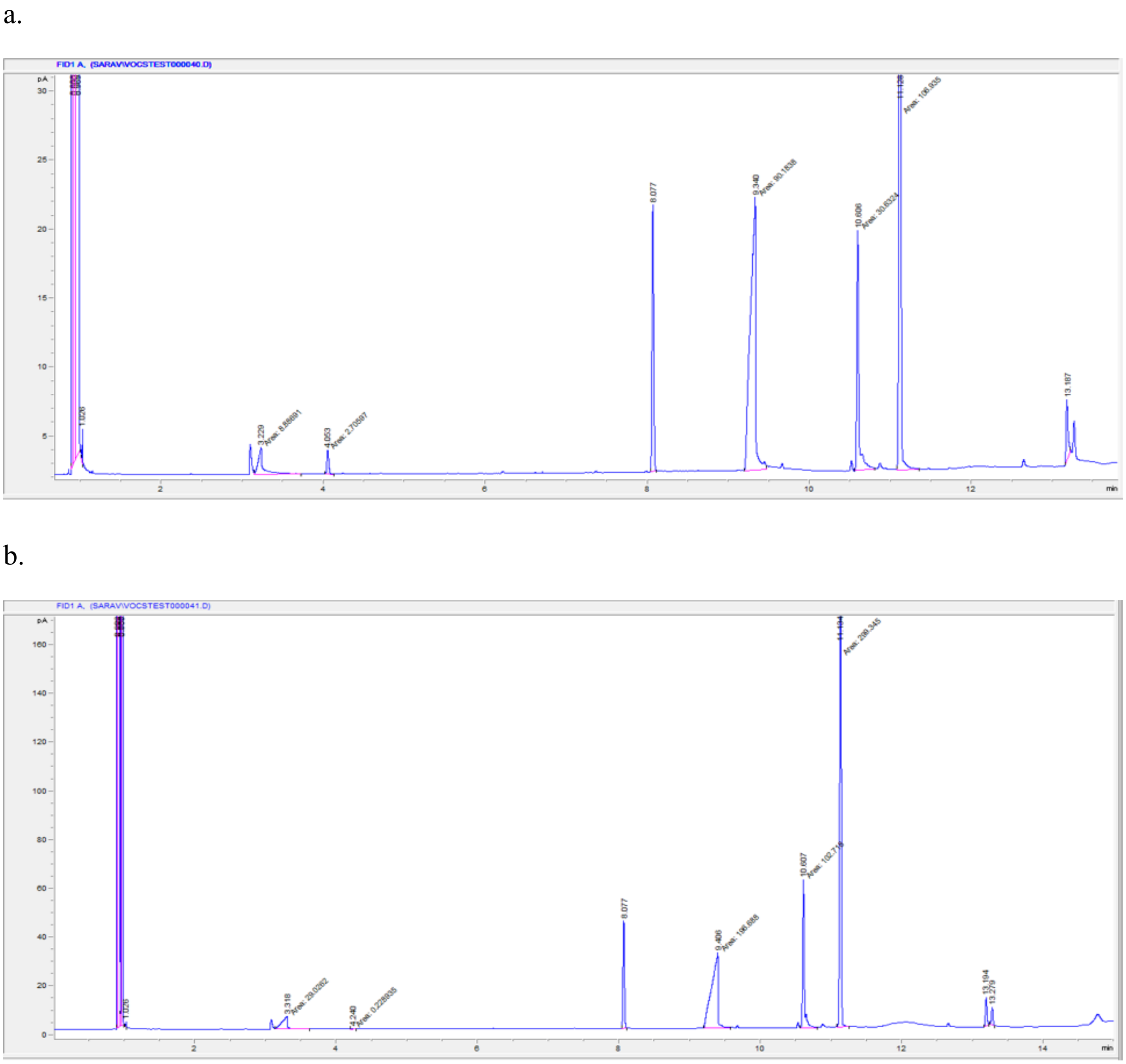

Figure B.1

Chromatograms of the extracted VOCs from; a) cotton and b) viscose swatches at 3 h

