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Environmental Assessment of Alternative Durable Water Repellent Chemicals

First steps towards a holistic assessment

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Abstract

Durable water repellent (DWR) finishes are applied to textiles to impart water and in some cases oil repellency. Water (and oil) repellency can be an important contribution to a textile's performance, for comfort or for the protection of human lives under extreme conditions. DWRs incorporating side-chain fluorinated polymers based on long-chain per- and polyfluoroalkyl substances (PFAS) are being phased out due to the recognition of the hazard they pose to humans and the environment. In this thesis the first steps towards a holistic environmental assessment of alternative DWRs are presented. A hazard assessment focussing on diffusively released substances showed that the available alternatives have better hazard profiles compared to the DWRs based on long-chain PFAS. Hydrocarbon based DWRs were assessed as most benign while properties of concern were identified for both side-chain-fluorinated polymers based on short-chain PFASs and silicones. To fully assess the human health and environmental toxicity impacts of the alternatives, including the possible trade-offs creating other types of negative impacts, risk assessment and life cycle assessment (LCA) are recommended methods and will be used to establish a substitution scheme. In addition to risks to human health and the environment due to chemical releases, a sound substitution scheme must also consider risks connected to DWR failure, and strive towards minimal release of hazardous substances. Further research needs to focus on filling the data gaps in the hazard profiles of the existing alternatives and to develop high performance DWRs with less problematic hazard profiles.

Keywords: CAA, dendrimers, diffuse emissions, DWR, LCA, PFAS, risk assessment, silicones, wax

Acknowledgements

List of Publications

This thesis is based on the research presented in the following papers, which are referred to in the text with roman numerals:

I. Holmquist, H.; Schellenberger, S.; van der Veen, I.; Peters, G.M.; Leonards, P.*E.G.*; Cousins, I.T. Properties, performance and associated hazards of state-of-the-art durable water repellent (DWR) chemistry for textile finishing. *Environment International*. 91:251-264; 2016

II. Harder, R.; Holmquist, H.; Molander, S.; Svanström, M.; Peters, G.M. Review of Environmental Assessment Case Studies Blending Elements of Risk Assessment and Life Cycle Assessment. *Environmental Science & Technology*. 49:13083-13093; 2015

The papers are reprinted at the end of the thesis with the kind permission of Environmental Science & Technology and Environment International.

Research related to the thesis has also been presented on the following posters:

A. Andersson[1], H., Harder, R., Peters, G. and Cousins, I. (2014) SUPFES: Environmental risk assessment on short-chain per- and polyfluoroalkyl substances applied to land in municipal sewage sludge. *Poster at the 6th INTERNATIONAL WORKSHOP on Per- and Polyfluorinated Alkyl Substances – PFASs, Idstein, Germany.*

B. Holmquist H., Schellenberger S., van der Veen I., Gillgard P., Peters G.M., Leonards P.E.G. and Cousins I.T. (2016) Performance and hazard assessment of alternative fluorinated and non-fluorinated DWR (Durable Water Repellent) technologies. *Poster at SETAC Europe's 26th annual meeting in Nantes, France.*

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[1] Since the publication of this poster, the author has changed her surname from Andersson to Holmquist.

Contribution report

Paper I

Co-author (shared first authorship) with Steffen Schellenberger (Stockholm University). Developed the idea of the study together with the co-authors. Performed the research and wrote the corresponding text for the hazard assessment parts of the article. Wrote large parts of the abstract, introduction, and discussion. Developed Figures 2 and 3 together with Steffen Schellenberger. Made adjustments based on feedback and contributions from all co-authors.

The hazard assessment includes a thorough review of the available literature on human toxicity, ecotoxicity and fate properties of selected substances related to DWR, modification of an established hazard assessment method, and use of the collected literature data and information to make a hazard assessment using the modified method. The results of the evaluation of the literature are described in detail in the 43-page Supplementary material of Paper I (Holmquist *et al.* 2016a).

Paper II

Co-author. Contributed to analysis and discussion of results of the literature review as well as conclusions and structure of the article. Robin Harder conducted the literature review.

List of abbreviations

Abbreviation	Explanation
ADI	Acceptable daily intake
alkyl FASE	Perfluoroalkane sulfonamidoethanol
BFR	Brominated flame retardant
BPA	Bisphenol A
CAA	Chemicals alternatives assessment
CRA	Chemical risk assessment
D4	Octamethylcyclotetrasiloxane
D5	Decamethylcyclopentasiloxane
DALY	Disability-adjusted life years
DfE	Design for the Environment
DMSD	Dimethylsilanediol
DWR	Durable water repellent
EEIOA	Extended input-output analysis
ERA	Environmental risk assessment
FTOH	Fluorotelomer alcohol
GHS	Globally Harmonized System of Classification and Labelling of Chemicals
ILCD	International Reference Life Cycle Data System
LCA	Life cycle assessment
LCI	Life cycle inventory
LCIA	Life cycle impact assessment
LOAEL	Lowest observed adverse effect level
MEC	Measured environmental concentration
NGO	Non-governmental organisation
NOAEL	No observed adverse effect level
PAF	Potentially affected fraction of species
PBDE	Polybrominated diphenyl ethers
PBT	Persistent, bioaccumulative and toxic
PCB	Polychlorinated biphenyl
PDF	Potentially disappeared fraction of species
PDMS	Polydimethylsiloxane
PEC	Predicted environmental concentration
PFAA	Perfluoroalkyl acid
PFAS	Perfluoroalkyl and polyfluoroalkyl substance
PFBS	Perfluorobutane sulfonic acid

PFCA	Perfluoroalkyl carboxylic acid
PFHxA	Perfluorohexanoic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonic acid
PFSA	Perfluoroalkane sulfonic acid
PNEC	Predicted no effect concentration
POP	Persistent organic pollutant
SVHC	Substances of very high concern
TDI	Tolerable daily intake
TMS	Trimethylsilanol
vPvB	Very persistent, very bioaccumulative
WWTP	Wastewater treatment plant

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1 Introduction

Chemical emissions from consumer products is an increasingly recognised problem worldwide (Massey *et al.* 2008; Molander 2015; Molander *et al.* 2012). Consumer health and safety can be put at risk due to chemical exposure from all kinds of products; from kitchen utensils to toys to clothes, just to mention a few examples. As these emissions eventually reach the environment, they contribute to a chemical burden that has been identified as a major threat to our planetary boundaries (MacLeod *et al.* 2014; Persson *et al.* 2013; Rockstrom *et al.* 2009; Rockström *et al.* 2009; Sala and Goralczyk 2013; Steffen *et al.* 2015). In the industrial world, diffuse emissions of chemicals, *e.g.* from consumer products, have been identified to be important contributors to the total environmental burden of chemicals (Molander *et al.* 2012; Molander and Rudén 2012). Substitution with less hazardous alternatives is one way to minimise the negative impacts of chemical release from consumer products (Hansson *et al.* 2011).

Chemical substitution in consumer products must meet two main criteria to be successful: i) the alternative must be able to provide the desired function, and ii) the alternative must lower the risk of negative effects on human health or the environment compared to the original chemical. The alternative can be a "drop-in" chemical but also a new construction or material. If the criteria of lowered risk is neglected, equal or larger negative impacts to human health and/or the environment than those caused by the original chemical may be the result (Fantke *et al.* 2015b; Harremoës *et al.* 2001). Substitutes are often placed on the market before they are sufficiently characterised for human health and environmental effects, and this can lead to unacceptable problems caused also by the substitute once the use is widespread. For example, Bergman *et al.* (2012) describe how the market for flame retardants has shifted from polychlorinated biphenyls (PCBs) to brominated flame retardants (BFRs), but when also these substances proved to be harmful to human health and the environment, the shift from PCBs to BFRs was followed by substitutions both within the BFR category and to other chlorine- or phosphorus-containing flame retardants. One of the main drivers for these market changes has been regulatory bans and restrictions due to human health and environmental concerns, *e.g.* on PCBs and the polybrominated diphenyl ethers (PBDEs). Further substitutions may be needed as de Wit *et al.* (2010) have reviewed available data on emerging BFRs and found that the substitutes have environmental behaviour that is similar to their predecessors, *e.g.* PBDEs, but that available data were not sufficient to evaluate possible risks to human health and the environment. Another example is the phase-out of bisphenol A (BPA). In many applications BPA has been

substituted with bisphenol F and bisphenol S, and a recent review shows that these substances have characteristics that may generate the same type of impacts as BPA (Rochester and Bolden 2015). The users, *e.g.* brands of outdoor garments, of durable water repellent (DWRs) textile finishes are currently facing the challenge of chemical substitution as chemicals originally used, the so called long-chain PFAS, *e.g.* perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), are being restricted or banned (UNEP 2012, 2014; ZDHC 2012). Available alternatives are currently being evaluated and this thesis is one contribution to that evaluation.

