

Textile Fibre Fragments in Marine Environments and their Interaction with Suspended Hydrocarbons

by

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## Abstract

Pollution by microplastics is one of the biggest current environmental problems, due to the great amount of plastic waste that is used worldwide, as well as the threat they represent to fauna that might ingest them, particularly in aquatic environments. One of the main sources of microplastics, is the shedding of synthetic fibre garments during laundering. The impact of these particles relies not only on the internal physical damage, but also on their capacity to absorb harmful pollutants in the water systems, acting as a concentrating vector. The effectiveness of these textiles fragments to absorb different pollutants is dependant on their physical morphology as well as their fibre chemistry. The purpose of this study was to evaluate the sorption capacity of four polyaromatic hydrocarbon (PAHs) pollutants by textiles fragments coming from three types of fabrics used in the textile industry. The experimental fabrics were 100% fibre content plain weave cotton, polyamide, and polyester. The selected PAHs are commonly found in by-products of fossil fuels combustion and tobacco smoke, phenanthrene, pyrene, fluoranthene and carbazole. Small fragments of each type of fabric were submerged in saturated solutions of each compound in deionized and artificial saltwater for 24 hours with gentle agitation twice per day. Aliquots of the aqueous phase was filtered and recovered via liquid-liquid extraction with dichloromethane, to be analyzed through gas chromatography – flame ionization detection.

The results showed a trend in the absorption capacity for the three fabrics. Cotton presented the lowest affinity towards the PAHs, followed by polyamide, while polyester showed the highest affinity towards them. Hydrophobic and hydrophilic sites in the fibres structure might be the main driving force that control these interaction pollutants-fibres. This work has showed that while both types of natural and synthetic textiles have the potential to absorb PAHs compounds from aquatic systems, synthetic fibres interact easier and at a higher degree with them.

## **Preface**

This thesis is an original work by Oscar Rene Arredondo Campos. No part of this thesis has been previously published.

## **Acknowledgments**

I would like to thank my supervisor Dr. Rachel McQueen for the opportunity to be part of her research group. I am deeply thankful for all the support, patience and understanding that she demonstrated towards me during the length of my program. I never felt lost or without direction during my academic journey, whether on program requirements, courses, or experimental phase of the research. I am also thankful for her support and words of encouragement during my hardest time of the program, as she always cared about my mental health and academic performance. Thanks to a great researcher and better human being.

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## List of definitions

Absorption	The process of one material being retained by another. This may be the physical solution of a gas, liquid, or solid in a liquid, attachment of molecules of a gas, vapour, liquid, or dissolved substance to a solid surface by physical forces (Calvert, 1990)
Adsorption	An increase in the concentration of a dissolved substance at the interface of a condensed and a liquid phase due to the operation of surface forces. Adsorption can also occur at the interface of a condensed and a gaseous phase (Calvert, 1990)
dtex	deci tex. In textile industry, unit used for linear density of a fibre. Denotes the weight in grams of 10,000 meters of yarn
Fibres	In textiles, a generic term for any one of the distinct types of materials that form the basic elements of a textile and that is characterized by having a length at least 100 times its diameter
Fibre fragments	Term proposed by the NOAA to avoid confusion between the concept of “microfibre” as in fragment of textile, and “microfibre” as the materials developed for use in different textile industries
Hydrophilicity	Hydrophilicity is the tendency of a molecule to be solvated by water (van de Waterbeemd et al., 1997)
Hydrophobicity	Hydrophobicity is the association of non-polar groups or molecules in an aqueous environment which arises from the tendency of water to exclude non-polar molecules (van de Waterbeemd et al., 1997)
Microfibre	Ultra fine synthetic fibres with a linear density less than 1 dtex
Microfibres	Microplastic particles smaller than 5 mm, with a length is 100 larger than their width (Gaylarde et al., 2021)
Microplastics	Plastic particles whose larger dimension do not exceed 5 mm (Auta et al., 2017)
Polar compound	A chemical compound whose molecules exhibit electrically positive characteristics at one extremity and negative characteristics at the other
Sorption	Physical and chemical process through which a substance become attached to another. It encompasses both absorption and adsorption phenomena

Non-polar  
compound

Any compound either with covalent molecules or lack of permanent dipole moment

## Chapter 1

### Introduction

Plastic products are commonly employed in every kind of human activity, from daily life necessities to industrial processes. However, plastic pollution represent a significant environmental problem and is a topic of major policy and scientific concern (Geyer et al., 2017; Jambeck et al., 2015). The United Nations has estimated that a staggering 400 million tonnes per year of plastic waste is released into the environment worldwide (United Nations environment, 2019), mainly due to the mismanagement of plastic waste at both the domestic and industrial scale. Plastics are not only pervasive within the environment, due to their high resistance to weathering (i.e., chemical and photo-oxidation) and to biological degradation they also persist within the environment (Browne et al., 2007; Liu et al., 2020; Schmidt et al., 2017). The half-life of plastics can be as high as 5000 years (Chamas et al., 2020).

Plastic waste can be present in a wide variety of size and shapes, with the largest objects being the scope of public attention due to global dependence on single-use plastics for many consumer products (Xanthos & Walker, 2017) and the graphic nature of impact on aquatic environments. However, plastics at a smaller scale, commonly referred to as microplastics, also represent an equally severe threat to every ecosystem, particularly to marine and freshwater aquatic environments (Bakir et al., 2014; Dris et al., 2015; Eerkes-Medrano et al., 2015). Microplastics include all kinds of plastic or synthetic particles that are smaller than 5 mm on their largest dimension (Auta et al., 2017).

Microplastics may arise from larger plastics as they are mechanically broken down into smaller particles (secondary microplastics) but microplastics can also enter the ecosystem in the micro-scale already (primary microplastics) (Estahbanati & Fahrenfeld, 2016). Sources of primary microplastics can vary from microbeads in cosmetics, rubber from tires and fragments of fibres released from synthetic textiles (e.g., polyester, acrylic). In fact, the release of primary microplastics in the form of textile fibres has been estimated as one of the largest contributors to microplastics in the oceans worldwide (Periyasamy & Tehrani-Bagha, 2022). Fibre fragments can be released during textile manufacture, but more importantly (and continuously), during domestic laundering (Hartline et al., 2016; McIlwraith et al., 2019). Approximately 35% of primary microplastics estimated to be released come from domestic laundering (Boucher & Friot, 2017). Some reports have estimated that in a single 6 kg load of laundry anywhere from 600 to over 700,000 fibrous microplastics can be released (Browne et al., 2011; Napper & Thompson, 2016; Zhang et al., 2019). Laundering of non-synthetic textiles such as natural

cellulose (e.g., cotton, linen), natural protein (e.g., wool, silk) and regenerated cellulose (e.g., rayon) also release and shed fragments of fibres during laundering. However, their environmental load has been deemed less concerning because natural and cellulosic fibres are more easily degraded by weathering or microbial activity, reducing significantly their lifespan in the environment (Periyasamy & Tehrani-Bagha, 2022).

The ecological threat of microplastics in the environment is due to their adverse interaction with marine organisms, from plankton and mollusks, to mammals and birds (Bosker et al., 2019; Giani et al., 2019; Holland et al., 2016; Zhu et al., 2019). Marine organisms can ingest these particles through breathing or during feeding, confusing microplastics as a food source. Once inside the body, microplastics can cause different effects, such as muscular tear, fake sense of satiety and subsequent nutrition deficiency (Eerkes-Medrano et al., 2015). Fibrous fragments (often referred to as microfibrils in the environmental science literature, and more recently, “fibre fragments” in the textile science literature) are also concerning for the ecology of aquatic biota, as their longer length can become entangled in gastrointestinal tracts causing blockages (Absher et al., 2019). Microplastics have also been identified as a potential “pathway for the transmission of pollutants, monomers, and plastic additives” (Browne et al., 2011). The potential to concentrate chemicals has also been raised as a concern for non-synthetic fibre fragments as well (Doucet et al., 2021). However, research in the area of chemical odorants suggest that in aqueous solutions cellulosic fibres take up less compounds than synthetic fibres (Abdul-Bari et al., 2020; Vaezafshar, 2019). Nonetheless, despite the recognition of microplastics and fibre fragments as potential sources of concentrating and transferring toxic chemicals to aquatic organisms there has been little research in this regard, as few studies have examined the contribution of chemical absorbed in the synthetic and non-synthetic fibre fragments.

### **1.1 Statement of the problem**

Fibre fragments released from synthetic and cellulosic clothing during laundering have the potential to absorb chemical pollutants present in the sewage system, and other environmental contaminants in aquatic environments such as lakes, rivers and the ocean. Sorption of these chemical pollutants onto fibre fragments can pre-concentrate these compounds which can lead to a higher exposure to aquatic organisms once they are ingested (Koelmans et al., 2016). The nature of chemical pollutants can vary considerably and may arise from sources such as improperly disposed medicine, chemical solvents and heavy metals (Brennecke et al., 2016; Turner, 2016). It is, therefore, important to understand the interactions between chemical pollutants and fibre fragments in order to better understand the behavior inside the bodies of aquatic organisms.

## **1.2 Justification**

The current state of the art for interaction between microplastics (which includes synthetic fibre fragments) and aquatic fauna has been mostly focused on the identification and quantification of these particles present in the organisms, and how they impact different behavioral aspects, such as feeding and fertility rate (Auta et al., 2017; Han et al., 2010). The quantification of synthetic fibre fragments released from domestic laundering related to textile and laundry parameters has also been another major focus in the current field of research on fibre fragment pollution. While important to know at what degree microplastics can accumulate in the organism, and the parameters that facilitate fibre fragment release via laundry, it is also important to identify what types of fibres are more likely to absorb and/or adsorb chemical pollutants.

This research is necessary to understand the harm that can be caused by microplastics and synthetic and cellulosic fibre fragments. To contribute to this goal, the present research focuses on the interaction between three types of fibres (cotton, polyester, and polyamide) and four chemical compounds (phenanthrene, pyrene, carbazole and fluoranthene) that are present as pollutants in the environment in two types of aqueous environments (freshwater and saltwater). Polyester and cotton make up the majority of consumer textiles fibres, while polyamide has very different chemical and physical properties from polyester and is also common synthetic fibre in consumer textiles. There is evidence to suggest that synthetic fibre fragments will accumulate more chemical pollutants than cellulosic fibre fragments. There is also evidence to suggest that among synthetic fibres that non-polar pollutants will have a higher affinity toward polyester than polyamide fibres (Vaezafshar, 2019). The research is conducted to evaluate the uptake capacity of each fibre type for each pollutant to assess the potential of different fibres to contribute to intensifying chemical toxicity.

## **1.3 Objectives**

The specific objectives of this study are to:

1. Evaluate the uptake of four selected chemicals (phenanthrene, pyrene, fluoranthene and carbazole) by fibre fragments which vary in fibre content (cotton, polyester, and polyamide) when exposed to chemicals mixed in deionized water.
2. Evaluate the uptake of four selected chemicals (phenanthrene, pyrene, carbazole and fluoranthene) by fibre fragments which vary in fibre content (cotton, polyester, and polyamide) when exposed to chemicals mixed in a saltwater solution.

## 1.4 Hypotheses

The following research hypotheses have been proposed:

Hypothesis 1:

- a) Cotton fibres will take up lower amounts of compounds than polyester and polyamide fibres, when exposed to compounds in freshwater solutions.
- b) Polyester fibres will take up higher amounts of compounds than polyamide fibres, when exposed to compounds in freshwater solutions.

Hypothesis 2:

- a) Cotton fibres will take up lower amounts of compounds than polyester and polyamide fibres, when exposed to compounds in saltwater solutions.
- b) Polyester fibres will take up higher amounts of compounds than polyamide fibres, when exposed to compounds in saltwater solutions.

## Chapter 2

### Review of Literature

#### 2.1 Microplastics and fibre fragments in the environment

##### 2.1.1 Microplastics

Although there is not an official definition of what constitutes a microplastic, it is well established in the literature that microplastics are plastic particles smaller than 5 mm (Auta et al., 2017; Browne et al., 2007; Ivar do Sul & Costa, 2014). Two categories of microplastics exist based on their origin, secondary and primary. Secondary microplastics are the result of fragmentation of larger plastics. Plastics are subjected to mechanical forces associated with exposure to wind, sand and water, as well as embrittlement by exposition to the sunlight, fragmenting them into smaller pieces (Browne et al., 2007a; Liu et al., 2020; Schmidt et al., 2017). Primary microplastics are particles that enter the environment already in a small size. They may be designed to be useful in small sizes (e.g., plastics used in cosmetics such as exfoliants and toothpaste) or are generated from the abrasion of larger plastics during production, use and/or maintenance (e.g., wearing of tires, fragments of fibres from synthetic clothing) (Boucher & Friot, 2017; Gaylarde et al., 2021). Secondary microplastics do not undergo any significant change in chemical properties, and as such they maintain their resistance to biodegradation.

Both primary and secondary microplastics (MP) small dimension allows them to increase their reach, not only in geographical distribution, but also in impact on living organisms. Miller et al., (2017) found evidence of MP across the Hudson River basin in New York State, US. The surveyed length of the river covered about 450 km starting from a mountainous area up to the Atlantic Ocean. MP were detected across the whole river at different concentrations, even in the mountain areas, suggesting transport of these particles through atmospheric mechanisms. Yang et al. (2015) examined the presence of MP in 15 brands of commercial table salt, from three different types of salt producing locations across China: sea-water lakes, inland salt lakes, and rock/well salts. Their results showed that salt-water lakes contained the highest concentration, followed by inland salt lakes and the rock/well salts contained the lowest quantities. The authors correlated the abundance of MP to population density, with far higher populations in the coastal zones compared to inland China. Furthermore, even remote areas like Antarctica are not exempt to MP pollution, as Munari et al. (2017) showed that from the total plastic debris found in the sediments near a research station, 78.4% were MP. In this case, the presence of MP is not due to transport from abroad, but local generation; 94.13% by weight of the MP corresponds to

styrene-butadiene-styrene copolymer (SBS), a type of polymer used among others in tires, shoes' soles, and waterproofing systems. MP presence has also been documented on the Arctic Ocean, from deep sea sediments (Bergmann et al., 2017) up to the surface, where some regions has been identified as accumulation zones for plastics (Cózar et al., 2017). The biological impact has been widely addressed in a broad range of marine species, from small filter feeders (Bosker et al., 2019; Cho et al., 2019; Luan et al., 2019) to mammals and birds (Holland et al., 2016; Zhu et al., 2019).

### **2.1.2 Fibre fragments**

Despite their small size (< 5 mm), not all microplastics are the same. Particles that are less than 5 mm in length and less than 10 µm in diameter, are now commonly referred to as microfibrils in the environmental science literature (Mishra et al., 2019). In the textile industry microfibrils are a common description for the ultra-fine synthetic fibres that have a linear density of less than 1 dtex knitted and woven into soft and supple clothing (Srinivasan et al., 2007). Therefore, within the textile industry literature these fibrous microplastics – and sometimes also natural and regenerated fibres – recognized as environmental pollutants, may instead be referred to as “fibre fragments” (FF) to avoid confusion (American Association for Textile Chemists and Colorists, 2021; Wood, 2020)

## **2.2 Release of microplastics into the environment.**

As previously mentioned before, microplastics have the potential to reach remote areas of the world (Bergmann et al., 2017; Munari et al., 2017; Yang et al., 2015), as due to their small size, these particles are easily transported by wind and water currents. Bank & Hansson (2019) coined the concept of the plastic cycle, as “the continuous and complex movement of plastic materials between different abiotic and biotic ecosystem compartments, including humans” (p. 7177). They argued that the presence and impact of plastics (including MP) is now a biogeochemical cycle, as it is not only limited by proximity to the source of waste, but is affected by natural cycles (e.g., water, wind, and carbon cycles). This approach is supported and expanded by other works ((Rochman et al., 2019; Y. Zhang et al., 2019; Zhang et al., 2022). After being produced or released around urban/industrial centres, MP can directly access aquatic environments through nearby waterbodies such as rivers and lakes; or by being carried over by wind currents. Particles present in aquatic environments can be mobilized to other locations, precipitate to the sea floor, be ingested by aquatic organisms. For those close to the surface, they can be dispersed into the air by evaporation of their surrounding water. MPs being transported by atmospheric phenomena, eventually precipitate to the surface of the Earth. This includes remote areas such as cryosphere regions (e.g., glaciers), where the relative darker



MPs reduce the albedo index of the icy surface and absorb the sun's energy increasing the temperature of ice and accelerates glacier thawing. In turn this accelerated melt of the ice pack causes the MP to return to the sea or lakes by run-off. All these mechanisms were condensed and illustrated by Zhang et al. (2022), as shown in Figure 2.1.

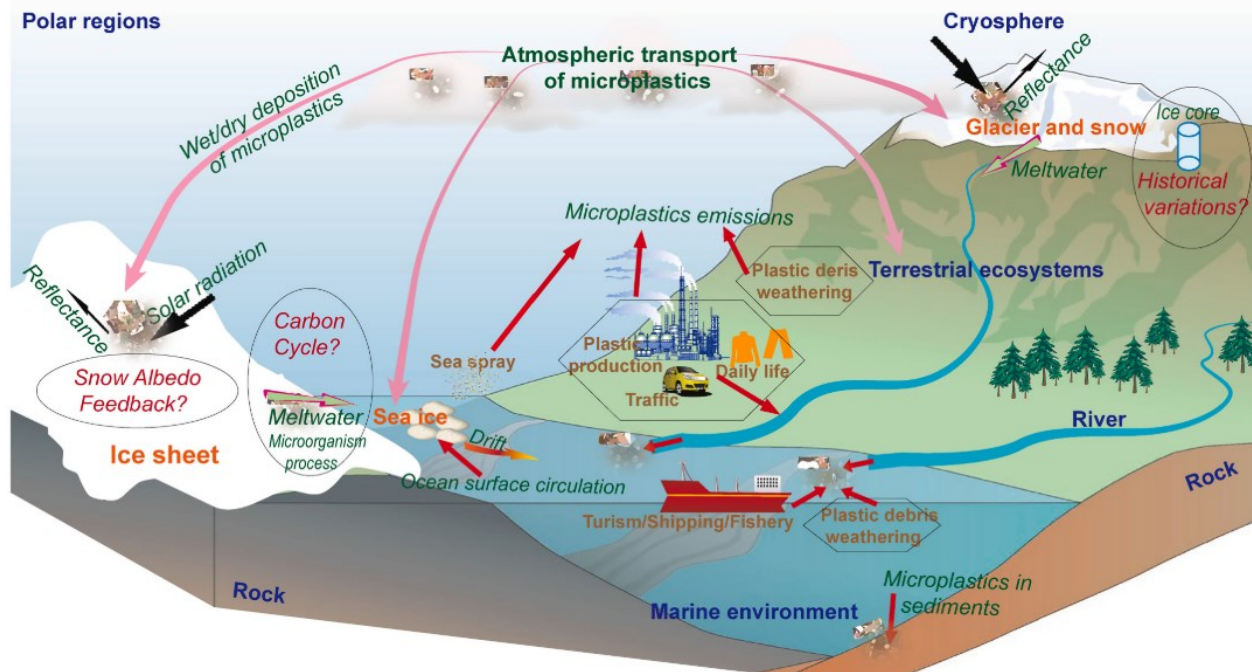


Figure 2.1 . Plastic and microplastic transportation in the environment (source, Zhang et al., 2022).