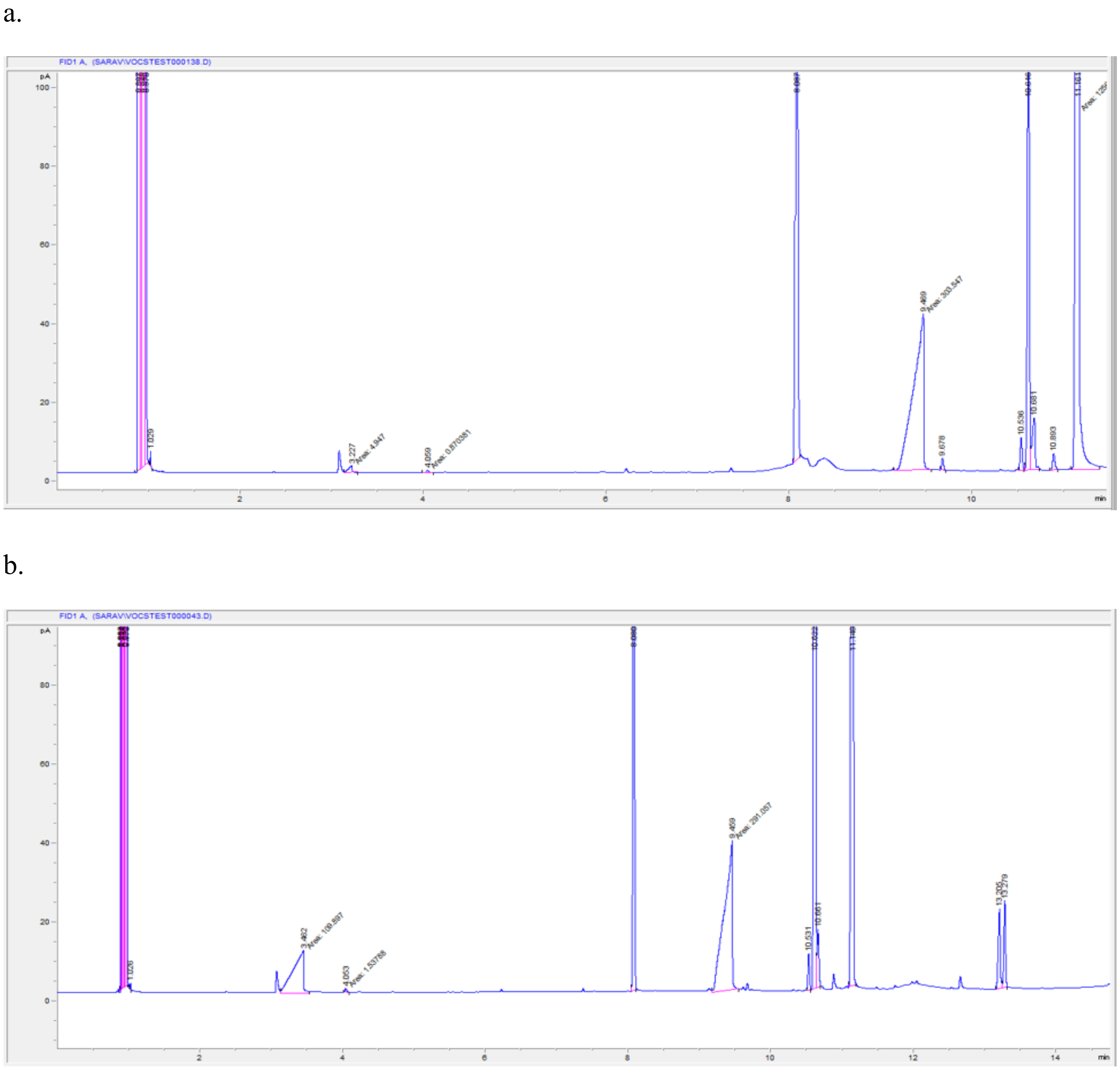

Figure B.2

Chromatograms of the extracted VOCs from; a) polyester and b) nylon swatches at 3 h

Appendix C

Percent recovery

Table C.1

Concentrations of directly injection of chemical mixture (4000 µg/mL) and extracted VOCs from fabrics

Source	Compounds					
	Isovaleric acid	2-heptanone	Nonanal	Octanoic acids	6-udecanone	Undecanal
Base line	4126.14	4196.08	4284.18	4329.11	3924.89	3898.78
Cotton	1485.31	1105.75	709.11	1475.47	705.50	1022.53
Nylon	1945.75	1196.11	848.38	1717.81	764.97	1286.92
Polyester	1139.96	881.19	582.02	1171.83	556.61	854.05
Viscose	1372.38	1096.06	719.88	1369.91	686.73	1099.70

Table C.2

Recovery percentages

Fabric	**Compounds**					
	Isovaleric acid	**2-heptanone**	**Nonanal**	**Octanoic acids**	**6-udecanone**	**Undecanal**
Cotton	36.00	26.35	16.55	34.08	17.98	26.23
Nylon	47.16	28.51	19.80	39.68	19.49	33.01
Polyester	27.63	21.00	13.59	27.07	14.18	21.91
Viscose	33.26	26.12	16.80	31.64	17.50	28.21