Research in this field is called for and necessary, and two of the main reasons are expanded upon below. Firstly, the way the European chemicals legislation (REACH; EC 1907/2006) works today, limited testing is required for low-use (low tonnage registered) chemicals (ECHA 2016). In a substitution process shifting use from one chemical to another, or another material/construction, change often occurs gradually. In the first phases before the substitute(s) have gained substantial market shares, chemicals will be used in low total amounts, if they are not used in substantial quantities in other applications. Also, the testing requirements may not incorporate effects relevant for certain types of substances, such as *e.g.* immunotoxicity and endocrine disruption of per- and polyfluoroalkyl substances (PFASs) (Scheringer *et al.* 2014). This means that hazard characteristics of concern may surface later on when used quantities have increased and more substantial testing is done, or when negative effects are observed on human health or in the environment once the chemical has been released. Secondly, brands and retailers may not have the competence or resources to make comparative assessments taking all relevant aspects into account, especially if such an assessment is not required by regulation. The better informed the brands and retailers are in the beginning of the substitution process, the likelier it is that sound and robust substitution will be achieved which will be beneficial for human health and the environment, and this will also be less costly than a repeated substitution process. Research activities, such as the ones conducted within the SUPFES project (see Section 2.3 below), are important contributors to the assessment of chemicals and can provide information and conclusions beyond those by the individual chemical industry or clothing brand. Furthermore, methodological improvements will always be needed as the chemicals on the market as well as regulations change.

1.1 Aims and approach

The research in this doctoral project aims to assess the overall human health and environmental consequences of the substitution of DWRs based on long-chain PFASs, focussing on diffuse emissions. This is done by exploring the hazards of diffusively emitted DWR chemicals (as presented in this thesis) as well as the associated risks connected to the use of DWR for selected scenarios and potential impacts generated over the life cycle of a DWR finished garment. Besides the addition of this research to an understanding of the alternative DWRs that are preferable from a human health and environmental perspective, it also scrutinises available methodological approaches and evaluates their relevance in chemical substitution cases. This research is performed within the SUPFES project (see Section 2.3) and benefits from research on the technical performance of DWR finished textile and from emission, fate and effect studies in other parts of the project. Thus, many research findings are (and will be) the result of a collaborative effort within the project, and the results will be best understood if considered in conjunction with other project outputs.

The primary aim of the research presented in this thesis is to identify relevant substances diffusively emitted from garments with a DWR finish and rank the assessed DWRs based on the hazards associated with the released substances. Furthermore, the secondary aim is to explore which methodological approaches, based on risk assessment and LCA that are appropriate for further assessment in chemical substitution in textile application cases.

1.1.1 Research questions

In order to fulfil the aims, the research presented in this thesis focusses on three questions:

Research question 1. What are the hazard characteristics of diffusively emitted substances from the main classes of DWRs on the market?

Research question 2. What is the hazard-based ranking of the available DWR alternatives (based on the characteristics as described in research question 1)?

Research question 3. How can hazard data be used in combination with other information to make holistic human health and environmental assessments of garments with a DWR finish as the basis for robust substitution recommendations?

1.2 Guide for readers

This consolidated thesis consists of two parts: i) the summary ("kappa") in which the research leading to the licentiate degree is presented in relation to the research questions, ii) the articles that form the basis for this thesis (Papers I and II).

Chapter 1 places this research in a context and describes the aims and research questions. In Chapter 2, the background of this research is described and in Chapter 3, methods and theory are described in more detail for selected items. In Chapter 4, the research questions are discussed based on the results in Papers I and II. Chapter 5 contains the conclusions, *i.e.* condensed answers to the three research questions. Finally, in Chapter 6, future research needs and opportunities are discussed.

1.2.1 Terminology

This thesis describes the work and results of two multidisciplinary research projects: my own doctoral project and the SUPFES project. The fields covered have more or less specified terminologies and these sometimes overlap and even contradict each other. The intended meaning of a number of terms, as used within this thesis, can be found in Appendix A.

2 Background

This chapter further elaborates on selected background information for items brought forward in the introduction.

2.1 Per- and polyfluoroalkyl substances (PFAS)

Per- and polyfluoroalkyl substances (PFAS) is an umbrella term for alkyl substances with all (perfluorinated) or several (polyfluorinated) hydrogen atoms exchanged for fluorine. This is a large family of substances that is described in detail elsewhere, *e.g.* by Buck *et al.* (2011). This thesis focuses on a few members of this substance family, namely the perfluoroalkyl acids (PFAA) which incorporate perfluoroalkyl carboxylic acids (PFCAs), and perfluoroalkyl sulfonic acids (PFSAs) and their precursors, *e.g.* side-chain fluorinated polymers and fluorotelomer alcohols (FTOHs). The PFAAs are both hydrophobic and lipophobic (Kissa 2001) and they are dissociating compounds. These properties, deviating from many conventional persistent organic pollutants, have implications for predictions of their fate as they may not behave as the conventional pollutants for which many models were developed, and because tests to obtain fate characteristics, *e.g.* water-octanol partitioning, may not be applicable (Armitage 2009).

2.1.1 Global use and global spread

PFAAs are used in many different products, both as auxiliary chemicals in fluoropolymer manufacture and in consumer and industrial products (as PFAAs or incorporated in more complex chemicals structures, which are precursors of the PFAAs) (OECD 2013). The use is global, and, thus, the contamination generated by both direct sources (the manufacture and use of PFCAs, as defined by Prevedouros *et al.* (2005)) and the indirect sources (PFCAs as reaction impurities or as generated by precursor degradation, as defined by Prevedouros *et al.* (2005)) is also global (Giesy and Kannan 2002; Prevedouros *et al.* 2005). As PFAAs are extremely persistent and have a transport potential in both air (via precursors) and water, they reach environments where they are not used (Armitage 2009; Dreyer *et al.* 2009; Suja *et al.* 2009). Prevedouros *et al.* (2005) have estimated the global historical industry-wide emissions to be 3200-7300 tonnes. PFAS-based DWRs have been one contributing source (Knepper *et al.* 2014).

2.1.2 Reasons for concern

There are no known environmental processes that efficiently degrade PFAAs under natural conditions (Butt *et al.* 2014; OECD 2013; Vierke *et al.* 2012). This means that once emitted those substances will accumulate in the environment. Environmental sinks (removal of a substance from circulation in

the biogeosphere) are sediment burial and the deep oceans (Prevedouros *et al.* 2005). Some of the PFAAs are known PBT (persistent, bioaccumulative and toxic) och vPvB (very persistent and very bioaccumulative) substances, *e.g.* perfluorooctanoic acid (PFOA) (Vierke *et al.* 2012) and perfluorooctanesulfonic acid (PFOS) (Swedish Chemicals Agency 2016) and other so-called long-chain PFASs (Swedish Chemicals Agency 2016). The long-chain PFASs have been defined as having an alkyl chain containing six or more carbons in molecules that are precursors to or are PFSAs ($C_nF_{2n+1}SO_3H$, n ≥ 6) and seven or more carbons in molecules that are precursors to or are PFCAs ($C_nF_{2n+1}COOH$, n ≥ 7) (Buck *et al.* 2011). The short-chain PFAS are not bioaccumulative and in many cases less toxic than their long-chain analogues (Holmquist *et al.* 2016a; Wang *et al.* 2015). However, continued emissions of these substances do lead to environmental accumulation and eventually human health and ecotoxic thresholds may be breached, and by that time, redeeming the situation will be very difficult or impossible (MacLeod *et al.* 2014).

2.1.3 Phase out of long-chain PFAS

The phase out of long-chain PFASs is an ongoing process. PFOS is restricted under the Stockholm Convention (Stockholm Convention 2014), and PFOA is identified as a substance of very high concern (SVHC) and is included in the REACH Candidate list (ECHA 2014a). PFOA has been proposed for an EU-wide restriction (ECHA 2014c) as well as a persistent organic pollutant (POP) under the Stockholm Convention (Stockholm Convention 2015). Also the PFCAs C11-C12 are included in the REACH Candidate list. Voluntary actions preceding the regulatory bans include, *e.g.* the US EPA initiated PFOA Stewardship Program incorporating the chemical industry (US EPA 2013) and the Zero Discharge of Hazardous Chemicals (ZDHC) Programme phase out action for PFOA within the apparel and footwear industry (ZDHC 2013).