### 2.2.1 Microfibre release from textiles due to laundering

During laundering, garments are subjected to mechanical forces favouring the fabric abrasion of the fabric. The quantity of fibre fragments shed from textiles can vary depending on the fibre, yarn, fabric and finishing processes applied to the fabric (De Falco et al., 2020). As well the detergent, water temperature, use of softeners, type of washing machine and water volume can also influence fibre fragments release (Rathinamoorthy & Raja Balasaraswathi, 2020).

Therefore, it is expected that a major source of environmental fibre fragments stems from household laundering of clothing and textiles (Browne et al., 2011; De Falco et al., 2019; Mishra et al., 2019; Vassilenko et al., 2021). However, sources from textile manufacture have also been found.

The connection between domestic laundering and synthetic microfibre release was first made by Browne et al., (2011). The research team sampled eighteen shoreline sediments from across

six different continents to identify the abundance of MP, and whether they present a correlation with the proportions of MP found in sewage effluents or not. They found substantial quantities of the tiny, elongated MP identified to be small fragments of textile fibres (i.e., fabric fragments). Higher concentration of these synthetic MF ranged from 2 to 31 fibres per 250 mL of sampled sediments, with an average predominant composition of polyester (56%) and acrylic (23%) MF, while the composition in sewage effluents was similar polyester (67%) and acrylic (17%). As such, the authors concluded that most of the FF in shore sediments comes from textile washing, rather than weathering fragmentation. Higher densities of microfibrils near sewage disposal sites and in high population areas provided further evidence that the microfibrils were released through the domestic laundering of synthetic clothing and linens (Browne et al., 2011).

Synthetic textiles represent the main source of microfibrils associated with shedding during the washing of synthetic garments, particularly synthetic “fleeces” that have had mechanical treatments to raise fibres on the surface (Vassilenko et al., 2021). However, synthetic textiles are not the only type of fabrics that require cleaning after use. Natural fibres of vegetable or animal origin such as cotton and wool, and other manufactured fibres such as the regenerated cellulosic fibres (e.g., viscose, modal) are also present in many types of consumer apparel and household textiles. In fact, non-synthetic textiles have been suggested to release high quantities of microfibrils due to their short staple and generally weaker strength (Browne et al., 2011). Cotton fibres, for example, are particularly prone to fracture during wet abrasion which makes them susceptible to fibre loss during laundering (McQueen et al., 2017). Cellulosic microfibrils have been identified as the main source of microfibrils in the Canadian Arctic and lakes in Ontario (Adams et al., 2021; Athey et al., 2020). Nonetheless, cellulosic microfibre pollution has generally been perceived to be less concerning. This might be attributed to the fact that natural and regenerated cellulosic fibres are more prone to natural mechanisms of degradation through weathering and microorganism metabolism (Brown, 1994; Cottonworks, 2018). Cotton demand in 2014 was estimated at 23.58 million tonnes, although considerably less than the 41.73 million tonnes of polyester (Carmichael, 2015), cotton still makes up a significant quantity of textiles requiring laundering. Due to its prevalence in the Arctic (Adams et al., 2021), understanding the potential environmental consequences of cotton is still relevant. Furthermore, despite cellulosic fibres being biodegradable under natural environmental conditions much more rapidly than polyester (Li, Frey and Browning, 2010), they can still take up to five years to decompose in some conditions (Henry et al., 2019), and have similar implications for malnutrition of aquatic life (Doucet et al., 2021).

Sillanpää & Sainio (2017), tested the quantity of fibres released by two cotton garments and four different polyester textiles due to laundering (water temp. 40°C, spin-dry rate 1200, for 75 min). The six textiles were brand new and unused and were each washed five times separately. To avoid cross contamination and allow easy identification, each textile was monochromatic (except one with two colours) and washed alternately. The washing effluent was collected in a polyethylene container, from which three replicate samples were taken for each textile and filtered with previously weighed 0.47 µm filters, to record the weight of the MF collected before MFs were examined under an optical stereoscopic microscope. They found that polyester textiles released from  $2.1 \times 10^5$  to  $1.3 \times 10^7$  fibres per kilogram of garment in the first wash (0.12 to 0.33% w/w) and decreased to a maximum of  $5.3 \times 10^6$  by the fifth wash. Cotton on the other hand, released up from  $3.6 \times 10^6$  to  $4.6 \times 10^6$  fibres per kilogram during the first wash (0.17 to 0.26% w/w), and  $1.1 \times 10^6$  after five washes. Based on the experimental data and based on the population of Finland and average laundry habits estimated the annual release of MF in Finland. They estimated that 110 trillion and 490 trillion MF may be released per year by polyester and cotton textiles respectively, corresponding to 154,000 kg and 411,000 kg for each textile respectively (Sillanpää & Sainio, 2017). The fabric of the textile (e.g., fleece, soft-shell) influenced the amount of fibre shedding among the polyester fabrics, accounting of the wide variability in fibre loss.

In a similar manner, Napper and Thompson (2016) performed an experiment to estimate the release of MF by new acrylic, polyester, and polyester/cotton shirts. They obtain an average value of  $7.3 \times 10^5$ ,  $5.0 \times 10^5$  and  $1.4 \times 10^5$  MF released per load (6 kg) of each type of fabric, equating to much lower quantities of fibre release per kilogram than those reported by Sillanpää & Sainio (2017). Differences among these values with those from Sillanpää & Sainio's (2017) study may be attributed to the use of detergent, softener and different temperature during the washing. However, the yarn and fabric structure and finishing treatments applied to the garments may also account for the large differences. Detailed information about the commercially purchased textiles were not provided. Although, Sillanpää & Sainio (2017) included fabrics that were clearly fleece (raised fibre surfaces). The textile structure was less clear in the study by Napper and Thompson (2016).

In the earliest work conducted by Browne et al., (2011), the authors compared three polyester garments (blanket, fleece and shirt), and reported a maximum release of >1,900 fibers per wash for the fleece clothing, which has been broadly referenced in the literature. It stands out the difference in three orders of magnitude between the values of this paper and the two previously mentioned, but the reason is not obvious with the content of the paper. Softener and detergent

were not used, commercial washing machines were employed, and effluent filtered sample was used to count the MF. However, there is no description of the methodology used for the counting, neither for the instrumentation nor for the statistical treatment of the data. Nonetheless, this pioneering work by Browne et al., (2011) highlighted this environmental concern and showed the dangers of particular types of polyester garments (e.g., fleece materials). Subsequent research by other environmental scientists have identified differences in the quantity of microfibre shedding, which has contributed to the literature significantly. Although, some are limited by insufficient information about the experimental fabrics (e.g. Napper & Thompson, 2016; Sillanpää & Sainio, 2017). Furthermore, various studies have used different methods for laundering and counting making it difficult to compare across studies (Gaylarde et al., 2021; Hartline et al., 2016). There are now many more studies which have examined fibre, fabric structure and laundering parameters on MF release during laundering (Lant Id et al., 2020; Rathinamoorthy & Raja Balasaraswathi, 2020). Recently the AATCC test method (American Association for Textile Chemists and Colorists, 2021) as been implemented which may help address the concerns of standardization and at least allow different fabrics to be compared.

### **2.2.2 Role of Wastewater Treatment Plants in reducing MF environmental release**

Despite the fact that MF abundance in washing machine effluents is somehow similar to those observed in shoreline sediments, these particles do not get directly from the washing machine to the sewage discharge. First, they pass through wastewater treatment plants (WWTP), which are the main facilities to remove solid particles from water. However, despite many of the MF which are released with the laundry effluent being captured by the filtering system in WWTPs a significant number pass through. As the research by Browne et al. (2011) originally indicated a fraction of the MF are not recovered from the waste water and therefore end up on shorelines. Even WWTP that meet the requirements for water quality established by the European Union's Wastewater Treatment Directive are not able to completely remove these particles. With the objective of assessing the role of WWTP as a route for the liberation of MP to the environment, Talvitie et al. (2015) conducted a study in the Viikinmäki WWTP, which provides treatment to sewage produced by about 800,000 habitants in the city of Helsinki. The samples were taken from four different stages of the treatment process (influent, after the primary and secondary sedimentation phases, and after the denitrification unit), as well as sea water and sediment samples from the underwater discharge line of the WWTP, and the archipelago next to the city. The concentration of MP present at the beginning of the process (i.e., raw sewage) was 180 fibres and 430 synthetic particles per liter. During the process, they observed a decrease in the amount of these particles, as after the primary sedimentation the concentration dropped down to

14.2 fibres and 291.7 synthetic particles per liter, while the secondary sedimentation the concentrations were of 13.8 and 68.6 particles per liter respectively. After the denitrification treatment, immediately before the release of the treated water, the concentrations were of 4.9 fibres and 8.6 synthetic particles. Overall, this indicate that the efficiency rate of this WWTP reached about 98% for the removal of fibres and microplastics in wastewater. The authors attribute the notable decrease of concentration to the deposition and capture of these particles in the sludges. On one hand sludges can be considered potential sinks to minimize the environmental impact of MF and MP as long as the sludge produced were subjected to proper control and containment measurement. On the other hand the sludge has the potential to release the MP back into the environment when they are used as fertilizer in crops (Henry et al., 2019). Therefore, this again highlights how imperative it is that MF and MP release are prevented at the source (e.g., washing machines, non-shedding textiles). Regarding the samples taken in the discharge zone and the archipelago, the authors reported concentrations of 1.7 fibres and 7.2 particles per kilogram of sediment for the former, and 0.01-0.65 fibres and 0.5-9.4 synthetic particles per liter. These findings show that MP settle near the source, but due to marine currents, can be transported into the open sea, and that although WWTP can remove a big fraction of MP, these facilities can be considered as an access point into the environment.

### **2.3 Prevalence and impact of MP and FF on aquatic organisms**

Independently of what is the driving source in a specific environment, pollution by these particles is a problem that has been identified worldwide. Because of this, many marine and fresh water living forms are currently at risk of being exposed to these materials. Many studies have been conducted to identify and evaluate the impact that MP have on the aquatic fauna that inhabit different regions of the marine and freshwater environment, from the sea floor to the surface. Impacts have been observed on different species of fish (Giani et al., 2019; Pozo et al., 2019; Rodrigues et al., 2019), mollusks (Bosker et al., 2019; Cho et al., 2019; del Carmen Alejo-Plata et al., 2019; Hermabessiere et al., 2019; Luan et al., 2019), sea mammals (Zhu et al., 2019) and even birds (Holland et al., 2016; Tanaka et al., 2013; Terepocki et al., 2017). For the purpose of this review, the diversity of affected animals will be grouped according to the zones of the column water they spend most of their time in. The first group of discussion encompass those organisms that by limited movement or living habits spend most of their time on the sea floor, like bivalves and coral; the second group refers to organism that are more activities and interactions along the water column, like fish and cephalopods; while the last group is focused on organisms that interact at higher degrees with the surface of the sea, like cetaceans, birds and plankton.

### 2.3.1 Sea floor

#### *Bivalves*

MP have the potential to be dispersed from the source point to the bulk of the sea, and denser particles can deposit at the bottom of the sea, whether in shallow coastal regions or in the open sea. This section of the water column is known as benthic zone, an ecological region where many types of organisms live (Scheer et al., 2004), from microorganisms (e.g. bacteria and fungi) to crustaceans, bivalves and even coral. Bivalves have been the object of attention for evaluation studies, from a health perspective they represent a significant fraction of human sea food consumption. For instance, between 2010-2015 an average of 15 million tonnes per year were produced making up 14% of total marine production. Furthermore, due to their attributes and feeding pattern bivalves (as with other benthic organisms) serve as a good living probe to monitor the presence of pollutants in the marine environment. Bivalves are broadly distributed across the world, sedentary, tolerant to environmental pollution, have a low capacity to metabolize enzymatically organic compounds, have a long life-span and are easy to identify due to their size (Zhou et al., 2008). These organisms obtain nutrients by filter feeding, a process that involves the suction of water to retain small organisms (plankton and algae) and suspended organic matter. It is during this process that pollutants, such as MP, enter the organism without being partially or completely expelled.

South-eastern countries have a high production rate of sea food. Four domestic species (oyster, scallop, mussel and Manila clam) representing 70-84% of shellfish consumption in South Korea were used as monitoring species (Cho et al., 2019). The samples were obtained in fishery markets of three major cities. The study identified an average of 0-1.08 MP particles per gram of bivalves (without shell), or 0-2.8 MP particles per individual. The most abundant types of polymers were polyethylene, polypropylene, polystyrene and polyester, which together they encompassed 80% of the MP observed. The authors also reported fibres, with polyester being the most abundant (82%), polypropylene and acrylic in second place (6% each) and lastly polyamide (3%). Due to this abundance, the authors suggested textiles as the source of the synthetic MF.

Meanwhile Hermabessiere et al. (2019) surveyed 100 mussels and 100 cockles obtained from two estuarine bays and one beach to evaluate the relationship between MP contamination and concentration of 40 pollutants (polycyclic aromatic hydrocarbons, polychlorinated biphenyl, polybrominated diphenyl esters, organochlorine pesticides and phthalates) in this region. MP presence was higher in bivalves coming from estuaries than beaches (58% and 34% respectively). In total 1,636 particles were observed, 324 of which were fibres (due to their thinness the authors could not analyse their composition by  $\mu$ -Raman). From the remaining

1,312 particles that could be analysed, 5-32.8% were MP, 0-2.5% pigment containing particles, 6.6-21.5% from natural origin (e.g., shell fragment and minerals), and 27-60.9% was not possible to identify. MP abundance was different from estuarine bays than the beach, as 0.7 MP per individual was observed in the former, while 2.46 MP per individual was identified in the latter. Observed FF may not all be included as MP, as cotton and other natural fibres may have been present. However, this research does support the relationship between laundering of textiles and MP/FF present in the environment.

Magni et al. (2019) identified the impact on proteins of zebra mussels coming from a freshwater environment, when exposed to two different concentrations of MP (i.e., low concentration:  $5 \times 10^5$  of  $1 \mu\text{m}$  and  $5 \times 10^5$  of  $10 \mu\text{m}$  MP; high concentration:  $2 \times 10^6$  of  $1 \mu\text{m}$  and  $2 \times 10^6$  of  $10 \mu\text{m}$  MP). When compared to a blank, mussels exposed to the lower concentration showed no significant difference, while those exposed to the higher concentration presented alterations in 78 proteins. These changes might be due to two different causes: the direct effect of MP on the cell by oxidative stress, and as a response of the organism to mitigate the stress. The proteins affected were related to the function of the protein synthesis, energy processes, cellular metabolism, and cytoskeleton. These observations in the protein profile might indicate that the mechanisms involved in the damage by MP on mussels is caused by oxidative stress processes.

### *Coral*

Corals are a type of marine polyp invertebrates well-known for their creation of coral reefs, submarine structures that work as an environment that can host a wide diversity of species. Coral reefs also serve to provide protection to the coast in cases of natural hazards, like tsunamis and hurricanes. So far, the impact of MP in these organisms have not been fully explored. A quantification study to identify the consumption of MP by a species of coral (*Dipsastrea pallida*) from the Australian Great Coral Barrier (Hall et al., 2015). Polypropylene shavings (0.395 g/L) were used to simulate and evaluate the exposure and intake of MP for two days. The identification on MP consumption was assessed by observing particles in the mouth and the mesentery (a radial structure of tissue that divides the cavity of the polyp where the digestion takes place). Once the consumption was confirmed, coral was exposed to two lower concentrations (0.197 and 0.24 g/L). MP particles were observed in about 21% of the polyps, and although they do not report a concentration per individual, they estimate the consumption of MP per hour, equivalent to 14-660  $\mu\text{g}/\text{cm}^2\text{h}$ . MP particles ingested may be difficult to excrete from the organism, as they were stored deep in the mesenterial tissue of the polyp, which may handicap their digestive mechanism, as this tissue is responsible of it.

### 2.3.2 Column water

#### *Fish*

Just like bivalves, fish species represent a considerable fraction of human consumption from marine sources, with a production of 90.3 million tonnes in capture (i.e. fishing of wild populations), of which 79.3 come from marine environments, and 80 million tonnes for aquaculture, with a marine contribution of 28.7 million tonnes (Food and Agriculture Organization of the United Nations, n.d.). Because of this, MP presence and effects on fish have been broadly studied. The retention of MP in the gastrointestinal tract of three oceanic fish species (*Trachurus murphy*, *Shangomera punctatus* and *Merluccius gayi*), and three coastal species (*Eleginopis macovinus*, *Aploactylus punctatus* and *Basilichtys australis*), from the Biobío region in Chile, which contributes to 36% of the fishery production of that country were examined (Pozo et al., 2019). The oceanic species cover from low to high trophic levels (i.e., from herbivores to carnivores in the food chain), while the coastal species are carnivore, herbivore and detritivore (feeding from organic matter in the sediments) respectively. Ten individuals of each species were analysed. Only MP particles were observed in both oceanic and coastal species, with sizes ranging from <0.5-5mm, with ~77% being polystyrene phthalate, and ~23% polyester. It is worth mentioning that FF were present in 20 out of 60 individuals. In the oceanic fishes *T. murphy*, *S. punctatus* and *M. gayi*, FF could be identified in 1, 3 and 1 individual of each species respectively. For the coastal fish species *E. macovinus*, *A. punctatus* and *B. australis*, FF were present in 3, 2 and 10 specimens of each. *B. australis* is a detritivore species, which feeds on dead organic matter, which might explain why every specimen had MF. Another factor is that the coastal zone receives the discharge of domestic and industrial wastewater, which contributes to a higher concentration of MP (FF in this case). The authors recognized the limitation that the small sample represents. Therefore, these results can be considered a preliminary, but not representative of the actual level of contamination by MP/MF.

Another study carried out in three different zones of the Mediterranean Sea around Italy reported the presence of MP in 19.7% and 26.8% specimens of *M. barbatus* and *M. merluccius*, respectively. Fibres were the most common type of particles (44% and 81%), while the sizes ranged from <0.3-25mm, with 0.5-1 mm being the predominant size (22% and 36% respectively) (Giani et al., 2019). On the slope of the South China Sea (L. Zhu et al., 2019), 35 fish from 13 species were collected from the sea bottom of the sea (200-1,500 m deep), with identified presence of MP in stomachs of 34 of the specimens (97.1%), and in intestines of 33 (94.3%), with an average concentration of 1.53 particles per gram in stomach, and 4.82 particles per gram in intestines, the maximum concentration in both cases were 3.8 and 17.87 particles per gram, respectively. The authors mention that a previous study identified the



presence of MP in planktonic organism in that region, therefore, the presence of these particles in fish might be related to their feeding habits.

### *Cephalopods*

The impact and presence of MP in cephalopods have not been broadly studied. In one work, *Argonauta nouryi*, an octopod was the focus of the research (del Carmen Alejo-Plata et al., 2019), with the aim to identify the presence of MP in the body of female specimens. The argonauts present a sexual dimorphism, where only females construct a shell that acts as a brood chamber. In order to do so, 177 predator fish specimens that prey on the argonauts were obtained from traditional fishers in the Gulf of Tehuantepec coast, Oaxaca, in southern Mexico. The stomach content was extracted, and only the individuals with undigested remains of the octopod were taken into account (137). All of the argonauts' remains contained microfibers across different sections of the body (gills, intestines, ovaries and oviducts). The average concentration was 67 FF per individual, with a minimum of 5 FF and a maximum of 914 MF. FF presence in the predator fishes where argonauts remain were observed were higher than on those without, but they were still present. This serves as evidence that FF can transfer across the trophic chain and can bioaccumulate in the highest levels.

