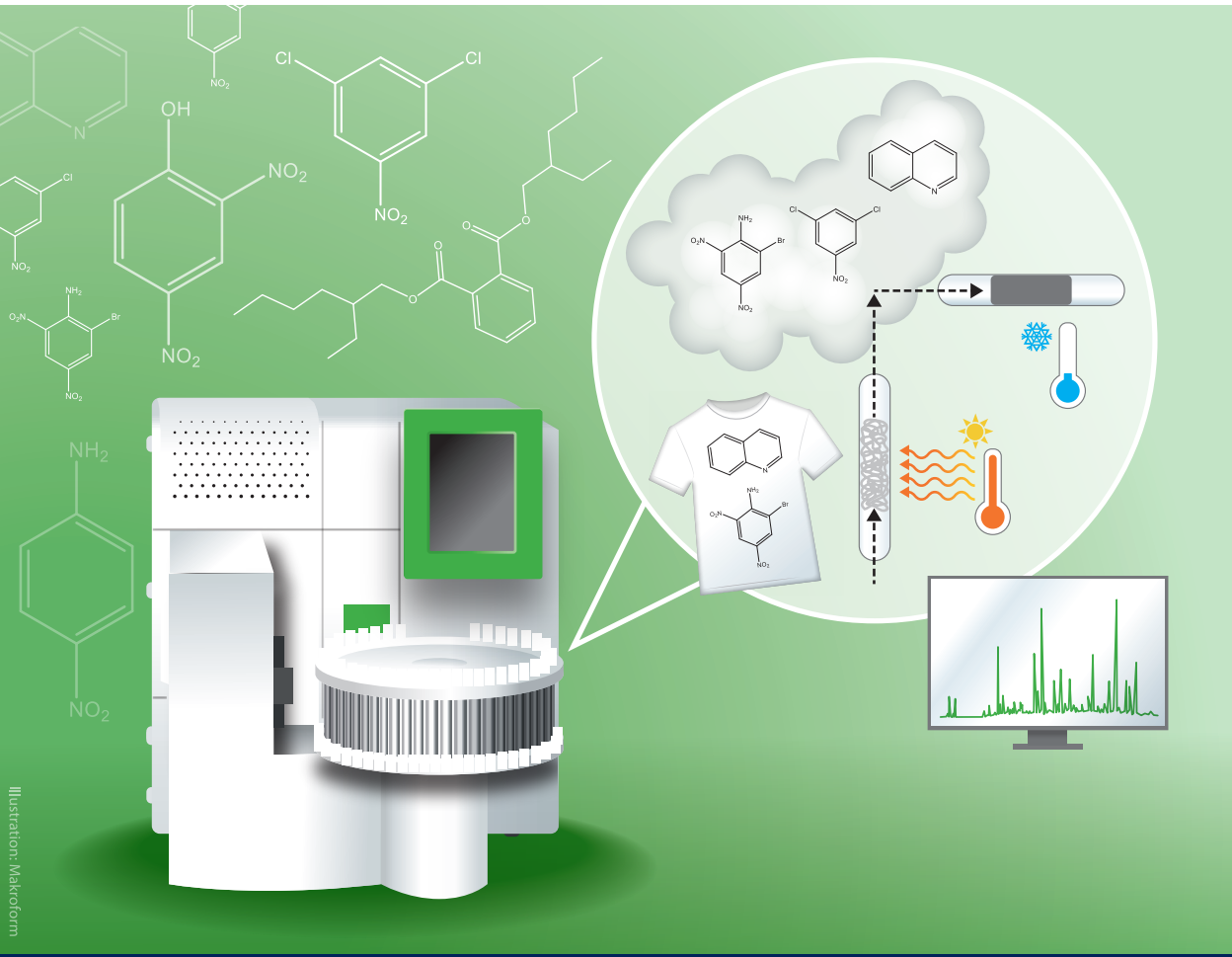
Stockholm University

Towards safe and sustainable fashion

Screening methodologies to detect health-hazardous chemicals in textiles and textile processing

Tim Åström



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Doctoral Thesis in Analytical Chemistry at Stockholm University, Sweden 2025

Towards safe and sustainable fashion

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Tim Åström

Academic dissertation for the Degree of Doctor of Philosophy in Analytical Chemistry at Stockholm University to be publicly defended on Wednesday 4 June 2025 at 13.00 in Magnelisalen, Kemiska övningslaboratoriet, Svante Arrenhius Väg 16B, and online via Zoom, public link is available at the department website.

Abstract

As one of the top global industries, textile manufacturing utilizes several thousands of industrial chemicals, many of which end up in the finished garments. These residues constitute a widespread, possibly hazardous, exposure of the general population, yet the long-term health effects remain largely unknown. Skin allergy - a life-long, incurable condition – is one health effect of repeated skin exposure to one or several chemicals. Among the Western population, textile allergy is estimated to have a prevalence of around 1%.

Fast-fashion trends make the chemical content in everyday textile apparel hard to predict, as non-regulated chemicals are rapidly introduced into production. Only a tiny fraction of the used chemicals is hitherto regulated, and there is a lack of oversight regarding the content in everyday garments. A recently introduced EU legislation concerning handling textile waste motivates the development of alternative recycling methods for worn-out textile apparel. Upcycling methods are also important to reduce the environmental burden from incineration and landfilling.

This thesis focuses on developing analytical tools for the quantitative chemical screening of textiles. A novel, fully automated analytical methodology based on thermal desorption - gas chromatography-mass spectrometry (ATD-GC/MS) was developed for polyester, synthetic polyester blends, and cotton, constituting at least 75% of the retail market. The method is especially suitable for detecting semi-volatile compounds capable of skin permeation. Recently, the method was proposed for evaluation as a potential EU standard. Ultimately, the method could help ensure regulatory compliance within the textile industry.

In addition, a high-resolution mass spectrometry workflow was developed to investigate the fate of hazardous substances during the upcycling of polycotton waste into cellulose nanocrystals. Most hazardous textile chemicals were found to remain in the polyester, while the upcycled product contained much less contaminants. Chemical release into waste streams is correlated with solubility under acidic conditions, highlighting target compounds for removal during upscaling.

Together, the developed methods contribute to a robust analytical toolbox with the potential to improve chemical oversight in textiles, support regulatory expansion, and promote safer, more sustainable fashion.

Keywords: *Sustainable fashion, Textile screening, Thermal desorption.*

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Department of Chemistry

Stockholm University, 106 91 Stockholm

TOWARDS SAFE AND SUSTAINABLE FASHION

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To my beloved family

All things are poison, and nothing is without poison. Solely the dose determines that a thing is not a poison" – **Paracelsus**

List of papers included in the thesis

I. Josefine Carlsson[*], **Tim Åström[*],** Conny Östman and Ulrika Nilsson
Disperse azo dyes, arylamines and halogenated dinitrobenzene compounds in synthetic garments on the Swedish market

Contact Dermatitis, Volume 87 Issue 6 pages: 558-558 (2022)
DOI: 10.1111/cod.14163

Contribution: Contributed to the study design, performed all experiments to screen arylamines and halogenated dinitrobenzene compounds, analyses, data processing and evaluation and wrote a major part of the original manuscript draft. [*]The authors contributed equally and shared the first authorship.

II. **Tim Åström,** Maria-Ximena Ruiz-Caldas, Lisa Skedung, Ioana Chelcea, Charlotte Nilsson, Aji P. Mathew, Ioannis Sadiktsis and Ulrika Nilsson
The fate of hazardous textile pollutants in an upcycling process for post-consumer garments

Cleaner Engineering and Technology, Volume 22, October 2024, 100794
DOI: 10.1016/j.clet.2024.100794

Contribution: Main contributor of the ideas behind the study and the study design, performed all experiments for non-target screening of samples using LC-ESI-Orbitrap, data analysis, processing and evaluation. Wrote the original draft of the manuscript.

III. Josefine Carlsson*, **Tim Åström***, Conny Östman and Ulrika Nilsson
Solvent-free automated thermal desorption-gas chromatography/mass spectrometry directly screening hazardous compounds in consumer textiles.
Analytical and bioanalytical chemistry, Volume 415, pages 4675–4687, (2023)
DOI: 10.1007/s00216-023-04780-x

Contribution: Contributed to the study design, performed part of the method development, analyses, data analysis, processing and evaluation. Wrote a major part of the original draft of the manuscript. *The authors contributed equally and shared the first authorship.

IV. **Tim Åström,** Ioannis Sadiktsis, Conny Östman, Maria-Ximena Ruiz Caldas and Ulrika Nilsson
Automated thermal desorption-gas chromatography/mass spectrometry for screening of hazardous chemicals in cotton and cotton blend garments – analytical challenges
[Submitted].

Contribution: Main contributor of the ideas behind the study and the study design. Performed all experiments, data analysis, processing, and evaluation. Wrote the original draft of the manuscript.

Papers not included in the thesis

V. Josefine Carlsson, Awat Dostberg, **Tim Åström**, Julia Matyjasiak, Anders Kallin, Sanja Juric, and Ulrika Nilsson
Health risks from exposure to chemicals in clothing - Non-regulated halogenated aromatic compounds

Chemosphere, Volume 363, September 2024, 142930
DOI: 10.1016/j.chemosphere.2024.142930

Abstract

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This thesis focuses on developing analytical tools for the quantitative chemical screening of textiles. A novel, fully automated analytical methodology based on thermal desorption - gas chromatography-mass spectrometry (ATD-GC/MS) was developed for polyester, synthetic polyester blends, and cotton, constituting at least 75% of the retail market. The method is especially suitable for detecting semi-volatile compounds capable of skin permeation. Recently, the method was proposed for evaluation as a potential EU standard. Ultimately, the method could help ensure regulatory compliance within the textile industry.

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Together, the developed methods contribute to a robust analytical toolbox with the potential to improve chemical oversight in textiles, support regulatory expansion, and promote safer, more sustainable fashion.

Populärvetenskaplig sammanfattning

Textilindustrin, en av världens största industrier, använder sig av tusentals kemikalier vid tillverkning av nya kläder, möbler och hushållstextilier. Det mesta tvättas ur materialen redan i slutskedet av tillverkningen, men en hel del finns också kvar i de färdiga plaggen. Många av kemikalierna är giftiga för människor, växt- och djurliv, exempelvis syntetiska färgämnen och de kemiska ämnen som tillsätts vid färgning och andra processer. Kemikalierna sitter inte fast i tyget och läcker därför ut från klädavfall i soptippar och via avloppssystemet vid tvätt. I mitt avhandlingsarbete har jag mestadels undersökt de kemikalier som vi människor kommer i kontakt med från vanliga kläder, som färgämnen och andra processkemikalier. När textilkemikalier migrerar från tygfibrerna och tas upp av huden, kan de ge upphov till textilallergi eller andra hälsoeffekter. Många är misstänkt eller påvisat allergiframkallande, cancerframkallande, mutagena (kan leda till förändringar av arvsmassan) eller fertilitetsstörande. Exponeringens påverkan på den allmänna hälsan är i stort sett outforskad, men är viktig att undersöka vidare med tanke på att miljarder människor varje dag bär kläder mot huden. En hittills välkänd effekt från kemikalier i kläder är textilallergi som beräknas drabba cirka en procent av befolkningen i västvärlden.

Mitt avhandlingsarbete har främst fokuserat på analytisk metodutveckling, för att kunna undersöka vilka textilkemikalier som är vanligast i kläder. I ett av projekten analyserades ett stort antal plagg från den svenska marknaden. Höga halter av möjliga textilallergener eller mutagener uppmättes, bland annat färgämnen och deras byggstenar, aromatiska aminer. En välkänd och kraftigt hudallergen substans, liksom andra liknande ämnen, upptäcktes i ungefär tio procent av plaggen. Förekomsten i kläder har hittills varit okänd och den eventuella betydelsen för textilallergi, som även beror på halten och hur mycket som släpper från kläderna, bör undersökas vidare.

En av metoderna som beskrivs i avhandlingen har utvecklats för att underlätta analyser av textiler med avseende på just de kemiska ämnen som lättast kan migrera från tyger till hud och sedan tas upp genom huden. Metoden kan inte användas för färgämnen eller metaller, men för hundratals andra kemiska ämnen, som bensotiasoler, kinoliner, aromatiska aminer, ftalater, med flera och är en snabb analysmetod som ersätter befintliga mer tidskrävande arbetssätt baserade på farliga lösningsmedel. Metoden, ATD-GC/MS, bygger på att ett textilprov snabbt värms upp till 175 °C så att kemikalier avdunstar från provet och den bildade ångan leds automatiskt vidare till analysinstrumentet, en gaskromatograf/masspektrometer, med vilken föreningarna identifieras och mäts. ATD-GC/MS är, just nu medan avhandlingen skrivs, under bearbetning som förslag till ny europeisk standardmetod för analys av textilier.

En annan av metoderna som jag har utvecklat undersöker hur, och i vilken omfattning, farliga kemikalier kan ta sig igenom en förädlingsprocess för textilier. Processen som innebär utvinning av cellulosa från avlagda kläder, t ex av polyester-bomull, är hittills i laboratorieskala och använder svavelsyra för att extrahera cellulosa i form av nanokristaller. Det är ju viktigt med miljövänliga förädlingsprocesser för att kunna ta vara på textilavfall och återvända en stor del av materialet istället för att bränna upp eller lagra avfallet på deponier. Den utvunna cellulosan är en biologisk nedbrytbar produkt som ska kunna användas för en rad olika områden, till exempel som isolerande material i byggnader. Innan uppskalning av denna och liknande förädlingsprocesser, så behövs kännedom om i vilken grad skadliga kemikalier läcker ut i miljön via processvatten och till den färdiga produkten, i detta fall cellulosan. I just det här exemplet resulterade återvinningen i en mindre giftig slutprodukt, men studien gav också insikten om att vissa åtgärder är viktiga vid en uppskalning. Avfallet från processen, polyestern, innehöll det mesta av färgämnen, aromatiska aminer och andra skadliga ämnen, men skadliga ämnen läckte även ut till processvattnet, bland annat färgämnen och PFAS. Ftalater fördes vidare till slutprodukten, dock i mycket lägre nivåer än de tillåtna.

Behovet av att kunna analysera kläder och textilier är stort och kommer att vara det även fortsättningsvis då modet snabbt växlar och nya kemikalier introduceras. Syftet med

de framtagna metoderna är förenklade analyser som kommer att kunna ge mer kunskap om den kemiska exponeringen. Min förhoppning är att användning av ATD-GC/MS kan leda till en bättre och mer omfattande kontroll av kläders kemikalieinnehåll. Krav på innehållsdeklaration för kläder, med redovisade halter av kemikalier, förutom materialkomposition, skulle leda till förbättrad konsumentsäkerhet, bättre miljö och en lägre förekomst av textilallergi.

Abbreviations

ACD	Allergic Contact Dermatitis	**MDL**	Method Detection Limit
ATD	Automated thermal desorption	**MQL**	Method Quantification Limit
C.I.	Colour Index	**NRC**	National Research Council
CLP	Classification, Labelling and Packaging	**NTS**	Non-Target Screening
DART	Direct Analysis in Real Time	**PFAS**	Perfluorinated Alkyl Substances
ECHA	European Chemical Agency	**Polycotton**	Polyester/Cotton blend
EEA	European Environmental Agency	**REACH**	Registration, Evaluation, Authorisation and Restriction of Chemicals
ESI	Electrospray ionization	**RMSE**	Root Mean Square Error
EU	European Union	**SPE**	Solid Phase Extraction
FC	Fold change	**SVHC**	Substances of Very High Concern
GC	Gas Chromatography	**SVOC**	Semi-Volatile Organic Compounds
GCB	Graphitized Carbon Black	**TDM**	Textile-Dye Mix
GHS	Global Harmonised System of Classification	**TRI**	Toxic Release Inventory
HPLC	High-Performance Liquid Chromatography	**TSCA**	Toxic Substances Control Act
HRMS	High-Resolution Mass Spectrometry	**US EPA**	United States Environmental Protection Agency
IRIS	Integrated Risk Information System	**UV**	Ultra-violet light
KEMI	Swedish Chemical Agency	**VOC**	Volatile Organic Compounds
***log*P**	Octanol-water partition coefficient for non-ionizable forms	**WFD**	Waste Framework Directive

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Preface

The human skin is the largest organ of our bodies, comprising a surface area of approximately $2m^2$, providing a physical barrier towards the outer environment. At the same time, the skin constitutes a route of exposure to chemicals, such as from the environment or consumer products. For example, clothing garments may release hazardous chemicals that can be absorbed through the skin. Skin uptake of small organic molecules from a garment was shown already in the 1970s. A mutagenic metabolite 2,3-dibromopropanol was identified in the morning urine from a child after having slept in a pyjamas containing the flame retardant tris(2,3-dibromo propyl) phosphate[1]. Benzothiazole is another textile chemical shown to penetrate through the epidermal barrier of the skin[2], likely to result in systemic exposure.

There are many possible adverse health effects associated with clothing-mediated exposure to chemicals, for example, skin sensitization, carcinogenicity, mutagenicity, reproductive problems or even heavy metal poisoning[3–6]. Many studies have revealed the prevalence of harmful substances in textile apparel[7–13]. Textile allergy, a life-long, non-curable health condition caused mainly by chemicals, has been studied for years[14–21]. The clinical manifestation is allergic contact dermatitis (ACD), a skin eczema that appears when the skin is exposed to the substance. Previous studies have shown several disperse dyes and some arylamines to be potent skin sensitizers, but the knowledge is limited regarding most textile-related chemicals[22–24,17].

Fast-fashion trends lead to the use of new substances in textile manufacturing processes. Today, several thousand are already used in the global textile industry. Apart from leading to possible human health issues, the number and amounts of chemicals constitute a huge environmental problem. During manufacturing, many process chemicals are released into the aquatic ecosystem. For example, the European Chemical

Agency (ECHA) has previously estimated the textile industry to be responsible for nearly half of the released nonylphenol ethoxylate and its transformation product, nonylphenol[25]. The release of benzothiazole and quinolines into sewage waste has been estimated to be around 0.5 g and 0.24 g, respectively, during the laundering of 5 kg of new polyester garments[26]. A study by Umeå University and others identified seventy-two compounds emitted into the sewage, such as phthalates, organophosphates, arylamines, bisphenols, perfluorinated alkyl substances, and formaldehyde[27].

Scope of the thesis

To protect human and environmental health, the regulation of textile chemicals would probably need to be expanded. Wearing clothes close to the skin may lead to the uptake of many likely hazardous compounds, which also contribute to environmental pollution when released during manufacturing and laundry. The knowledge gap regarding the contents of ordinary clothes and other textiles for daily use is still large. Although various analytical methods are available, they are mostly tedious and laborious for comprehensive surveys. Simpler-to-use analytical workflows would facilitate an improved oversight of the complex and varying chemical contents in clothing.