2.2 Durable Water Repellent (DWR) for textile finishing

DWR is applied to a textile to provide water and in some cases also stain and oil repellency (Kadolph 2014). Repellence is desirable for many types of textile products such as carpets, upholstery, medical equipment, and garments. In this thesis, the focus lies on the DWR used on outdoor garments such as workwear and outdoor clothes for leisure and sports. Many of the water repellent garments on the market today have membranes or coatings through which water droplets cannot penetrate but that can be passed by evaporated water. This means that the main function of the DWR is to hinder the garment from becoming heavy and cold due to absorbed water since the membrane or coating hinders water droplets from penetrating and wetting the wearer.

The DWR is applied as a finish to the garment's outer fabric to make it resistant to water absorption. The water forms droplets that roll off the fabric and the user stays dry and warm. Some DWRs provide oil repellency in addition to water repellency (UNEP 2012). In those cases, even oils form droplets and roll off the fabric. Oil repellency is specifically needed in some cases, *e.g.* in workwear used in traffic accident situations, on oil rigs, or during the work with non-polar harmful liquids. In addition, oil repellency makes the fabric stain resistant. This can be desirable considering that it decreases the care needed for a garment, but it has also been alleged that oil/stain repellency is a prerequisite for durable water repellence (ZDHC 2012).

As mentioned above (Section 2.1.3), the apparel and footwear industry is involved in the on-going phase-out of long-chain PFAS, and products with new DWRs (fluorinated and non-fluorinated) are being placed on the market.

2.3 Project SUPFES

SUPFES (Substitution of prioritised poly- and perfluorinated chemicals to eliminate diffuse sources) is a four-year long project funded by the Swedish Research Council Formas and is focussed on the diffuse emissions of PFAS. The project is being carried out by an international consortium with researchers from VU University in Holland, Stockholm University, Chalmers University of Technology, and Swerea IVF, who is also the lead partner. The municipal wastewater treatment plant (WWTP) Käppala as well as the outdoor brand Haglöfs are also project members. In addition to its members, the project also has stakeholders in several fields, such as chemical industry, outdoor clothing and equipment companies, and policy makers tied to the project. The aims of the project are to: i) characterise the diffuse emissions of fluorinated chemicals from consumer products such as textiles, ii) explore possible alternatives, and iii) assess the substitutions for functionality in case studies. The goal is to provide policy makers with a basis for legislation and industry with guidelines for reduced human health and environmental impacts with retained competitiveness.

The intended work scheme/method in the SUPFES project is outlined in Figure 1 (starting with the task of characterising the PFASs in use). In the practical project execution, all four activities are being conducted in parallel.
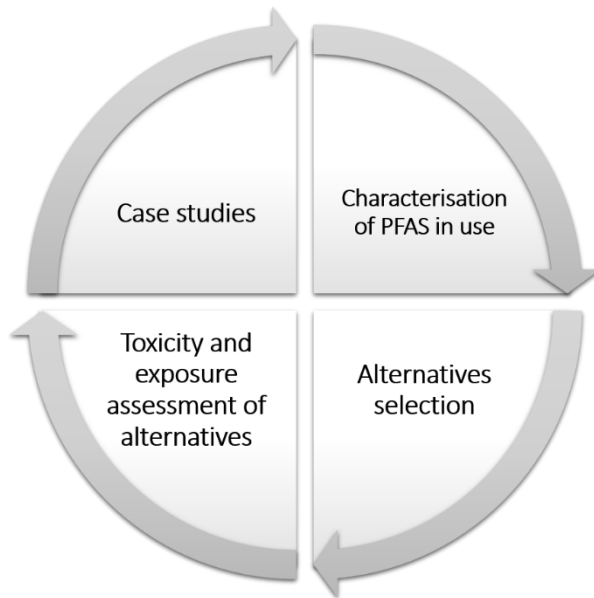
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Figure 1: Illustration of the SUPFES project method (adapted from the project proposal). The case studies include prototype manufacture, technical performance testing, risk assessment, emission studies, LCA and life cycle costing.

3 Theory and methods

A robust substitution process is a complex procedure that need to take human health and environment considerations as well as functionality and economic considerations. In practice, a substitution process can look like the SUBSPORT substitution steps (Figure 2). The assessment and comparison of alternatives can be made within a chemicals alternatives assessment (CAA) framework. In this chapter the general principles of CAA as well as selected environmental assessment methods that can be used within the CAA, in part or in full, are described. The selection is based on the SUPFES project work plan, complemented with methods frequently used by brands within the DWR field, *e.g.* the chemical industry. Other key parts of a CAA, such as functionality and performance assessment as well as cost effectiveness assessment, are not described here as those parts are being performed by other researchers in the SUPFES project.

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│      Define the problem       │
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│     Set substitution criteria │
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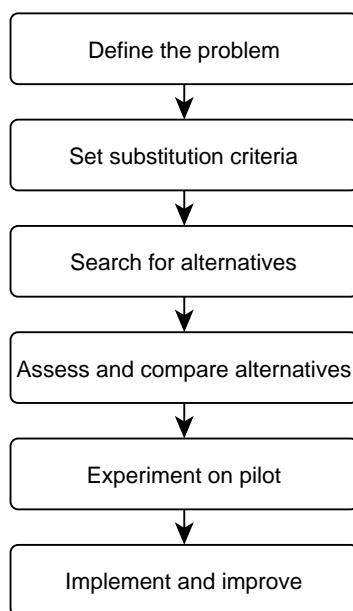
Figure 2: Substitution steps according to the Substitution Support Portal, SUBSPORT (SUBSPORT 2016). The portal provide, *inter alia*, information on tools and guidance for substance evaluation and substitution management.

3.1 Chemicals alternatives assessment (CAA)

CAA is an umbrella term for a general assessment procedure intended to lower the risk to human health and the environment from chemicals of concern by substitution (Geiser *et al.* 2015). This is done by selecting a safer alternative that is still cost effective and delivers the same function and performance (BizNGO 2013; Geiser *et al.* 2015; Hester and Harrison 2013; Jacobs *et al.* 2016; Lavoie *et al.* 2010). An alternative can be a drop-in chemical, a change of material and/or construction, or even discontinuing the activity (BizNGO 2013). A CAA is an important part of a substitution process as alternatives must be assessed and compared (see Figure 2). It has also been argued that the substitution principle should not give absolute priority to the functional criteria but that the alternative should reduce the hazard as much as possible and retain the functionality as much as possible (Hansson *et al.* 2011). Geiser *et al.* (2015) list common principles for alternatives assessment that capture the general idea and at the same time describe the complexity of the assessment; reduce hazard, minimize exposure, use best available information, require disclosure and transparency throughout the supply chain, resolve trade-offs, and take action.

For commercial companies, the driver of substitution is often an existing or foreseeable regulation process banning or restricting the use of "their" chemicals. As substitution can be very costly, the incentive is strong to find a long-lasting alternative and thus avoid multiple substitution processes. To accomplish this, CAA has been recognised as a useful tool (Geiser *et al.* 2015; Lavoie *et al.* 2010). Also authorities have use for a CAA as an extensive overview of available alternatives that can provide an important part of risk management when a substance is restricted or banned (see *e.g.* UNEP (2009)).

One of the key parts of a CAA (for chemical alternatives) is a hazard assessment in which a substance's intrinsic human health, ecotoxicological and fate properties are assessed. The inclusion of a hazard assessment, rather than a full risk assessment, is based on the principle that the risk depends on both the hazard and the exposure, and, with a drop-in substitute, the exposure will remain unchanged, and, thus, the risk will solely depend on the hazard. Whether or not this is the case depends on the properties of the substitute, *i.e.* it may have other fate characteristics that change exposure routes, and whether or not manufacturing processes or amounts applied need to be changed. In an extensive CAA, such things should be highlighted or even further assessed.

3.2 Environmental assessment tools suitable for chemicals alternatives assessment

3.2.1 Hazard assessment

A chemical's hazardousness is related to its intrinsic properties, *i.e.* its acute and chronic human toxicity, ecotoxicity and fate characteristics. Results from human toxicity, ecotoxicity and fate testing are evaluated according to criteria for a number of endpoints, and the substance under assessment is classified as a low, moderate or high hazard (or similar wordings). As described above (Section 3.1), an alternative with a lower hazard for a certain endpoint will also be associated with lower risks, given that the exposure is the same. In an analogy, an alternative with a higher hazard will be associated with higher risks, given that the exposure is the same. However, a high hazard does not necessarily mean that the risks are high, as risks would depend on the expected exposure. Hazard assessment methods do not have to consider specific user scenarios or geography and are, in that sense, universal and less time consuming and extensive than a risk assessment.