### **2.3.3 Sea surface**

#### *Cetaceans*

Cetaceans and marine mammals that function as apex predator (i.e., top of the food chain). Because of this, it is expected to observe the occurrence of different pollutants obtained through bioaccumulation. Being a bigger species, and sometimes classified as endangered, they can play three important roles regarding environmental preservation: monitor species, attract public awareness for ecosystem protection and conservation, and as a result, the protection of co-occurring species, as recounted by Zhu et al. (2019). However, the impact of MP/FF in cetaceans is mostly unexplored. The authors aimed to identify the abundance, size and type of MP in the intestinal tract of the Indo-Pacific humpback dolphin (*Sousa chinensis*). The specimens were stranded individuals, two adults and one calf retrieved from the Guangxi Beibu Gulf, China. Of the observed particles, 68% were MP, 24% non-MP, and 8% unidentified particles. MP abundance across the three specimens were of 30 and 45 for the adults, and 2 in the calf. The most abundant types of MP were polyester, polypropylene, polyethylene, polyamide, and polybutyrate phthalate, but cellulose, wool and cotton FF were also identified.

#### *Birds*

Coastal birds feed largely on a broad variety of marine species thus, they are prone to ingest a great amount of MP consumed by their prey. Tanaka et al. (2013) examined the occurrence of

polybrominated diphenyl ethers (a flame retardant applied to plastics and textiles) in twelve birds individuals (*Puffinus tenuirostris*), in the Hokkaido Prefecture in Japan. Additionally, three lanternfish and one squid were collected from the same region, which are common prey of the *P. tenuirostris*. Plastic fragments were observed in all of the birds, and nine of them presented different types of polybrominated compounds that have been observed in their prey. However, three birds contained other heavier types of these compounds that have not been observed in their prey. This finding suggests that the plastic debris found in the birds are responsible for the liberation of chemicals that otherwise are not present in the food chain. In contrast, Holland et al. (2016) conducted an study on freshwater birds (ducks, geese and loons) across Canada, to identify anthropogenic debris in the stomach of these birds. Common eiders were used as a marine bird control. It is important to note that some of these species live in marine environment but move to inland freshwater for breeding purposes). There were 350 specimens studied, and MP were observed in 39 (11%) of them, with no significant difference when compared to the marine species. This suggests that the geographic distribution and closeness to urban centers does not play an important role on the amount of MP that is ingested by birds across the country.

## **2.4 Fibre chemistry**

### **2.4.1 Cotton**

Cotton can be considered the most important natural fibre used for textile purposes, with an estimated production of 26.2 million tonnes worldwide (representing 24% of the total fibre production) (Textile Exchange, 2021). Raw cotton fibres consist primarily of cellulose (95%), with the remaining percentage corresponding to proteins, ashes, wax, sugars among other compounds (Wakelyn et al., 2007). Cellulose is a natural polymer built by hundreds to thousands of  $\beta(1\rightarrow4)$ -D-glucose units (Cook, 2001), named in this way due to the bonding sites of the glucose monomers through the carbons in the first and fourth position, as shown in Figure 2.2a.

Each cotton fibre is a seed-hair composed by an elongated single cell composed by several layers arranged in a concentric structure. The lumen is located at the center, surrounded by the secondary cell wall, a transition layer, followed by the primary wall and finally the cuticle as the external layer. During the development of the fibres, liquid cellulose is added into the inner layers to thicken the fibre (Wakelyn et al., 2007). The general structure of a cotton fibre is shown in Figure 2.3b. Figure 2.2c shows the appearance of cotton fibers used in this work under optical microscopy, with an objective of 400x, with the lumen visible and the typical helicoidal structure throughout the fibre.

As with all textile fibres structures, cotton presents zones with crystalline and amorphous array, but due to the slow addition and accumulation of cellulose in the inner layers of the fibre, it forms microfibrils in a mostly crystalline array. These crystalline microfibrils provide a strong and rigid structure to the fibres (Hsieh, 2006). The polymer chain does not only provide a solid structure to the fibre, but also plays an important role in the interaction with other compounds. Due to the abundant presence of hydroxyl groups (three per glucose unit), cotton fibres' surface have a strong affinity towards polar compounds through the formation of hydrogen bonds via inter- and intra-molecular interactions, as well as the pore structure (Hsieh, 2006; Wakelyn et al., 2007).

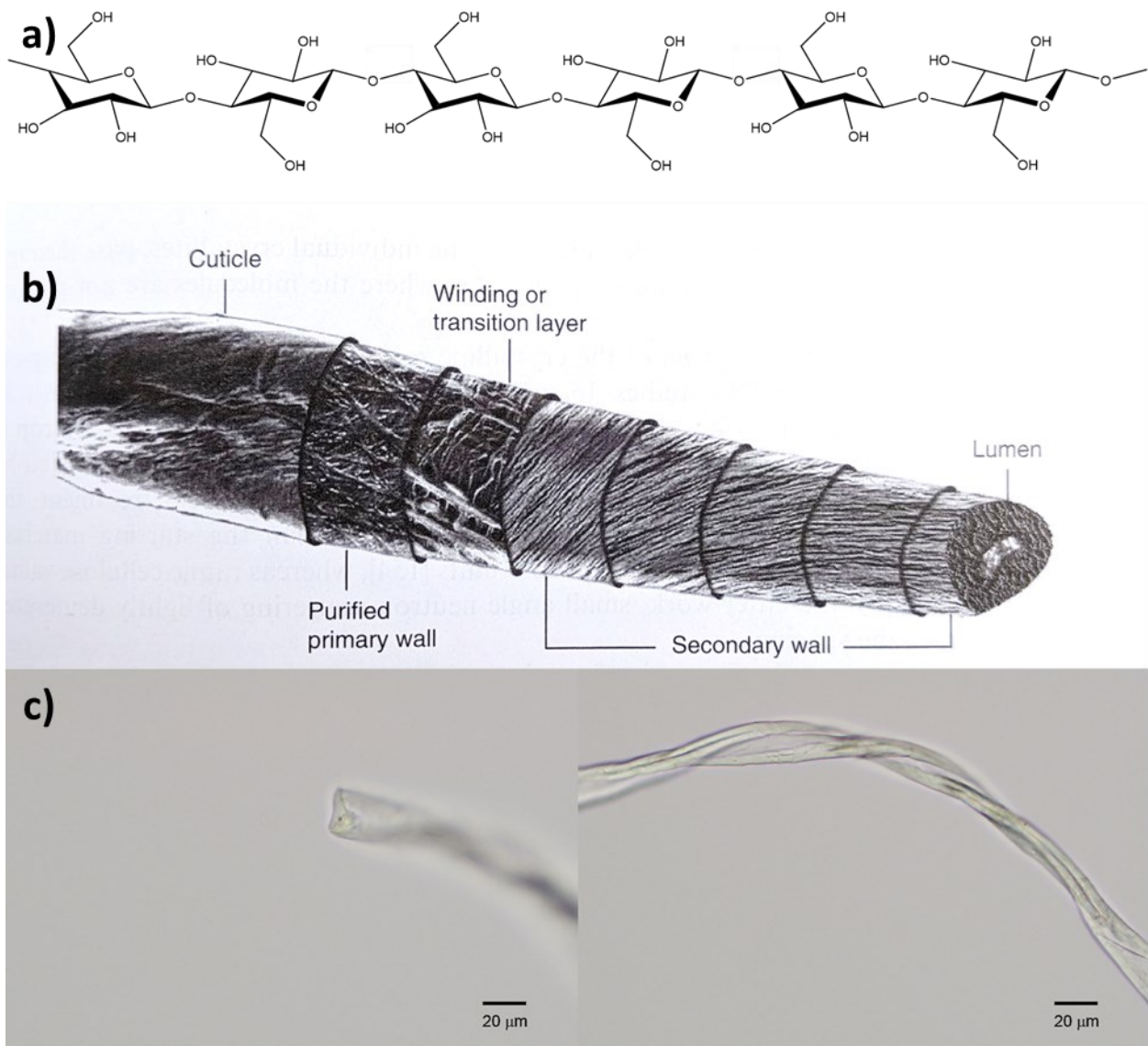


Figure 2.2 a) Chemical structure of cotton; b) general layer structure of cotton (Wakelyn et al., 2007); c) lumen and helicoidal structure observed in cotton fibres (Wakelyn et al., 2007)

## 2.4.2 Polyester

Just like cotton represents the most important natural fibre used for textiles purposes, polyester is the most popular among the synthetic fibres. Polyester had a total production of 57.1 million tonnes during 2020, almost twice as much as cotton, which represented 52% of the fibre production worldwide (Textile Exchange, 2021). Although polyester encompasses a group of polymers containing ester functional groups, in the textile world polyester fibres refer most commonly to poly(ethylene terephthalate) (Figure 2.3a), a long-chain polymer consisting by repeating units of the monomer ethylene terephthalate (at least 85%) (Cook, 2005). Polyester is synthesized through the reaction of terephthalic acid and ethylene glycol, in which the removal of water is crucial for the correct production of the polymer (Jaffe & East, 2007). Polyester fibres are composed of regions with alternating amorphous and crystalline arrangements. In Figure 2.3b, polyester fibres observed under the microscope with 400x magnification, these regions can be observed, shown as dark spots throughout the fibre.

Due to the high content of aromatic rings along the polymer chain, it is possible to obtain  $\pi$ - $\pi$  interactions between the rings. This also confers a hydrophobic property to the fibres, limiting their interaction with polar compounds, and reducing the permeability to water to the inner structure. As a result, polyester fibres present a higher affinity towards non-polar compounds (e.g., compounds containing aromatic rings, mostly organic compounds) (Cook, 2005; Jaffe & East, 2007).

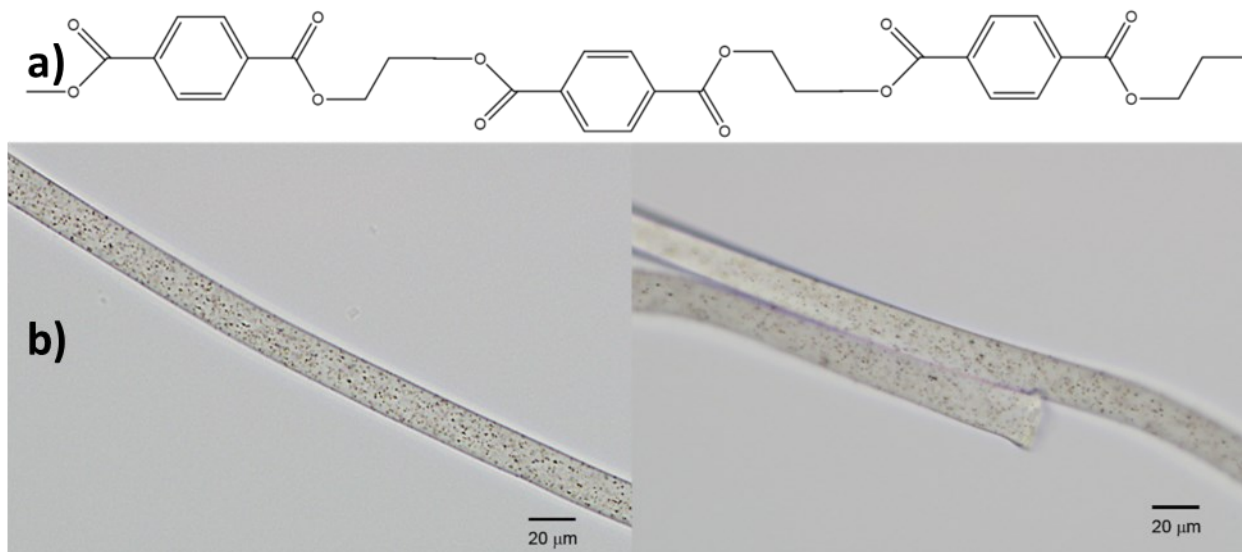


Figure 2.3 a) Polyester chemical structure; b) optical microscopy image of polyester fibres.

### 2.4.3 Polyamide

Polyamide, also known in the textile world as nylon, is the second most used synthetic fibre; with 5.4 million tonnes produced each year. This represents only 5% of textile production worldwide, so in terms of market share remains well behind cotton and polyester (Textile Exchange, 2021). Polyamide (nylon) refers to a group of similar compounds where the monomers are linked to each other through an amide group (Clark, 2020). Polyamides can be compounds which are either aliphatic (e.g., nylon 6) or aromatic (e.g., para-aramids such as Kevlar®).

In the case of aliphatic polyamides, they are distinguished from each other based on the number of carbons present in the monomers. For example, the two most popular polyamides used for consumer apparel applications are nylon 6 and nylon 6,6. The former is composed by at least 85% of the 6 carbon monomer  $[\text{NH}-(\text{CH}_2)_5-\text{CO}]$ , while the latter is made out of two different alternating 6 carbon monomers  $[\text{NH}-(\text{CH}_2)_6-\text{NH}-\text{CO}-(\text{CH}_2)_4-\text{CO}] - [\text{NH}-(\text{CH}_2)_5-\text{CO}]$  (The Essential Chemical Industry, 2018). The chemical structure for both can be seen in Figure 2.4a.

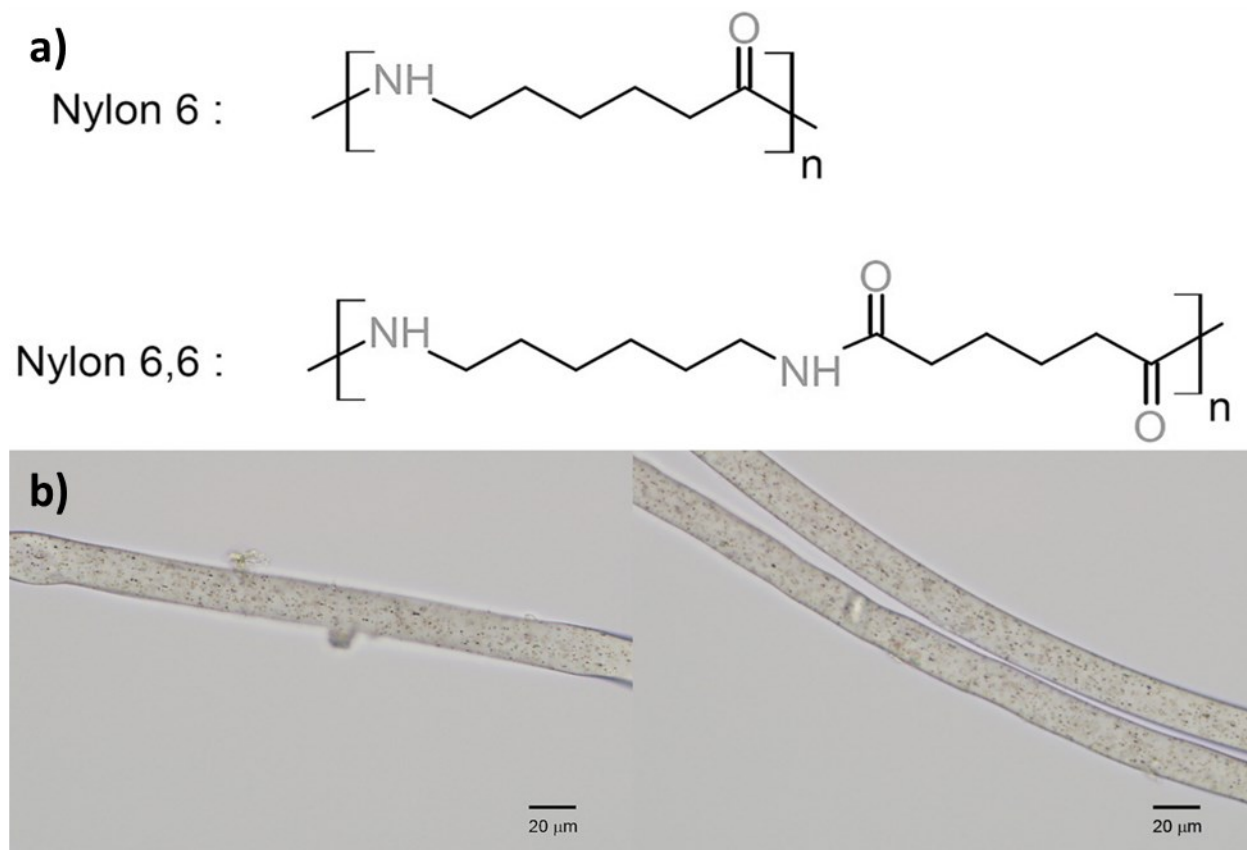


Figure 2.4 a) Chemical structure of the monomer units in nylon 6 and nylon 6,6; b) optical microscopy image of polyamide (nylon) fibres.

For all polyamides, the high content of amide groups in the polymer creates sites with partially hydrophobic properties (aliphatic chain), and hydrophilic zones, due to the presence of oxygen and nitrogen atoms, which can form hydrogen bonds with polar compounds. And similarly, to polyester and other polymer fibres, polyamides present sites with crystalline and amorphous arrangement of the monomers. The nylon 6 fibres used in this work were observed under optical microscopy, where these amorphous/crystalline regions can be observed as black spots along the fibres (Figure 2.4b)

## **2.5 Polycyclic Aromatic Hydrocarbons (PAHs)**

Amongst the many types of pollutants present in the environment, one heavily associated with anthropogenic activity is polycyclic aromatic hydrocarbons (PAHs). The structure of these compounds consists of only carbon and hydrogen atoms arranged in at least two aromatic rings (benzene), which can be ordered in linear, angular or cluster groupings (Park & Penning, 2008). PAHs can be classified in small and large PAHs, based on the number of aromatic rings in their structures, with six being the limiting number (Abdel-shafy & Mansour, 2016; Fetzer & Fetzer, 2010).

### **2.5.1 Sources of PAHs**

PAHs are mainly produced during incomplete combustion of fossil fuels (coal, oil and wood) (Masih et al., 2012), as well as in tobacco, mainly produced during its combustion (i.e. environmental tobacco smoke), or as accidental deposition during the curing of the tobacco leaves. Despite PAHs being by-products of other processes, these compounds can be used in the production and consumption of other compounds of interest, such as medicaments, agricultural products, pesticides, dyes, and pigment. Furthermore they are also present in roadways made of asphalt (Dutson et al., 1997).

The generation of PAHs can be divided in three processes; pyrogenic PAHs are produced when organic compounds are exposed to high temperatures (300-1200 C), and the oxygen levels are low or nonexistent. Examples of this type of generation are in the distillation of coke, incomplete combustion of wood, fossil fuels and oils. Petrogenic PAHs are produced during the formation of crude oil, or volcanic activity. These compounds can be released into the environment mainly through crude oil spills in the ocean, spills of petroleum products in-land, or volcanic fumes. Lastly, PAHs can be biologically produced by degradation of organic matter by bacteria (Chen et al., 2018; Zelinkova & Wenzl, 2015).

The release of PAHs can be from natural or anthropogenic causes, with anthropogenic being the more abundant and noticeable. Anthropogenic release is particularly evident in the

combustion of fuel in cities, as well as the erosion of asphalt roads. In the case of pyrogenic production, PAHs can be easily transported by air currents, where they can come in contact with animals, humans, and plants. Whereas petrogenic PAHs can get into aquatic environments via run-off from populated areas, highways and anywhere where petroleum products can be stored in or transported through. Because of these sources and routes for environment pollution, it is common to find higher concentrations of PAHs around populated areas, both through water run-off and wind transportation (Burgess et al., 2003).