Therefore, the present thesis has focused on analytical strategies for screening textile chemicals in various contexts. The primary aims of the work behind this thesis were to contribute with:

1. **More knowledge regarding the content of potentially health-hazardous substances in clothing, focusing on compounds most prone to be released from textile fibres that might be taken up by human skin.**
2. **A simpler-to-use method for comprehensive screening of chemicals in standard clothing fabrics, such as polyester and cotton, focusing on substances available for skin uptake.**

Considering the escalating environmental issues with worn-out apparel subjected to incineration and landfilling, there is an increased need for methods to upcycle post-consumer textiles. Since such fabrics may contain large amounts of chemicals, another aim was to:

3. **Develop a quantitative screening workflow to follow the fate of hazardous chemicals in a textile upcycling process, from post-consumer polycotton garments to extracted cellulose.**

Background

The average annual consumption of household textiles is estimated to be 12-26 kg/EU citizen[28–31]. In 2017, the textile industry was valued at 1.3 trillion US dollars, and among all textiles produced, clothing is expected to remain the most extensive application, accounting for around 60% of the global textile production in 2017. Still, less than 1% of the worn-out textile apparel is recycled into new garments, resulting in economic loss and increased environmental impact from incineration and landfilling[32]. Textile production within the EU mainly focuses on fashion and clothing, while household- and industrial/technical textiles constitute around 10-20%[33].

On average, each EU citizen spends €630 yearly on textiles, of which a vast majority, >70%, are imported from outside the EU, mainly from Southeast Asia[33]. The countries within the EU-27 represent the world´s 2nd largest textile exporters, among which Italy is the most significant[33,34], **Figure 1.**

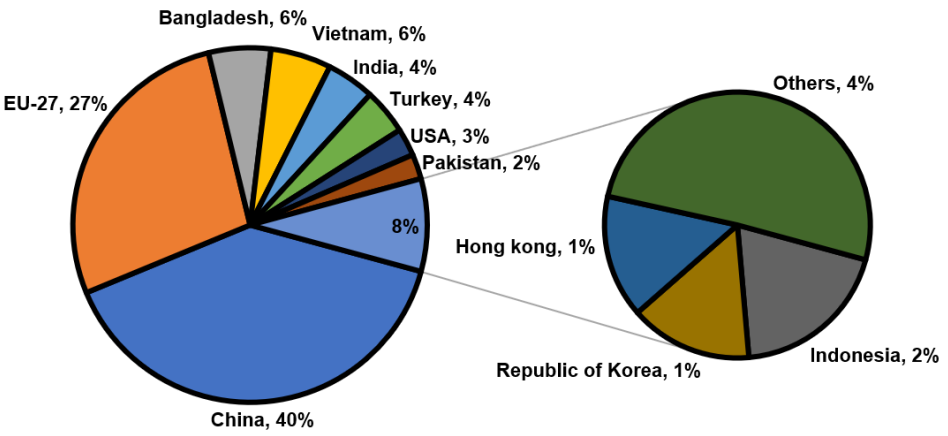

Figure 1: Top ten global textile exports based on 2022 data[33]

The average consumption of reused textiles was 2.3 kg/EU citizen, corresponding to only 13% of the total consumption in 2021[35]. In 2022, the combined textile waste within the EU-27 was nearly 7 million tonnes, of which around 75% was subject to incineration or landfilling[35]. To resolve this, a Waste Framework Directive[36] (WFD) is valid from 2025, forcing EU members to establish separate textile collection systems at the municipal level for all worn-out textile apparel to establish a circular textile economy. As a result, it is no longer allowed within the EU to mix textiles in household municipal waste[37,38].

Raw fibres in textile production

The raw fibre materials are natural, semi-synthetic or synthetic, consisting of repeating subunits of polymeric structures. Natural fibres include plant-based and animal-based fibres and are perceived as more eco-friendly alternatives since they are biodegradable. The major types are:

- Cellulose, e.g., cotton, linen, hemp and jute
- Protein, e.g., wool, silk, mohair and cashmere

Artificial fibres include three sub-categories:

- Cellulosic, e.g., viscose, lyocell, modal and cupro
- Semi-synthetic, e.g., acetate, tri-acetate and promix
- Synthetic, e.g., polyester, polyamide, acrylic, elastane etc.

The environmental impact of standard synthetic fibres, such as polyester, is of great concern due to the petrochemicals involved during production. It has been estimated that around 8% of the total release of microplastics into the oceans within the EU originates from synthetic textiles[39].

The tendency towards bio-based synthetic polymers derived from living organisms, renewable-based plastic materials, e.g., polylactic acid, polyhydroxyalkanoates, and polymers derived from agricultural resources, such as wood or fibre crops, but also algae, fungi, and waste from agriculture, is growing yearly. Worn-out textile apparel is another source of these bio-based polymers. The only commercially available bio-based synthetic fibre today is polylactic acid (**Figure 2**), possessing inferior performance compared to polyester. With growing awareness and demand for sustainable fashion, bio-based alternatives may outcompete traditional plastic-based polymers in the future, and shifting towards sustainable options may decrease the dependency on fossil-based polymers. In 2021, the total produced value of bio-based textiles in the EU was around €25 billion[40].

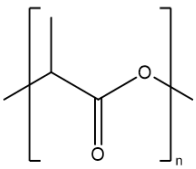

Figure 2: The only commercially available bio-based synthetic polymer, polylactic acid.

Figure 3 shows some of the synthetic fibre materials used for garment textiles. Polyester is the most common textile fibre[41]. Polyamide is also widely used, often synthetic, and exists naturally in silk and wool. Nylon is a synthetic polyamide fibre; two variants of nylon are illustrated (**Figure 3**). Acrylic fibres are synthesized from polyacrylonitrile[42]. Acrylic

fibres are mechanically strong and possess good abrasion resistance[43]. Elastane (spandex or lycra) is composed of a long-chain polyurethane polymer. In clothing, elastane blends with other fibres to combine various features, giving a better quality, e.g., breathable, durable and elastic articles with a smooth texture[44].

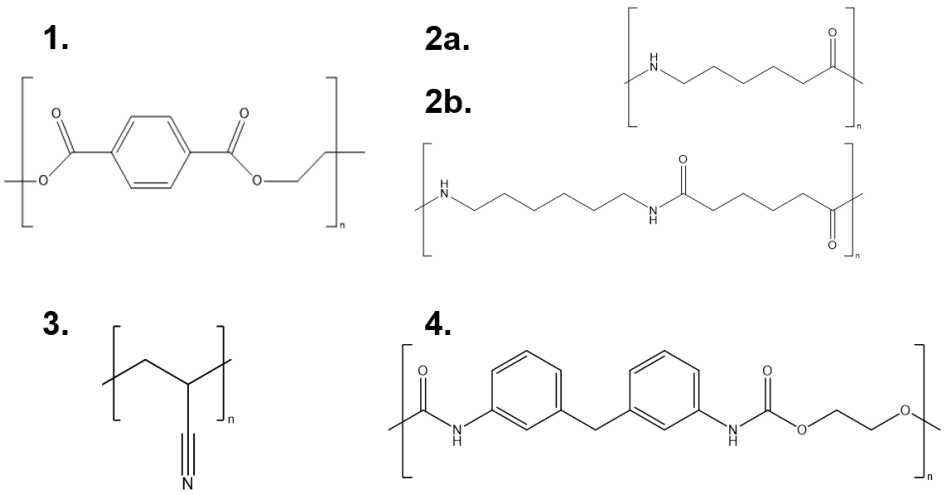

Figure 3: Some standard synthetic textile fibres 1) polyethylene terephthalate, 2a) Nylon 6, 2b) Nylon 6.6, 3) polyacrylonitrile and 4) polyurethane

Natural fibres

Cotton, wool, jute and silk are the most common natural fibres. Plant-based fibres include cellulose, hemicellulose, and lignin, while animal fibres, e.g., wool and silk, are protein-based**.** It has been estimated that approximately 300 million people are involved in natural fibre production, primarily cotton[45].

Cotton, **Figure 4,** comprises 88-96.5% α-cellulose; the rest are proteins, organic acids, inorganic substances, and other sugars[46]. The cellulose polymer is a linear 1,4-β-glucan polymer with repeating subunits of D-anhydroglucose[47]. The strength, durability, high fibrillar and crystalline nature of cellulose depend on the formation of intra- and intermolecular hydrogen bonding between hydroxyl groups in the glucose ring, which makes the molecule hydrophilic[47]. Cotton crops enable an income source for more than

250 million people worldwide[48]. Negative environmental impacts of cotton include enormous water consumption during cultivation[49], production, washing and drying[50]. As a result, attempts have been made to mitigate and promote an eco-friendly manufacturing process on behalf of the World Wildlife Fund (WWF), resulting in an organization called the Better Cotton initiative, a commitment involving a wide range of members from the agriculture to the commercial top-selling brands[48,51].

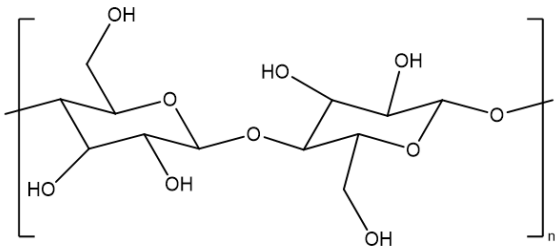

Figure 4: Cellulose structure

Wool is mainly produced from fur from sheep, such as Merino, Lincoln, and Sussex goats and camelids. Wool is the most hydrophilic type of all fibres and consists of an α-keratin protein[52]. Wool possesses elasticity, resilience, and good wrinkle-recovery properties.
For over 4000 years, silk has been highly valued for textile applications. Certain insects and spiders produce it in their web or cocoon construction. The most widely used silk is obtained from cocoons of mulberry silkworms (*Bombyx mori*) and consists of two proteins, 70-75% fibroin and 25-30% sericin. Due to its high strength in binding dyes and luster, silk fibres are still considered the premium textile fibre today[53].

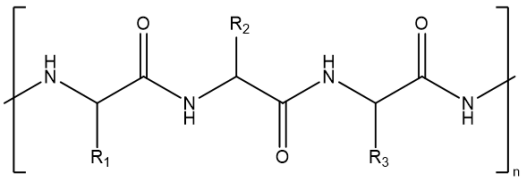

Figure 5: *G*eneric peptide illustrating the chemistry of protein fibres, e.g., wool and silk. The substituents R_1 – R_3 represent the side chains of an amino acid.

Linen originates from the flax plant, comprises 70% cellulose and 30% pectin, and is mainly recognized for its coolness and freshness, especially during warm days. The main characteristics are strong plant-based fibre and smooth absorbing material but poor elasticity[54].

The natural mineral-based fibres are derived from rock, metal clay or glass materials and have outstanding features against corrosion, humidity, and thermal insulation. In addition, these fibres offer unique fire resistance and durability and provide long-lasting textiles. Typical mineral examples include asbestos, ceramic, carbon, and glass-based mineral fibres. Asbestos, traditionally used as insulation material, is banned; ceramic fibres are very resilient to heat; carbon fibres are lightweight materials exhibiting good mechanical strength typically used in aerospace applications; and glass fibres are usually used for fibre-glass insulation and filters. In the fashion industry, mineral fibres, e.g. basalt and slag wool, are versatile textiles due to their high durability and sustainability, which makes them suitable for sportswear and outdoor gear[55].

Global fibre production

In 2023, the fibre production was 124 million tonnes globally[56]. The manufacturing of synthetic fibres, mainly polyester, has dominated the market since the mid-1990s when it overtook cotton fibre production[57]. The second most produced fibre is cotton, while other synthetic fibres account for around 10%. The global sheep wool production was around 1%. Recycled polyester is below 15 % of the total polyester production, and the

corresponding share for recycled polyamide was only 2% in 2023. Of the annual total fibre production, less than 1% originates from worn-out textile apparel. Most of the recycled polyester originates from plastic bottles[56].

Man-made cellulosic (MMC) fibres accounted for 6% of the global fibre production in 2023, with viscose (rayon) as the most popular product. MMC fibres are derived from wood pulp, which could be problematic from the perspective of deforestation. Lyocell (Tencel) is regenerated cellulose from eucalyptus[58] and does not require irrigation or pesticides. Bemberg® (cupro) is derived from cotton linter, and Pinatex® from pineapple leaves[57].

Textile manufacturing

The textile production constitutes a multistep procedure, as illustrated in **Figure 6.** The pretreatment steps of any fabric before weaving, knitting, and dyeing are necessary to remove any residual content in the raw fibres, e.g., pectins, cotton seeds, waxes, dirt, and oils., to maintain the desired properties of the material, *i.e.,* enhance dyeability and attachment of functional chemicals at a later stage.

The intended properties of fabrics are several, such as softness, durability, flexibility, strength, water absorbency/repellency, dyeability, elasticity, chemical resistance and insulation capabilities. They may involve adding chemicals, from raw fibre to finished garment, in each step. The production steps are listed below:

1. **Raw fibre -** Raw fibre synthesis or fibre harvesting from plants and animal-based fibres
2. **Yarn –** Spinning, twisting and drawing. Spinning oils are added to protect the fibres.
3. **Sizing** – to warp the yarn, which strengthens the fibres and minimizes the risk of depolymerization by adding sizing agents, e.g. starch, polyvinyl alcohol and carboxymethyl cellulose, helps to withstand any mechanical stress during the weaving or knitting[59].

4. **De-sizing** – removes unwanted chemicals and sizing agents on the yarn after weaving or knitting using enzymes and auxiliary agents[59]. Current methods typically involve bacterial enzymes and mineral acids. It also improves the absorbency of the yarn.
5. **Scouring** – a high-temperature alkaline environment using various scouring agents, e.g. anionic- and non-ionic surfactants, alkali agents to remove non-cellulosic impurities, like fats, waxes, pectins and proteins, and to improve the hydrophilicity of the cotton fibre and the dyeability by increasing its wettability[60].
6. **Bleaching** – reduction or oxidation of the chromophore with hydrogen peroxide, sodium hypochlorite or sulphur dioxide[61].
7. **Mercerization** - cotton is treated with caustic soda to improve its strength, smoothness/luster and dyeability[62].
8. **Carbonizing** – to remove wool grease and residues from plant-based fibres[63]
9. **Weaving and knitting –** Lubricants are added to make sportswear, underwear, and casual textiles more comfortable.
10. **Dyeing, printing, and washing –** a wide variety of synthetic or natural dyes are available, such as disperse dyes, reactive dyes, direct dyes, pigments, or metal-complex dyes. Many additional chemicals, dispersive agents, facilitate the dye-fibre interaction, altogether making the colouring step the "dirtiest" of all the steps. Plasticizers, often phthalates, are used in screen prints. After colouring and printing, the fabric is washed using non-ionic or anionic surfactants.
11. **Cutting and sewing**
12. **Finishing** is a step that may include anti-fading, water-repellent, flame-retardant, luster-improving chemicals and substances enhancing flexibility and durability. Functional chemicals include biocides, flame retardants, perfluorinated acids, softeners, anti-wrinkling agents, plasticizers and UV stabilisers[64].

13. **Transport preparation** – the finished articles are protected from mould and insects during storage and long transportation routes. Examples of biocides are dimethyl fumarate, ethylene oxide, methyl bromide and 1,2-dichloroethane[65].

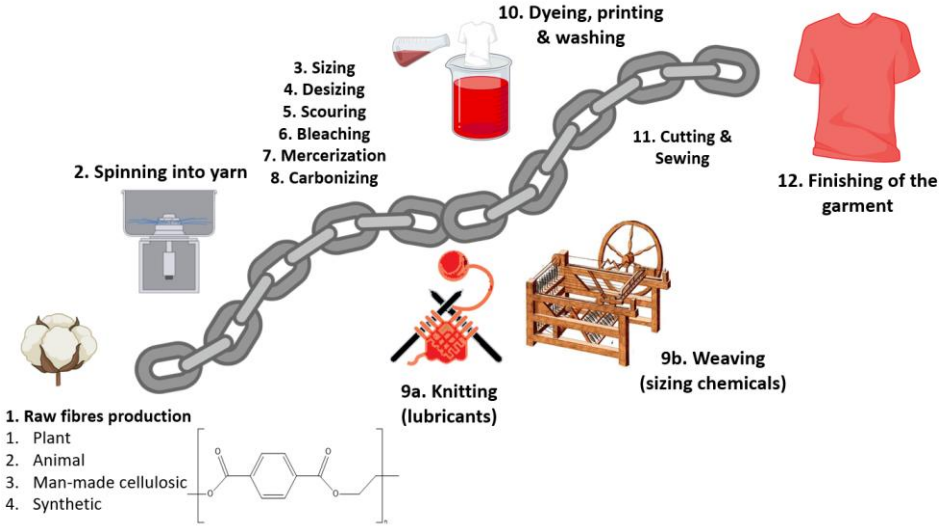

Figure 6: A multistep textile manufacturing process from raw fibres to a finished fabric [created with Biorender.com].

Types of textile chemicals

The used chemicals can be divided into the following main categories.

1. **Process chemicals** include detergents, dispersive agents, alkaline agents, acids, solvents, chelating agents, and bleaching agents.
2. **Functional chemicals** include dyes, water repellants, softeners, plasticizers, anti-wrinkle agents, UV stabilizers, and anti-molding agents.
3. **Unwanted/unintentional chemicals** are not meant to remain in the finished garment but end up as residues, such as dye precursors, synthetic fibre precursors, surfactants, detergents, inorganic salts, stabilizers, acids, bases, and enzymes.

Dyeing textiles

Dyes are classified by the Color Index™ (C.I.) and are available to manufacturers to register dye chemicals. The index is organized according to dye structure and methods of application[66]. Dyes are chemically defined as chromophoric molecules capable of interacting with fibres physically or chemically, and typical examples include azo (-N=N-), carbonyl (-C=O), nitro ($-NO_2$), methine (-CH=) and quinoid groups[67]. In addition, auxochromes enhance the colour intensity of a dye by shifting the absorption spectrum[67], improve the stability and solubility of dyes and facilitate the attachment to fibres[68].

Three different application methods are used for dyeing textiles, namely:

- **Mass dyeing**: a synthetic polymer is dyed before the fibre formation.
- **Pigment dyeing**: a dye binder is used to facilitate the fixation of an insoluble dye.
- **Dye exhaustion**: dyes with an affinity for the fibres applied from an aqueous environment, usually under heat/pressure or specific dye carrier molecules, are adsorbed to the surface and further diffused into the fibre material.