There are several hazard assessment methods available, both within regulatory contexts, *e.g.* Global Harmonisation System (GHS), and for commercial purposes, *e.g.* GreenScreen (Clean Production Action 2013) , and the GHS Column Model (IFA 2014). In the present project, the hazard assessment criteria for the Design for the Environment programme (DfE) were used (further described below in Section 3.2.1.1). The DfE criteria are, to a large extent, based on globally accepted criteria in the GHS, and they are very similar to the GreenScreen method, used by many actors in the DWR industry.

If there are no indications of ameliorating effects, *e.g.* fast removal from environmental compartments important for exposure of sensitive safeguard subjects, an alternative substance with higher hazards than the substance to be substituted can be ruled out already after a hazard assessment and need not be evaluated further.

3.2.1.1 Design for the Environment Program Alternatives Assessment Criteria for Hazard Evaluation

The US EPA programme Safer Choice includes product labelling and chemical lists to guide consumers and industry to select safer chemicals. The Design for the Environment (DfE) Alternatives Assessments is a related programme and within that programme, CAA criteria for hazard assessment have been developed (US EPA 2011). The criteria cover 10 human health endpoints (acute mammalian toxicity, carcinogenicity,

mutagenicity/genotoxicity, reproductive and developmental toxicity, neurotoxicity, repeated dose toxicity, sensitisation, irritation/corrosivity, and endocrine activity), acute and chronic aquatic toxicity as well as persistence, and bioaccumulation. For each endpoint, data for all relevant exposure routes, *e.g.* no observed adverse effect level/lowest observed adverse effect level (NOAEL/LOAEL), are compared with the respective threshold levels to arrive at a hazard classification on a scale from low to high (and for some endpoints very low/high, see Table 2 in Paper I). The DfE criteria do not allow for weighting the hazard classifications into a single score; instead, the hazard classification is shown for each endpoint.

3.2.1   Risk assessment

Risk is defined as "the probability of an unwanted event that results in negative consequences" (Ostrom and Wilhelmsen 2012). Risk assessments are conducted in many different contexts and can be both prospective (are the risks associated with this action acceptable?) or retrospective (are measures needed to ameliorate current risks?). There is no single method for risk assessment, but all risk assessments bear a number of common traits. The risk assessments aim to describe the likelihood that the event will occur, *i.e.* the probability, and the hazard or threat that, if it occurs, will lead to negative consequences, *i.e.* the event, which together make up the risk. The result of a risk assessment provides decision support for further actions within a risk management framework.

Environmental risk assessment (ERA) can deal with chemical exposure and/or other stressors and is often conducted in response to regulatory demands, *e.g.* when a new industry is being established and applies for an environmental permit or when a chemical is registered for use. In such cases, there is extensive guidance available under each relevant regulation. Ostrom and Wilhelmsen (2012) describe the process of ERA, based on the US EPA ERA[2] practices, and this is reproduced in Figure 3.

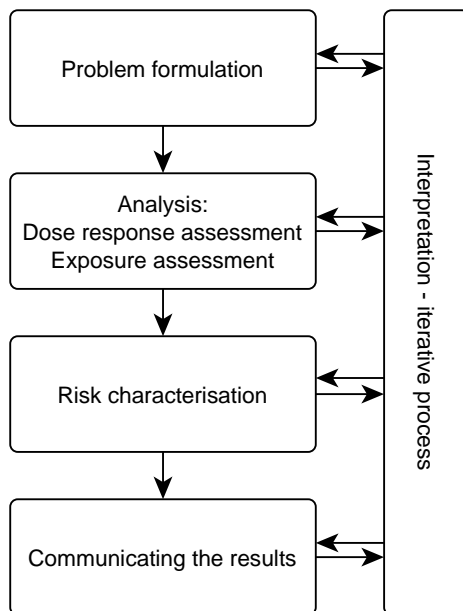[2] ERA is called ecological risk assessment in the US setting

Figure 3: General procedure in environmental risk assessment (adapted from Ostrom and Wilhelmsen (2012)

The ERA process is started by a problem formulation, *i.e.* answering why an ERA is needed, assessment endpoints are identified, and a conceptual model of the system is developed. The analysis phase incorporates a dose-response assessment, *i.e.* the probability of an effect depending on the dose (Gao *et al.* 2015), and an exposure assessment. The latter can also include a probability component, *e.g.* to quantify the likelihood of an accidental spill, using different scenarios (Engelen *et al.* 2007). The risk characterisation combines the exposure and effect profiles, which results in a quantification of the risk associated with the action being assessed (or a qualitative assessment if qualitative data are used). The process is iterative, meaning that understanding of the system can feed into earlier stages. Additionally, identification of risks based on worst case assumptions may initiate generation of more data, *e.g.* by further testing or additional measurements.

Chemical risk assessment (CRA) is a type of risk assessment that in essence is chemical hazard assessment and exposure assessment combined, normally in a quantitative assessment. For the environmental part, in general, the predicted or measured environmental concentration (PEC/MEC) for an

environmental compartment is compared with a threshold value for the same compartment to determine a risk quotient. The threshold is often the predicted no effect concentrations (PNEC) or a quality standard. The threshold can be determined with a deterministic approach (the "assessment factor method") or a probabilistic approach (by species sensitivity distributions (SSD)) (see *e.g.* European Commission (2011a)). In the same way, human health risks are characterised by comparing the estimated (or known) dose with a threshold such as, *e.g.* an acceptable/tolerable daily intake (A/TDI). A risk quotient above one means that there is a risk of (unacceptable) negative effects. What is seen as an unacceptable effect depends on the context; for example, in human health risk assessment, the aim is to protect even the most sensitive individuals in a population. An environmental risk assessment, on the other hand, often deals with the ecosystem function rather than protection of individuals (Molander 2015). Even a threshold such as a PNEC, where the name implies complete protection (on a scientific basis), has a component of normative assumption(s). This is because, at some stage, a decision has been made about what is to be regarded as "no effect", *e.g.* 10% growth reduction or 10% of species reaching their NOEC.

Regulators have argued that current quantitative risk assessment methods are not sufficient to establish safe concentrations for PBT or vPvB substances (ECHA 2014b). The reason is that the environmental accumulation that can be expected for such substances is very difficult to predict, and if negative effects manifest, eventually they will be very difficult to reverse as environmental concentrations will continue to persist after the cessation of the emissions. Additionally, it has been proposed that high persistence alone is a reason for similar concern, based on the precautionary principle (with today's knowledge we may not be able to predict all relevant effects of a substance), since effects currently unknown may manifest with a time delay or on a global scale only and be poorly reversible (MacLeod *et al.* 2014; Persson *et al.* 2013; Steffen *et al.* 2015). Industrial representatives argue that quantitative risk assessment is possible for PBT and vPvB substances, although better refined methods than the standard procedure are needed (ECETOC 2011).

3.2.2 Life Cycle Assessment (LCA)

LCA is a method for assessing the potential impacts of a product or service over its life cycle. An LCA can be conducted with a focus on social impacts as well as environmental impacts. In an environmental LCA, resource use and emissions generated throughout the life cycle of a product or service and potential impacts on human health and the environment associated with those flows are quantified. The principles and framework for LCA are outlined in the

ISO standard 14040:2006 and in many guidelines such as the International Reference Life Cycle Data System (ILCD) handbook (Wolf *et al.* 2012). The present research focuses solely on environmental LCA, and, hereafter, the term LCA will be used for environmental LCA. An LCA can be conducted either using an attributional approach or a consequential approach, where the former (also called a retrospective LCA) can be defined by "its focus on describing the environmentally relevant physical flows to and from a life cycle and its subsystems", and the latter (also called a prospective or change-oriented LCA) can be defined by "its aim to describe how environmentally relevant flows will change in response to possible decisions" (Ekvall *et al.* 2005).