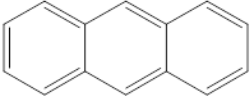
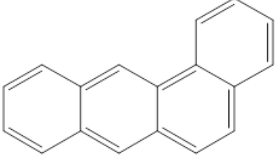
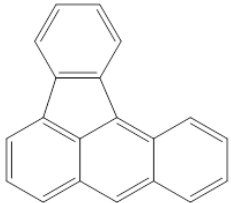
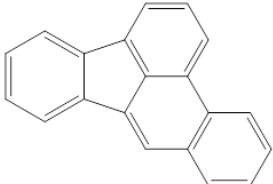
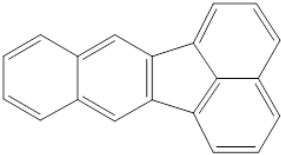
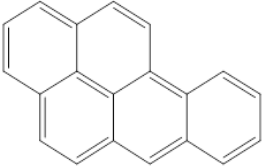
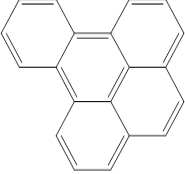
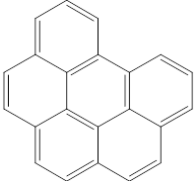
In terms of interactions with fibre fragments, PAHs have a greater chance to being in contact with these particles while in aquatic systems rather than during aerial transportation. Although a general property of PAHs low solubility in water, the solubility is inversely proportional with the size of the compound (Abdel-shafy & Mansour, 2016). Therefore, small PAHs will be more likely found dissolved or suspended in the water column, while large PAHs will be mainly precipitated at the bottom. In this way, larger PAHs will see reduced their opportunities to interact with fibre fragments.

### **2.5.2 Impact of PAHs on the environment**

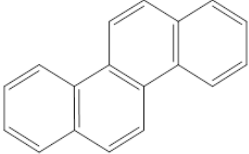
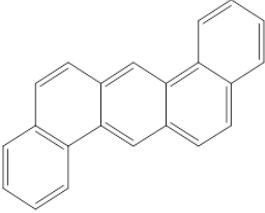
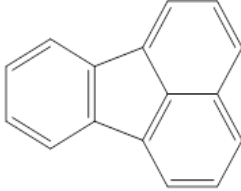
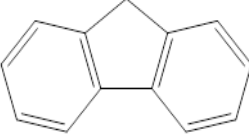
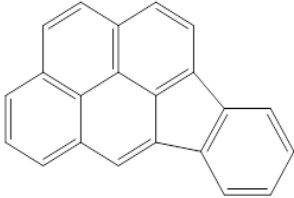
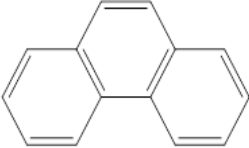
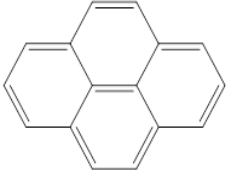
Within the environment, PAHs represent a high hazard towards fauna and humans exposed to them. According to various national and international health and environmental protection agencies, at present, 15 PAHs are considered to have different degrees of carcinogenicity in humans and animals. This classification of carcinogenic PAHs by three health/environmental protection organizations are presented in Table 2.1. The keywords used in the graphic refer to different levels of scientific evidence of causality between a compound and the occurrence of cancer. Known, enough evidence has been collected; probable, limited evidence has been observed (Probably carcinogenic, IARC; Likely to be carcinogenic, EPA); possible, evidence is not statistically significant (Possibly carcinogenic, IARC; Suggestive evidence, EPA); not classifiable, not enough causality evidence has been observed in humans (Not classifiable as carcinogenic, IARC; Not likely to be carcinogenic, EPA) (EPA, 2005; IARC, 2019).

Out of the compounds listed in said table, pyrene, phenanthrene and fluoranthene were selected for the current study. They were selected, as they are part of the lowest level of carcinogenicity risk, as well as being among the smallest PAHs, which was taking in account to work with aqueous solutions, without the help of surfactants or organic solvents. Despite their low carcinogenicity classification towards human, the effects that these compounds have in aquatic fauna has been previously explored.

Table 2.1 List of PAHs and their different carcinogenic classification assigned by IARC, EPA & HHS

	Chemical Structure	Carcinogenic risk in humans	Carcinogenic risk in animals
Anthracene		Not classifiable <sup>2</sup>	
Benzo(a)anthracene		Probable <sup>2</sup> Not classifiable <sup>3</sup>	Known <sup>1</sup>
Benzo(a)fluoranthene		Possible <sup>2</sup> Not classifiable <sup>3</sup>	
Benzo(b)fluoranthene			Known <sup>1</sup>
Benzo(k)fluoranthene		Possible <sup>2</sup> Not classifiable <sup>3</sup>	
Benzo(a)pyrene		Probable <sup>2</sup> Not classifiable <sup>3</sup>	Known <sup>1</sup>
Benzo(e)pyrene		Not classifiable <sup>2</sup>	
Benzo(g,h,i)perylene		Not classifiable <sup>2</sup>	



Chrysene		Not classifiable <sup>2,3</sup>	
Dibenz(a,h)anthracene		Not classifiable <sup>3</sup>	Known <sup>1</sup>
Fluoranthene		Not classifiable <sup>2</sup>	
Fluorene		Not classifiable <sup>2</sup>	
Indeno(1,2,3-c,d)pyrene		Possible <sup>2</sup> Not classifiable <sup>3</sup>	Known <sup>1</sup>
Phenanthrene		Not classifiable <sup>2</sup>	
Pyrene		Not classifiable <sup>2</sup>	

Carcinogenic hazard of each compound assigned by different agencies. Empty boxes mean that said agency has no current classification for that compound. 1=US Department of Health and Human Services; 2=International Agency for Research on Cancer; 3=US Environmental Protection Agency.

### 2.5.3 Properties of selected PAHs and carbazole

#### *Pyrene*

Pyrene is a generally colorless solid but might have yellow hues if impurities are present. It is composed of 4 aromatic rings arranged in a cluster order. These type of PAHs are known as peri-fused, as the aromatic rings are joined by more than one side (Pyrene, n.d.). Pyrene can be obtained from the distillation of coal tar, and from pyrolytic processes like the pyrolysis of acetylene and hydrogen, along with the combustion of fossil fuels (Figueira-Duarte & Klaus, 2011). Pyrene is used in the production of dyes, plastics, and pesticides (EPA, n.d. -b), but also has been widely used in research due to its photophysical properties, as is used as a probe in microenvironments via fluorescence (Figueira-duarte & Klaus, 2011).

Despite their uses in research, pyrene has been observed to cause negative impact on marine fauna. Oliveira et al., (2013) observed an absolute mortality rate (100%) of goby fish (*Pomatoschistus microps*) exposed to a concentration of 200 µg/L after 48 h. But when the fish were exposed to the same concentration plus 18.4 and 184 µg/L of polyethylene microspheres, the mortality rate of 100% was observed after 60 h. The authors also reported an increase of pyrene metabolites in the bile of individual fish exposed to microplastics and pyrene, which might indicate that microplastics can delay the impact of pollutants present in the environment. However, it is not clearly stated if the mixture of microplastics and pyrene were given time to reach equilibrium with each other, raising the question if the delay in the mortality rate was due to a slow release of pyrene by the microplastics, or if the microplastics absorbed a fraction of pyrene, reducing its concentration, thus delaying the death of the individuals.

Avio et al., (2017) conducted a similar study, in which they exposed mussels (*Mytilus galloprovincialis*) saturated polyethylene and polystyrene powder (<100 µm) with pyrene in saltwater. The authors observed a transference of pyrene from the powder into the tissue of the mussels, specially in the stomach, where the concentration was 3 times higher than the original concentration in the powder.

#### *Phenanthrene*

Phenanthrene is also a white looking solid when pure, but yellow if impurities are present. It is composed of three aromatic rings (Phenanthrene, n.d.), and it is an ortho-fused PAHs, which refers to molecules in which the aromatic rings in the structure have only two carbon atoms in common (IUPAC, n.d.) with an angular arrangement. Its solubility in water ranges from 1.15-1.6 mg/L in deionized water, and 0.6 mg/L in seawater. Phenanthrene is obtained mostly during the

incomplete combustion of coal, oil, gas and organic matter. It is used in the elaboration of dyes, plastics, pesticides, explosives, and also in pharmaceutical applications, such as bile acids, cholesterol, steroids and drugs (EPA, n.d. -a).

Phenanthrene and microplastics interactions have been studied at different degrees. Wang et al., (2019) (ecotoxicology and environmental safety) explored the effect that polystyrene microplastic size have on the sorption of phenanthrene and nitrobenzene. The sizes ranged from micrometers (30-170  $\mu\text{m}$ ) to nanometers (50-800 nm), while the concentrations of the analytes were 0-800  $\mu\text{g/L}$  (phenanthrene) and 0-30 mg/L (nitrobenzene). Overall nitrobenzene presented a higher sorption in the particles, which the authors attribute to the higher affinity between the substrate (weakly polar) and nitrobenzene (slightly polar, when compared with phenanthrene (non-polar). The effect of particle size was observed as smaller particles having increased sorption rates per weight unit, which might be linked to the higher specific surface area.

Other researchers have examined the impact of phenanthrene on aquatic fauna, Chen et al. (2018) assessed the impact of phenanthrene on *Chlorella salina* while present at different pH conditions (pH 6-10) They observed an inhibition rate of ~40% when using more than 0.3 mg/L phenanthrene, which increased to >75% when using at least 2 mg/L. The increase of pH did not seem to have a significant effect on the inhibition rate.

### *Fluoranthene*

Fluoranthene is a light-yellow solid. It consists of three aromatic rings connected by a cyclopentane, thus being considered a ortho- and peri-fused PAH (Fluoranthene, n.d.). Its solubility is 0.26 mg/L in water. Fluoranthene is another by-product of the incomplete combustion of coal, wood, fuels, (Minnesota Department of Health, 2015) and organic matter, fluoranthene has a diverse range of applications besides production of pesticides and dyes industries. It can be also used to line storage tanks and pipes, for cancer research (to assess its carcinogenicity ), and as eczema treatment (Government of Canada, n.d.).

In their work, Paul-Pont et al., (2016) assess the impact that fluoranthene has when exposed to mussels (*Mytilus edulis* and *galloprovincialis*. Mussels were exposed to 30  $\mu\text{g/g} \cdot \text{day}$  of fluoranthene, polystyrene microbeads or both for 7 days. At this time, the concentration of fluoranthene in the digestive glands was lower in fluoranthene exposed mussels ( $12.1 \pm 0.8 \mu\text{g/g}$ ) than in the fluoranthene + microbeads group ( $13.5 \pm 1.1 \mu\text{g/g}$ ), but the difference was more noticeable after the depuration period at 14 days ( $36.9 \pm 6.7 \mu\text{g/g}$  and  $61.3 \pm 4.8 \mu\text{g/g}$  respectively). Histopathological lesions were also observed in the three groups, as well as

higher hemocyte infiltration in the digestive system for those exposed to fluoranthene. The authors discussed that the presence of microbeads does not have a major impact on the fluoranthene concentration during the exposure phase. However, it seems to be a more noticeable effect after the exposure has stopped, which might be due to the presence of microbeads slowing the metabolism or delayed release of the fluoranthene sorbed in the microbeads.

A similar work was performed by Magara et al., (2018), where they compared the effect of single (fluoranthene only), combined (fluoranthene + microplastic), and previously incubated (fluoranthene + microplastic interaction, time not specified) exposure of fluoranthene and polyethylene microplastics by *Mytilus edulis*. After an exposure of 96 h, the fluoranthene concentration in the digestive gland followed the order single > combined > incubated exposure ( $45.25 \pm 22.23 \mu\text{g/g}$  >  $25.02 \pm 11.64 \mu\text{g/g}$  >  $2.16 \pm 1.47 \mu\text{g/g}$  respectively). However, the single and combined exposures were not significantly different.

This research is very similar to the one of Paul-Pont et al., (2016). However, it is important to note that the two studies had different exposure times; as well as how the exposure solution was applied. While Paul-Pont et al., (2016) added the fluoranthene along with the food of the mussels, Magara et al. (2018) did not specify the method of addition. Lastly, Magara et al. (2018) used two concentration levels for each exposure condition but grouped them as one result for each condition. Nonetheless, the findings of both authors show that their results were congruent, as presence of microplastics did not cause a significant difference in concentration in the tissues of mussels.

### *Carbazole*

Carbazole is an aromatic heterocyclic organic compound (HETs). Although HETs are greatly similar to PAHs, they differ in that they include at least one atom other than carbon and hydrogen in their molecular structure. Due to the presence of another atom (usually nitrogen or oxygen), these compounds have in general a higher solubility and polarity (Salam et al., 2017). Carbazole is composed of two aromatic rings connected through a pyrrole (cyclopentane which “middle” carbon has been substituted by a nitrogen atom (Georgiades & Nicolaou, 2019). Carbazole has the appearance of white crystals. Carbazole occurs naturally in some plants, but it is also part of coal tar, and it is present in the combustion of nitrogen containing organic matter, such as tobacco smoke. Carbazole is commonly used in the production of dyes (Ziarani et al., 2018), and some of its derivatives are used in health treatment research (Georgiades & Nicolaou, 2019)

Carbazole has not been found to be carcinogenic in mice or humans (EPA, 2008), but other negatives effects have been observed, such as development and reproductive toxicity, as well as being found to be mutagen and neoplasms inducing (Salam et al., 2017).

Peddinghaus et al., (2012) studied the toxicity of fourteen HETs containing nitrogen, oxygen or sulphur (NSO-HET) in embryo specimens of zebrafish (*Danio rerio*), one of which was carbazole. Carbazole was observed to decrease its concentration by 82% after 48 h in solution pre-exposure to fish, which might indicate a fast-decaying rate of carbazole in aqueous systems or a high volatilisation. In terms of toxicity, carbazole was the second most toxic compound with a lethal concentration 50 (LC50) of 1.07 mg/L, with other compounds ranging from 3.6 to 103.51 mg/L.

## **2.6 Fibre interactions with other compounds**

Given the difference in structure and molecular composition between natural and synthetic fibres, it is clear they present different behaviour and affinity to absorb and/or interact with other compounds. For example, Chien et al. (2011) compared the release of volatile organic compounds (VOCs) from eight types of fabrics exposed to tobacco smoke. They observed that as a general trend, fabrics released higher concentrations of compounds that have either high or low molecular weight. However, it is important to note that the compounds observed to have a higher release were polar compounds, or compound without an aromatic ring in their structure (i.e., phenol, furfural, n-hexadecanoic acid), while the ones with the lowest release were non-polar compounds (i.e., naphthalene, benzonitrile, d-limonene). Cotton released the highest amount for compounds with low molecular weight and polar characteristics, which might indicate that it does not create strong bonds with organic compounds. One thing to note from this work, is that cotton and polyester had a similar release rate for less polar and bigger compounds.

Vaezafshar (2019) compared the rate of sorption of six different volatile compounds that can be present in axillary odour by four different fabrics (cotton, viscose, polyester, and polyamide) when immersed in an aqueous sweat solution. She observed that cotton and viscose absorbed lower concentrations for five compounds, while polyester presented the highest affinity for three of them, while polyamide adsorbed the most for two of the compounds. The author suggested that the cellulosic fibres had the lower absorption capacity due to the active sites to create hydrogen bonds used by water molecules instead of the compounds of interest. While for polyester fibres, their structure and chemical surface increases their affinity to non-polar compounds, even when subjected to washing. Polyamide behaved similar to polyester, but due

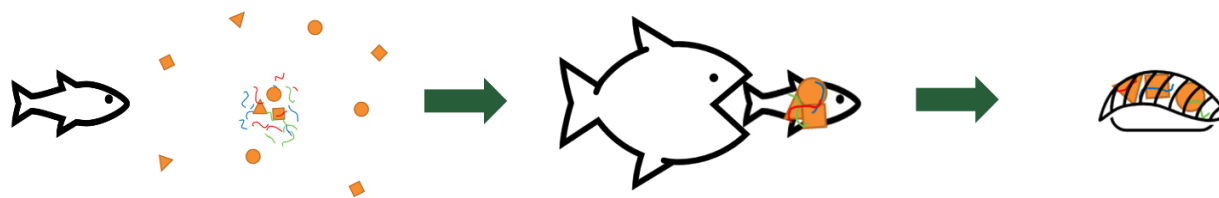
to the presence of the amino and carbonyl groups, it can interact to a higher degree with polar compounds.

A similar result was observed by Abdul-Bari et al. (2020), who also compared the release of three axillary volatile compounds absorbed in cotton and polyester fabrics, before and after subjecting them to washing cycles. Prior to being washed, cotton released a higher concentration of a polar compound (octanoic acid), while polyester released more of the non-polar compounds (2-nonenal, dodecane). The released amount of these compounds can reflect how much each is absorbed in the two fabrics, supporting the assumption that cotton has a higher interaction with polar compounds, even if the difference is as small as changing from a carboxylic acid to an aldehyde. After one wash cycle, it was observed that cotton lost >90% of both compounds, while the concentration in polyester decreased by 59 and 86.2%. This result indicates that regardless of the polarity of the compounds, cotton has not only a lower absorbency rate, but also a less strong retention capacity with these compounds than polyester.

For a comparison between two synthetic fibres and their uptake of phenanthrene, Wang et al. (2018) tested polyester and polyamide fragments simulating those shed by fishnets in a mariculture farm. They observed that phenanthrene has a slightly higher affinity towards polyester than polyamide (146.4 and 131.8  $\mu\text{g g}^{-1}$  respectively). In congruence with Abdul-Bari et al. (2020), the difference between both fibres is associated with their difference in functional groups, which in the case of polyamide, limits the interaction with an aromatic compounds to those regions of the chain that do not have these sites capable of creating an hydrogen bond (hydrophilic)

Diverging away from synthetic and natural textiles to put the fibre/compounds interactions back into perspective of the overall problem of microplastics is the study by Rochman et al. (2013), in which it was assessed the sorption rate between high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP), polyvinyl chloride (PVC), and polyethylene terephthalate (PET) pellets, and 27 polychlorinated biphenyl's and 15 polycyclic aromatic compounds (including three used in the current study). Overall, the concentration for all compounds were significantly higher (one order of magnitude difference) in HDPE, LDPE, and PP than in PVC and PET. This difference in sorption rates was attributed to the first three polymers having a more rubber-like structure, which allowed them to have a higher diffusion and permeability, in contrast to a more ordered and crystalline structure of the last two polymers. Therefore, fibre fine structure can also influence sorption capacity.

Considering the widespread occurrence of MP on aquatic organisms, as well as their interaction with different groups of compounds, it can be considered that MP have the potential to work as a vector through which pollutant chemicals can get an easier and direct point of entry into the food chain, where they can bioaccumulate affecting not only aquatic organisms, but also humans, mainly through seafood consumption (Fig. 2.5).



*Figure 2.5 Bioaccumulation of chemicals absorbed by MP through the food chain*

## 2.7 Summary

Although very small in size microplastics and fibre fragments pose significant hazards within aquatic ecosystems. Not only are these microplastics difficult to remove from the environment, but due to their increased relative surface area they have the potential to adsorb a relatively high number of chemical contaminants. Although plastics are mostly inert, the high surface area allows them to increase their interaction and adsorption of harmful pollutants (e.g., metals and pesticides) that they may be exposed to while they are in an aquatic environment, like rivers and waste water effluents (Brennecke et al., 2016; Haap et al., 2019; Naidu, 2019; Rodrigues et al., 2019), in addition to the compounds they may retain from the original product they came from. Fibres which have different chemical compositions and morphological structures can take up and retain chemical compounds to different degrees or intensities. Within the aqueous environment the chemical-water-fibre interactions will influence the affinity of certain compounds to certain fibres. As such, this study is evaluating the affinity of select compounds to three common textile apparel fibres that can be present in freshwater and marine environments following release via laundering.