In most cases, the liquid solvent is water, and after dye diffusion into the fibres, a chemical or physical fixation, depending on the dye-fibre interaction, is necessary to obtain wash fastness. High-temperature conditions are typically required to get higher dyeing rates and improved colour fastness of the fibre. It is common to perform the dyeing at elevated temperatures of up to 135 °C under pressurized conditions[69].

Dyeing of synthetic fibres occurs according to two main principles: (1) elevated pressure and high-temperature conditions and (2) atmospheric conditions using a dye carrier[70]. Firstly introduced by DuPont company in 1949, the thermosol process facilitates thermal fixation of disperse dyes into the fibres at elevated temperatures, typically 180-220 °C for one minute[71]. To further promote thermal fixation, compounds such as ethoxylated fatty alcohols or fatty acids capable of dissolving the dyes and wetting the fibre are added to obtain a homogenous distribution of the dyes on the fibre surface. During the thermal fixation, the high temperature causes the dyes to melt, dissolving them in the liquid film of additives on the fibre surface. Dyes typically processed at elevated temperatures include direct, disperse, acid and basic dyes[72].

In 1856, William Henry Perkin accidentally discovered the first synthetic dye, Mauveine, from coal tar derivatives while attempting to synthesize quinine. Non-biodegradable synthetic dyes from petrochemicals are the most widely used dyes globally due to their greater colour variety, consistency, cost-effectiveness, and efficiency. A wide range of applications, e.g., textiles, leather, cosmetics, pharmaceuticals, plastics, and food, are examples of products where synthetic dyes are utilized. Different organic structures with chromophores, e.g., azo, anthraquinone, polymethine, nitro, nitroso aryl methyl, xanthine and coumarin, are responsible for the perceived colour of the molecule. The major types are disperse dyes for synthetic textiles and direct and reactive dyes for natural fibres[70]. Other dyes are basic, acidic and vat dyes. Natural dyes, such as indigo for denim, also exist. In the work behind this thesis, the dyes of focus were disperse azo dyes. Disperse dyes are described briefly below.

Disperse dyes

Disperse dyes constitute the most widely used dye class and are water-insoluble, non-ionic chemicals intended for hydrophobic materials, mainly polyester, polyamide, and acetate fibres. Azo dyes account for over 50% of all disperse dyes, anthraquinone dyes approximately 25%, and the remaining part constitutes methinine, nitro and naphthoquinone dyes.

Disperse dyes are most stable at pH 4-5, *i.e.,* the dye-fibre adsorption depends much on controlling the pH. Due to poor water solubility, a dispersive agent, typically a surfactant, is required to prevent dye aggregation and maintain a smooth dispersion, resulting in a uniform dyeing of the fibre. Dyeing at high temperatures and elevated pressures allows a temperature of 125-135 °C, causing the fibre to swell, facilitating dye diffusion. Further improvement of the dye absorption is achieved using levelling agents, resulting in a homogenous colouring of the fibre material.

To enable dyeing at ambient conditions below 100 °C, dye carriers, such as phenylphenol, chlorobenzenes and benzoic acid, are used. However, hydrophobic and highly toxic carriers, such as dichloro- and trichlorobenzenes, have been replaced by benzoic acid[73].

Chemical stability of dyes

The desired colour and appearance of dyes must be maintained over a long period, *i.e.*, chemically resistant and stable to various conditions, e.g. pH stability, UV resistance and humidity. Stable structures, including conjugated aromatic systems or protective functional groups, may be more resistant to subsequent reactions, such as UV degradation. In addition, dyes applied at elevated temperatures must be resistant to thermal degradation and resilient to laundry detergents. Another example concerns the susceptibility of natural dyes since they exhibit their maximum colour intensity at specific pH ranges, which may be affected by either acidic or alkaline environments, such as laundry detergents. Hence, the stability is crucial depending on the application, e.g., if the clothes are produced for indoor or outdoor activities.

Chemicals previously identified in textiles

In a previous report to the Swedish government, Report No 6/14 by the Swedish Chemical Agency[74], 3500 substances were identified as possible components used in textile production. The list was compiled based on a literature survey of multiple databases, including the International Uniform Chemical Information Database at ECHA (IUCLID 5) containing registered substances in the European regulatory act, *i.e.*, Registration, Evaluation, Authorization and Restriction of Chemicals (REACH), and national authority databases and chemical lists obtained from the textile industry and organizations. Among the non-confidential registrations, 2450 chemicals were reviewed, and around 10% of these were considered to be of concern for human health. Chemicals we might be exposed to via fibre loss include plasticizers and flame retardants. Regarding environmental pollution, around 5% of textile-related compounds possessed any form of severe consequence upon discharge. However, these numbers are likely underestimated because of (1) the rapid introduction of new chemicals due to fast-fashion trends and (2) the vast majority of chemicals have not yet been evaluated for adverse toxicity effects. For example, textile allergy has long been mainly attributed to a few azo- and

anthraquinone-disperse dyes, covering only a tiny fraction of all possible sensitizing textile compounds. Hence, there is a high likelihood of possibly unrecorded cases[74].

Previously detected textile-related substances of possible health concern include functional and unintentionally introduced compounds. Typical examples are disperse dyes[75–77], arylamines[7,10,76–81], quinoline, isoquinoline and methylated derivatives[7,8,11,26,82], benzothiazoles and benzotriazoles[9,26,83], dioxins and furans[84], polychlorinated biphenyls (PCBs)[85,86], organophosphorus pesticides (OPPs)[87], halogenated flame retardants[88–90], perfluorinated alkyl substances[91–94], phthalate esters[95], glycol-based solvents[96], formaldehyde[19,20,97,98], common substances in fuels, e.g. linear and branched C_{10}-C_{16} alkanes, C_3 alkylbenzenes and straight-chained C_2-C_{10} aldehydes[99], as well as heavy metals[6,100,101].

Environmental release and bioremediation technologies

The sewage effluents from textile-dye industries contain many potentially toxic substances. Synthetic dyes lack a firm interaction with the fibre, leading to an inefficient dyeing process and a discharge that adversely affects animals, plants and humans[102]. The composition of textile effluents is a mixture of many different substances from different production stages, e.g., trace elements, salts, sizing agents, caustic soda, surfactants, detergents, dyes and pigments, resulting in severe consequences to aquatic life[103]. A previous review summarizes typical characteristics of textile effluents and reported studies on real-world wastewater from textile factories[104].

Oliveira et al. (2007) have published a study in which they screened effluents from a Brazilian wastewater treatment plant[105]. Tentative identification was performed of multiple chemical classes, such as the mutagenic dyes Disperse Violet 93, Disperse Blue 373 and Disperse Orange 37. In addition, subsequent screening of potentially mutagenic molecules using gas chromatography/mass spectrometry (GC/MS) revealed the presence of several other textile chemicals, such as quinoline, arylamines, and nitrophenols. Eleven per- and polyfluorinated alkyl substances (PFAS), originating from textile wastewater, were detected in wastewater treatment effluents in China[106]. When applying a non-target

workflow, they identified around 650 individual substances, both regulated and *a priori* unknown compounds. Although an anaerobic and aerobic treatment was employed, the average removal efficiency of these recalcitrant molecules was only 22%, indicating severe environmental pollution[106].

Remediation methods for water stream purification are not a topic of this thesis and are only mentioned here. The methods can be based on physicochemical treatment, including oxidation processes, adsorption, ion exchange, membrane filtration or nanotechnology[107–109]. Alternatives based on a more eco-friendly approach are the bio-based remediation processes, e.g. plant adsorption and microorganisms, the latter including various species of bacteria, yeast, and fungi, and enzymes capable of degrading azo dye-containing wastewater[110–112].

Human exposure to textile chemicals

The human skin protects our bodies from the surrounding environment, *i.e.* toxic chemicals and pathogens. It can be divided into three main layers: epidermis, dermis, and *hypodermis*. Dermal exposure is attributed to the outermost layer of the *epidermis*, called *stratum corneum,* possessing a thickness of 10-30 µm. This layer is very hydrophobic; the barrier mechanism of the *stratum corneum* depends on the corneocytes[113] embedded in a lipid matrix, forming a brick-and-mortar arrangement. The bricks are the corneocytes providing strength to the skin, while the mortar is the surrounding lipid matrix[114].

Textile allergy is widespread, with a prevalence of around 1% among the general population. The most common reason for developing this type of T-cell-mediated delayed skin hypersensitivity is repeated dermal exposure to skin-sensitizing chemicals in skin-close clothing[18]. Penetration to the *epidermis* is a prerequisite for chemicals to cause sensitization and is facilitated by suitable lipophilicity (*log*P 2-3)[115] and molecular weight (below 500 Da)[116]. In addition, a recent study has shown that the exposure may increase through sweating[117].

A skin allergy, or skin sensitization, is initiated by a reactive hapten, commonly an electrophile, binding to a macromolecule and forming an antigen, which eventually

causes an inflammatory response. Not all molecules are sensitizing *per se*, but so-called prohaptens or prehaptens become sensitizing after metabolic activation in the skin or activation to a hapten outside the skin, respectively. Prehaptens can be produced from autoxidation, such as the case with the well-known allergen p-phenylenediamine (PPD), occurring in hair dyes[118] and textiles[119]. This compound is easily autoxidized to the electrophilic and potent skin sensitizer Brandowskii´s base. Among textile chemicals, disperse dyes of both anthraquinone and azo type are the most well-known textile allergens[17,120,121].

Numerous disperse dyes have been clinically evaluated in Sweden regarding skin sensitization[21–23]. Azo dyes are commonly not electrophilic, but metabolic activation might produce a reactive hapten. Arylamines, other than PPD, are also suspected of playing a role in textile allergy as pre- or prohaptens, but there is still a knowledge gap regarding most textile chemicals as allergens. Three skin sensitizers, 2,4-dinitrochlorobenzene, 2,5-dinitrochlorobenzene, and 2,6-dichlorobenzene-1,4-diamine, were recently identified as frequently occurring compounds in common polyester garments[77,117]. The two formers are electrophiles, able to bind directly to cysteines in skin peptides/proteins, while the latter requires oxidation to an electrophile to become sensitizing. A risk assessment was performed, and the risk was considered low based on garment levels and a 16-hour daily exposure to individual compounds[117]. However, the risk might be more prominent due to additive and synergistic effects from all compounds in the textiles, as they usually contain hundreds of detectable compounds.

Compound classes of focus

Besides textile allergy, a systemic bioavailability of toxic textile chemicals may lead to non-negligible adverse health effects, such as mutagenic, reproductive effects and cancer. Below, I discuss some of the most prevalent low-molecular, semi-volatile chemicals detected in clothing garments and the focus of this work. Other semi-volatile compound classes found in textiles include benzotriazoles (UV filters),
organophosphate esters (plasticisers/flame retardants), polycyclic aromatic compounds, nitrophenols (dye/insecticide/fungicide synthesis) and PFAS (water repellents). Formaldehyde was incompatible with our analytical methods, but to my knowledge, it is rarely used in skin-close garments. Most of these have reported health effects but are not further discussed here.
Furthermore, health-hazardous air pollutants from indoor- and outdoor environments can adsorb to clothing textiles, such as phthalates and halogenated flame retardants, and lead to dermal exposure[122,]

Phthalate esters

Phthalate esters are widely used as plasticizers to soften polymer chains. Typical plasticizers used in polyvinylchloride include high molecular mass phthalates, e.g., DEHP, BBP and di-isononyl phthalate (DiNP), while dimethyl phthalate (DMP), diethyl phthalate (DEP) and DBP are more attributed to personal care products[113].
Since phthalates are ubiquitous and utilized in multiple applications besides textiles, they often cause contamination problems in chemical analyses. Phthalates are recognized for their reproductive health effects and for causing developmental issues in both males[123] and females[124], endocrine disruption[125–128], respiratory issues[129], behaviour problems from exposure during pregnancy[130,131], the possible correlation with obesity in children[132], and risk of type-2 diabetes[133].
In a Chinese study, fifteen phthalates were identified in children's clothing manufactured in Asia, ranging between 3 – 220 µg/g, with DEHP, DiBP and DBP as the most abundant contaminants. Estimations of the total reproductive risk using several garment types

simultaneously surpassed the acceptance threshold, indicating severe dermal exposure when wearers are exposed to a combined mixture of several phthalates[134].

A previous study indicates that the removal of phthalates from jeans upon laundry increases with lower lipophilicities (*log*P) of the compounds. In addition, the wash program, garment composition, use of detergents, and drying method also influence the final phthalate content in the treated fabric[135].

The physical-chemical properties of 22 phthalate esters at ambient conditions have been calculated, with *log*P from 1.6 to 12.1[136]. The bioavailability from dermal uptake of phthalates varies between congeners due to different lipophilicities and chain lengths[137,138]. As indicated by a previous study, factors such as lipophilicity and molecular weight may influence the extent of dermal absorption of phthalates in rats, *i.e.* longer alkyl chains may exhibit a low skin permeability. In contrast, others with a shorter length may show a higher permeation rate (maximum around *log*P of 2) through the epidermal barrier of the skin[139].

Halogenated and non-halogenated nitrobenzene compounds

Nitrobenzene compounds are widely used to synthesize arylamines, precursors of azo dyes. The synthesis pathway is a selective hydrogenation of halogenated nitroaromatic substances, *e.g.* 3,4-dichloronitrobenzene converted to 3,4-dichloroaniline[140]. A study of the mutagenic effects of nitrobenzenes following *in vivo* transformation[141], has been presented. Halogenated nitrobenzenes frequently detected in clothing have recently been shown to possess mutagenic effects[141]. Another adverse health effect is skin allergy, and 2,4-dinitrochlorobenzene (2,4-DNCB) is known as an extreme skin sensitizer[142]. Recent work also characterised its structural isomer 2,5-DNCB as a firm skin sensitizer[143]. In addition, several halogenated and non-halogenated aromatic nitrobenzene substances are listed in the priority pollutants lists controlled by US EPA[144].

Arylamines

Arylamines are mainly used as azo dye precursors[79], biocides[145] and in rubber processing[146]. Their prevalence in textiles has been studied before, and a previous study reported 11 arylamines ranging from 0.1 – 600 μg/g in seven garments purchased on the Swedish retail market[7]. Adverse health effects from several arylamines are well-documented, such as allergenic effects[147], genotoxic potential[148] and mutagenicity[76].

Two previous studies indicated microbial degradation of azo dyes on the skin, posing difficulties concerning the risk assessment of arylamines. Microbial reduction may lead to the production of bioaccessible toxic arylamines[149,150].

Arylamines may become bioactive after metabolism, and phase-I cytochrome p450s (CYP450), monoxygenases[151] and peroxidases[152] activate the molecule by oxidizing the amino group, producing more potent molecules, such as hydroxylamines. A common detoxification of arylamines involves phase-I ring oxidation, followed by N-acetylation, catalyzed by N-acetyltransferase.

The bioactivation of arylamines to haptens in contact allergy, as for PPD and 2,6-dichlorobenzene-1,4-diamine, has been studied and may follow similar pathways as in the liver metabolism, such as N-acetylation[153], although the levels of enzymes in skin differ from the liver.

Quinolines

Previous studies have reported the presence of this class of pollutants in textiles[7,8], with levels from 0.01 to 6 μg/g[7]. Quinoline congeners are employed in the textile industry as precursors for dye manufacturing[154]. A typical adverse health effect is genotoxicity, but this varies depending on the position of the methyl group[155]. Quinoline itself is a human carcinogen and a suspected mutagen, according to the European Chemical Agency[156].

Benzothiazoles

Benzothiazoles are used in many industrial processes, e.g. as vulcanization accelerators in rubber production, typically above 1% by weight[157], and corrosion inhibition[157], but also

as biocides and fungicides[158], and constitute some of the significant sources of wastewater pollution[158,159]. Several techniques have been developed for determining these compounds in aqueous matrices using LC-ESI-MS/MS[158,160]. Their prevalence in textile clothing has previously been investigated in twenty-six garments purchased on the Swedish retail market, and their high detection frequency suggests a common occurrence in clothes, varying between 0.05 – 51 μg/g[9], with benzothiazole detected in almost 90% of the analyzed textiles as the most abundant compound. Their occurrence has also been identified in 79 textiles, including fabrics and infant clothing of various fibres, e.g., cotton, polyester and nylon, from the US market. Benzothiazole was detected in most garments, almost 90%, ranging from 0.01 to 1 μg/g[161]. A considerable release of benzothiazoles into the sewage system has been found after 5- and 10 laundry cycles, indicating a potential source of environmental pollution[26]. The occurrence of benzothiazoles in industrial wastewater has been shown as well[162].

Toxicity-related issues associated with these compounds have been reported, for instance, genotoxicity and cytotoxic effects of nine benzothiazoles[163], carcinogenicity[164], dermal sensitization potency in guinea pigs[165], as allergens in tennis shoes[166] and their endocrine-disrupting adverse impact on the thyroid gland[167]. In addition, dermal sensitization, depression in the central nervous system, hepatotoxicity, kidney damage and pulmonary irritation may be severe health consequences of exposure to benzothiazole[168]. The possibility of benzothiazole migrating from a textile and penetrating a skin-mimicking artificial membrane using Franz- and flow-through diffusion cells has been investigated earlier[2].

Labelling of garments – protection of consumers

Certification of textiles as eco-friendly products is voluntary. A textile producer certifies a material according to a standard, such as OEKO-TEX®[169], Global Organic Textile Standard (GOTS)[170], Nordic Swan Ecolabel[171], or EU ecolabel[172], assuring that the manufacturing company complies with social and ecological qualities by taking preventative action

against environmental pollution as well as allowing sufficient tests of the chemical content of the product.

Chemical regulation

Risk assessment is the foundation of any regulated chemical placed or identified on the market. According to the US National Research Council (NRC), a risk assessment is a four-step process, and a proper risk assessment requires information such as hazards, dose-response relationships, and exposure to characterize a risk.

European REACH

The European Chemical Agency (ECHA) is responsible for the primary regulation act within the EU, summarized under REACH, including rules for registration of chemicals, bans or restrictions, authorization requirements for specifically harmful substances and regulations regarding customer notice. REACH has compiled more than 26.000 substances[173], and the original legal act from 2006 has been summarized in EC No 1907/2006[174]. A summary of the European legislation can be divided into three groups controlled by REACH.

- **SVHC list:** A candidate list of substances of very high concern, currently containing 247 registered compounds[175].
- **Annex XIV:** Prioritized chemicals from the SVHC candidate list are subject to ECHA authorization, with 59 registered substances[176].
- **Annex XVII:** Restricted substances, *i.e.*, harmful substances with an associated threshold value for industrial use or presence in finished products, currently containing 74 regulated substances[177].