Figure 4 shows a general description of the process of an LCA. The process starts by defining the goal and scope; stating the goal of the study as well as how the assessment will be made, including the definition of system borders and selection of impact categories. The next step is a life cycle inventory (LCI) in which data on resource use and emissions are collected and related to the functional unit. The functional unit quantifies the function or service that is being assessed, *e.g.* illuminating a $40\,m^2$ room located in Sweden during one year in a comparison of light sources, or keeping one person in Sweden warm and dry for one year in the comparison of a DWR finish for an outdoor jacket. The LCI is followed by an impact assessment (life cycle impact assessment, LCIA) with the use of so called characterisation factors that convert the elementary flows in the LCI to potential impacts. LCA is an iterative process in which the results from each phase can feed back to the previous phases as the analyst learns more about the system.
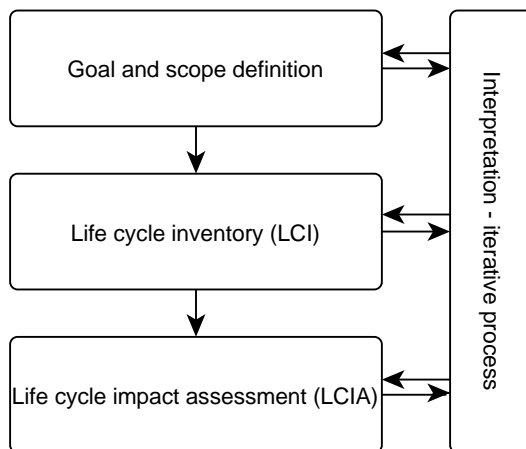
Figure 4: General procedure in life cycle assessment (LCA), adapted from the ISO standard 14040:2006

As a holistic method, LCA should, in principle, incorporate all relevant environmental effects of a product or service. In reality, all methods are limited by the available knowledge and data. Therefore human toxicity and ecotoxicity effects have often been excluded from LCAs, even in cases in which chemical emissions are foreseen and deemed to be relevant (Roos 2015). This is a field that is developing. There are a number of LCIA models for human toxicity and ecotoxicity available today, and there is also a so-called consensus model, USEtox (Fantke *et al.* 2015a; Hauschild *et al.* 2008; Rosenbaum *et al.* 2008), which is also the ILCD recommended model (European Commission 2011b). The different human toxicity and ecotoxicity LCIA models incorporate fate processes to a varying degree (European Commission 2011b) and characterise effects in different ways. Impacts can *e.g.* be expressed in relation to a known toxic compound, as in the CML2001 model where the impact assessment is based on 1,4-dichlorobenzene equivalents, or as human health cases and potentially affected fraction of species (PAF), as in the USEtox model. In USEtox, the fate of an emitted substance is modelled in a multimedia nested box model and effects on human health (cancer and non-cancer) as well as freshwater aquatic wildlife are characterised. Since USEtox is a consensus model, compartments and effects that fall outside the consensus are not included. As a result oceans are modelled only as sinks (Rosenbaum *et al.* 2008). This means that potential impacts from the accumulation of a substance in the oceans will not be quantified using USEtox characterisation factors. Other limitations are the exclusion of terrestrial wildlife and the modelling of

sediments and groundwater also only as sinks (Fantke *et al.* 2015a; Henderson *et al.* 2011; Rosenbaum *et al.* 2011).

LCA (on toxicity impacts) and CRA bear many similarities but generate different types of results. An LCA is used to assess the (potential) impacts associated with the life cycle of a product or service relative to the functional unit. This provides a basis for a comparison of environmental performance or consequences, either within the life cycle of one product/service, *i.e.* between life cycle stages and/or processes, or between product or service systems. This means that an LCA, unless adjusted from the traditional approach (Harder *et al.* 2015a; Harder *et al.* 2015b), does not assess impacts from absolute exposure, solely the proportion of impacts associated with the functional unit. In addition, an LCA is generally static in time and unspecific with regards to geography. CRA, on the other hand, is generally aimed at assessing the probability of absolute impacts on the safeguard subjects but not necessarily covering the full life cycle of a product or service. This means that emissions are quantified in full mode operation and that background exposure is considered, often in a site- and time-specific model.

4   Discussion of research findings

The research presented in this thesis is based on two papers: Paper I in which the properties and performance as well as associated hazards of state-of-the-art DWR chemistry are described, and Paper II in which environmental assessment case studies blending elements of risk assessment and LCA are reviewed. This chapter gives overview of each paper followed by a discussion of the research in the papers in relation to the three research questions (Section 1.1.1). For references to the content in the overview of Papers I and II (Sections 4.1 and 4.2), see the full version of the papers (appended).

4.1   Overview of Paper I

Paper I is divided into three interlinked sections; identifying state-of-the-art DWRs, identifying mechanisms for diffuse emissions during the use phase of a fabric, and characterising the hazards associated with the diffuse emission of DWR chemicals.

The basic property that generates the water repellency of all DWRs is that hydrophobic side chains are attached to a backbone. The hydrophobic side chains are either carbon-hydrogen (CH) or carbon-fluoride (CF) based with CF_3 or CH_3 end-groups, and the backbone is either a carbon- or silicone-based polymer, a dendritic structure or inorganic particles (see Fig 1. and S3-S6 in Paper I). The repellency of water results from the dense packing of the hydrophobic side chains, which makes the CF_3 or CH_3 end-groups appear on the fibre surface. Based on these general characteristics, DWRs can be divided into four broad groups: polymeric repellent finishes based on side-chain-fluorinated polymers, silicones or hydrocarbons, and other chemistries including dendrimers (hyperbranched polymeric structures) and nanoparticles. All DWR alternatives provide water repellency, but the side-chain-fluorinated polymer DWRs also provide oil repellency due to the ability of per- and polyfluoralkyl side chains to repel both polar and non-polar liquids. This effective liquid repellency is due to the hydro- and oleophobic nature of the CF groups and the ability of per- and polyfluorinated side chains to be densely packed. In contrast to the side-chain-fluorinated polymers based on short-chain PFAS, long-chain PFAS form a crystallised structure which gives optimal repellency. The side-chain-fluorinated polymers based on short-chain PFAS do not crystallise but form a sufficiently dense structure to provide both water and oil repellency. Silicone DWRs are based on polydimethylsiloxane (PDMS; $[-Si(CH_3)_2O-]$) which provides the fabric with good water repellency and a soft texture to the human hand, but the durability of the DWR to laundering may be only moderate. Hydrocarbon-based DWRs use crystallised n-alkyl chains $[-(CH_2)_n-$

CH$_3$] to mimic the structure of the natural coating on plant leaves, which makes them water repellent. Hydrocarbon-based DWRs are linear alkyl hydrophobic moieties which are linked to hydrocarbon-based copolymers. Dendrimers and nanoparticles provide water repellency via the employment of hydrophobic groups (CH-, CF-, or Si-based) attached to the dendrimer/particle and the structure created on the fabric. The durability of a DWR varies between chemistries, and it depends on how the DWR is bonded to the fibre. In modern DWRs, the DWR agent (polymer/dendrimer/particle) is modified with functional groups that bind covalently with the fibre or create a cross-linked network around the fibre.

Diffuse emissions during the use phase of the fabric are generated either by loss of impurities in the DWR not bound to the fabric fibre and that can be washed out with water or evaporated to air, *i.e.* unreacted chemicals, or by degradation processes either on the fabric surface or on fibre/fabric fragments lost to the environment by wear and tear (see Fig. 2 in Paper I). Degradation of the polymer requires certain conditions such as, *e.g.* accessible photoactive or hydrolysable groups in the polymer. In the present work, the focus has been on diffuse emissions of substances related to the DWR agent, while other constituents, *e.g.* cross-linkers and extenders in the DWR formulation have not been considered. This limitation in scope is justified because, irrespective of other hazardous substances contained in or generated from the DWR formulations, the chemical moiety providing the water (and oil) repellent function is key when assessing alternative DWRs, as other moieties may be substitutable. For the side-chain-fluorinated polymer DWRs, documentation is available on the loss of residual PFASs, *i.e.* impurities such as FTOHs, perfluoroalkane sulfonamidoethanols (alkyl FASEs) and PFAAs, from the finished fabric and the industry is actively striving to reduce the level of such impurities. The degradation rate of the side-chain-fluorinated polymer is, however, debated; in aerobic soils, degradation half-lives span from 100s to 1000s of years, depending on the experimental set up. The degradation of side-chain-fluorinated polymers and impurities in such products generate PFAAs as terminal degradation products. Silicone-based DWRs have similar issues with loss of impurities as side-chain-fluorinated polymers. Two substances identified as impurities in PDMS-based products are the cyclic siloxanes octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5), and those can be lost from the fabric mainly to air due to their volatility. Degradation of the PDMS generates shorter chain silanols, dimethylsilanediol (DMSD) and trimethylsilanol (TMS), and eventually silicic acid or silica. The hydrocarbon-based DWRs have a great chance of complete degradation over time.

Hazard assessment of the diffusively emitted substances related to the DWR has shown that also the alternative DWRs have hazard profiles of concern, which are described further below.