## Chapter 3

### Methods

#### 3.1 Experimental design

The experimental design used in this work was a 3 x 2 x 4 factorial design, with three types of apparel fibres (cotton, polyamide, and polyester); two types of aqueous solutions (deionized water and saltwater); and four pollutant compounds (phenanthrene, carbazole, pyrene and fluoranthene). All these factors represent the independent variables of the study, while the dependent variables were the number of compounds not absorbed to the fibres (remaining in solution) expressed as part per billion.

*Table 3.1 Factorial design 3x2x4 used in this project*

Fabric	Matrix	Analytes			
		Phenanthrene	Pyrene	Carbazole	Fluoranthene
Cotton	Deionized water	x	x	x	x
	Saltwater	x	x	x	x
Polyamide	Deionized water	x	x	x	x
	Saltwater	x	x	x	x
Polyester	Deionized water	x	x	x	x
	Saltwater	x	x	x	x

#### 3.2 Materials and reagents

##### 3.2.1 Experimental fabrics and preparation of yarns/fibres

The experimental fabrics were ISO standard fabrics and were purchased from TestFabrics Inc. (Delaware, PA, USA). All fabrics were of 100% in fibre content and plain weave structures. Polyester (ISO 105-F04) was 136 g/m<sup>2</sup>, polyamide was (ISO 105-F03) was 134 g/m<sup>2</sup> and cotton (ISO 105-F02) was 119 g/m<sup>2</sup>. The specific surface areas was determined in a previous study (Vaezafshar, 2019), with values of 0.302, 0.493 and 0.967 respectively.

To obtain the fibres from the fabrics, lengths of yarns (~70 cm) were individually removed from the weave structure, then the yarns were cut into shorter lengths. To do this, the yarns were first wrapped around a pair of tweezers (2 cm per cycle), and a circular blade was used to cut them through the middle. This resulted in two groups of yarns with a length of 1 cm. Each of these groups were cut again to obtain yarn fragments of 0.5 cm. To avoid cross contamination due to



fibres getting stuck in the wounds of the cutting surface made by the cutting blade, a different cutting mat was used for each fibre type.

The yarn fragments were collected in 20 mL screwed cap vials. In order to remove as much possible residual cross contamination during handling and sample prep, all of the fragments were subjected first to a methanol (MeOH) wash, for hydrophilic compounds, followed by an overnight wash with dichloromethane (DCM) to target hydrophobic compounds. This washing procedure was done in order to remove any impurities that may have come from the skin or environment prior to and during the cutting procedure. After this period, the DCM was removed from the vial and the yarn fragments were left to dry with the cap unscrewed but not removed. Once dry, the yarn fragments were stored in clean petri dishes in a conditioning room ( $21 \pm 2$  °C,  $65 \pm 4\%$  relative humidity) for at least 24 hours before being used.

### **3.2.2 Chemical reagents**

The compounds selected to simulate pollutants present in wastewater were phenanthrene (Matheson, Coleman & Bell, OH, USA), pyrene (Aldrich Chemical Company, WI, USA), carbazole (Fisher Chemical, ON, Can), and fluoranthene (Eastman Organic Chemicals, TN, USA). For the validation of the quantification analysis, 1-methoxynaphtalene (Aldrich Chemical Company, WI, USA), was used as the internal standard. Synthetic saltwater was selected to simulate the ionic strength of sea water and its effect on the selected pollutants solubility. Synthetic saltwater was prepared with sodium chloride (NaCl), magnesium chloride (MgCl<sub>2</sub>), sodium sulphate (Na<sub>2</sub>SO<sub>4</sub>), calcium chloride (CaCl<sub>2</sub>), potassium chloride (KCl), sodium bicarbonate (NaHCO<sub>3</sub>). The salts compounds were acquired from Fisher Chemical, ON, Can. Deionized water was used to simulate freshwater conditions. Deionized water was preferred over tap water to compare more notably the effect of the dissolved salts in the solubility of the compounds. Methanol and dichloromethane were acquired from Sigma-Aldrich (Aldrich Chemical Company, WI, USA)

### **3.2.3 Gas chromatography**

All the quantification analysis was carried out using a Gas chromatograph coupled with Flame Ionization detection (GC-FID), using a 30.0 m x 250 µm x 0.25 µm Restek Rxt®-5MS column (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.

### 3.3 Experimental procedure

#### 3.3.1 Pollutants saturated solutions

To increase the probability of interactions between the compounds and the yarn fragments, saturated solutions of each compound were used. Saltwater solutions were prepared by using a modified formula of the solution reported in ASTM D1141-98, consisting in 24 g NaCl, 5.2 g, MgCl<sub>2</sub>, 4.1 g Na<sub>2</sub>SO<sub>4</sub>, 1.16 g CaCl<sub>2</sub>, 0.69 g KCl, 0.2 g NaHCO<sub>3</sub>. “Freshwater” solutions were prepared with deionized water. The preparation of the pollutant saturated solutions was done by adding independently the mass of each analyte shown in Table 3.1 into a 2 L volumetric flask, filling up to the mark with either deionized water or saltwater solution, and heating the flask on a hot plate at 80 °C for 4 h to enhance the solubility of the compounds, using a magnetic stirrer. After 4 h the heat was turned off, but the agitation was kept on overnight. Each solution was prepared the day prior to it being used and stored in a cabinet afterwards.

Table 3.2 Mass of the analytes added to the fresh and saltwater solutions (2 L)

Analyte	Fresh water (g)	Saltwater (g)	Solubility in water (mg/L)*	Solubility in saltwater (mg/L)*	Log P*
Phenanthrene	2.3	2.35	1.15	0.6	4.46
Pyrene	0.280	0.295	0.135	N/A	4.88
Carbazole	2.5	2.5	1.2/1.8	N/A	3.72
Fluoranthene	0.4	0.43	0.26	0.12	5.16

\*Values obtained from pubchem.com; N/A= data not available

#### 3.3.2 Fibre-pollutants absorption

The interaction between fibres and analytes was evaluated by immersing the yarn fragments in the saturated solutions. The analysis of each solution was performed by adding 100 mL of the stock solutions into 12 amber 125 mL glass bottles. Three samples of  $0.0503 \pm 0.00016$  mg of yarn fragments for each fibre type were weighed and added to the bottles and shaken softly to facilitate the dispersion of the fibres/yarn fragments.

Three bottles of each solution were used to serve as the control in order to evaluate the initial concentration of the solution. The bottles were left for 24 hours, with gentle shaking twice per day to increase the contact between fibres and diluted chemicals. After this period, 20 mL of the solution was recovered into screwed cap vials using a cellulose acetate membrane 0.45 µm to prevent the pass of solid particles.

### 3.3.3 Extraction and concentration

The aliquots collected were subjected to a liquid-liquid extraction, spiked with 1-methoxynaphtalene as the internal standard. Each sample was transferred into a 50 mL conical glass tube. Aliquots of 750  $\mu\text{L}$  of DCM with the internal standard were added to each tube and agitated vigorously using a vortex for 5 minutes. They were then placed in a centrifuge for 5 minutes at (2000 rpm) to concentrate the small bubbles of DCM created during the agitation. Two aliquots of 150  $\mu\text{L}$  were collected from the bottom layer and transferred to 300  $\mu\text{L}$  insert GC labeled vials. A visual representation of the method is presented in Figure 3.1.

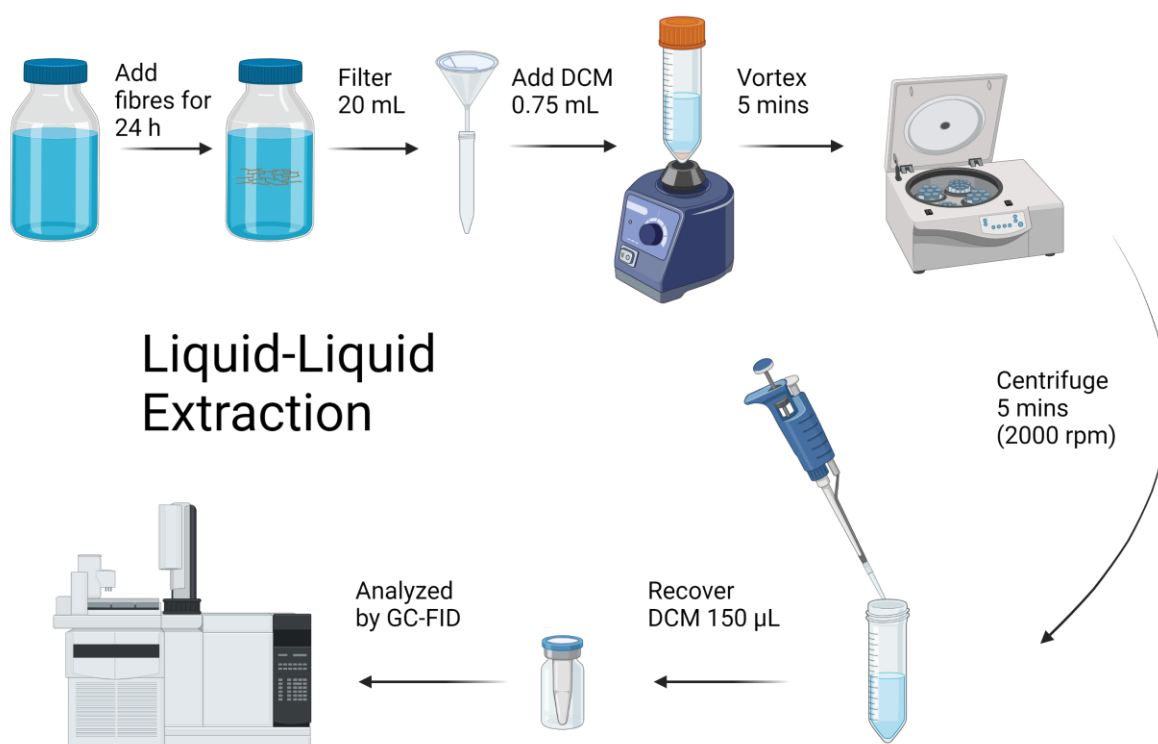


Figure 3.1 Methodology flowchart

The concentrations of the analytes ( $\mu\text{g/L}$ ) remaining in the solution are calculated with a dilution factor corresponding to the 0.75 mL of DCM used to extract the analytes from 20 mL of each solution using Equation 3.1, and later normalized by the mass of fabric present in each bottle, as indicated in Equation 3.2:

$$\text{Concentration in solution} = \text{observed concentration} * \frac{0.75\text{mL}}{20\text{mL}} \quad \text{Eq. 3.1}$$

$$\text{Normalized concentration} = \frac{\text{concentration in solution}}{\text{fabric mass (g)}}$$

### 3.3.4 Calibration curves

Prior to the analysis of the obtained sample aliquots, a calibration curve was created for each compound individually with an internal standard by serial dilutions normalize the areas and reduce interferences due to random errors. The concentration of the analytes used in the calibration curves is shown in Table 3.3. The peak area of each compound in the resulting chromatograms was recorded to generate the regression curves for each compound. The peak areas for the analysis of the resuspended aliquots will be collected and input in the regression curve equation to calculate the concentration in each sample.

*Table 3.3 Concentrations used in the calibration curve*

Calibration point	Phenanthrene	Pyrene	Carbazole	Fluoranthene
1	0.05	0.01	0.5	0.025
2	0.1	0.025	0.75	0.05
3	0.416	0.075	1	0.2
4	0.833	0.1	1.5	0.416
5	1.667	0.125	2	0.833

### 3.4 Data Analysis

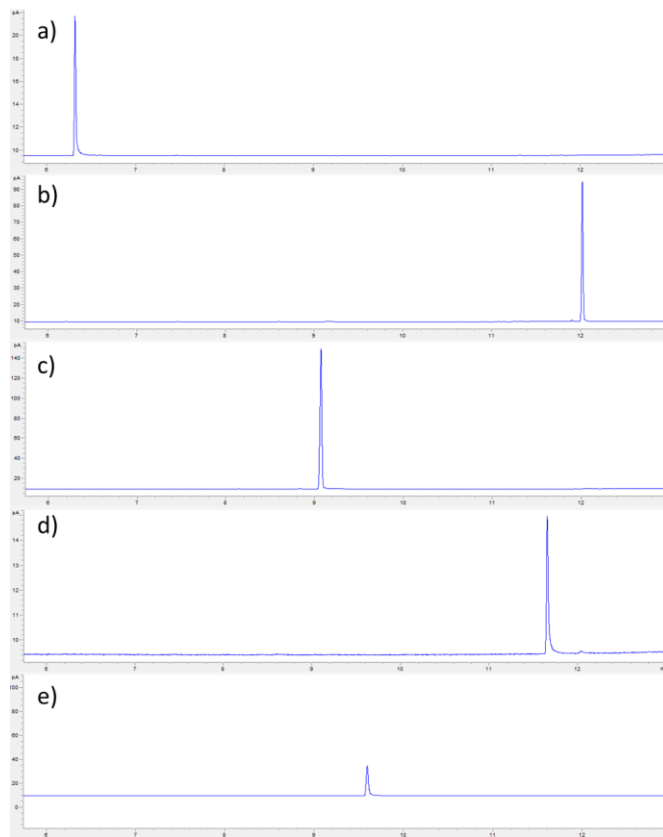
Descriptive statistics such as the mean (M) and standard deviation (SD) were calculated of the concentration of analytes remaining in solution ( $\mu\text{g/L}$ ) for each fibre/compound/water. A series of one-way analysis of variance (ANOVA) tests were performed to evaluate the null hypothesis that there were no significant differences among the fibres in concentration of each compound for each type of water. The Welch's test was performed as an alternative to the standard one-way ANOVA as the assumptions of equal variance were not met (i.e., Levene's test of equality of variances were significant). For the same reason (unequal variances), the Games-Howell test was used as the post-hoc test to identify which fibres differed significantly from each other when the ANOVA showed significant differences among the three fibres. All the data analysis was performed using IBM® SPSS® Statistics 28.0.

## Chapter 4

### Results

#### 4.1 Retention times of analytes.

Before conducting the experiments, it is important to identify the retention times of the analytes and the internal standard, to ensure that there is no overlapping between them. Individual solutions of 100 mg/mL for each compound were prepared. The obtained chromatograms for 1-methoxynaphthalene, pyrene, phenanthrene, fluoranthene and carbazole are shown in Figure 4.1, with retention times of 6.31, 12.1, 9.08, 11.67 and 9.58 minutes respectively.



*Figure 4.1 Retention times in minutes for a) 1-methoxynaphthalene (6.31), b) pyrene (12.1), c) phenanthrene (9.08), d) fluoranthene (11.67), and e) carbazole (9.58)*

#### 4.1 Calibration curves for pollutants

The concentration of the analytes remaining in the water after interacting with the fibres were calculated using calibration curves for each compound. These calibration curves were linear in

the range of 0.01 – 0.125 mg/L, 0.5 – 1.66 mg/L, 0.025 – 0.833 mg/L, and 0.05 – 1.666 mg/L for pyrene, phenanthrene, fluoranthene and carbazole, respectively. The corresponding least squares linear regression equation for each compound are:

Pyrene  $y = 21.312x - 0.1837$   $R^2 = 0.9965$  Eq. 4.1

Phenanthrene  $y = 1.68x - 0.0032$   $R^2 = 0.9991$  Eq. 4.2

Fluoranthene  $y = 0.1318x - 0.0011$   $R^2 = 0.9983$  Eq. 4.3

Carbazole  $y = 0.823x - 0.1359$   $R^2 = 0.9823$  Eq. 4.4

#### 4.2 Concentration of analytes in salt and deionized water saturated solutions

The concentrations of the individual saturated solutions of the analytes were analyzed, and representative chromatograms for each compound are presented in Figure 4.2 and 4.3 for deionized and saltwater conditions respectively, where well defined peaks can be observed at the previously identified retention times.

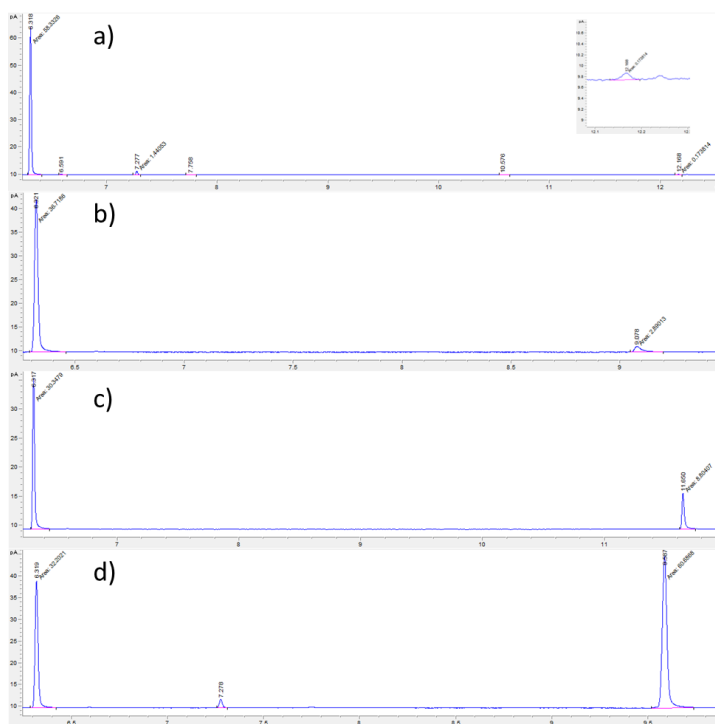


Figure 4.2 . Peak intensity observed for of a) pyrene, b) phenanthrene, c) fluoranthene, and d) carbazole in deionized water saturated solutions

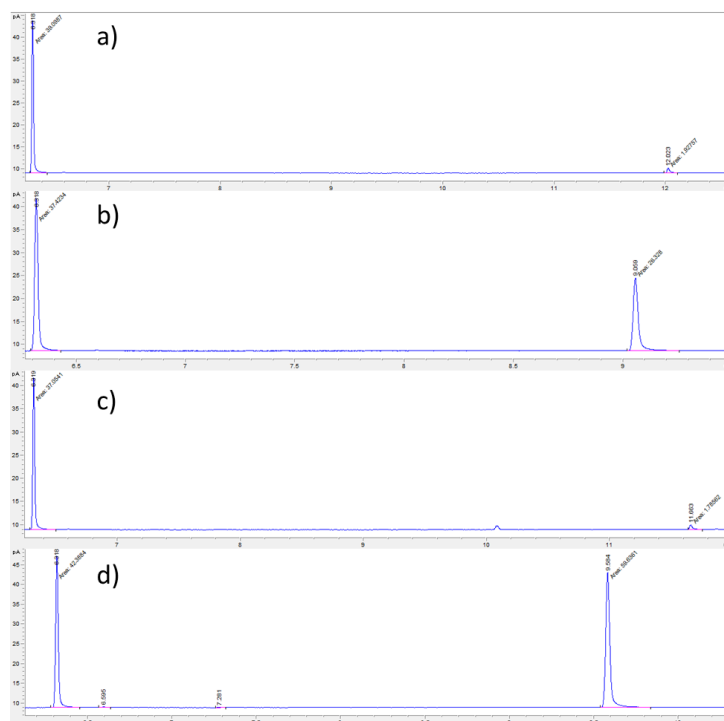


Figure 4.3 Peak intensity observed for of a) pyrene, b) phenanthrene, c) fluoranthene, and d) carbazole in saltwater water saturated solutions

The quantitative results are presented graphically in Figure 4.4 and Table 4.1. It can be observed that carbazole and fluoranthene present a higher concentration when compared to phenanthrene and pyrene. The concentration observed is considerably lower than the theoretical solubility of these compounds in water (see Table 3.2). This discrepancy with the reported values might be due to the conditions in the laboratory, or the water used. It is also interesting to note that pyrene and phenanthrene present a lower concentration when deionized water was used for the solutions, but the concentration increases when using saltwater. On the other hand, fluoranthene and carbazole exhibit the reverse behaviour, with higher concentrations in deionized water compared to that in saltwater.