Registration of a pure chemical or mixture is required if the total annual amount exceeds one tonne per year, according to REACH, with information about its properties. In addition, Annex XVII of REACH states that any substance exceeding 0.1% by weight must be reported to ECHA, which applies to all manufacturing industries within the EU and

imported goods. The Classification, Labelling, and Packaging (CLP), EC No 1272/2008, based on the United Nations Global Harmonized System (GHS), is the only legislative act within the EU regarding the classification of substances and mixtures[178].

A textile-specific EU regulation, Regulation No 1007/2011[179], summarizes the labelling requirements of textile articles comprised of at least 80% of textile fibres by weight. Other examples of textile chemicals included in REACH are azo dyes, which, by reductive cleavage of one or several azo groups, can release any of 22 restricted arylamines at levels > 30 µg/g in a finished garment[180]. Another restricted textile chemical at levels > 50 µg/g is the human carcinogen quinoline[181]. A few potentially endocrine-disrupting phthalates are prohibited if the detectable total concentration exceeds 1000 µg/g (0.1% by weight), namely bis(2-ethylhexyl) phthalate (DEHP), dibutyl phthalate (DBP), benzyl butyl phthalate (BBP) and diisobutyl phthalate (DiBP)[182].

American TSCA

The primary chemical regulation in the US is summarized under the Toxic Substances Control Act[183], which should contain all known chemical substances produced, processed, or imported to the US. It allows the US Environmental Protection Agency (US EPA) to review any adverse effects associated with any new chemical produced, processed or imported to the market. By mid-2024, the total number of recorded chemical substances was more than 86.000.

As a part of their mission to protect humans and the environment, the US EPA has initiated a program about the integrated risk information system (IRIS)[184], *i.e.,* risk assessments that summarize toxicity information about health hazards found in the environment. The current IRIS assessment contains a total of 572 compounds[185], and there are several textile-related substances assessed as probable carcinogens of category 2B, e.g. quinoline, aniline, and 4,4'-methylene bis(N,N'-dimethyl)aniline[186–188].

As a part of the EPA regulatory review process concerning chemicals of health concern, the authority has compiled a Toxic Release Inventory (TRI) list for chemicals that may

cause chronic human adverse effects, e.g. cancer, acute toxicity effects, or adverse effects within environmental systems[189].

Analytical methods

Textile fibre characterization

Since the authenticity of textile fibres depends much on the fibre composition, and fibre fraud is a growing concern where the specified composition does not match the actual fibre content[190], there is a need for material characterization methods. This is essential for quality control during production, in forensic or historic fibre identification, and in confirming imported and recycled textiles. Typical methods include mid-infrared spectroscopy[191–193], near-infrared spectroscopy[194], and a semi-quantitative classification approach using attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR)[195].

Textile chemicals

The prevalence of possibly health-hazardous substances, e.g., skin-sensitizing compounds, in new and recycled garments, have been investigated mainly using extraction with organic solvents[7–10,13,75,77,80,83] before offline GC/MS analysis. Disperse azo dyes should be removed since they are not sufficiently volatile. As was found in this work, they are also thermally unstable, *i.e.*, they may decompose to arylamines in the GC injector. Solid-phase extraction can remove these dyes on a graphitized carbon black (GCB) sorbent[196,197]. A standard method for measuring the total levels of arylamines involves reducing disperse azo dyes and subsequent analysis by LC/MS/MS[12,198], as described in ISO 143621:2017[199]. As far as I know, the quantitative performance of this method has not been reported, and no internal standard is suggested. Further, this method cannot differentiate between free arylamines in textiles and their presence as

part of azo-dye molecules since all free-occurring nitro-based arylamines are reduced into the corresponding amine groups.

Automated thermal desorption

Automated thermal desorption coupled to GC/MS (ATD-GC/MS) was used in **Papers III** and **IV** to extract textile chemicals from garments. This technique does not utilize any solvent for the extraction but is based on heating the sample to release sufficiently volatile analytes directly for further transfer into the analytical instrument. ATD was introduced over four decades ago for air samples collected on sorbent tubes filled with charcoal. It is sometimes recognized as a fully automated methodology combining sampling, extraction, and focusing of chemical components, followed by a smooth introduction to GC/MS. TD requires an analyte to be sufficiently volatile, such as SVOCs. An initial purge using an inert carrier gas, such as N_2, at ambient conditions is needed to vent a sample tube before desorption and to remove unwanted interferences, such as CO_2, CH_4, and H_2O. In addition, it also extends the capillary column lifetime by preventing large amounts of air and H_2O in the system. The key parameters during TD are (1) the desorption temperature, (2) desorption time, (3) desorption flow rate, (4) focusing temperature and (5) optional split flows, e.g., inlet and outlet split[200].

Two-stage ATD instruments

A two-stage ATD system obtains narrow chromatographic peaks by thermal desorption of the sample and rapidly condensing the target analytes at a low temperature in a glass tube with an adsorbent, *i.e.* a cold trap. The trap enriches and focuses the sample components before introducing them onto the GC by fast-heating the trap. Typical adsorbents are materials based on quartz, graphitized carbon black and Tenax[200].

After focusing the chemical vapour, the trap is rapidly heated to release the compounds, and a reversed gas flow, usually He, transfers the analytes onto the analytical column. Although cryogenic focusing offers a wide range of advantages considering detection limits, these systems also possess limitations, e.g. poor retention of VOCs due to aerosol

formation leading to breakthrough[201]. Apart from the temperature, the flow rate and the trap geometry influence the trapping efficiency[202].

Sampling split

Direct chemical extraction from a solid sample has been possible due to the double-splitting technology to dilute highly concentrated samples. This feature was introduced on the ATD 50 instrument to minimize the sample load on the cold trap during primary desorption and the subsequent secondary desorption from the cold trap before introduction to the GC column. Double-splitting prevents system overload and allows for faster sample extraction. Higher desorption flows can be applied during the primary desorption using inlet splitting to avoid analyte loss on the cold trap by maintaining a sufficiently low flow through the adsorbent. The subsequent secondary desorption flow rate also speeds up the analyte desorption from the focusing trap and injection to the GC using an outlet split[200].

Adsorbent selection

Commercially available cold traps are empty glass tubes or prepacked with various adsorbents. Typical sorbent tubes are available for non-polar substances ranging from C_3 to C_{26}[203], but previous studies have shown the retention of N_2O[204] and CS_2[205] at ambient conditions. Water is a common interference that may cause issues during the cryogenic focusing with ice formation.

Combining sorbents to cover a wider volatility range of analytes is common. An appropriate sorbent is selected based on its thermal stability, collection efficiency, retention of certain compound classes, and thermal desorption efficiency. Tenax-TA is the most popular organic polymer used as a trap material. The most commonly used adsorbents for ATD applications are based on the volatility and boiling point of the analytes, see **Table 1.**

Table 1: Common trap absorbents used in ATD applications[206–208]

Trap adsorbent	Material	Surface area (m2/g)	Maximum temperature (°C)	Approx. volatility range (°C)
Molecular sieves**	Aluminosilicates (zeolites)	400-1200	350	-60-80
Carbosieve SIII	Carbonaceous	820	400	-60-80
Carboxen®	Carbonaceous	75-1200	400	-90-150
Tenax®-TA	2,6-Diphenyl p-phenylene oxide	35	350	100-400
Tenax®-GR	2,6-Diphenyl p-phenylene oxide, 30% Graphite	24	350	100-450
Carbotrap®	Graphitized Carbon Black	100	400	0-250
Carbotrap® C	Graphitized Carbon Black	12	400	125-350
Chromosorb® 102/106	Styrene/Divinylbenzene	350-800	250	50-200
Chromosorb® 107/108	Crosslinked acrylic ester	100-500	150	≤ 150
Spherocarb*	Activated charcoal	1200	400	-30-150
Porapak®	Polymeric poly (Divinylbenzene)	300-550	180-250	50-200
Anasorb® CSC	Carbonaceous	800-7000	400	-60-80
Anasorb® 747	Carbonaceous	980	350	-90-40

***Exhibits water retention, **Significantly hydrophilic**

Non-target workflows for screening

Harmonized guidelines are available for broad non-target screening of environmental samples and consumer products and were summarized by the NORMAN Association members[209].

Non-target screening workflows commonly use liquid chromatography/high-resolution MS (LC/HRMS), which generates an accurate mass of detected features. Electrospray (ESI) is the most common ionization mode in positive and/or negative modes. The amount of acquired data is often large, so data filtering steps using computerized data mining are required, for instance, with software like MS Dial or Compound Discoverer™ (Thermo Scientific). The identification confidence of a detected *a priori* unknown compound is based on five levels[210], namely:

- **Level 5:** Only an exact mass
- **Level 4:** A definitive molecular formula exits, but insufficient MS/MS information
- **Level 3:** Tentative structure supported by experimental information, e.g., fragmentation spectrum, isotopic pattern, retention information, molecular adducts
- **Level 2:** A sufficient match with a library spectrum and/or diagnostic fragments
- **Level 1:** Confirmation using an authentic reference standard

In the analytical work behind this thesis, targeted analyses and non-target screening have been used to identify chemicals in clothing. GC/MS with electron ionization (EI) and a low-resolving (LR) quadrupole analyzer, LC/MS/MS with a triple quadrupole, and LC/HRMS with an Orbitrap analyzer were used. Screening of cotton garments using a non-targeted approach with GC/EI-LRMS was recently described[211]. Non-target screening using a combination of GC/EI-LRMS and LC/HRMS was recently performed to study a process for extracting nanocellulose from a polycotton post-consumer garment[212]. The present thesis used such a workflow to screen a similar process quantitatively.

2 Results and discussion

Paper I

Paper I focused on chemicals possibly relevant as textile allergens, mainly disperse azo dyes and dye-related textile chemicals. Disperse dyes have long been considered major textile allergens, and eight of these, proven as potent skin sensitizers, are used in a textile-dye mix[213] (TDM) for patch testing to diagnose textile allergy. However, there have been previous indications that these eight dyes are rarely present in clothing[214], although the prevalence of textile allergy has not decreased. Thus, one aim was to investigate their occurrence in everyday garments. Screening of 82 synthetic fabrics was performed using LC/HRMS, and 65 disperse dyes were identified, of which 14 could be confirmed using commercially available reference compounds. Other dye-related chemicals determined by a targeted approach using GC/LRMS were arylamines and halogenated dinitrobenzenes. To our knowledge, this was the first time halogenated nitrobenzene compounds were detected in clothing. One of the compounds was identified as 2,4-dinitrochlorobenzene, a well-known extreme skin sensitizer often used as a positive control in skin sensitization assays. Both arylamines and the halogenated dinitrobenzenes are most likely mainly present in clothing as residues from the crude synthesis of disperse azo dyes.

In **Figure 7**, an overview of the analytical workflow used in **Paper I** is illustrated, starting with (1) suspect screening of disperse dyes with LC/HRMS, (2) quantification of selected disperse dyes using triple-quadrupole LC/MS/MS and available reference standards, and (3) identification and quantification of arylamines and halogenated nitrobenzene compounds with GC/LRMS. The sample preparation involved only solvent extraction with

dichloromethane, evaporation, and syringe filtration before injection into each instrument.

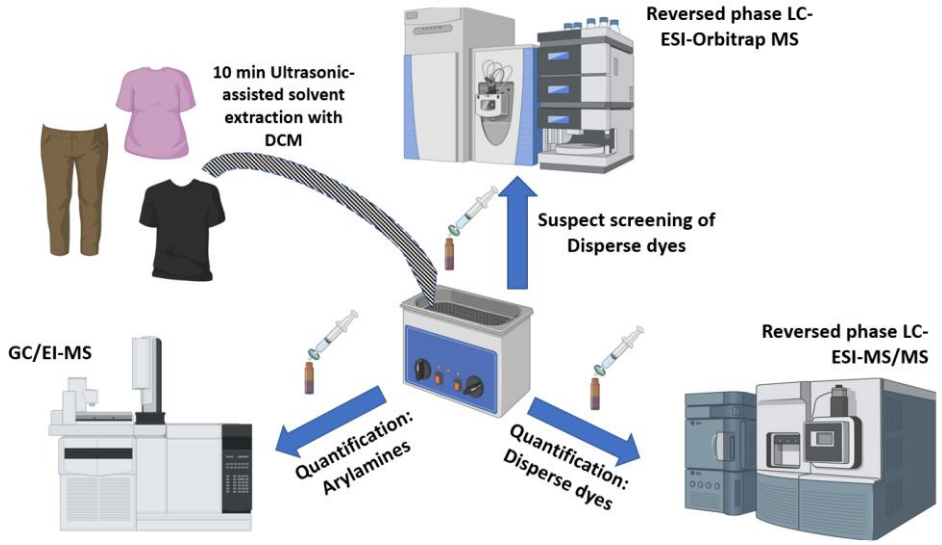

Figure 7: The analytical workflow utilized for the suspect screening of disperse dyes and subsequent quantification of disperse dyes, arylamines and halogenated dinitrobenzene compounds [created with Biorender.com].

Disperse dyes

A previously developed data mining workflow[10] employing the Compound Discoverer 3.0 software was used to assign tentative identification of disperse dyes. The five identification levels discussed above were considered during the evaluation process. Only those features assigned as tentatively identified had an associated fragmentation spectrum (MS^2), isotopic pattern within max ±5% deviation from the theoretical, and retention time deviating at maximum ± 2 min from the predicted. **Figure 8** shows the correlation between experimental retention times using 21 disperse dyes and their *log*P.

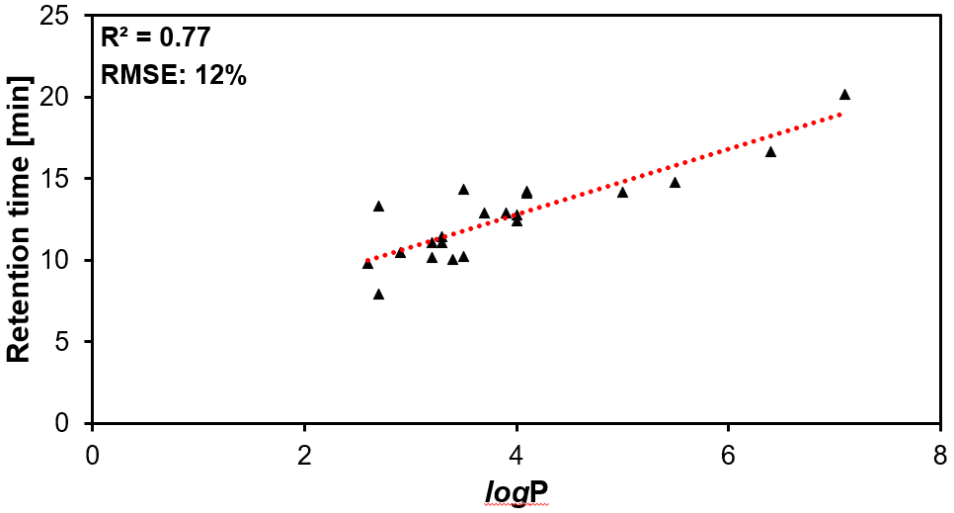

Figure 8: A prediction model for the retention times based on corresponding *log*P values for 21 reference disperse dyes utilized in the data filtering of suggested dyes from the suspect screening. All *log*P values were obtained from PubChem. Adopted from Paper I.

Figure 9 presents dyes detected in ≥ 10% of the garments in descending order of frequency. Most of the detected dyes were identified as only level 3 features since reference MS^2 spectra for dyes are scarce. The identity of the most frequent dye, Disperse Red 167:1, was further strengthened by matching with an *in-silico* predicted spectrum using the software CFM-ID[215].

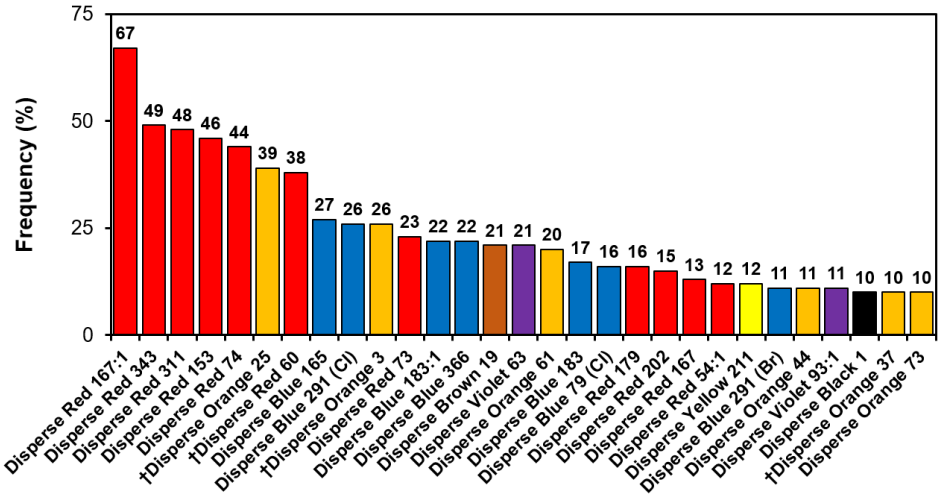

Figure 9: A comprehensive screening of 82 synthetic textiles resulted in many detected disperse dyes. Those with a frequency ≥ 10% are shown in the diagram. Dyes marked with † were confirmed with an authentic reference standard. Adopted from Paper I.

As shown in **Figure 10**, the most frequently detected dye among the confirmed dyes was Disperse Orange 25 (39%), ranging from 0.01 – 100 µg/g. The dye with the highest measured concentration was Disperse Red 60 (EC list no: 241-442-6), ranging from 0.02 – 500 µg/g, and according to ECHA, this anthraquinone substance is likely a skin-sensitizer and may cause an allergic skin reaction[216]. Anthraquinones are electrophiles and may be directly active as haptens. Apart from Disperse Orange 3, the dyes included in TDM were not among the most frequently detected dyes in this screening survey, as seen in **Table 2**. This could imply that other dyes, which are more regularly occurring nowadays, would be more suitable for patch testing.