4.1.1 Hazard characteristics of the diffusively emitted substances from the main classes of DWRs on the market

The hazard assessment included selected substances related to the DWR agent which were also identified as being diffusively emitted (Table 1). Side-chain-fluorinated polymer DWRs based on long-chain PFAS were selected as the benchmark for the hazard assessment, and PFOA was selected as a representative substance for hazard assessment since it is both relevant as an impurity in DWR formulation and a terminal degradation product of both impurities and polymers. Perfluorohexanoic acid (PFHxA) and perfluorobutanesulfonic acid (PFBS) were selected as representative substances for the hazard assessment of side-chain-fluorinated polymer DWRs based on short-chain PFAS on the same grounds as PFOA was selected. For silicone DWRs, the degradation products DMSD, TMS, and short-chain silanols were selected as representative degradation products, and D4 and D5 were selected as representative impurities. Paraffin wax was selected as a representative degradation product (and possible impurity) of hydrocarbon-based DWRs. For the group including dendrimers and nanoparticles, no representative substances could be found owing to the lack of available information. A justification for the approach can be found in Paper I Section 2.3 and 5.

Table 1: Substances selected to be included in the hazard assessment

Substance name	Abbreviation	CAS No.	Impurity	Degr. Prod.
Benchmark				
Perfluorooctanoic acid	PFOA	335-67-1	X	X
Side-chain fluorinated polymers				
Perfluorohexanoic acid	PFHxA	307-24-4	X	X
Perfluorobutane sulfonic acid	PFBS	375-73-5	X	X
Silicones				
Short-chain silanols				X
Dimethylsilanediol	DMSD	1066-42-8		X
Hydroxytrimethylsilane (trimethylsilanol)	TMS	1066-40-6		X
Octamethylcyclotetrasiloxane	D4	556-67-2	X	
Decamethylcyclopentasiloxane	D5	541-02-6	X	
Hydrocarbons				
Paraffin Wax		8002-74-2	X	X
Other chemistries (dendrimers, inorg. nano particles)				
Unknown				

The hazard assessment of substances relevant for each of the four groups of DWR is summarised in Table 3 in Paper I. PFOA is a PBT substance, *i.e.* a substance with hazard properties of concern in both fate and toxicity categories. PFOA is extremely persistent and degradation rates under environmental conditions are negligible. PFOA also has high bioaccumulation potential in mammals. In standardised testing, PFOA has low ecotoxicity, although non-standard tests (including sensitive endpoints but not directly comparable with the hazard criteria) indicate effects at lower concentrations. However, in toxicity tests on mammals, relevant for the assessment of human health effects, PFOA has high toxicity for several important endpoints; carcinogenicity, reproductive toxicity, developmental toxicity, and repeated dose toxicity. Furthermore, PFOA is a potential endocrine disruptor, *e.g.* by increasing serum estradiol levels in rats.

The side-chain-fluorinated polymers based on short-chain PFAS have a better hazard profile compared to the benchmark; only the endpoint for persistence was classified as a high hazard (both PFHxA and PFBS were

classified with very high hazard). In contrast to PFOA, both PFHxA and PFBS have low bioaccumulation potential, which could be one important contributor to the lower toxicity of these substances. PFHxA was classified as being moderately hazardous for three human health endpoints; developmental toxicity, reproductive toxicity, and repeated dose toxicity while PFBS was classified as having low toxicity in the same categories. Whether this is a true difference in hazard characteristics between the substances or due to differences in test set-ups in the toxicity tests on which the classification is based is not known. Both PFHxA and PFBS were classified as having potential for endocrine disruption although the endocrine activity seems to be limited. Ecotoxicity was classified as low but, similar to PFOA, non-standardised tests indicated effects at lower concentrations than the standard test results, which resulted in a high uncertainty score.

Silicon-based DWRs have a hazard profile that looks more problematic than the profile for the side-chain-fluorinated polymers based on short-chain PFAS (as described above), given that some of the substances representative for this group were classified to constitute high or very high hazard for several endpoints. For the degradation products (short-chain silanols, DMSD, and TMS) comparisons were difficult due to the many data gaps, but with the data available, it is apparent that those substances are at least moderately hazardous to human health and that DMSD is highly persistent. More toxicity data are available for D4 and D5, which are possible impurities in silicone DWRs. D4 was classified with high hazard for human health, ecotoxicity and fate endpoints and D5 was classified with high hazard for human health and fate endpoints.

The hydrocarbon DWRs were not classified with a high hazard for any endpoint. For the endpoint repeated dose toxicity, the paraffin waxes were classified as moderately hazardous (with high uncertainty), but, for all other endpoints, the hazard was classified as low (endocrine effects and neurotoxicity could not be classified due to data gaps).

The available information on the chemical structure that provide the water (and oil) repellency of dendrimer-based and nanoparticle-based DWRs was not sufficient to select representative substances for hazard assessment (based on the criteria set up for this purpose, see Section 2.3. in Paper I).

4.1.2 Hazard-based ranking of the available DWR alternatives

The DfE hazard assessment method does not summarise the hazard classifications for all endpoints into one single classification for a substance. This lack of a single hazard score makes ranking less obvious. However there are some distinct differences between the substance groups assessed here that provide a good basis for the ranking:

i) The benchmark PFOA is a PBT substance and, thus, has a very problematic hazard profile.

ii) PFAS are extremely persistent and although short-chain PFAS are not bioaccumulative, and at most moderately toxic (based on current knowledge), their persistence will lead to environmental accumulation if emissions continue.

iii) The substances selected as representative for silicone DWRs have hazard profiles giving rise to concern. However, despite being persistent enough to be classified as a very high hazard for the persistence endpoint, these substances do degrade under environmental conditions.

iv) Waxes have a fairly benign hazard profile, especially considering that the classification of moderate hazard for chronic repeated dose toxicity is highly uncertain and could very well be classified as low hazard with additional data.

Based on i-iv above, it is apparent that all alternatives are an improvement over side-chain-fluorinated polymer DWRs based on long-chain PFAS (represented here by PFOA). The hydrocarbon-based DWRs get the best ranking (most benign hazard profile). Based solely on the hazard profile, silicone DWRs and side-chain-fluorinated polymer DWRs based on short-chain PFAS share the next best ranking since PFASs are extremely persistent and silicones are less persistent but more hazardous in other categories.

The many data gaps in the hazard assessment (see Table 3 in Paper I) add uncertainty to the ranking above. In particular with regard to the "other chemistries" that could not be assessed at all due to the lack of information on their chemistries. There are two types of data gaps in the hazard assessment: those in which data on human toxicity and ecotoxicity and fate are not available and the effects not known, and those in which data are available but proprietary. One may hope that the information missing in Paper I is actually available although not accessible to researchers and adequate risk assessment has been performed showing that the alternative DWRs will not give rise to unacceptable human health or environmental risk. However, low production volumes,

naturally associated with new developments still gaining market shares, do not warrant extensive testing or assessment under chemical legislation such as REACH. Thus, at worst, risks associated with the alternative DWRs not yet (publicly) characterised may be unknown even to the chemical companies and could surface as use continues and/or increases. The issue of proprietary data and low testing requirements is under discussion in the academic community (see *e.g.* Scheringer *et al.* (2014)), and finding a way forward is important for the selection of long-lasting safer alternatives to hazardous chemicals. This lies also in the interest of the industry in order to avoid multiple substitution processes.

4.2 Overview of Paper II

Paper II maps and discusses different approaches to combine elements of (or integrate, hybridise, complement) risk assessment and LCA in case studies of chemical pollutants and/or pathogens. A literature search resulted in 30 case studies in which elements of risk assessment and LCA were combined in one way or another in environmental assessments and those could be categorised into three different clusters:

1. **Site-dependent assessment**
   Studies using environmentally extended input-output analysis (EEIOA) as a starting point for a spatially differentiated assessment of human health impacts. Five studies were categorised to this cluster.
2. **Application of life-cycle thinking to risk assessment**
   Studies in which chemical emissions from different life cycle stages of a product or service were considered in a risk assessment. Two studies were categorised to this cluster.
3. **Trade-off between local and global effects**
   Studies in which the recognition that local risk remediation for contaminated land or wastewater treatment, for instance, may lead to problem-shifting, initiated environmental assessments in which the local risk assessment was complemented with an LCA on risk mitigation measures. In these studies, results were often reported separately for the LCA and the risk assessment. Some studies expressed the outcomes of human health assessments in disability-adjusted life years (DALY) as a common indicator allowing for comparisons of the results between LCA and the risk assessment. Other studies applied multicriteria analysis methods to weight and aggregate results. Twenty-three studies were categorised to this cluster.