Figure 4.4 shows the concentration of the four analytes in a) deionized water and b) saltwater, where the difference in the solubility of the compounds is more visually appreciated. In both cases, carbazole is the compound with the highest concentration (90.82 and 70.82  $\mu\text{g/L}$ ). Carbazole has the smallest proportional change in concentration between deionized water and saltwater, as it only decreased by 22%. On the contrary, pyrene is the compound with the lowest concentration in both solutions (0.34 and 1.74  $\mu\text{g/L}$ ). The concentration of pyrene in saltwater increased by 394% compared to its concentration in deionized water. Phenanthrene

presented the highest proportional change in solubility at 1,125% between deionized water and saltwater (1.57 and 17.67  $\mu\text{g/L}$  respectively). While fluoranthene has a relatively high concentration in deionized water at 82.8  $\mu\text{g/L}$  but decreased by 83% in saltwater (14.02  $\mu\text{g/L}$ ).

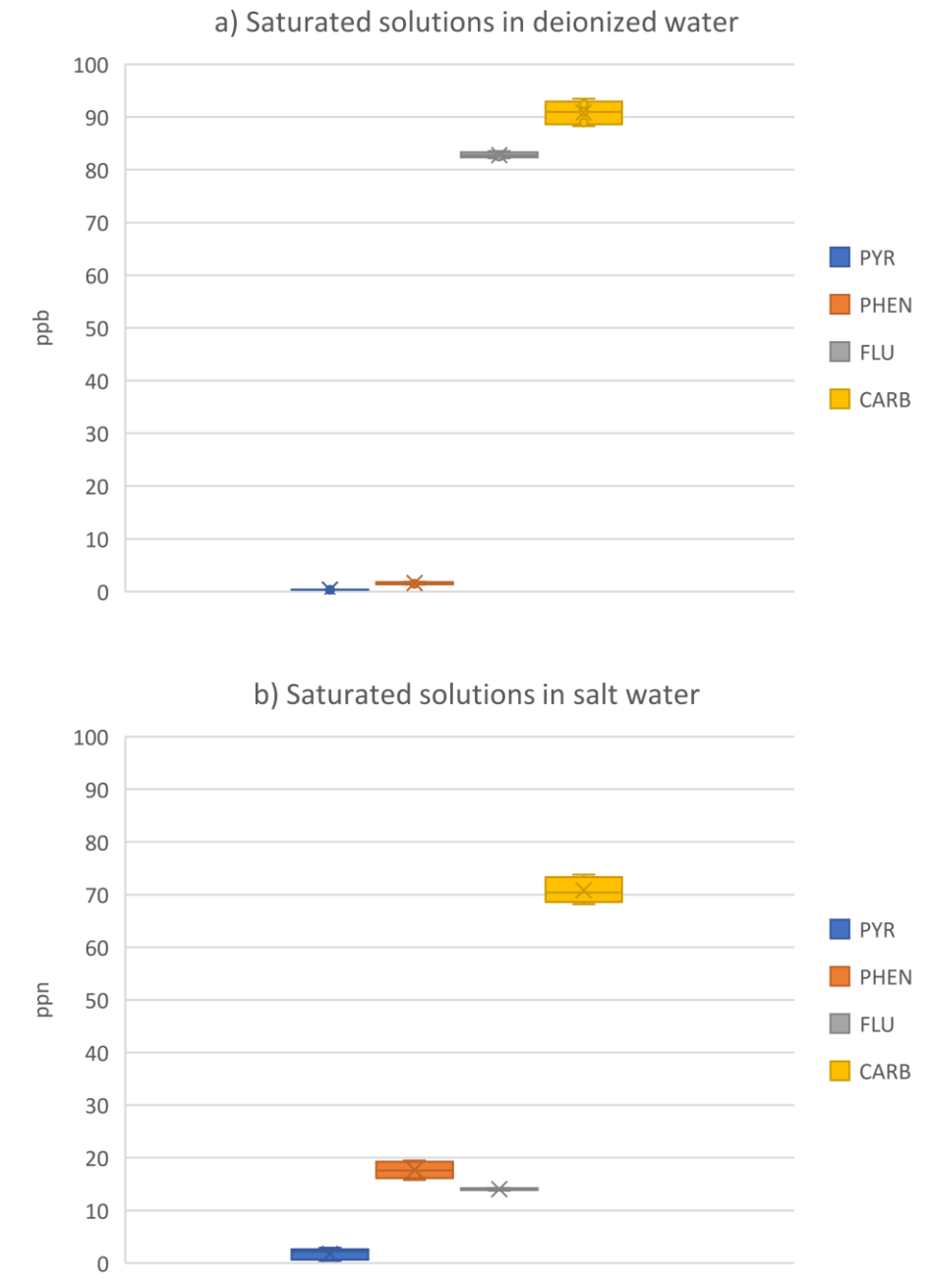


Figure 4.4 Boxplot of concentration ( $\mu\text{g/L}$ ) of pyrene, phenanthrene, fluoranthene and carbazole in a) deionized water and b) saltwater



Table 4.1 Observed concentrations of analytes ( $\mu\text{g/L}$ ) in saturated deionized and saltwater solutions.

	Phenanthrene		Pyrene		Carbazole		Fluoranthene	
	<i>M</i>	<i>SD</i>	<i>M</i>	<i>SD</i>	<i>M</i>	<i>SD</i>	<i>M</i>	<i>SD</i>
Deionized water	1.57	0.21	0.34	0.00	90.82	2.21	82.8	0.58
Saltwater	17.67	1.57	1.74	1.06	70.82	2.43	14.02	0.19

### 4.3 Concentrations of analytes in water following exposure to fibres

The analytes' remaining concentration in the aqueous phase after the 24 h exposition period to the fibres were measured following the extraction process. It was possible to observe detectable signals for all fibres in both water solutions. Representative chromatograms for all compounds and conditions are presented in Appendix A. However, during the analysis of pyrene it was not possible to obtain peak signals with an area large enough to be integrated. Not being able to quantify all of the analytes was not ideal, but also not completely unexpected, as pyrene was the analyte with the lowest concentration in both deionized and saltwater saturated solutions. Therefore, results from pyrene will not be examined further in the results chapter.

#### 4.3.1 Analytes remaining in deionized water

The concentrations of the analytes remaining in the solutions of deionized water after being exposed to the fibres for 24 h is shown in Figure 4.5, and summarized in Table 4.2, which also shows the analysis of variance (ANOVA) results. The results for phenanthrene (Figure 4.2a) showed that solutions exposed to cotton had the highest concentration at  $0.706 \pm 0.041 \mu\text{g/L}$ , followed by polyamide, which showed a larger variance ( $0.45 \pm 0.134 \mu\text{g/L}$ ), and polyester at  $0.26 \pm 0.007 \mu\text{g/L}$ . All three samples were significantly different from each other ( $F_{2,6.91} = 302.37$ ,  $p < 0.001$ ).

For fluoranthene (Figure 4.2b) the highest concentration remaining was in the solution containing cotton fibres with a mean of  $34.3 \pm 2.06 \mu\text{g/L}$ . This was followed by polyamide at  $4.5 \pm 1.23 \mu\text{g/L}$ , and then polyester with the lowest concentration at  $3.08 \pm 0.0046 \mu\text{g/L}$ . Significant differences among the three fibres were found for fluoranthene ( $F_{2,6.98} = 620.65$ ,  $p < 0.001$ ). However, polyamide and polyester did not differ significantly from one another.

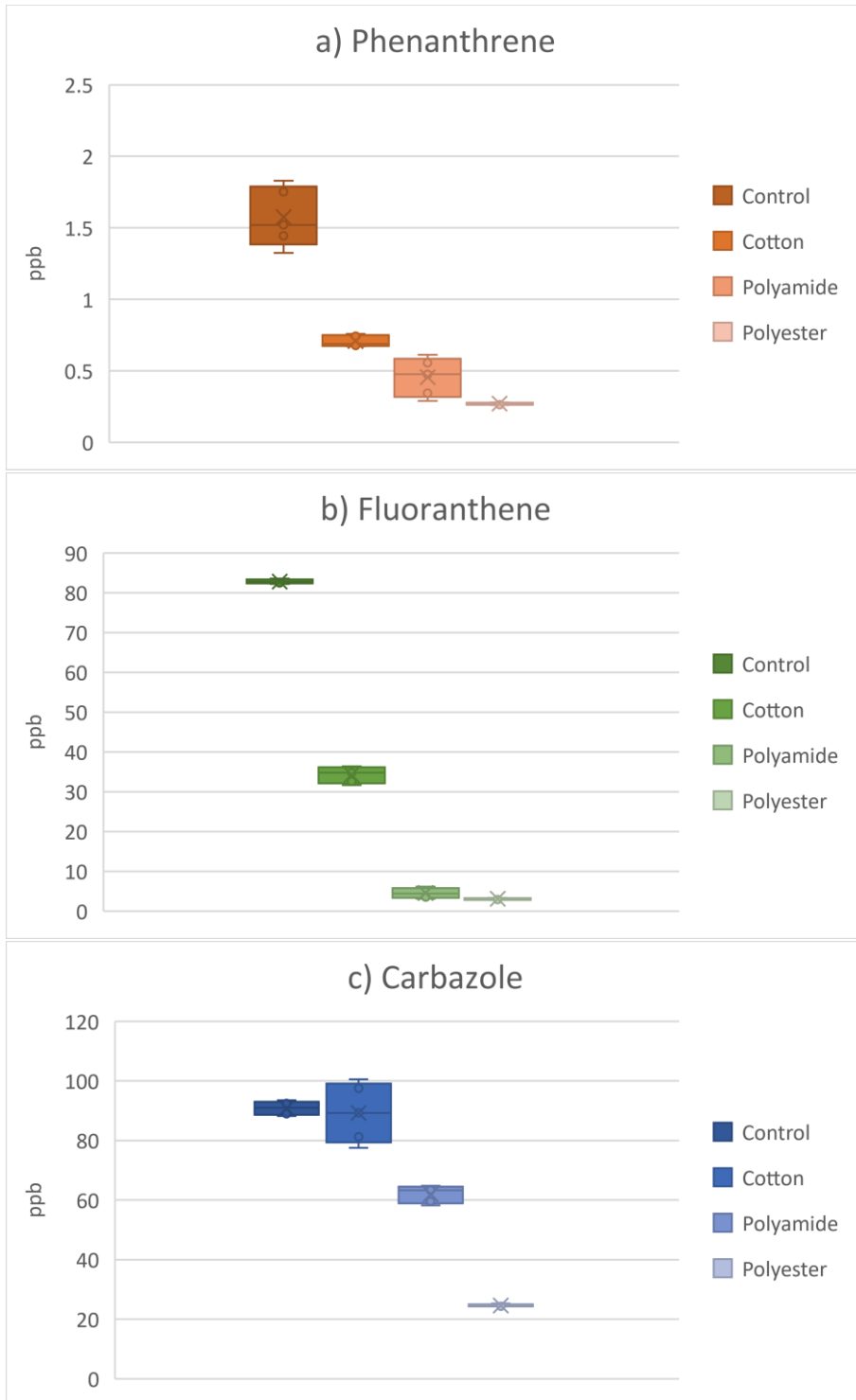


Figure 4.5 Boxplot with the mean concentration ( $\mu\text{g/L}$ ) of each analyte after being exposed to the different fibres in deionized water for a) phenanthrene, b) fluoranthene and c) carbazole

Lastly, the same trend was apparent for carbazole (Figure 4.2c) with the highest concentration found in the solution containing cotton fibres at  $89.23 \pm 9.96 \mu\text{g/L}$ . Then the solution that contained polyamide fibres at  $62.03 \pm 2.97 \mu\text{g/L}$ , and finally polyester showed the lowest concentration at  $24.6 \pm 0.307 \mu\text{g/L}$ . The concentrations depending on fibre type were significantly different ( $F_{2,6.78} = 538.37$ ,  $p < 0.001$ ) with all fibres being significantly different from one another.

As the results from the one-way ANOVA tests show that for every condition the means were significantly different ( $p < 0.001$ ). A Games-Howell post hoc analysis was performed to determine which fibre types among the three were significantly different between each other (identified by the superscripts letters in Table 4.2). For phenanthrene and carbazole, all fibres were significantly difference from each other (i.e., phenanthrene: cotton [ $M = 0.706$ ] > polyamide [ $M = 0.45$ ] > polyester [ $M = 0.26$ ]; and carbazole: cotton [ $M = 89.23$ ] > polyamide [ $M = 62.03$ ] > polyester [ $M = 24.6$ ]). However, in the case of fluoranthene polyamide and polyester were not significantly different from one another, yet cotton differed significantly from both synthetic fibres (i.e., cotton [ $M = 34.3$ ] > polyamide [ $M = 4.5$ ] = polyester [ $M = 3.08$ ]).

Table 4.2 ANOVA test results when comparing remaining analytes in deionized water.

Analytes		Descriptive statistics ( $\mu\text{g/L}$ )			N	ANOVA results		
		Cotton	Polyamide	Polyester		F	df	Sig.
Phenanthrene	M	0.706 <sup>a</sup>	0.45 <sup>b</sup>	0.26 <sup>c</sup>	6	302.368	2, 6.91	<0.001
	SD	0.041	0.134	0.007				
Carbazole	M	89.23 <sup>a</sup>	62.03 <sup>b</sup>	24.6 <sup>c</sup>	6	538.37	2, 6.78	<0.001
	SD	9.96	2.977	0.3605				
Fluoranthene	M	34.30 <sup>a</sup>	4.50 <sup>b</sup>	3.08 <sup>b</sup>	6	620.65	2, 6.98	<0.001
	SD	2.06	1.233	0.0046				

N/Q = non-Quantifiable; <sup>a, b, c</sup> = means followed by the same letter are not significantly different from one another at  $p > 0.05$  by the Games-Howell post-hoc test

Hypothesis 1a proposed *that cotton fibres will take up lower amounts of compounds than polyester and polyamide fibres, when exposed to compounds in saltwater solutions*; and Hypothesis 1b proposed *that polyester fibres will take up higher amounts of compounds than polyamide fibres, when exposed to compounds in deionized water solutions*. From the above analysis it is clear that Hypothesis 1a is supported as it can be observed that for all compounds, the remaining concentration in the solution after exposition to cotton, is higher than those when exposed to polyester and polyamide. Hypothesis 1b is partially supported, as the solutions after being exposed to polyester presented the lowest concentration for phenanthrene and carbazole, but not for fluoranthene. In the case of fluoranthene there were no significant differences in the amount of the compound between polyester and polyamide.

#### **4.3.2 Analytes remaining in saltwater**

The concentrations of the analytes remaining in the solutions of deionized water after being exposed to the fibres for 24 h is shown in Figure 4.6, while the descriptive results and one-way ANOVA results are further summarized in Table 4.3. The results for phenanthrene (Figure 4.3a) showed that solutions exposed to cotton had the highest concentration at  $11.51 \pm 0.23 \mu\text{g/L}$ . This was followed by polyamide at  $4.98 \pm 0.447 \mu\text{g/L}$ , and polyester at  $4.81 \pm 0.613 \mu\text{g/L}$ ; significant differences among the three fibres were found ( $F_{2,8.59} = 657.33, p < 0.001$ ).

For fluoranthene (Figure 4.6b) the highest remaining concentration was in the solution exposed to cotton with a mean of  $6.69 \pm 0.376 \mu\text{g/L}$ . This was followed by the solution containing polyamide fibres at  $5.18 \pm 0.549 \mu\text{g/L}$ , and polyester with  $1.68 \pm 0.335 \mu\text{g/L}$ ; significant differences were found among the three types of fibres ( $F_{2,9.68} = 2568.9, p < 0.001$ ). Finally, the highest concentration of carbazole (Figure 4.6c) in salt-water solution was found for the cotton fibres at  $79.28 \pm 3.139 \mu\text{g/L}$ . This was again followed by polyamide fibres at  $51.26 \pm 16.44 \mu\text{g/L}$ , and polyester with the lowest concentration remaining in the water at  $34.12 \pm 2.599 \mu\text{g/L}$ . Significant differences were observed among the three fibres ( $F_{2,8.92} = 342.65, p < 0.001$ ).

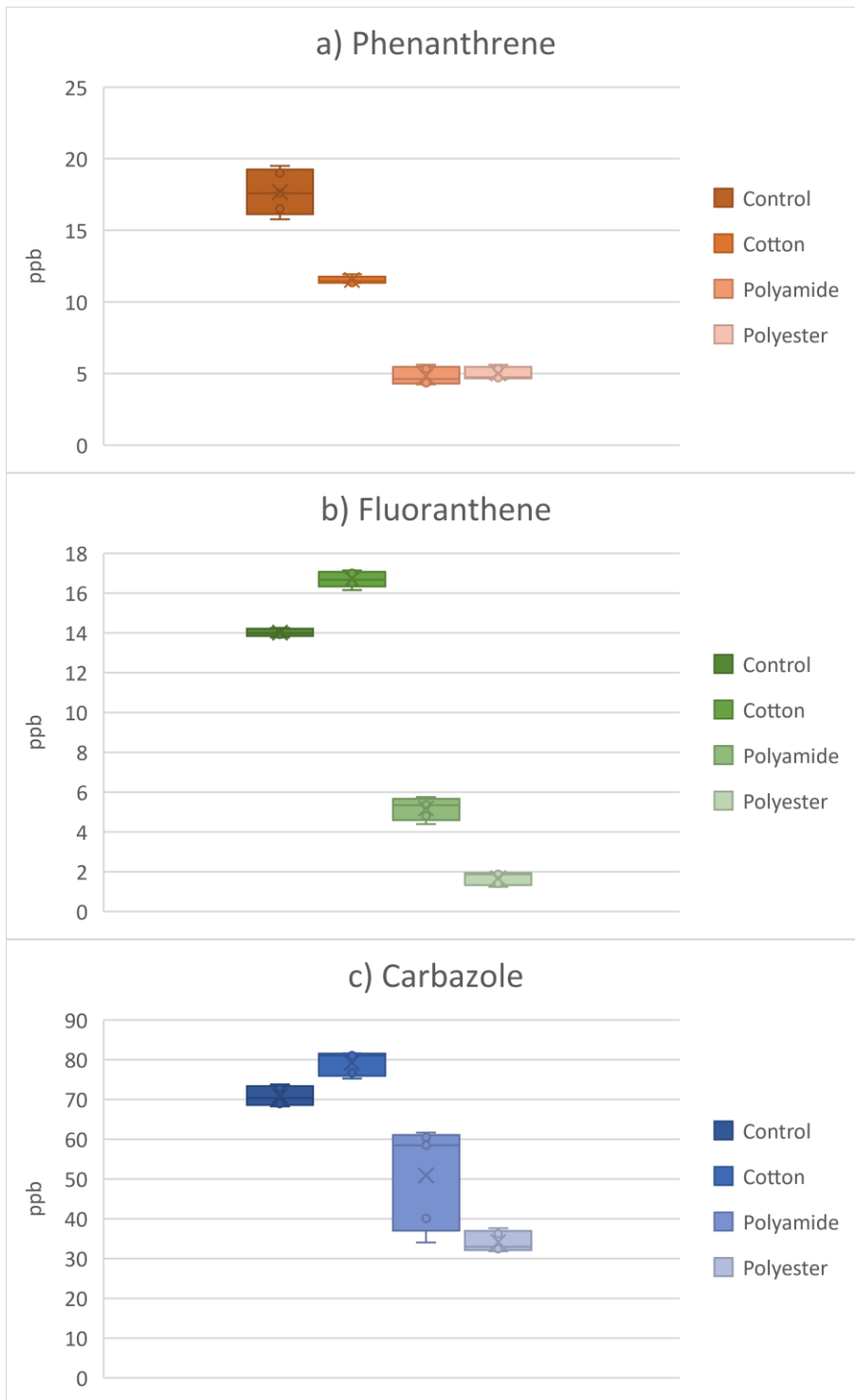


Figure 4.6 Boxplots with the mean concentration of each analyte after being exposed to the different fibres in saltwater for a) phenanthrene, b) fluoranthene & c) carbazole

One-way ANOVA tests found that there were significantly different concentrations of analytes remaining in the solution among the three types of fibres in saltwater solution ( $p < 0.05$ ). The Games-Howell test showed which fibres were significantly different from one another. In the case of phenanthrene, cotton was significantly different from the other two fibres, but polyester and polyamide did not significant differ between each other (i.e., cotton [ $M = 11.51$ ] > polyester [ $M = 4.98$ ] = polyamide [ $M = 4.81$ ]). However, for both fluoranthene and carbazole, all three fibre types were significantly different from one another (i.e., carbazole: cotton [ $M = 79.28$ ] > polyamide [ $M = 51.26$ ] > polyester [ $M = 34.12$ ]; and fluoranthene: cotton [ $M = 6.69$ ] > polyamide [ $M = 5.18$ ] > polyester [ $M = 1.68$ ]).