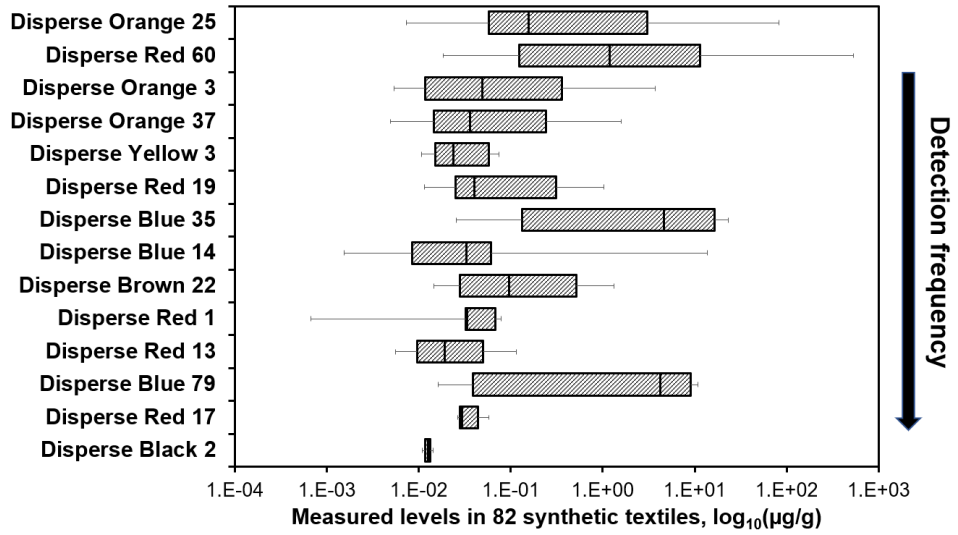

Figure 10: Quantification levels (log_{10}[µg/g]) of disperse dyes in 82 synthetic textiles with available reference standards (n=3).

Table 2: Quantification and detection frequency of five TDM dyes, n=3.

Compound	CASRN	Frequency (%)	Range [µg/g]
Disperse Orange 3	730-40-5	26%	0.01 - 4 µg/g
Disperse Yellow 3	2832-40-8	9%	0.01 - 0.07 µg/g
Disperse Blue 35	12222-75-2	7%	0.03 - 20 µg/g
Disperse Red 1	2872-52-8	6%	0.001 - 0.08 µg/g
Disperse Red 17	3179-89-3	4%	0.03 - 0.06 µg/g

Dye precursors

Altogether, 13 arylamines and three halogenated nitrobenzene compounds were identified and quantified in the 82 analyzed garments. In **Figure 11**, the 15 most frequently detected are displayed in descending order, with 4-nitroaniline having the highest frequency (44%). It is a constituent of several most common dyes, such as Disperse Red 74, Disperse Orange 3, and Disperse Orange 25. Most studies show that 4-nitroaniline is a weak/non-sensitizer. Still, according to ECHA (EC list no: 202-810-1), it might be persistent and bioaccumulative, and based on its CLP, it is poisonous to humans and the aquatic environment.

The detected arylamine levels were generally very high, and the maximum levels of 6-chloro- and 2-bromo-4,6-dinitroaniline were approximately 3 mg/g, 100 times higher than the levels allowed for regulated amines. The congener 6-chloro-2,4-dinitroaniline is a precursor of the tentatively identified halogenated dyes Disperse Blue 291 (Cl) and Disperse Blue 79 (Cl), while 2-bromo-4,6-dinitroaniline may originate from Disperse Blue 291 (Br), Disperse Violet 93:1 and Disperse Blue 79 (Br). Another abundant halogenated arylamine, 2-chloro-4-nitroaniline, is a precursor of Disperse Red 167:1. According to a previous study[76], 2-chloro-4-nitroaniline has shown positive effects in the Ames test for mutagenicity, and this supports the need for an improved toxicity assessment of non-regulated arylamines identified in textiles.

During my PhD work, it was found that the levels of at least some of the free arylamines reported in **Paper I** had most likely been overestimated. This assumption was based on the observation that some of the available reference dyes exhibited thermal decomposition into arylamines in the split/splitless injector of the GC. Thus, the reported levels may not reflect only free levels *per se* but also a portion originating from azo dyes. To what extent this is the case for the reported 82 analyzed samples was not further investigated, but in the following work, azo dyes were removed before GC/MS[7]. In the

ATD-GC/MS, described below (**Paper III and IV**), the desorption temperature was thoroughly investigated to ensure no dyes were degraded.

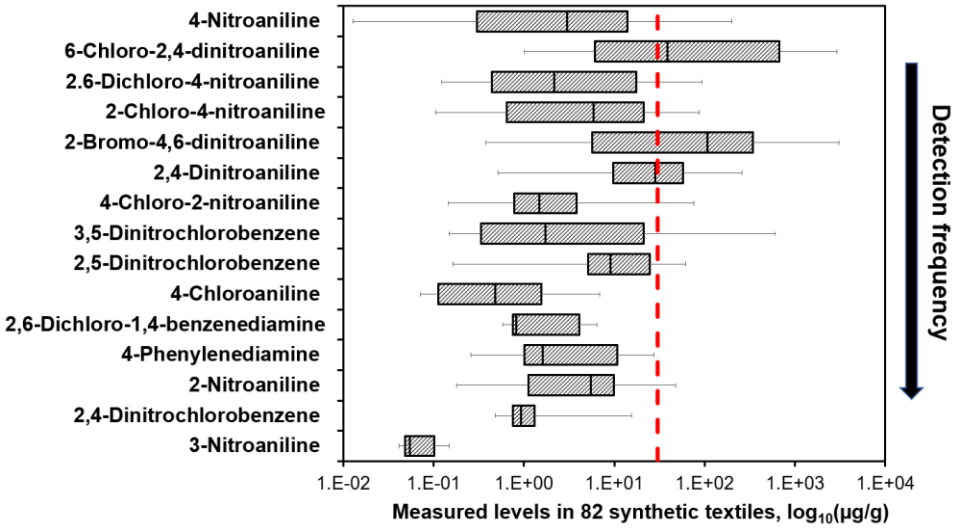

Figure 11: Quantification levels of (Log_{10}[µg/g]) of dye precursor molecules, identified as either arylamine or halogenated nitrobenzene compounds in 82 synthetic garments (n=3). The dashed red line corresponds to the REACH limit for regulated arylamines, 30 µg/g.

Paper II

As a part of the environmental goals concerning circular textile consumption and production, environmental-friendly recycling and/or upcycling methodologies are necessary. In **Paper II**, the fate of textile chemicals was investigated in a process for upcycling post-consumer cotton garments by extracting the cellulose in the form of cellulose nanocrystals (CNCs) under strongly acidic conditions using diluted sulphuric acid. Similar methods have been presented previously[212,217–226]. As shown in **Figure 12**, the synthesis of CNCs is a multistep process starting from worn-out textile apparel. Here, an analysis of the post-consumer polycotton garments was compared with the synthesized product and the polyester residual obtained after the cellulose extraction. In addition, the chemicals were tracked by developing a method to investigate process effluents, and a target analysis using LC/ESI-MS/MS was performed.

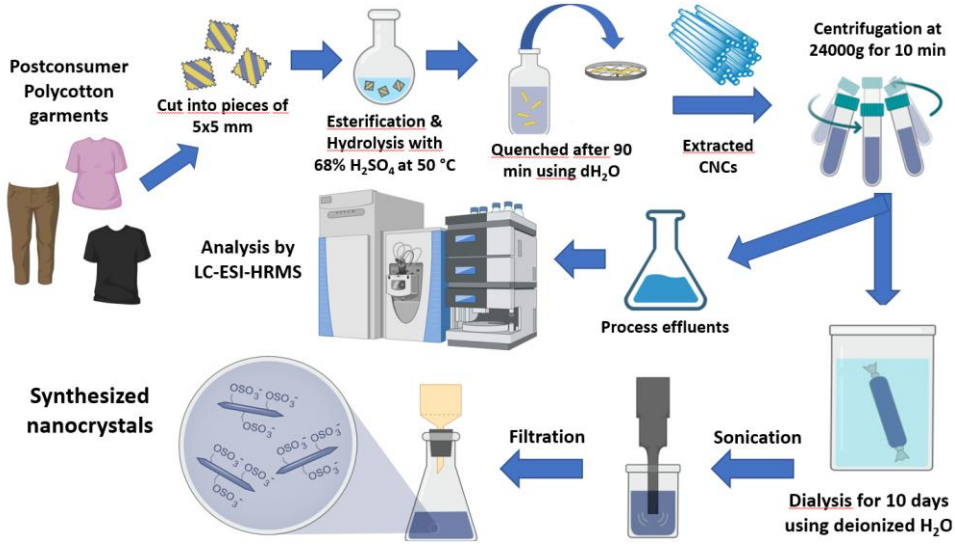

Figure 12: Simplified scheme illustrating the process of making cellulose nanocrystals from worn-out textile apparel. The effluent obtained following centrifugation was subjected to LC/ESI-MS/MS analysis. Adopted from an illustration by M-X Ruiz Caldas[212].

The mixed starting material from ten polycotton garments was analyzed using GC/MS (not shown in **Figure 12**). A previously developed data mining workflow with MS dial[212] was used to assign chemical features using two mass spectral libraries, Mass Bank of North America (MoNA) with 19 000 EI-spectra and the National Institutes of Standards and Technology (NIST17) with approximately 300 000 EI-spectra. Altogether, 147 compounds were tentatively identified, considering those peaks at least 10 times higher than those in a blank sample. The number of confirmed and quantified analytes was 40, see **Figure 13**, and 35 compounds were assigned level 2. Some health or potential environmental hazards were confirmed in the starting material, *i.e*. the mix of polycotton post-consumer garments, such as benzyl benzoate, a weak/moderate skin sensitizer[227]. The sunscreen chemical octocrylene was also confirmed at 2 µg/g. A degradation product from octocrylene, benzophenone, was detected at 0.2 µg/g[228]. Various adverse health effects[228], such as genotoxicity[229], carcinogenicity[230] and endocrine disruption[231], are associated with this compound. Together with its metabolites, benzophenone has shown positive effects in the Ames test for mutagenicity[232].

Some arylamines were also detected in the starting materials, for instance, 2-bromo-4,6-dinitroaniline (70 µg/g), 2-chloro-4,6-dinitroaniline (30 µg/g), and 2,4-dinitroaniline (30 µg/g), which is close to or exceeding the regulated limit set by REACH.

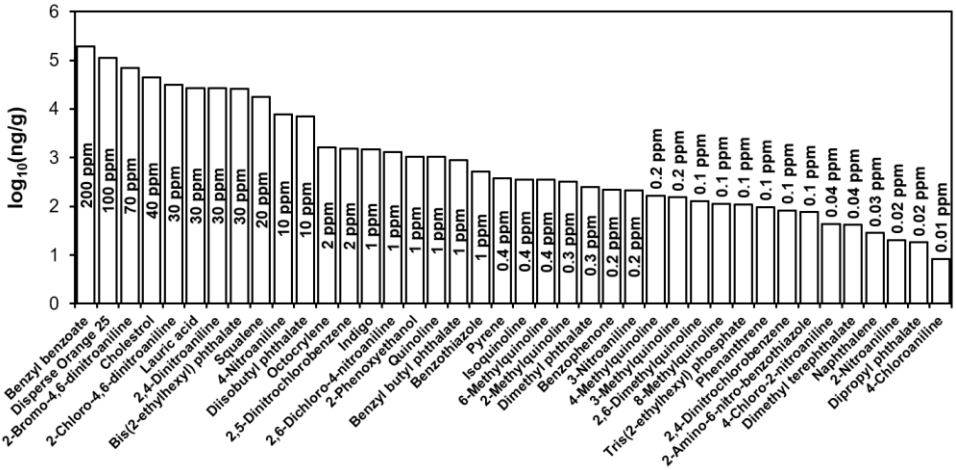

Figure 13: Quantified textile chemicals within a mixture of ten postconsumer polycotton garments using solvent extraction and offline GC/MS.

In LC/HRMS analysis, the total number of features detected in the starting material was almost 800 after blank correction (fold change, FC ≥ 10), of which 27 compounds were assigned as level 2, and the number of confirmed (level 1) compounds was 22. In **Figure 14,** the transfer of chemicals within the process from the starting material to the CNCs is illustrated by a volcano plot. The relative levels of most identified chemicals, expressed as $\log_2$(fold change), are significantly reduced in the CNCs compared to the starting material. Only 11% of the identified chemicals were higher in the CNCs. Notably, bis(2-ethylhexyl) phthalate (4 µg/g) and dibutyl phthalate (0.5 µg/g) remained attached entirely to the extracted cellulose. They were thus transferred to the product, however, at levels 200 times below the current REACH threshold of 0.1% (1000 µg/g) for individual or combined concentrations of phthalates.

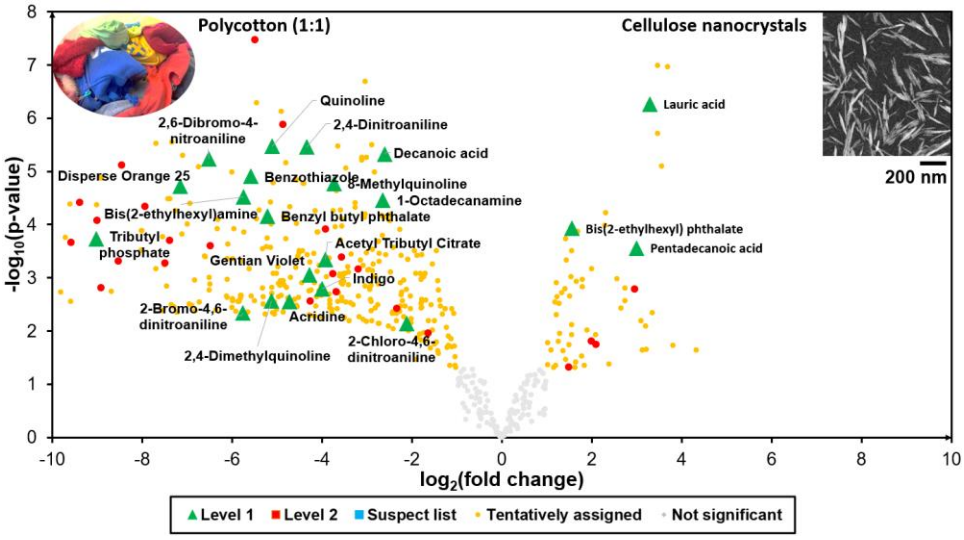

Figure 14: Relative distribution of the identified features, log_2(fold change), from an upcycling process of postconsumer polycotton textiles (left) and CNCs (right) using LC/HRMS in a non-target screening survey. Adopted from Paper II.

Many textile chemicals were detected in the polyester residual following the CNC extraction process, as illustrated in **Figure 15**. In total, 829 features were detected in the recovered polyester residual, of which 30 were assigned level 2, while 23 compounds were confirmed (level 1). The number of detected disperse dyes was 23, with a majority (65%) at higher residual levels than in the polycotton. This result could be expected since these dyes are firmly affixed to synthetic fibres. Hence, with the polyester residual acting as an adsorbent of hazardous textile pollutants, this waste fraction is easy to destroy, e.g., through incineration.

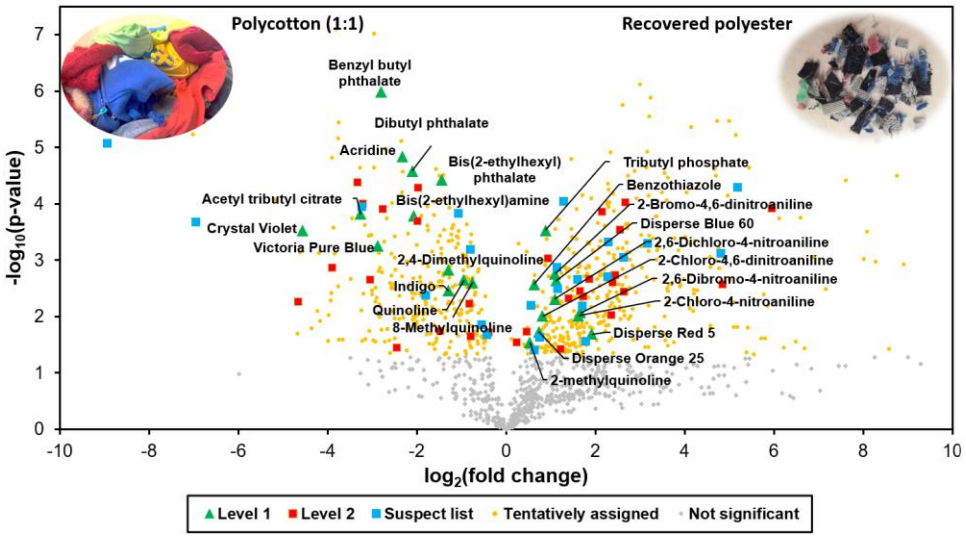

Figure 15: Relative distribution of the identified features, log_2(fold change), identified textile chemicals at higher levels in the polycotton mix (left) versus the recovered polyester residual (right) using LC/HRMS in a non-target screening survey. Adopted from Paper II.

A targeted screening, including 24 selected compounds using LC/ESI-MS/MS, was performed to screen chemicals in the process effluents quantitatively. In **Figure 16**, the distribution in % within the process is shown for each measured compound. For instance, some analytes were degraded/transformed in the process by the strongly acidic conditions, defined as "analyte loss", *i.e.*, the total amount detected within the entire process minus the amount in the polycotton starting materials. At least 13 compounds possessed a recovery of >70%.

Three analytes were almost wholly released into the effluents, indicating the necessity of wastewater treatment in an industrial upscaling: perfluorooctanesulfonic acid (PFOS), Victoria Pure Blue (VPB) and Crystal Violet. PFOS is a "forever chemical" with possible carcinogenic effects[233], Crystal Violet (EC list no: 208-953-6) is also a carcinogen and, according to CLP, toxic to the aquatic environment with long-lasting effects, and VPB (EC list no: 219-232-0) is genotoxic[234] and harmful to marine life.

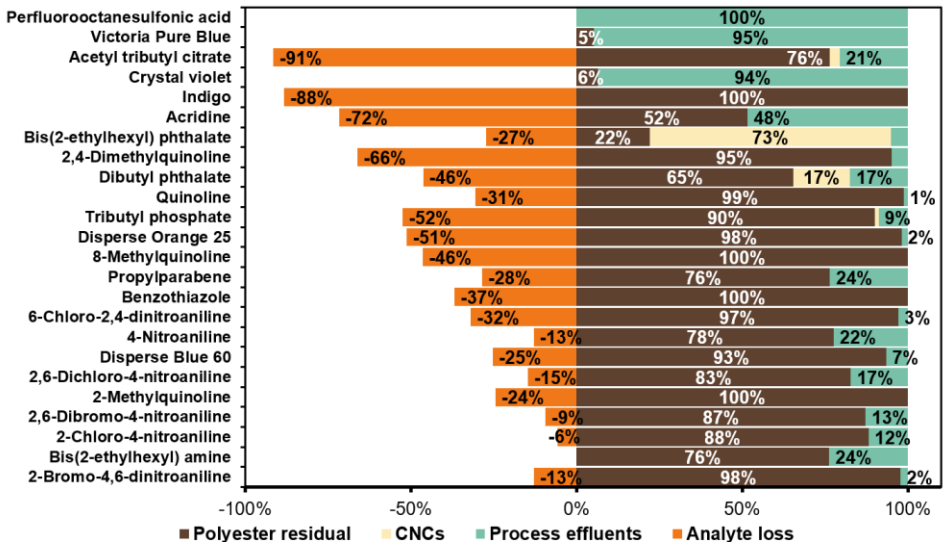

Figure 16: Analyte loss versus the distribution of target compounds in the three investigated sample matrices (polyester residual, CNCs and the process effluent) relative to the detected amount in polycotton. Adopted from Paper II.