The review identified a number of potential pitfalls important to consider when blending elements of the two methods:

- Bias due to model asymmetry if the acceptability of impacts is only assessed for parts of the system. For example: comparing exposures in the part of the system of direct concern for the decision maker and thus giving less weight to possible unacceptable effects in other parts of the system.
- Bias due to model asymmetry if certain parts of the system or certain impact categories are modelled differently. For example: inclusion of site-specific models may result in lower dilution of emissions and thus higher exposures.
- Double counting. For example: including site-specific characterisation models in parallel with characterisation models on a larger spatial scale, and including local emissions in both models.
- Inadvertent transfer of assumptions and parameter value choices between the methods. For example: modelling parts of the system or selected impact categories based on conservative or worst-case exposure scenarios (as is often practised in risk assessment) and the remainder of the system based on average data.

The review in Paper II clearly highlights that, in many cases, neither risk assessment nor LCA according to standard procedures will be sufficient for a complete environmental assessment, but a combination of the two methods could be used to achieve the needed results. The review also makes it clear that it is not easy to draw the line between what is a risk assessment and what is an LCA, and, furthermore, such a differentiation may not be necessary. In Paper II, a design space is proposed to facilitate the conscious and purposeful set-up of environmental assessments including elements of risk assessment and LCA.

4.3 Implications of risk and life cycle thinking for holistic human health and environmental assessment

Papers I and II provide a good basis for discussion of the third research question "How can hazard data be used in combination with other information to make holistic human health and environmental assessments of garments with DWR finish as basis for robust substitution recommendations?". The answer to this question bridges the gap between the first (this licentiate thesis) and the second half of this doctoral project, and as such this discussion also covers future research needs. In this chapter, the focus is on theoretical considerations for methodological choices for the further studies, and, in the last chapter of this thesis (Section 6), future research needs are concretised.

The hazard-based ranking that could be made based on the results in Paper I (Section 4.1.2) need to be complemented with further environmental assessment, beyond what is most often included in CAA, to achieve a sound substitution scheme. Firstly, the hazard profiles need to be complemented with exposure assessments since both emission patterns and fate processes can be expected to differ between the alternatives, and, thus, the risk profiles may be different from the hazard profiles. Secondly, there are indications that a change of DWR can lead to a change in the life length of garments and a change in washing needs (W. L. Gore & Associates GmbH 2015), which means that possible trade-offs need to be analysed. Thirdly, Fantke *et al.* (2015b) point out the need for fundamental rather than incremental substitution in chemical alternatives assessment, in which the alternatives would be fundamentally different and, for this purpose, the focus should be on function. An expanded scope, beyond drop-in chemicals, may be needed to achieve such fundamental substitution.

To further distinguish between the alternative DWRs by means of an exposure assessment of DWR-related substances, a risk assessment is a suitable tool. Use-phase emissions, as described in Fig. 2 in Paper I, can be expected to reach quite different levels for different DWRs, as the level of impurities vary between DWRs and degradation rates of polymers and other precursors differ. Where the substances can be expected to accumulate will also differ between alternatives as some substances are volatile, *e.g.* cyclic siloxanes, and others are water soluble, *e.g.* PFAAs. In addition, the amount of DWR applied in textile finishing can differ between the DWRs, and it has been discussed that side-chain-fluorinated polymer DWRs based on short-chain PFAS may require larger amounts for finishing to achieve the same level of water and oil repellency as their long-chain equivalents (Scheringer *et al.* 2014). In a risk assessment, the difference in the amount of emissions and the fate of the different substances are to be accounted for. As absolute amounts in emissions and exposure can be accounted for, a risk assessment can also provide information on the share of DWR to the total risk from a certain substance or substance group.

Indications of changes in life length and washing needs of a DWR-finished garment after substitution mean that the environmental burden of a garment over its life cycle may shift from one type of impact category to another, or between life cycle phases, with a change of DWR. This makes LCA a suitable method for further assessments that take into account potential trade-offs, *i.e.* the risks of problem-shifting. Furthermore, including a garment's life cycle from cradle to grave, which is a must when life lengths of the garments differ, and selecting an LCIA method for the human health and ecotoxicological effects

which takes into account exposure and fate processes, will give possibilities to compare potential human health and ecotoxicological impacts between different life cycle phases and give an idea of the importance of diffuse emissions in relation to point source emissions. Moreover, an LCA, with its basis in a functional unit, allows for the assessment of other alternatives than only chemical drop-ins if such are identified. This adds to the chances of achieving a fundamental rather than an incremental substitution (Fantke *et al.* 2015b).

As is obvious in the discussion above, both risk assessment and LCA perspectives (Harder *et al.* 2015a) are needed in further environmental assessments of the substitution of long-chain PFASs in DWRs, *i.e.* research performed in the second part of the doctoral project. To be able to easily communicate results of risk assessment and LCA, the assessments can be kept separate. However, it is desirable to be able to discuss the magnitude of impacts as predicted by each method, *e.g.* by reaching a common unit. Comparing results from assessments made within different frameworks must however be done with careful consideration of the potential pitfalls as identified in Paper II. The use of DALYs for endpoint characterisation of human health impacts was described in Paper II as part of an effort to reach results of risk assessment and LCA that could be compared between the methods. In LCA DALY is a relevant endpoint (impacts characterised at damage level) unit for human health damage in many impact categories, including toxicity (European Commission 2011b). For ecosystem effects, in LCA, potentially disappeared fraction of species (PDF) is a possible common unit at endpoint level for a number of impact categories, including ecotoxicity (European Commission 2011b). In the toxicity assessment these units are possible to reach *e.g.* by use of the latest version of USEtox (2.01) as characterisation factors are calculated on both mid-point and endpoint level (Fantke *et al.* 2015a). The data required to reach these common units in risk assessment, via DALY calculations (Gao *et al.* 2015) and SSDs (European Commission 2011a), may, however, limit the possibilities to reach the common units. Adjustments of available methods may be needed, in particular for alternatives based on emerging chemistries, not extensively tested. Parallel execution of risk assessment and LCA also aid data collection and problem understanding for each assessment method. As previously described, the risk assessment of PBT, vPvB, and possibly also persistent (P) substances warrants particular carefulness and refined methods (see Section 3.2.1), and it is inevitable to think that this is also valid for LCIA. Thus, while setting up a risk assessment relevant for PBT, vPvB, or persistent (P) substances, the transfer of relevant components to an LCIA to incorporate environmental accumulation processes relevant for these types of substances should be considered.

There are different demands for performance, *e.g.* durability and oil repellency, for different applications of DWR, and the environmentally most benign DWR may not be suitable for all uses (Fig. 3, Paper I; Holmquist *et al.* (2016b)). Therefore, a substitution scheme is needed that considers the risks to humans connected to DWR failure and the risks to human health and the environment connected to the hazard characteristics of DWR-related substances. There are examples of LCA studies that incorporate similar trade-off situations, *e.g.* environmental impacts of flame retardants vs. risks from fires (Simonson *et al.* 2002) and social impacts from the production of an airbag vs. increased traffic safety (Baumann *et al.* 2013). In SUPFES, however, four different types of garments are included in the LCA study, representing different wearer protection needs (from leisure rain wear to workwear). The approach is to only include the DWRs that fulfil the functional unit of each garment. This approach will show the viable alternatives for different types of garments and protection needs. The results will be an important basis for a discussion of how to achieve the lowest possible overall risk, not putting the user of DWR in danger and still minimising emissions of hazardous substances as far as possible, *i.e.* only use the most hazardous substances when absolutely necessary and thus minimise used amounts and emissions. Here it will be important, as highlighted by Hansson *et al.* (2011), to give equal weight to human health and environmental risks as to functional properties, *i.e.* not to necessarily set the functionality criteria as delivering the exact same function as the original chemical.

5 Conclusions

The results of the hazard assessment in Paper I provided answers to the first two research questions:

***Research question 1*. What are the hazard characteristics of diffusively emitted substances from the main classes of DWRs on the market?**

The side-chain-fluorinated DWRs and the silicone-based DWRs have hazard profiles that are clearly of concern with very high hazards for at least one endpoint (based on representative substances, see Section 4.1.1). The hydrocarbon-based DWRs have a better hazard profile with, at most, moderate hazard. A number of data gaps on the hazardous properties were identified, in particular for the degradation products of the silicone-based DWRs. The group of "other chemistries", including dendrimers and inorganic nanoparticles was not possible to characterise at all due to the lack of information about the chemical structure providing the water (and oil) repellent function in these chemistries. In other words, the hazard profile of this group is not known even though these substances are available on the market.

***Research question 2*. What is the hazard-based ranking of the available DWR alternatives (based on the characteristics as described in research question 1)?**

Based only on the substances' intrinsic hazard characteristics, hydrocarbon-based DWRs were ranked higher (more environmentally benign) than side-chain-fluorinated DWRs based on short-chain PFAS and silicone-based DWRs. The latter two could not be differentiated between based on hazard characteristics alone. The ranking is uncertain due to the data gaps identified and the lack of information about the "other chemistries", and those need to be filled for robust hazard assessment and fair comparison between alternatives.