Table 4.3 ANOVA test results when comparing remaining analytes in saltwater.

Analytes		Descriptive statistics ( $\mu\text{g/L}$ )				ANOVA results		
		Cotton	Polyamide	Polyester	N	F	df	Sig.
Phenanthrene	M	11.51 <sup>a</sup>	4.81 <sup>b</sup>	4.98 <sup>b</sup>	6	657.33	2, 8.59	<0.001
	SD	0.23	0.613	0.447				
Carbazole	M	79.28 <sup>a</sup>	51.26 <sup>b</sup>	34.12 <sup>c</sup>	6	342.65	2, 8.92	<0.001
	SD	3.139	16.44	2.599				
Fluoranthene	M	16.69 <sup>a</sup>	5.18 <sup>b</sup>	1.68 <sup>c</sup>	6	2568.90	2, 9.68	<0.001
	SD	0.376	0.549	0.335				

N/Q = non-Quantifiable; <sup>a, b, c</sup> = means followed by the same letter are not significantly different from one another at  $p > .05$  by the Games-Howell post-hoc test

Hypothesis 2a proposed that cotton fibres will take up lower amounts of compounds than polyester and polyamide fibres when exposed to compounds in saltwater solutions; and Hypothesis 1b proposed that polyester fibres will take up higher amounts of compounds than polyamide fibres when exposed to compounds in deionized water solutions. Based on the observed results, Hypothesis 1a is supported as for every compound, their concentration in the solution after being exposed to cotton is higher than when exposed to polyester and polyamide. Hypothesis 1b is partially supported, as the concentration in the solution exposed to polyester is lower for carbazole and fluoranthene, but not for phenanthrene where there is no significant difference in the concentration.

## Chapter 5

### Discussion

Fibre fragments released from domestic laundering provide a main source of primary microplastics and cellulose-based anthropogenic particles that pollute aquatic environments (Athey et al., 2020; Browne et al., 2011; Napper & Thompson, 2016). Release of these fibrous particles contribute considerably to the overall global microplastic pollution (Boucher & Friot, 2017). The presence of microplastics and fibre fragments in the environment in of themselves creates an ecological threat due to their persistence and disruption they cause to metabolic and development processes of aquatic organisms. It has also been suggested that due to textile fibres high sorption capacities that synthetic and natural fibre fragments provide an important role in the “transport and fate of chemical pollutants in the aquatic environment” (Sillanpää & Sainio, 2017). The authors suggested that more research needed to be conducted, and the current study begins to fill the gap in the literature.

Findings from the current study show that sorption capacities among two synthetic fibres (polyester and polyamide) and cotton fibres do differ in their uptake of chemicals when presented in aqueous solutions. This was done by a liquid-liquid extraction with dichloromethane. The recovered concentrate was analyzed by a GC-FID equipment, with the values obtained correspond to the concentration of the compounds left in the solution (not in the fabrics). As such, it must be understood that a higher reported value equals to a lower adsorption/interaction with the fabric.

Among the three fibres examined in this study, greater quantities of analytes remained in the aqueous solution which has been exposed to cotton, meaning that cotton absorbed the lowest amounts of compounds. This lower uptake by cotton was observed for all three compounds where detectable amounts were be obtained (i.e., phenanthrene, carbazole and fluoranthene). The relative trend among the three types of fibres where cotton absorbed the least and polyester the most (cotton < polyamide ≤ polyester) was found in both deionized water and saltwater. This behaviour is congruent to the one observed in other studies (Abdul-Bari et al., 2020; Vaezafshar, 2019).

The low interaction between cotton and the analytes can be attributed mainly to the cellulose chemistry of the fibres. The four analytes used in this study are composed by aromatics rings, providing them with non-polar (hydrophobic) properties. The cellulose chain is heavily charged with polar functional groups, so it is easier to create hydrogen bonds with another polar molecules (i.e., water) than creating intramolecular attractions (such as Van der Waals) with

non-polar molecules. As hydrogen bonding is the major form of intermolecular bonding between cellulose and other compounds, cellulose has a far higher affinity for water. In aqueous solutions, non-polar compounds can present increased partitioning toward fibrous surfaces (including cellulosic fibres), than the polar compounds (Liu et al., 2005). This may account for still high sorption of the most non-polar compound pyrene to cotton fibres so that it was difficult to quantify pyrene remaining in water.

The surface chemistry of polyester is very different from cotton, with the main difference being the benzene ring. Also, despite containing two polar ester groups in each monomer, the polar moment can be cancelled when the polymer is formed, as the negatively charged oxygen can be attracted to the positively charged carbon. The high interaction between polyester and aromatic compounds was observed previously (Chien et al., 2011; Rochman et al., 2013), and in particular for phenanthrene when compared to polyamide (Wang et al., 2018). Both the hydrophobic polyester fibres and non-polar compounds have low affinity for water, therefore, in aqueous solutions the non-polar compounds have a much higher affinity for adsorption to polyester than remaining in water (Aspland, 1992).

Polyamide fibres have both hydrophobic and hydrophilic sections distributed throughout the polymer structure. The methylene chains within polyamide enable non-polar interactions to occur, while the hydrophilic amide groups enable the sorption of water molecules into the fibre interior (Bortolato et al., 2008). The aliphatic sections of the chain made possible to create interactions with the non-polar compounds to a higher degree than cotton, but not as strong as polyester. These results are supported by the findings of Abdul-Bari et al. (2018), who observed that polyester was capable of absorbing higher amounts of non-polar 2-nonenal than the polar isovaleric acid, whereas the reverse was the case for polyamide. The relatively lower hydrophobicity of nylon compared with polyester, may indicate that polyester fibres have a greater affinity for non-polar compounds in aqueous solutions than polyamide. Similar results were found by Vaezafshar (2019) in the initial sorption of odorous VOCs in a synthetic sweat solution. Polyamide had lower affinity for the three more non-polar compounds, nonanal, 6-undecanone and undecanal, than polyester, whereas more water-soluble compounds such as octanoic acid and 2-heptanone with lower Log P values there were no differences between nylon and polyester in initial uptake.

The interaction between the fabric fragments and the analytes of interest can be also attributed to the analytes Log P values. Since Log P (Partition coefficient) indicates the ratio of concentration of a compound when two immiscible liquid phases are present in the same



system (e.g., water and octanol), it can be used as a reference to understand the preference of a compound to be more easily solubilized in an aqueous or organic solvent (Eq. 5.1).

$$\text{Log}P = \frac{[\text{analyte}]_{\text{octanol}}}{[\text{analyte}]_{\text{water}}} \quad \text{Eq. 5.1}$$

Despite not having two immiscible liquids during the exposition time between fabrics and saturated solutions, the fabrics can be considered as the second phase. The partition coefficients for phenanthrene, carbazole and fluoranthene are 4.46, 3.72 and 5.16, respectively. This could explain why even though carbazole has the highest solubility, is the least absorbed compound by the synthetic fibres.

It was unfortunate in the method carried out in the current study that it was not possible to quantify the amount of pyrene remaining in the solution following exposure to the fibres. However, that pyrene was not able to be quantified does not necessarily imply that the three fibre types had a much higher affinity towards it, and that it was significantly more absorbed than the other analytes. At this stage it is only possible to state that the interaction between fibres and pyrene was enough to reduce the concentration in the solution below the quantification limit of the equipment. As pyrene had much lower concentrations in both deionized water and saltwater saturated solutions to begin with. Extracting pyrene, and the other compounds, from the fibres directly would be necessary in future work to confirm whether the fibres had a higher overall affinity for pyrene compared with the other compounds in this study.

In the current study it was not possible to make a clear direct comparison between the absorption of compounds from deionized water compared with saltwater solutions. This in part was due to the different initial concentrations of compounds in the saturation solutions between the two conditions. This difference in concentration might be due to the salting out effect that takes place when a solution has a higher concentration of salts dissolved. This salting out effect is more noticeable when the analytes of interest are bigger or have a higher degree of hydrophobicity (Endo et al., 2012). This might be the reason of the sharp decrease in the concentration of fluoranthene in saltwater, but not for carbazole, which has an amino group in the central ring and is more water soluble.

## Chapter 6

### Conclusions

#### 6.1 Summary

The purpose of this work was to evaluate the absorption capacity of three common consumer apparel fibres (cotton, polyester, and polyamide) when exposed to four polyaromatic hydrocarbon compounds (pyrene, phenanthrene, fluoranthene, and carbazole) in two different types of aqueous environments (deionized water and saltwater). The fibres were selected to represent common consumer apparel and household textiles that undergo frequent domestic laundering. The four compounds were selected as they are widely spread by-products of human activity, especially the combustion of fossil fuels and represent a major hazard towards the environment due to their toxicity when ingested by freshwater and marine organisms.

Eight saturated solutions were prepared by dissolving each compound in deionized water and artificial saltwater until the solubility limit was reached. The concentration in the saturated solutions in deionized water ranged from 0.34 to 90.82 µg/L for pyrene and carbazole respectively; and in saltwater from 1.74 to 70.82 µg/L for pyrene and carbazole respectively. Small amounts (50 mg) of each type of fibres were added into each solution as yarn fragments and fibres were suspended in solution for 24 hours. Aliquots of solution were filtered to remove solid particles of fibres and subjected to liquid-liquid extraction with dichloromethane. The concentration of the compounds left in the solution were measured. As such, a higher value of analyte in solution corresponded to a relatively lower sorption/interaction with the fibre.

For phenanthrene, fluoranthene, and carbazole a trend was observed in the sorption of these three compounds based on fibre type. Cotton fibres had the lowest uptake towards the analytes used with the highest concentrations remaining in solution. This was followed by polyamide that had a higher affinity for the compounds than cotton, but typically lower than polyester. Lastly, polyester had the highest affinity for the compounds, as the concentration in all the solutions were considerably lower compared to cotton, and in most cases with polyamide. This relationship among compounds that exhibit low solubility in water can be attributed to the different polymer chain chemistry of cotton, polyester, and polyamide.

Pyrene was not included in the analysis as the concentrations of pyrene in the aliquots taken from solutions following exposure for all fibres were barely identified in both deionized and saltwater solutions.

## 6.2 Conclusions

The results obtained in this study show that among the three types of fibres, differences in the affinity of polyaromatic hydrocarbons toward fibres when exposed in an aqueous environment occur. Polyester exhibits the greatest affinity for the polyaromatic hydrocarbons when exposed to the analytes in aqueous solutions while cotton fibres have the lowest affinity to polyaromatic hydrocarbons in aqueous solutions. Polyamide fibres have lower affinity toward sorption of compounds than polyester, although they are more but a higher affinity than cotton.

Explanations for these findings relates to the inherent fibre chemistry and the preferential sorption of water to the polar groups in the fibres' polymer structure (cellulose or synthetic).

The result from this study is limited to the fibres used, the compounds selected and the conditions under which the experiments were conducted. Nonetheless, some pertinent findings related to the selective sorption of selected synthetic versus cellulosic fibres in aqueous environments have been shown. The results provide evidence that synthetic fibres make a greater contribution to environmental pollution than cellulosic fibres.

## 6.3 Limitations and Recommendations

The following limitations were apparent in the current research:

1. Yarn fragments were used in this study rather than fibre fragments that would be present in real world situations. Yarns were unravelled from standard textile fabrics as it had not been possible to source synthetic fibres without additional treatments in sufficiently small amount quantities. As such, the yarn fragments represent an aggregate of longer fibre fragments than would represent fibre fragments within aquatic environments. Therefore, the surface of each individual fibre may be less accessible to the analytes in the experiment and the overall surface area would have been smaller than fibre fragments in the environment. Therefore, the size and availability of surface area in the experimental work does not accurately represent the impact of the morphology of each fibre in the absorption of the compounds in real life conditions.
2. A limited range of chemical compounds was used in the current study. In real life conditions fibre fragments will be exposed to a high number of other diverse types of environmental pollutants (e.g., heavy metals, pesticides, medical active ingredients, etc.)
3. Only liquid-to-liquid extraction was used in the experimental and analysis of analytes remaining in the aliquot of liquid was measured. This limited the ability to calculate the number of compounds ad/absorbed by the fibres. In particular, a comparison in sorption between deionized and saltwater solutions was not possible. As well, the low solubility of

pyrene proved to be a drawback, as it was not possible to measure the most non-polar analyte in the study.

To address some of the limitations outlined above and/or to extend the research related to the sorption of chemical contaminants in aqueous environments the following recommendations for future research are made:

1. Use fibres that more closely represent the size of fibre fragments that would be found in real life conditions, rather than yarn fragments.
2. To confirm that the observations in this study, extract compounds directly from the recovered fibres. This way, the analytes observed in the solution plus the concentration in the fibres should be equal to the concentration on the saturated solutions prior to the exposition to fibres.
3. A wider range of compounds should be used, including those with higher solubility in water. This may prevent repeating the problem with pyrene of too low solubility.
4. Carry out experiments with a mixture of the analytes, to observe possible synergetic or antagonist effect between the compounds when interacting with the fibres.
5. Include other groups of chemicals, to simulate real conditions and evaluate the affinity of the fibres with analytes that have different properties, such as hydrophobicity, molecular weight and size, as well as different purpose/origin in human activities (e.g., heavy metals, pesticides, medical active ingredients, etc.).

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## Appendix A.

### Chromatography results.

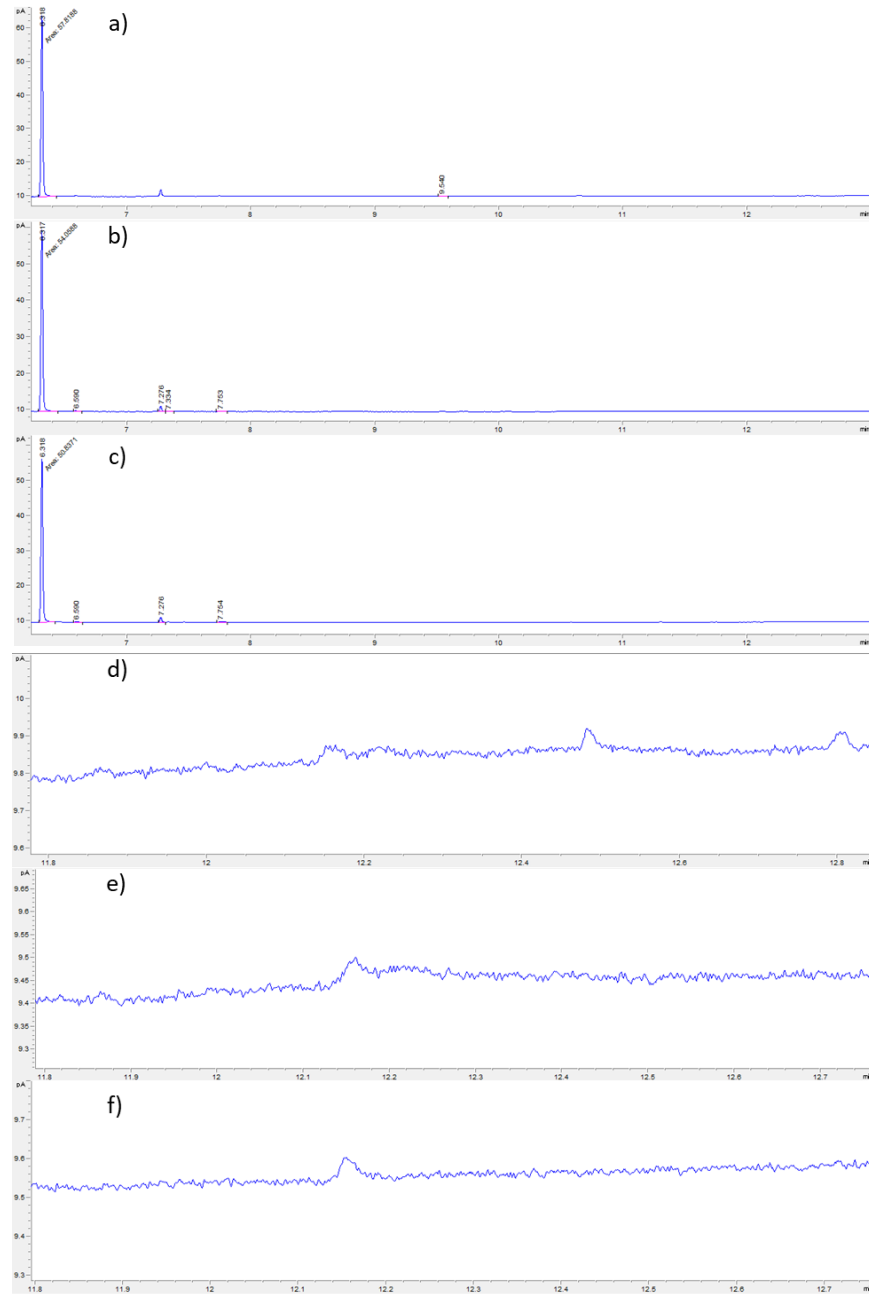


Figure A.1 Chromatographic signal for pyrene after exposure to a) cotton, b) polyamide, and c) polyester, and extraction in deionized water solutions. Images d), e) and f) detail the pyrene peaks corresponding to a) b) and c), but can not be quantified