The acidic conditions may reduce the disperse azo dyes to arylamines. A preliminary simulation (unpublished data) of the process was performed by subjecting a black synthetic sports jacket made of 100% polyester to strongly acidic conditions in diluted sulfuric acid. According to LC/HRMS analysis, the garment contained 21 tentatively identified disperse azo dyes before the acidic treatment, as seen in **Table 3.**

Table 3: A list of tentatively identified disperse azo dyes in the investigated synthetic sports jacket made of 100% polyester and corresponding theoretical cleavage products with available reference standards.

Name	Theoret. MW	RT [min]	Investigated cleavage product
Disperse Red 167:1	505.1356	12.1	2-Chloro-4-nitroaniline
Disperse Blue 79:1 (Cl)	580.1306	11.9	2-Chloro-4,6-dinitroaniline
Disperse Blue 291	508.0701	13.5	2-Bromo-4,6-dinitroaniline
Disperse Red 74	471.1743	11.1	4-Nitroaniline
Disperse Blue 291 (Cl)	464.1205	13.4	6-Chloro-2,4-dinitroaniline
Disperse Blue 79:1	624.0819	12.0	2-Bromo-4,6-dinitroaniline
Disperse Violet 93:1	478.0594	13.0	2-Bromo-4,6-dinitroanilin
Disperse Blue 291:1 (Cl)	488.1206	13.6	6-Chloro-2,4-dinitroaniline
Disperse Red 311	516.1598	11.2	2,4-Dinitroaniline
Disperse Orange 30	449.0649	11.8	2,6-Dichloro-4-nitroaniline
Disperse Red 54	415.1041	11.7	2-Chloro-4-nitroaniline
Disperse Blue 373	532.0705	13.7	2-Bromo-4,6-dinitroaniline
Disperse orange 25	323.1377	11.7	4-Nitroaniline
Disperse Yellow 211	361.0574	7.4	4-Chloro-2-nitroaniline
Disperse Brown 22	398.0543	10.0	2,6-Dichloro-4-nitroaniline
Disperse Orange 73	443.1589	12.4	4-Nitroaniline
Disperse Red 167	519.1516	12.6	2-Chloro-4-nitroaniline
Disperse Yellow 119	327.0968	10.7	2-Nitroaniline
Disperse Brown 19	526.0276	11.5	2,6-Dibromo-4-nitroaniline
Disperse Orange 3	242.0806	10.3	4-Nitroaniline
Disperse Yellow 241	336.0184	11.5	3,4-Dichloroaniline

In **Table 4,** an ATD-GC/MS analysis of the black sports jacket before and after acidic hydrolysis is presented. A t-test indicated the formation of 12 dye precursors as cleavage products after acidic hydrolysis ($p < 0.05$). Although this was a preliminary study, it probably explains, at least partly, the detection of arylamines in the process effluents **(Figure 16),** indicating one possible route of environmental pollution upon discharge into the sewage water system. Acidic hydrolysis is not a primary treatment of synthetic fibres, but it should be considered in any upscaling of this process.

Table 4: A quantitative comparison of a black sports jacket (100% polyester) subjected to acid hydrolysis using 68% H_2SO_4 and analysis with ATD-GC/MS at 175 °C primary desorption (n=3). n.d. = not detected. Sig = Significant.

Compounds	RT [min]	Before analysis [µg/g]	Hydrolysis [µg/g]	Change	Sig?
Benzothiazole	9.7	1.0 ± 0.2	1.0 ± 0.02	-1%	
Quinoline	9.8	0.9 ± 0.1	0.7 ± 0.05	-14%	
Isoquinoline	10.2	0.3 ± 0.05	0.1 ± 0.01	-97%	**Sig.**
2-Methylquinoline	10.8	0.1 ± 0.02	0.1 ± 0.003	-12%	
8-Methylquinoline	11.0	0.04 ± 0.01	0.03 ± 0.001	-13%	
6-Methylquinoline	11.5	0.1 ± 0.01	0.08 ± 0.005	-30%	
3-Methylquinoline	11.5	0.04 ± 0.01	0.04 ± 0.001	-13%	
4-Methylquinoline	11.8	0.03 ± 0.005	0.02 ± 0.001	-30%	
2-Nitroaniline	12.1	n.d.	0.2 ± 0.05	100%	**Sig.**
2,6-Dimethylquinoline	12.3	0.02 ± 0.003	0.02 ± 0.001	-14%	
3,4-Dichloroaniline	12.4	0.06 ± 0.01	0.3 ± 0.1	82%	**Sig.**
2,4-Dimethylquinoline	12.6	0.04 ± 0.004	0.03 ± 0.001	-24%	**Sig.**
3,5-Dinitrochlorobenzene	13.5	1.4 ± 0.1	2.0 ± 0.3	29%	**Sig.**
2-Bromo-4,6-dinitroaniline	13.5	2.2 ± 0.3	3.0 ± 0.6	28%	
2,6-Dichloro-1,4-benzenediamine	14.5	1.0 ± 0.5	1.4 ± 0.4	26%	
4-Chloro-2-nitroaniline	14.6	n.d.	0.2 ± 0.1	100%	**Sig.**
4-Nitroaniline	14.6	3.6 ± 0.1	10 ± 3	73%	**Sig.**
3,5-Dinitrobromobenzene	14.7	0.3 ± 0.04	0.5 ± 0.1	35%	**Sig.**
2-Chloro-4-nitroaniline	15.7	3 ± 0.1	20 ± 6	86%	**Sig.**
2,6-Dichloro-4-nitroaniline	16.0	18 ± 1.2	180 ± 50	90%	**Sig.**
6-Chloro2,4-dinitroaniline	17.9	40 ± 3	60 ± 10	35%	**Sig.**
2,6-Dibromo-4-nitroaniline	18.2	12 ± 0.8	10 ± 0.6	4%	
2,4-Dintroaniline	18.4	0.4 ± 0.04	1.0 ± 0.2	58%	**Sig.**

Paper III

This part of the work aimed to develop a simplified, comprehensive method for screening health-hazardous compounds in clothing not bound to the textile fibres, which can migrate to the skin and be capable of skin uptake. Such a textile screening method would make chemical surveillance of garments easier and hopefully lead to improved knowledge and control. The novel method, shown in **Figure 17**, was first (**Paper III**) developed for the most common clothing fabrics, polyester and synthetic blends. It requires minimal sample handling and laboratory supplies. With a total run time of around 40 minutes, the textile analysis is significantly faster than conventional methods with solvent extraction and offline analysis[7]. In the full scan mode of the MS, the quantification limit (MQL) is less than one µg/g for most of the analytes, including quinolines, arylamines, and nitrobenzene derivatives. In addition, electron ionization (EI) provides informative fragmentation spectra and a linear response range covering six orders of magnitude. The method was evaluated for the analytes between 1 – 100 µg/g textile to cover the current REACH limits, 50 µg/g for quinoline and 30 µg/g for twenty-two regulated arylamines.

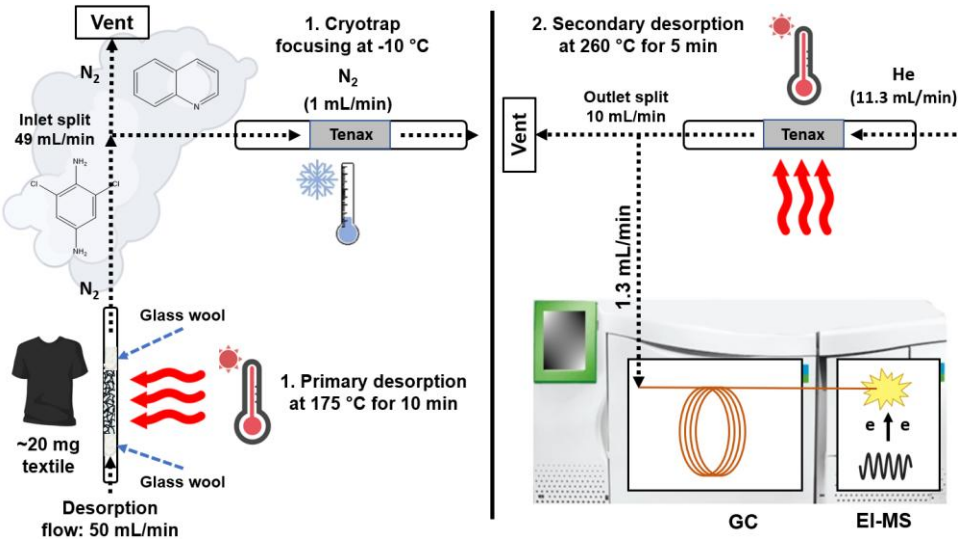

Figure 17: A schematic principle of the two-stage ATD-GC/MS instrumentation.

Thermal degradation of disperse azo dyes

The ATD-GC/MS is developed for semi-volatile chemicals and is generally incompatible with thermo-labile, non-volatile textile chemicals, e.g. disperse dyes and trace elements. However, as mentioned above, disperse dyes may still be desorbed and decomposed to arylamines, depending on the desorption temperature. Thus, setting a suitable temperature and time to achieve an exhaustive desorption of volatiles from the textiles was essential. At a temperature of 175 °C, the thermal degradation was found to be minimal or not observable. However, when the temperature was increased, arylamines were shown to be generated as artefacts from dye degradation. This is illustrated by analyzing a solvent extract from a black sports jacket with ATD at different temperatures, including some dyes. An increase in the temperature to 250 °C revealed an emanating peak corresponding to Disperse Orange 30 and a peak from its precursor, 2,6-dichloro-4-nitroaniline, as illustrated in **Figure 18. Figure 19** shows the results from the corresponding analysis at 175 °C. In the latter, the peak from 2,6-dichloro-4-nitroaniline represents the free form, not the degradation product.

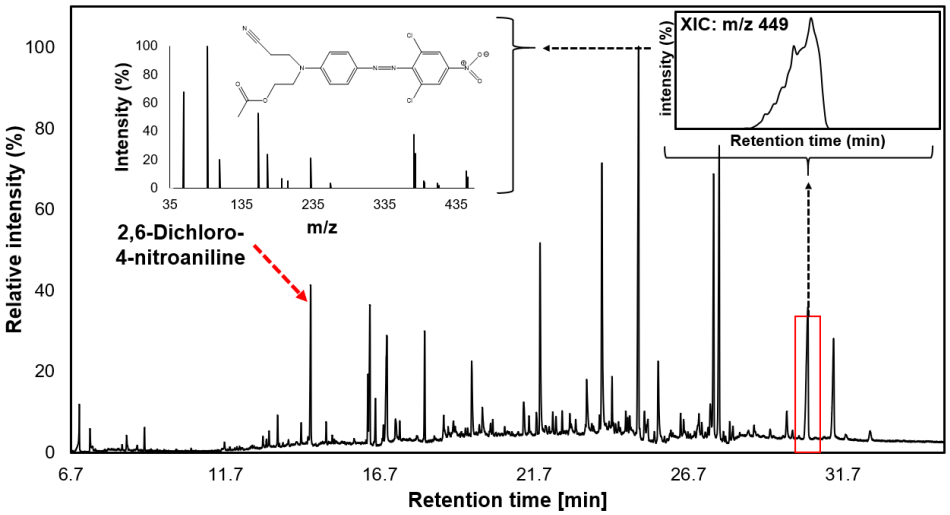

Figure 18: ATD-GC/MS chromatogram of a black sports jacket desorbed at 250 °C. Adopted from Paper III.

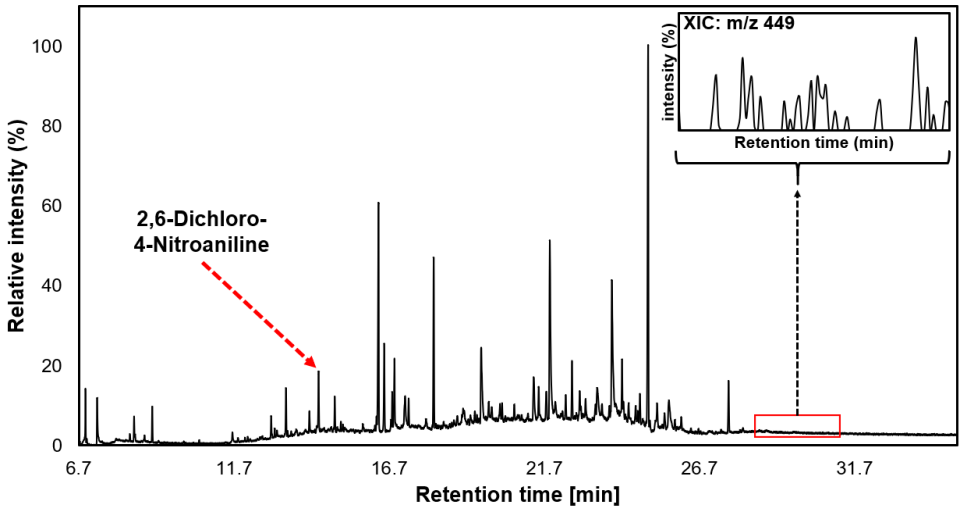

Figure 19: ATD-GC/MS chromatogram of a black sports jacket desorbed at 175 °C. Adopted from Paper III.

The desorption efficiency from polyester was further investigated at 175 °C (**Figure 20**) by repeating the desorption cycle for the same sample. As shown, the extraction was almost complete for all analytes at the first desorption, and artefact formation was not the case since the fourth cycle was empty.

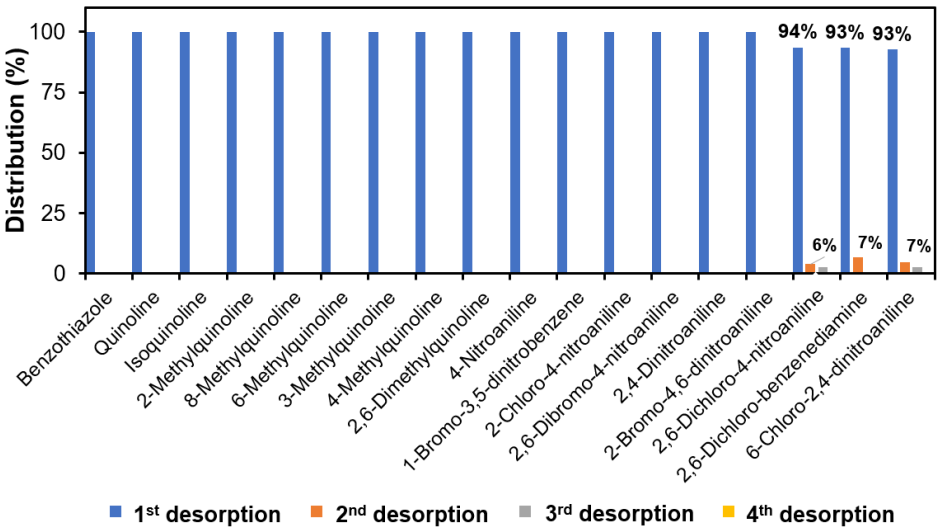

Figure 20: Repeated ATD-GC/MS analysis of native compounds in a black sports jacket (100% polyester) desorbed at 175 °C for 10 min (n=3). Adopted from Paper III.

A method cross-validation was performed by comparing the ATD-GC/MS analyses of native compounds present in two garments (100% polyester and 91% polyester, 9% elastane, respectively) with solvent extraction and off-line GC/MS (SE-GC/MS), results shown in **Figure 21**. In total, 18 individual compounds were identified using reference standards and a linear correlation was found between the two analytical methods (R^2 = 0.91). However, the regression coefficient/slope (≈0.9) reveals a slight favour for solvent extraction, but the developed ATD-GC/MS method is an acceptable extraction technique considering an error margin of ±15%.

As a result of the broad applicability of the ATD-GC/MS methodology for textile screening, it was 2024 proposed as a European standard method by the standardisation authority (CEN) for textile screening. A round-robin test of the technique, including several international laboratories, is currently planned.

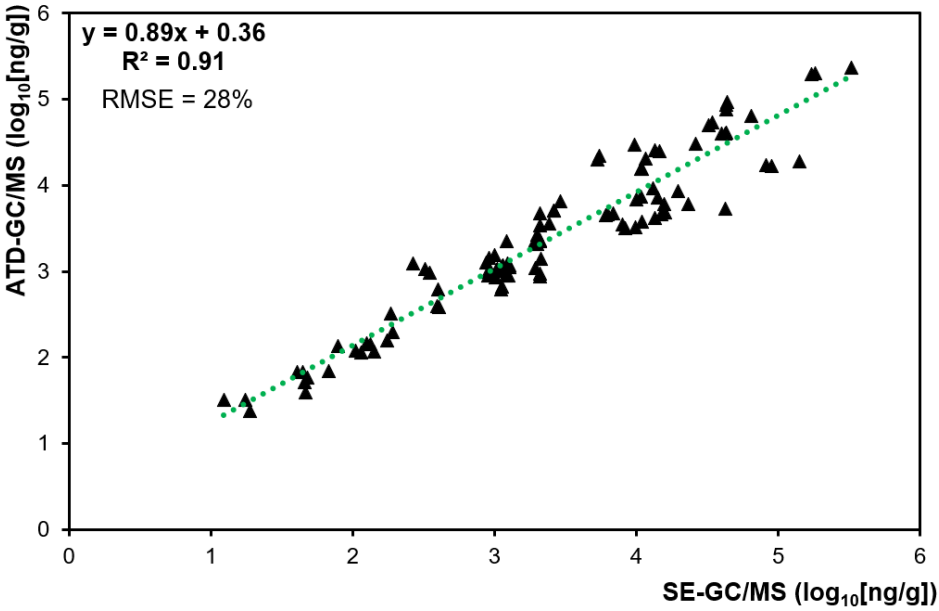

Figure 21: Analysis of native compounds in a black sports jacket (100% polyester) and a blue sports T-shirt (91% polyester, 9% elastane) using the ATD-GC/MS with 175 °C desorption and solvent extraction with offline GC/MS (SE-GC/MS)

Paper IV

Paper IV aimed to evaluate ATD-GC/MS for expanded applicability, including cotton analysis. A pilot study found that thermal desorption from cotton at 175 °C was much less efficient than synthetic fabrics. Despite this, the desorption temperature cannot be further increased due to the risk of degrading present azo dyes. Lower cotton content and higher synthetic fibres generally improved desorption efficiency. However, there was a considerable variation in desorption yields between analytes. The analytes presented in retention order from the GC show that this is not due to different vapour pressures. The desorption yields for internal standards are shown in **Figure 22**. Since nitrogen-containing analytes are the most difficult to desorb, the interaction between analytes and cellulose is considered hydrogen bonding and/or polar-polar interactions. The 100% cotton samples S1-S4 also showed different yields. Since all four materials are made from pure cellulose and should have similar surface chemistry, physical parameters, such as thread density and wettability, were investigated. The optical spectroscopy photographs in **Figure 23** reveal differences in thread thickness and porosity. Sample S4 possesses a less dense structure than the other cotton materials, which may explain the higher desorption yield due to fewer site-specific interactions with the cellulose.