The results in Paper II provided a basis for the selection of further environmental assessment actions to fulfil the goal of the doctoral project and the SUPFES project:

Research question 3. **How can hazard data be used in combination with other information to make holistic human health and environmental assessments of garments with a DWR finish as the basis for robust substitution recommendations?**

A hazard assessment should be complemented with exposure considerations, which could be made with use of risk assessments for selected scenarios. The environmental assessment should also include LCA for DWR application on textiles with differing performance requirements, *e.g.* from leisure to workwear. The LCA should make it possible to avoid problem shifting and thus resolve trade-offs between different types of impacts. The LCA should also allow for assessment of other alternatives than only drop-in chemicals. To aid the discussion of the magnitude of predicted impacts, LCA and risk assessment results should be possible to compare, *e.g.* by expressing the results in the same units. Comparing results from assessments made within different frameworks must be done with careful consideration of the potential pitfalls as identified in Paper II. The results for the hazard assessment, risk assessment and the LCA should feed into a substitution scheme with the aim of achieving the lowest possible overall risk and avoid putting the user of a DWR in danger. The result of the substitution scheme should be to minimise emissions of hazardous substances as far as possible, *i.e.* only use the most hazardous substances when absolutely needed due to performance requirements. The substitution scheme should also point out research needs to further reduce the risk, both regarding the properties of DWRs already in use and development of new chemistries or other solutions to fulfil the water repellent function.

6 Recommendations for future research

Future research within this doctoral project (executed in collaboration with other project members) will include environmental assessments that combine the use of risk assessment and LCA, as one contribution to the substitution study of the SUPFES project.

In the risk assessment(s) of the project, a focus on emissions from municipal WWTPs is inevitable since a substantial part of the diffuse emissions during the use phase may end up in the WWTP via wash water. In a pilot study on land applied PFAS contaminated sludge, it was shown that a shift from contamination from long-chain PFAS to short-chain PFAS contamination would lead to a lower risk to human health and the environment. This is due to the more benign hazard profile of the short-chain PFAS and the lower soil accumulation. However, a larger portion of the amount applied would be further dispersed and contribute to global contamination (Andersson *et al.* 2014). Data on PFAS in incoming and outgoing flows from Käppala WWTP, on the Swedish east coast, are currently being obtained by colleagues at Stockholm University. In that study, a new technique, molecular absorption spectrometry (MAS) is being applied, to quantify the fraction of organofluorines not captured using routine techniques. These new data will allow for further risk assessments of emissions via WWTPs. Emission factors and trade statistics can be used to estimate the contribution of DWR to the total emissions and thus the contribution of DWR to risks. The study of risks connected to WWTP emissions of DWR chemicals also has interesting potential because wastewater and sludge treatment are a natural object for studying problem-shifting. This is a matter of assessing whether or not additional treatment to lower risks leads to increased risks (potential impacts) elsewhere, *e.g.* through increased energy use. Additional scenarios for which risk assessment may be warranted (but not necessarily covered within the SUPFES project) are, *e.g.* risk to workers and the environment during manufacturing processes and risks to the wearer of the garments with a DWR finish. Risk assessment(s) must consider the particular challenges posed by PBT, vPvB, and persistent (P) substances.

The upcoming LCA study including four different types of garments representing different protection needs of the wearer (from leisure rain wear to workwear) will show viable alternatives for different types of protection needs. To realise this study, several challenges need to be addressed:

- Selection of a suitable LCA method. Since a substitution is a change, and the aim is to assess the possible consequences of that change, the use of consequential LCA is inevitable (see Section 3.2.2). However, an

attributional LCA in a future setting may be another option (see *e.g.* Arvidsson *et al.* (2015a); Arvidsson *et al.* (2015b); Sandén and Karlström (2007)).

- Finding a suitable zero option, *i.e.* a solution that provides the function of keeping a person warm and dry but without a DWR, in other words, assessing an alternative that is not a drop-in chemical.
- DWR effects on garment life lengths, *i.e.* finding appropriate ways to translate durability results in technical testing to quantify the difference in the life length of products with different DWR finishes.
- DWR fulfilment of the functional unit, *i.e.* finding appropriate ways to incorporate results from the technical performance testing conducted within the SUPFES project into an LCA to ensure that the comparison of DWR alternatives are made on a fair basis. This would include estimations of life length and performance requirements, such as oil and stain repellency.
- Specify how the DWR formulation should be modelled, including all ingredients, as such information is generally proprietary.
- DWR characterisation factors, *i.e.* currently, LCIA characterisation factors for several DWR-related chemicals are lacking. To be able to make a relevant assessment of alternative DWRs with the use of an LCA, characterisation factors must be developed. The hazard assessment in Paper I provides a good basis for such work, however, developing LCIA characterisation factors still involves many challenges, *e.g.* how to deal with PBT, vPvB, and persistent (P) substances, how to incorporate persistent degradation products and how to consider the particular fate properties of PFAS.

For the combined use of results from the risk assessment and LCA studies future work should include efforts to achieve results that can be compared between the two methods, *e.g.* by the use of common units.

One of the aims of the SUPFES project is to develop an improved substitution method with widespread applicability. The combined use of risk assessment and LCA in the upcoming doctoral project will be further explored with the aim of contributing to this substitution method.

Research performed in other, not the upcoming doctoral project, parts of the SUPFES project will also help resolve issues highlighted in this thesis as well as future issues that may arise in LCA and risk assessment work:

- Emission studies on the generation of emission factors to air and water.

- Human toxicity and ecotoxicity studies that further characterise DWR-related chemicals.
- Technical performance testing including water and oil repellency before and after ageing as well as testing for repellency of other types of stains.

In addition to the environmental assessment efforts described above, further research, not necessarily executed within the SUPFES project, needs to focus on filling the data gaps in the hazard profiles of the existing alternatives and to develop high performance DWRs with less problematic hazard profiles.

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Appendix A

Terminology of this thesis:

Term	Specification
Alternative	An option which is an alternative to the original solution, i.e. another chemical or another material or construction or some other solution to meet the functional needs of the user of the product/service.
Areas of protection	Term used within LCA for categories of impacts that need consideration; human health, ecological consequences, and resource use (as defined by Baumann and Tillman (2004)).
Background system	All processes within the system in the LCA study, that are not part of the foreground system (as defined by Baumann and Tillman (2004)).
Characterisation	In LCA, characterisation is the process of using characterisation factors to aggregate emissions that contribute to a particular potential impact. In this thesis, the word is also used in a wider sense, e.g. about a chemical's properties.
DWR agents	The chemicals (polymer, dendrimer or nanoparticle) in the DWR formulation that provide the water (and oil) repellent function.
DWR chemicals	Any chemical in or related to the DWR formulation.
DWR-related substances	Chemicals in the DWR formulation, including impurities, or transformation products of those chemicals.
Endpoint	In LCA this is the characterisation at (or close to) the level of areas of protection (as defined by European Commission (2011b)). In toxicity and ecotoxicity assessments the endpoint is the type of effect observed in a study. In this thesis the term is used with both

	these meanings, in their respective context.
Environmental assessment	Assessment of the effects of an activity on the environment and human health.
Foreground system	Processes that can be directly influenced (e.g. by change of mode of operation) by the decisions taken based on the LCA study (as defined by Baumann and Tillman (2004)).
Impact	In this thesis, the term impact is used synonymously to the word effect.
Midpoint	Characterisation at a level of cause-effect chain between missions/resource consumption and the endpoint level (as defined by European Commission (2011b)).
Risk	The probability of an adverse effect (the combination of the probability and the severity of an effect). In chemical risk assessment that means the probability of an adverse effect on humans or the environment occurring as a result of a given exposure to a chemical or mixture (Van Leeuwen 2007).
Safeguard subject	In LCA synonymous to areas of protection (Baumann and Tillman 2004). In this thesis used, with the same meaning, also within other methodological frameworks, such as hazard and risk assessment.
Safer alternative	As it is defined in The commons principles for alternatives assessment (BizNGO, 2013): "An option, including the option of not continuing an activity, that is healthier for humans and the environment than the existing means of meeting that need."
Substitute	Replacement, in this thesis used for chemical alternatives (i.e. "drop-in" chemicals).This is narrower than the definition of "alternative" used in this thesis.

Water (and oil) repellency	Water repellency and in some cases also oil repellency. This use of brackets around "and oil" is used to allow description of DWRs giving only water repellency and DWRs giving both water and oil repellency in the same sentence.