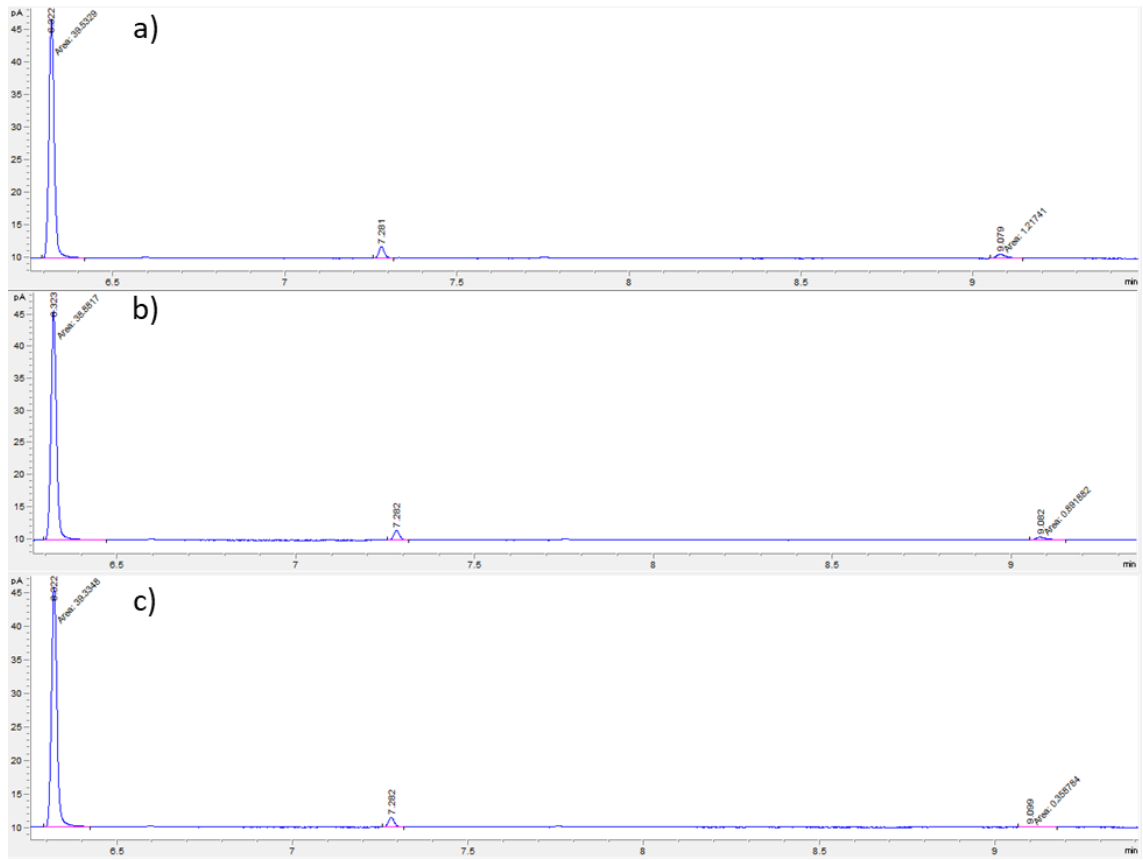


Figure A.2 Chromatographic signal for phenanthrene after exposure to a) cotton, b) polyamide, and c) polyester, and extraction in deionized water solutions



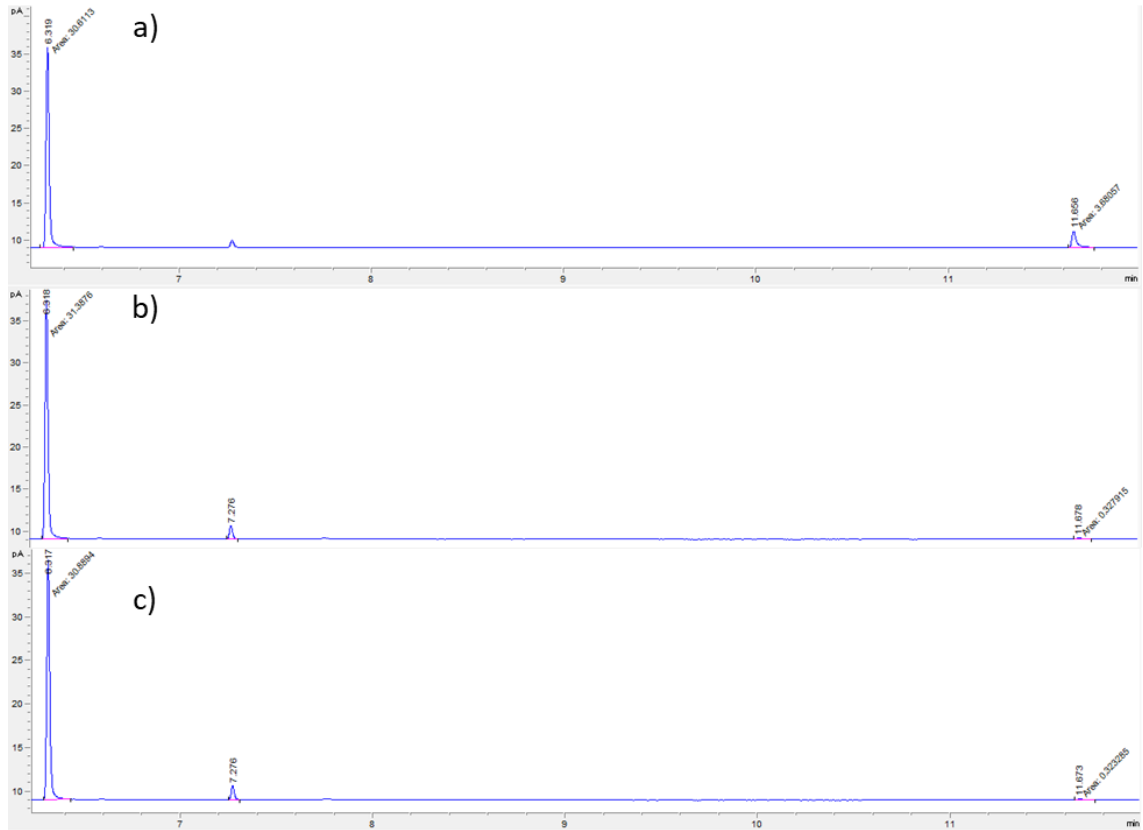


Figure A.3 Chromatographic signal for fluoranthene after exposure to a) cotton, b) polyamide, and c) polyester, and extraction in deionized water solutions

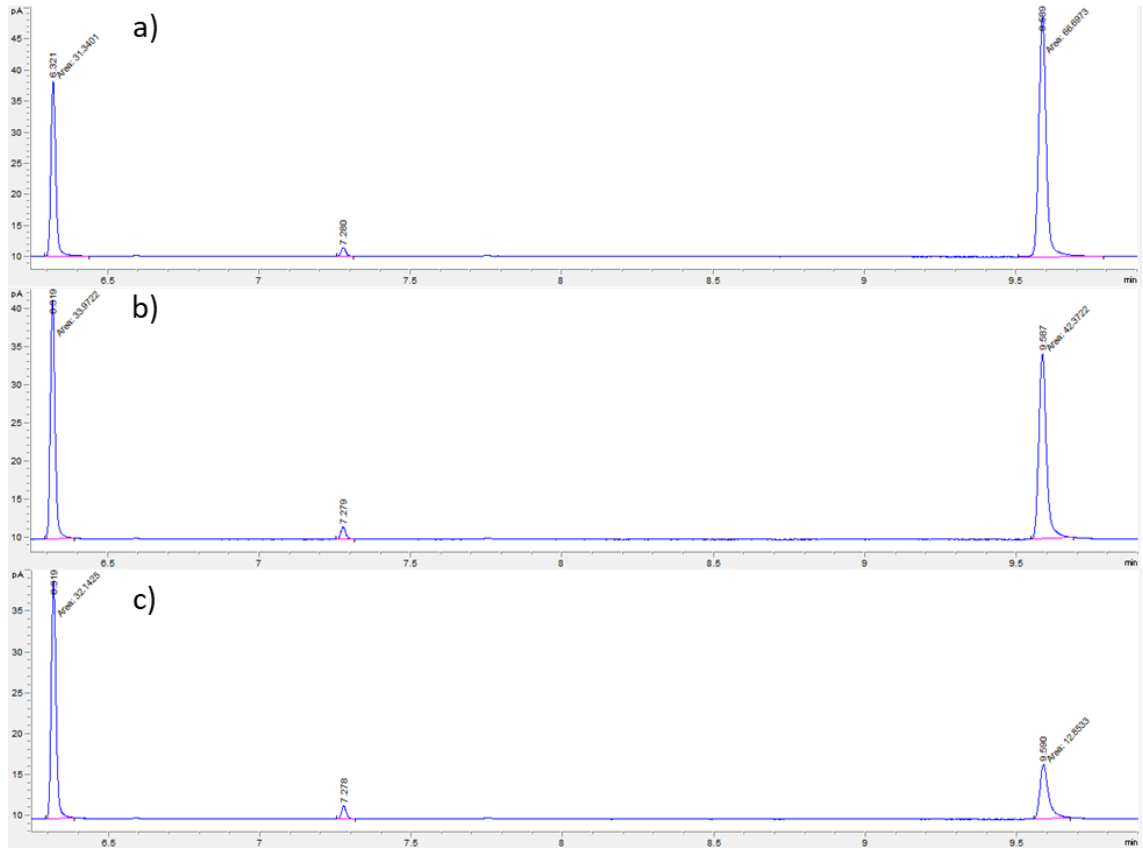


Figure A..4 Chromatographic signal for carbazole after exposure to a) cotton, b) polyamide, and c) polyester, and extraction in deionized water solutions

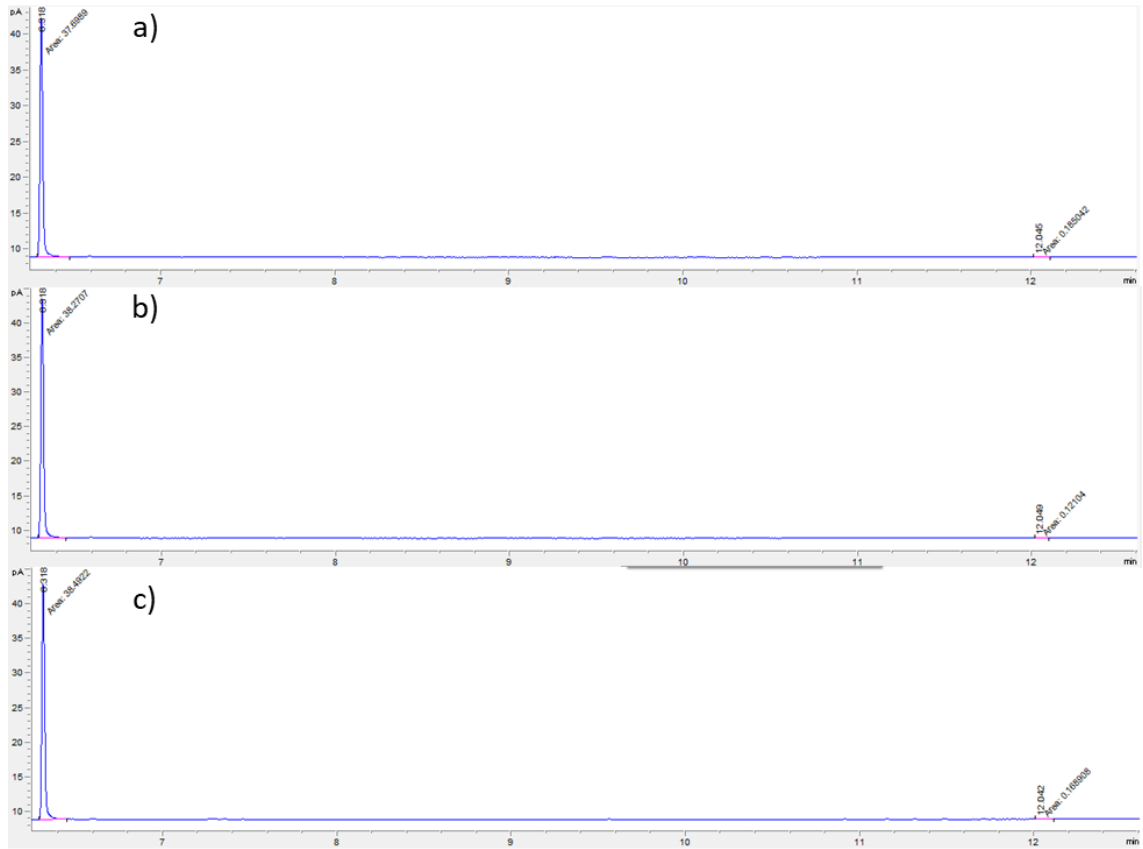


Figure A.5 Chromatographic signal for pyrene after exposure to a) cotton, b) polyamide, and c) polyester, and extraction in saltwater solutions

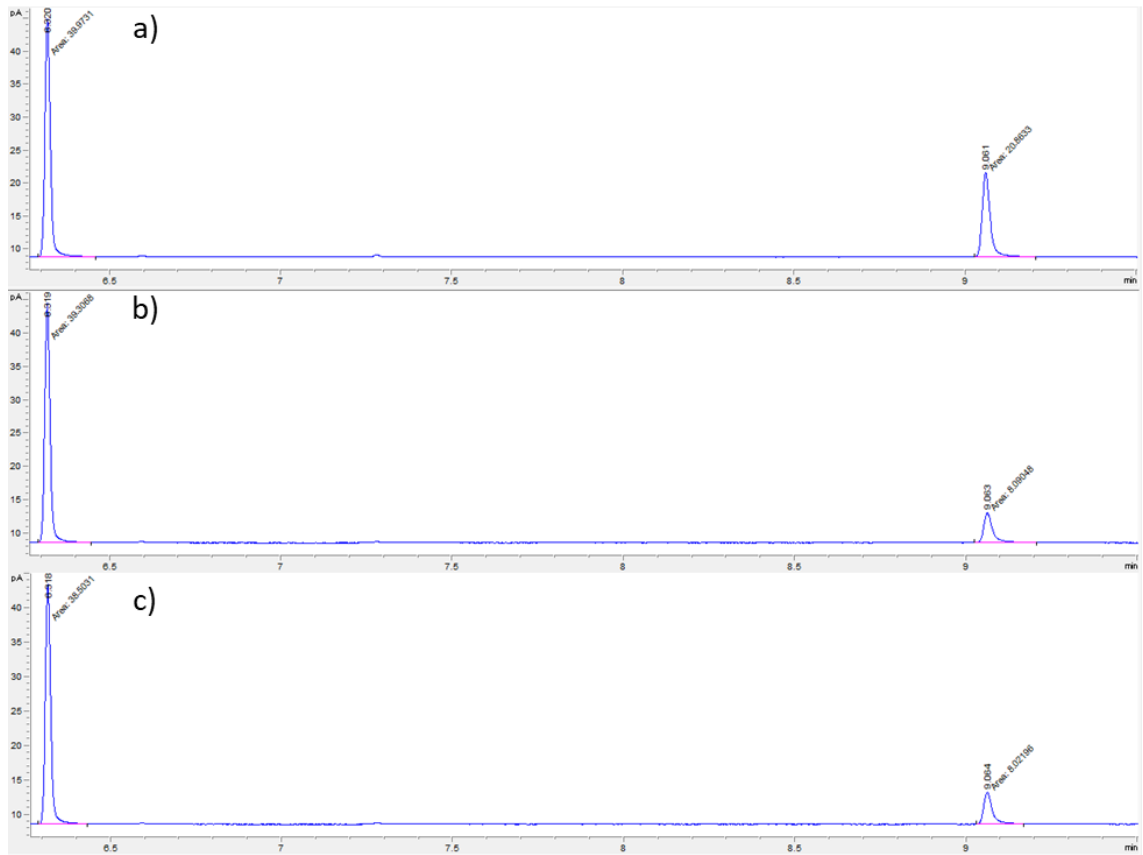


Figure A.6 Chromatographic signal for phenanthrene after exposure to a) cotton, b) polyamide, and c) polyester, and extraction in saltwater solutions



Figure A.7 Chromatographic signal for fluoranthene after exposure to a) cotton, b) polyamide, and c) polyester, and extraction in saltwater solutions

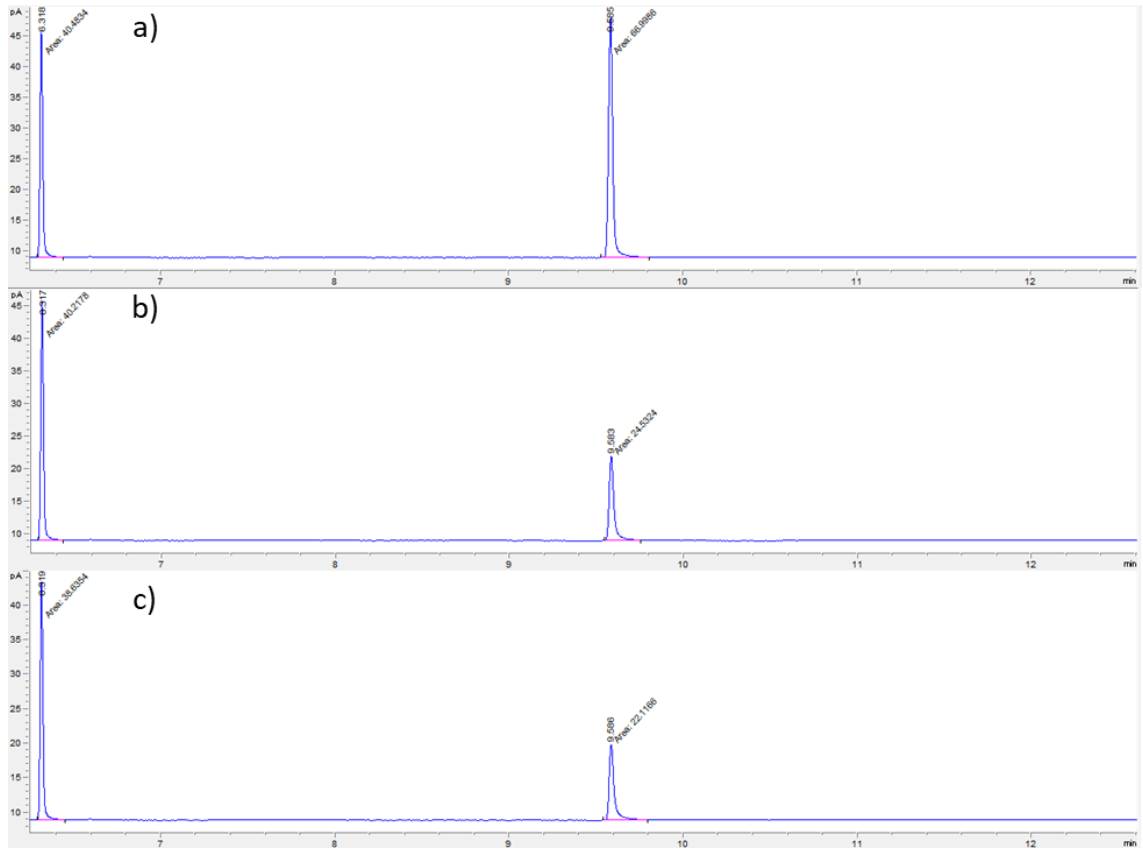


Figure A.8 Chromatographic signal for carbazole after exposure to a) cotton, b) polyamide, and c) polyester, and extraction in saltwater solutions