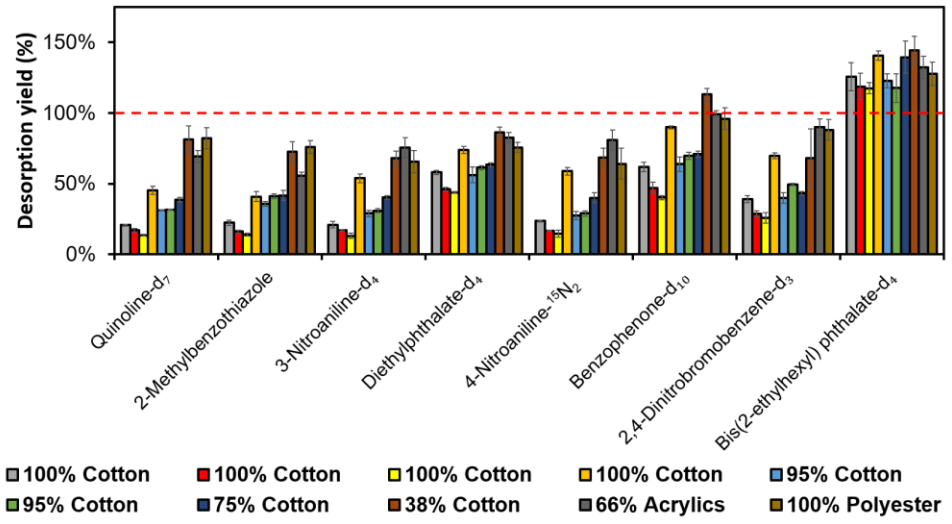

Figure 22: Desorption yield of eight internal standards, added to 10 different textile garments with a varying cotton composition. Samples (S1–S10) with a decreasing composition of cotton are presented from left to right. Adopted from Paper IV.

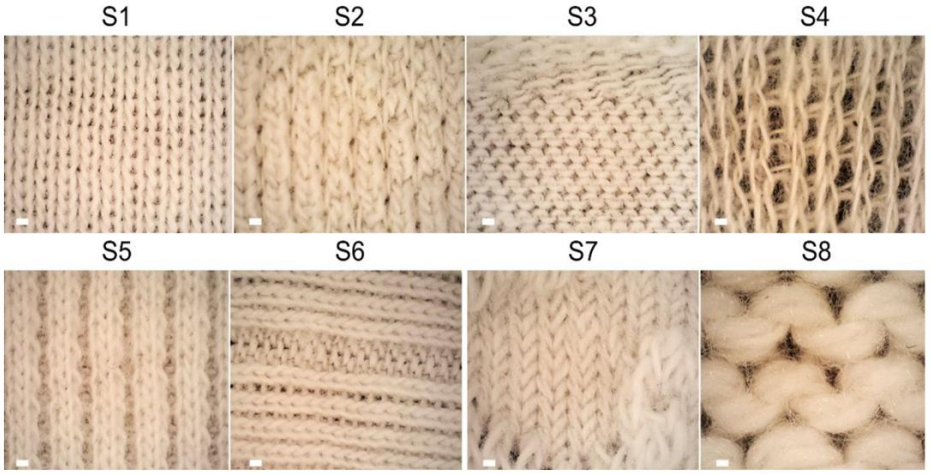

Figure 23: Optical microscopic images of samples S1-S8. Scale bar: 500 µm. S1-S4 are pure cotton. Adopted from Paper IV.

The desorption temperature was not solely limited to the thermal decomposition of disperse azo dyes but also the thermal stability of the fibres. The thermal properties of the individual components, i.e., cellulose, hemicellulose, and lignin, have been studied

before by thermal gravimetric analysis (TGA) in an inert atmosphere[235]. Thus, the susceptibility to thermal degradation suggests that the processing temperatures of natural fibre composite polymers should be kept below 200 °C to minimize the possibility of thermal degradation since the effect of heating lignocellulosic fibres in the range from 100 – 250 °C emphasizes various chemical- or physical changes in the material properties[236]. In **Paper IV**, experimental observations of pure cotton subjected to primary desorption at 220 °C resulted in a colour change from white to brownish, indicating that the higher thermal conditions affected the material properties, which was not observed at 175 °C.

The desorption time was investigated to check the influence on the yield, but there was no considerable improvement by increasing the time. In **Figure 24,** a comparison of a 10-minute primary sample desorption is compared with a 30-minute desorption. The regression coefficient (≈0.96) indicates a small or non-existent difference since there is almost a 1:1 ratio between 10-min and 30-min desorption time (R^2 = 0.93).

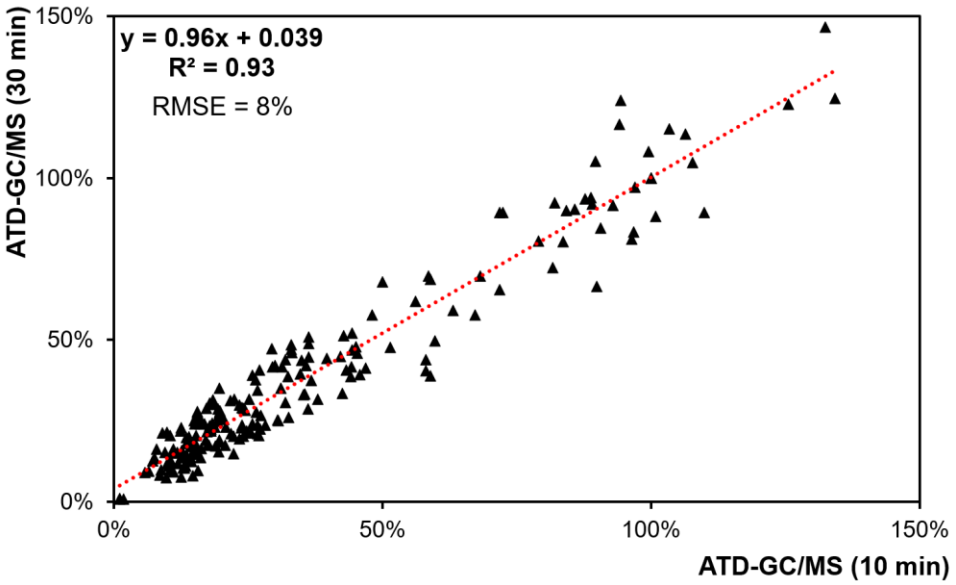

Figure 24: Evaluation of the desorption time (10 and 30 min) for 71 target analytes added to 100% Cotton (Cotton-2 in Paper IV).

To summarise, most analytes were stronger adsorbed to cotton than polyester. The absolute yield from cotton was as low as 10-15% for some compounds. The desorption efficiency also varied between materials because of different thread densities and porosities. Then, the question followed: *How can the ATD-GC/MS method be used best for quantitative screening surveys of different textiles of varying compositions?*
The quantification was acceptable irrespective of textile composition when using absolute response factors from several carefully selected, mostly isotope-labelled internal standards, spiked onto the samples into the desorption tubes. This is an excellent advantage in obtaining a fast, reliable, and user-friendly method.

Validation of the process was performed by comparison with SE-GC/MS. The ultrasonic-assisted solvent extraction with dichloromethane also showed low absolute recoveries, as did the ATD-GC/MS. This result differs from those of synthetic fibres, for which the same solvent extraction method is generally exhaustive. **Figure 25** shows the comparison between the methods (R^2= 0.80). The regression coefficient (≈1.5) does not indicate a 1:1 ratio between the two techniques but rather an improved extraction/desorption efficiency with the ATD-GC/MS methodology compared to the selected solvent extraction technique with dichloromethane.

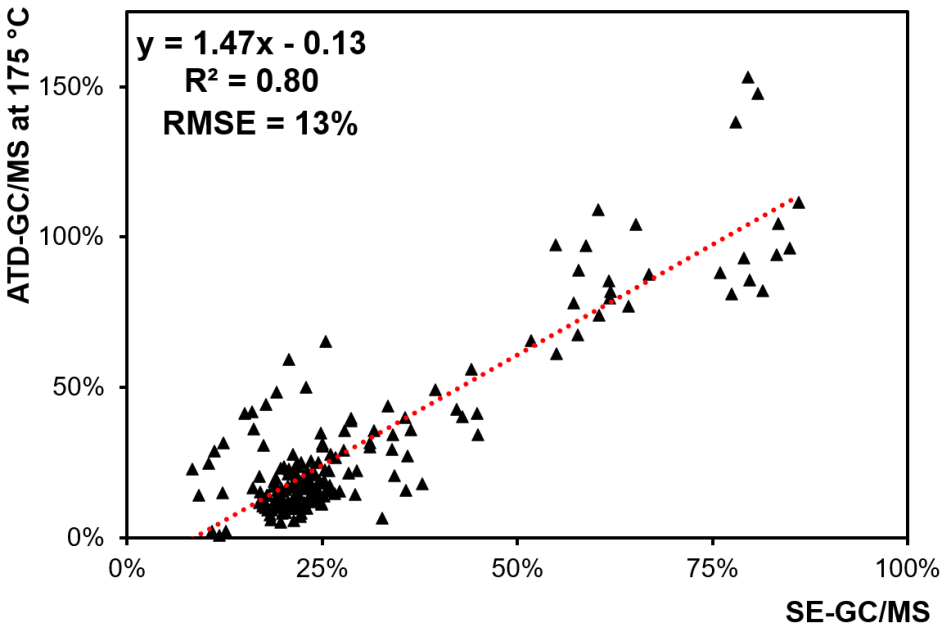

Figure 25: The yields from ultrasonic-assisted extraction with offline GC/MS versus ATD-GC/MS at 175 °C for 59 target compounds added to 100% cotton (Cotton-2).

In **Figure 26,** the comparison between ATD-GC/MS and SE-GC/MS is illustrated by a scatter plot using the selected internal standards to compensate for analyte loss. Absolute trueness, represented by the red centre circle (100%), has a radius indicating a tolerance of ±30%. The red dashed circle encloses more than 90% of the investigated compounds. This suggests that the method is fit for quantification purposes, assuming that structurally similar or isotopically labelled internal standards have been equilibrated on the textile matrix before extraction and desorption, respectively.

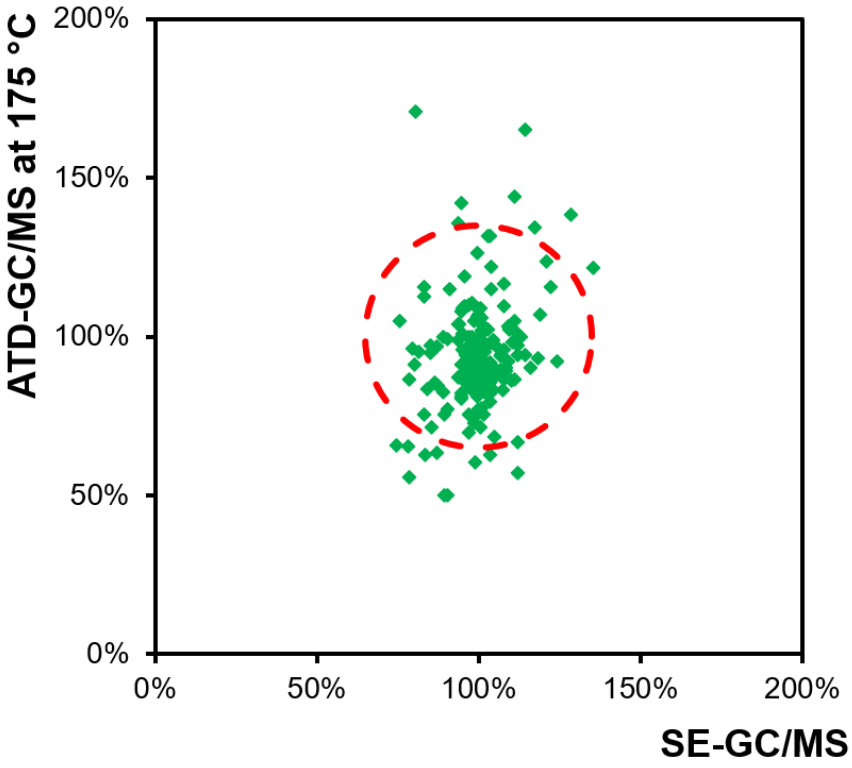

Figure 26: Method accuracy using a structurally similar or close-eluting IS of the 51 target compounds added to the cotton matrix (n=3).

Comparing the extractable amount with other solvents in SE-GC/MS rather than dichloromethane might lead to lower or higher extraction recoveries. For curiosity, the extraction of spiked cotton into artificial sweat (pH 5.4) was tested (unpublished results) and showed much higher extraction yields than dichloromethane for the nitrogen-containing analytes. This further indicates the strong adsorption of analytes based on polar-polar interactions and hydrogen bonding with the hydroxyl groups on the cellulose structure.

Characterization of textile fibres

A non-destructive control of finished garments is crucial for the characterization of textile fibre composition, not only within the textile industry *per se* but also in forensic- and archaeological applications and for fashion designers. The regulatory framework is a comprehensive legal act within the EU[179] and US[237]. However, textile manufacturers might exaggerate the content of natural fibres, which are often associated with higher costs and are labour-intensive. A study conducted by Circular Economy in 2019 observed that approximately 40% of the tested garments (N=10000) were inappropriately labelled, i.e. did not match the actual content specified[238].

In **Paper IV**, two commercial materials specified as 100% cotton were utilized as standard textile matrices in the ATD desorption tests. One of the materials gave similar desorption efficiencies as 100% polyester, leading to questions about whether the product was mislabelled. Fourier-transform infrared analysis was performed on the two materials to investigate this further. In **Figure 27,** a 100% polyester material is shown, and in **Figure 28**, a 100% cotton material is shown.

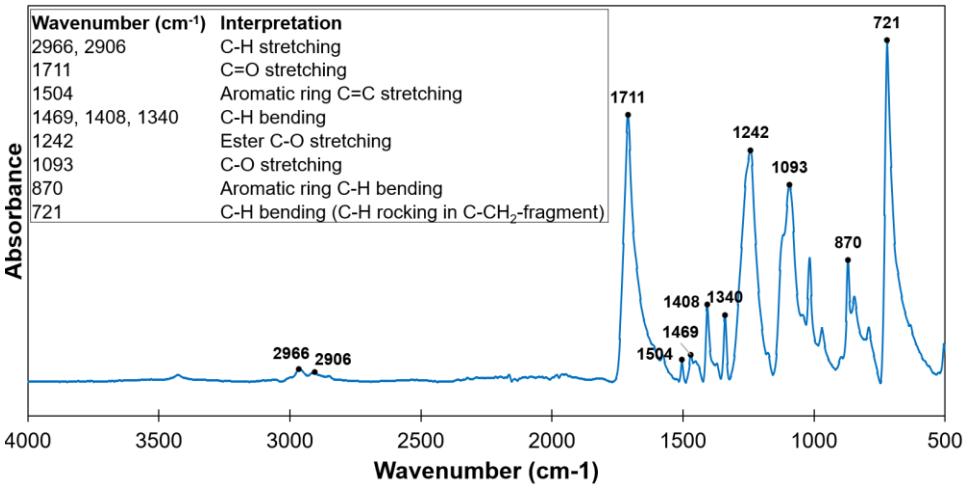

Figure 27: FTIR characterization of 100% polyester[239,240].

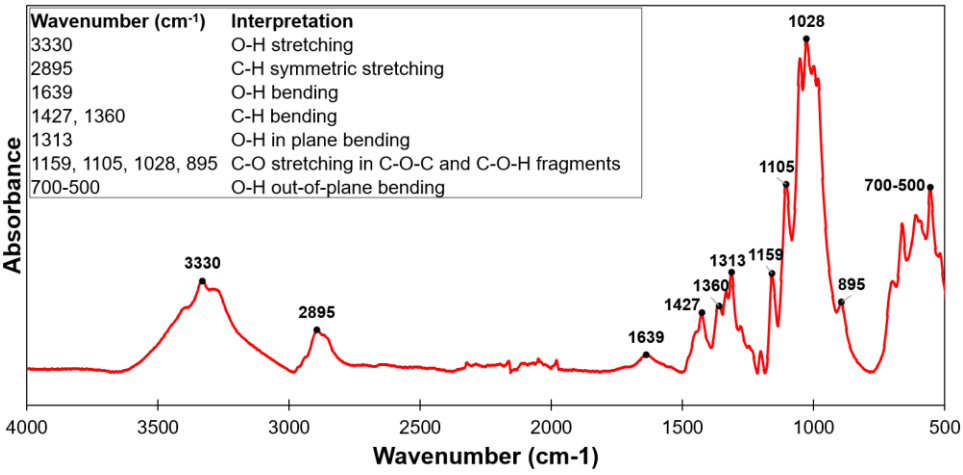

Figure 28: FTIR characterization of 100% Cotton[239,240].

The results (**Figure 27**) indicated that the used material was mislabelled as 100% cotton, emphasising the need for textile fibre characterization, especially for upcycling of worn-out textile apparel.

Preliminary study not included in the papers:

Wash-out of chemicals during laundry

Since many health-hazardous chemicals have been detected as residuals in garments from the open retail market, an obvious follow-up question is: *To what extent can laundry wash them out?* This has been investigated previously for several substances, such as benzothiazoles and quinolines, but as far as I know, not for arylamines and nitrobenzenes. The laundry effect was not a focus of the present thesis, but I performed some preliminary experiments out of curiosity. Four different textiles were each subjected to one and ten laundry cycles, and the results are presented in **Table 5.** As observed, the results reveal possible losses of chemicals upon laundry, calculated as the difference between the unwashed and one-cycle washed garments. However, the variations in measured amounts between the replicates were too large, and hence, the losses were non-significant ($p>0.05$), except for the arylamines in textile-3 ($p<0.05$). However, more considerable losses were observed after ten laundry cycles for most of the investigated classes, and the results were generally statistically significant ($p<0.05$).

Table 5: The washout effect considering 5kg of textile, including quinolines, arylamines, phthalates, nitrobenzenes and benzothiazole, detected in four different garments, textile-1 (100% polyester), textile-2: 71% cotton, 26% polyester, 3% elastane, textile-3: 100% polyester and textile-4: 100% polyester (n=3). A standard laundry program was used at 40°C with two rinse cycles.

Compounds	Mean ± STD (mg/ 5kg textile)	One cycle (%)	Ten cycles (%)
Textile-1 (100% Polyester)			
Σ Quinolines	16 ± 1.2	-11 ± 5	-26 ± 9
Σ Arylamines	470 ± 50	-13 ± 6	-18 ± 5
Σ Phthalates	55 ± 4	-14 ± 5	-39 ± 2
Σ Nitrobenzenes	n.d	n.d	n.d
Benzothiazole	14.8 ± 1.1	18 ± 12	-30 ± 7
Textile-2 (71% Cotton, 26% Polyester, 3% Elastane)			
Σ Quinolines	12 ± 1.1	-11 ± 8	-20 ± 19
Σ Arylamines	14 ± 3	-12 ± 7	-26 ± 35
Σ Phthalates	15 ± 2	-5 ± 18	-30 ± 19
Σ Nitrobenzenes	n.d	n.d	n.d
Benzothiazole	8.3 ± 0.4	-41 ± 7	-26 ± 16
Textile-3 (100% Polyester)			
Σ Quinolines	3.0 ± 2.4	-65 ± 6	-42 ± 17
Σ Arylamines	680 ± 50	-31 ± 8	-36 ± 9
Σ Phthalates	10 ± 3	-36 ± 9	-55 ± 5
Σ Nitrobenzenes	n.d.	n.d.	n.d.
Benzothiazole	10 ± 0.5	-42 ± 9	-37 ± 7
Textile-4 (100% Polyester)			
Σ Quinolines	220 ± 40	-8 ± 4	-17 ± 13
Σ Arylamines	1000 ± 200	-12 ± 13	-16 ± 8
Σ Phthalates	20 ± 2	-49 ± 5	-28 ± 5
Σ Nitrobenzenes	170 ± 20	-3 ± 15	-8 ± 12
Benzothiazole	3 ± 0.5	-24 ± 4	-42 ± 6

To sum up, a major amount (>50%) seems to remain within the ten-cycle washed garments; textile laundering might not be the most effective solution to remove pollutants. The results indicate that laundry is ineffective in removing significant amounts from polyester garments before usage. However, this should be investigated more thoroughly, including many different fabrics. Also, it should be investigated if arylamines

may be released from azo dyes by the action of enzymes or chemicals in the washing powder.

Chemical- vs electrospray ionization

LC/ESI-HRMS has previously been used for non-targeted textile screening[10]. However, a drawback with ESI is the tendency of matrix effects on the ionization[241,242], *i.e.* ion suppression or enhancement, especially in highly complex samples such as textile extracts. Further, the selectivity of ESI makes it "blind" to many chemicals. To expand the chemical space in the non-targeted analysis and include chemicals missed in ESI, atmospheric pressure chemical ionization (APCI) could be added to the non-targeted workflow[243]. The responses in APCI may depend on ionization efficiencies from several possible in-source reactions apart from protonation and deprotonation, such as electron ionization, interaction with a solvent radical ion, or proton exchange[244].

For curiosity, I performed a brief comparison of the responses of thirty-one model textile substances using both ESI-HRMS and APCI-HRMS. LC/MS is sometimes more useful than ATD-GC/MS, such as for textile chemicals in waste effluents or sweat extracts. The absolute response of each compound was evaluated by multiple linear regression of eight calibration levels, ranging from 0.05-10 ng, and injected on a reversed-phase (C_{18}) column to derive the slope of the calibration graph. The acquisition runs were divided into positive and negative ionization modes, and the results are presented in **Table 6** and **Table 7.** Most of the investigated chemicals were found to possess a higher absolute response with APCI, with a few exceptions. The studied nitrobenzenes, *i.e.* 1,4-dinitrobenzene, 2,4-dinitrochlorobenzene, and 3,5-dinitrobromobenzene, resulted in the greatest difference, from 200-4000 times more intense using negative APCI compared to ESI.

Table 6: Comparison of the absolute response using APCI- and ESI-HRMS in positive ionization mode. n.d = not detected.

Compounds	Molecular formula	RT (min)	Adduct type	Experimental m/z	$Slope_{APCI}$	R^2	$Slope_{ESI}$	R^2	Slope APCI/Slope ESI
2,6-Dichloro-1,4-phenylenediamine	$C_6H_6Cl_2N_2$	6.4	$[M+H]^+$	176.9986	7.6E+06	0.8834	n.d.	n.d.	-
2-Hydroxybenzothiazole	C_7H_5NOS	6.9	$[M+H]^+$	152.0170	1.6E+06	0.9987	2.5E+05	0.9682	6
Quinoline	C_9H_7N	7.4	$[M+H]^+$	130.0657	7.9E+08	0.9992	1.3E+08	0.9871	6
Benzothiazole	C_7H_5NS	7.6	$[M+H]^+$	136.0221	2.7E+08	0.9989	1.5E+07	0.9819	20
4-Chloroaniline	C_6H_6ClN	7.9	$[M+H]^+$	128.0267	1.1E+06	0.9979	1.3E+05	0.9783	8
Dibenzylamine	$C_{14}H_{15}N$	8.0	$[M+H]^+$	198.1283	4.4E+08	0.9987	1.1E+09	0.9945	0.4
2-Methylquinoline	$C_{10}H_9N$	8.1	$[M+H]^+$	144.0813	7.4E+08	0.9992	1.4E+08	0.9842	5
Dimethyl phthalate	$C_{10}H_{10}O_4$	8.3	$[M+H]^+$	163.0390	2.9E+07	0.9996	4.1E+06	0.9844	7
2,4-Dimethylquinoline	$C_{11}H_{11}N$	9.1	$[M+H]^+$	158.0970	5.9E+08	0.9989	1.3E+08	0.9858	5
Benzophenone	$C_{13}H_{10}O$	11.1	$[M+H]^+$	183.0810	1.5E+06	0.9976	3.8E+05	0.9802	4
Dipropyl phthalate	$C_{14}H_{18}O_4$	12.2	$[M+H]^+$	251.1283	2.1E+07	0.9963	4.9E+06	0.9874	4
Triphenyl phosphate	$C_{18}H_{15}O_4P$	12.7	$[M+H]^+$	327.0786	6.5E+07	0.9993	7.2E+07	0.9980	1
Tributyl phosphate	$C_{12}H_{27}O_4P$	12.7	$[M+H]^+$	267.1725	3.8E+08	0.9979	7.7E+08	0.9958	0.5
Benzyl butyl phthalate	$C_{19}H_{20}O_4$	13.6	$[M+H]^+$	313.1440	3.6E+07	0.9979	1.8E+07	0.9945	2
Isobutyl phthalate	$C_{16}H_{22}O_4$	13.8	$[M+H]^+$	279.1596	3.4E+07	0.9930	7.1E+06	0.9846	5
Bis (2-ethylhexyl) phthalate	$C_{24}H_{38}O_4$	19.5	$[M+H]^+$	391.2848	1.6E+08	0.9950	1.2E+07	0.9919	10
Dioctyl phthalate	$C_{24}H_{38}O_4$	20.2	$[M+H]^+$	391.2848	6.0E+07	0.9980	3.0E+06	0.9898	20
Tris (2-ethylhexyl) phosphate	$C_{24}H_{51}O_4P$	23.9	$[M+H]^+$	435.3603	3.5E+08	0.9994	1.2E+09	0.9968	0.3

Table 7: Comparison of the absolute response using APCI- and ESI-HRMS in negative ionization mode. n.d = not detected.

Compounds	Molecular formula	RT (min)	Adduct type	Experimental m/z	$Slope_{APCI}$	R^2	$Slope_{ESI}$	R^2	Slope APCI/Slope ESI
2,4-Dinitrophenol	$C_6H_4N_2O_5$	4.0	$[M-H]^-$	183.0042	2.3E+08	0.9913	4.8E+08	0.9927	0.5
4-Nitroaniline	$C_6H_6N_2O_2$	6.2	$M^{+\bullet}$	138.0197	1.9E+09	0.9995	2.5E+09	0.9785	0.7
4-Nitrophenol	$C_6H_5NO_3$	6.2	$[M-OH]^-$	122.0242	4.2E+07	0.9912	n.d.	n.d.	-
2,4-Dinitroaniline	$C_6H_5N_3O_4$	7.9	$[M-H]^-$	182.0202	2.0E+09	0.9988	2.4E+09	0.9812	0.8
1,4-Dinitrobenzene	$C_6H_4N_2O_4$	8.5	$M^{+\bullet}$	168.0171	4.4E+08	0.9679	1.8E+05	0.9920	2500
2-Chloro-4-nitroaniline	$C_6H_5ClN_2O_2$	8.6	$[M-H]^-$	170.9961	5.6E+08	0.9973	6.3E+08	0.9931	0.9
2-Chloro-4,6-dinitroaniline	$C_6H_4ClN_3O_4$	9.1	$[M-H]^-$	215.9818	1.5E+09	0.9978	5.8E+08	0.9979	2.6
2-Bromo-4,6-dinitroaniline	$C_6H_4BrN_3O_4$	9.4	$[M-H]^-$	259.9307	1.1E+09	0.9979	3.4E+08	0.9982	3.1
2,4-Dinitrochlorobenzene	$C_6H_3ClN_2O_4$	9.7	$[M-Cl+O]^-$	183.0042	6.5E+08	0.9786	3.3E+06	0.9999	200
2,6-Dichloro-4-nitroaniline	$C_6H_4Cl_2N_2O_2$	10.0	$[M-H]^-$	204.9572	1.0E+09	0.9943	1.8E+08	0.9999	6
3,5-Dinitrobromobenzene	$C_6H_3BrN_2O_4$	10.2	$[M-H]^-$	245.9282	5.7E+08	0.9778	1.4E+05	0.9916	4000
2,6-Dibromo-4-nitroaniline	$C_6H_4Br_2N_2O_2$	10.6	$[M-H]^-$	294.8548	6.5E+08	0.9989	2.1E+08	0.9995	3
3,5-Dichloronitrobenzene	$C_6H_3Cl_2NO_2$	11.6	$M^{+\bullet}$	190.9541	3.2E+07	0.9907	n.d.	n.d.	-

The quantitative performance of the two ionization techniques in both positive and negative modes was compared by analyzing four textile samples in triplicate. **Figure 29** shows a linear (1:1) relationship between the two ionization techniques, indicating a good agreement regardless of possible matrix interferences obstructing the analyte response in ESI.

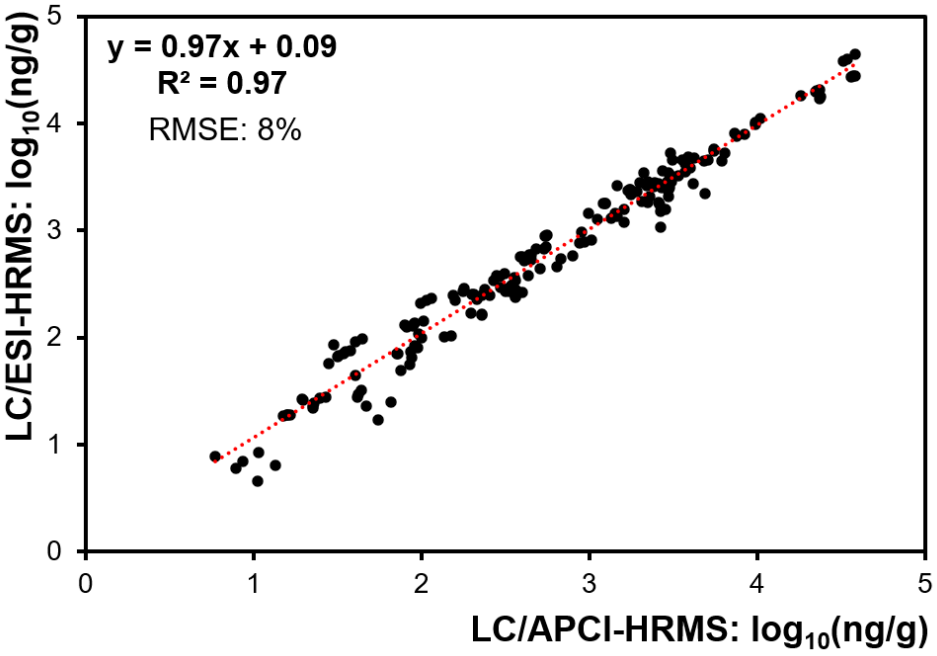

Figure 29: Quantification of twenty-two target compounds detected as native analytes in four textile extracts obtained from Textile-1: 71% cotton, 26% polyester, 3% elastane, and Textiles 2-4: 100% polyester.

To sum up, APCI should be helpful in further non-target screening of aqueous samples containing textile chemicals. It would be interesting to study further the correlations between responses and analyte properties, such as pKa, ionization potential, and proton affinity.

Conclusions

The analytical methodologies presented in this thesis have generated more knowledge concerning the chemicals occurring in ordinary clothing, which most of us are exposed to daily. **Paper I** focused on screening for possible skin sensitizers since textile allergy is a widespread problem among the general population. Many dyes not yet evaluated in skin-sensitization assays were frequently detected. At the same time, those used for patch testing in a textile-dye mix (TDM) were much less common, except for Disperse Orange 3. It is possible that including other, more common dyes would improve the diagnosis of textile allergy. It was also found that the dyes used in textile manufacturing are not pure but contribute to potentially health-hazardous dye precursors in the finished garments.

Several of the arylamines presented in **Paper I** have chemical structures similar to those of the regulated ones and may thus pose comparable risks for skin sensitization and/or mutagenicity. Regarding the latter, the arylamines are considered more important than the corresponding parent azo dyes. In some cases, levels at mg/g were detected, almost 100 times the current EU regulation of individual arylamines. The arylamines measured in **Paper I** were likely measured as a combination of free compounds and azo dye degradation products, *i.e*. overestimated due to degradation of azo dyes in the GC injector, and measures were taken to remove azo dyes prior to GC/MS in the following studies.

An interesting finding in **Paper I** was the regular occurrence of halogenated dinitrobenzenes in clothing, such as 2,4-DNCB, an extreme skin allergen. Other detected compounds of the same class were 2,5-DNCB, which was later found to be both skin-sensitizing and mutagenic, and the bromine-containing 3,5-DNBB, which was shown to be a mutagen.

In **Paper II**, the fate of hazardous chemicals in a novel textile upcycling method was studied. The extracted cellulose product was cleaner than the textile apparel used as starting material, and the transfer of health-hazardous chemicals was minimal. Selected toxic chemicals detected in the starting material were followed through the entire process to the finished upcycled material, and the analytical methodology made it possible to quantify the distribution of the chemicals within the process. The low transfer of chemicals to the product could be explained by their strong attachment to the polyester residual. A few phthalates were, however, shown to stay attached to the cellulose and thus transferred to the CNCs. Measures to handle this should thus be taken in the future, such as removal by thermal desorption or laundry. The emission of some water-soluble pollutants, such as PFAS, was detected in the waste effluent, and it was possible to predict its extent based on their water solubilities under acidic conditions. As for the phthalates, it is important to consider them in any future industrial upscaling process.

In **Paper III**, ATD-GC/MS is presented as a novel analytical methodology for screening synthetic garments, targeting those potential health-hazardous substances most prone to be absorbed by human skin. Among these compound classes are quinolines, arylamines, halogenated dinitrobenzenes, phthalates, and a wide range of semi-volatile compounds. The advantage is the automated approach, shorter analysis time and no need for solvent extraction or consumables for cleanup, reducing both environmental impact and laborious sample preparation. It should be mentioned that the method has some limitations, such that it cannot be used for disperse dyes or trace elements.

In **Paper IV**, the ATD-GC/MS method was shown to also apply to the analysis of the most abundant natural fibres used in textile production, i.e., cotton. Although a challenging material for ATD-GC/MS due to strong and varying chemical adsorption and thermal adsorption efficiency, it was still possible to quantify the adsorbed chemicals with acceptable accuracies by using absolute responses from carefully chosen internal standards spiked to the samples.

The ATD-GC/MS method can be applied to most skin-close garments from the retail market, potentially measuring chemicals well below EU-regulated levels. If accepted as a European standard method for textile screening, this will hopefully lead to more control of the chemical content in produced and recycled textiles and improved compliance with regulations.

Future perspectives

For a sustainable textile manufacturing and circular economy, as well as for consumer safety and environmental health, it is essential to improve the general control of chemicals in new, recycled, and post-consumer textiles aimed for upcycling. Current chemical legislation only embraces a small fraction of all potentially harmful textile chemicals. Due to the fast fashion trends and changes in colours and textile materials, analytical methods will also be needed to screen for new emerging compounds that could threaten human health and/or the environment. Knowledge regarding the chemical content is a foundation for further regulation. Several identified chemicals are already suspected or proven skin-sensitizers, mutagens, or carcinogens. Still, an important question remains unanswered, *i.e.,* how the complex chemical mixtures in some garments, including hundreds of substances, influence the total toxicity of a garment.

In addition, future research should investigate which textile chemicals or chemical classes are most relevant in skin allergy. This knowledge would be highly valuable in preventing and diagnosing textile allergy. In a longer perspective, more research may lead to the conclusion that new compounds should be included in the patch tests to diagnose textile allergy more efficiently.

The laundry effect and discharge of textile pollutants into the environment are also relevant for further research, as chemicals might be more firmly or loosely bound depending on the fibre composition. It seems that compounds such as quinolines and arylamines are firmly bound to polyester, as indicated by the laundry test, artificial sweat extraction, and the upcycling process.

As this thesis has indicated, the content and fate of potentially harmful substances should be determined as part of a life cycle analysis before transforming a laboratory upcycling

process to a pilot or an industrial scale. Analytical methodologies for this are now available.

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