MIDWOR - LIFE14 ENV/ES/000670

With the contribution of the LIFE financial instrument of the European Commission

PROJECT MIDWOR Deliverable

Environmental Life Cycle Assessment Studies of the Alternative DWOR Chemicals

Project acronym:	MIDWOR-LIFE
Project full title:	Mitigation of environmental impact caused by DWOR textile finishing chemicals studying their nontoxic alternatives
Grant agreement no.:	LIFE14 ENV/ES/000670
Responsible partner for deliverable:	CETIM
Contributing partners:	Haga clic aquí para escribir texto.
Author(s):	Julio Fierro, Cristina Martínez
Nature[1]:	R
Dissemination level[2]:	PU
Total number of pages:	16
Version:	Draft versión
Contract delivery date:	Haga clic aquí para escribir una fecha.
Actual delivery date:	Haga clic aquí para escribir una fecha.

Version control

Number	Date	Description	Publisher	Reviewer
0.1	24/05/2018	Draft deliverable with results from DWORs	AD, CM	AD, CM

[1] **Nature of Deliverable**: **P**= Prototype, **R**= Report, **S**= Specification, **T**= Tool, **O**= Other.

[2] **Dissemination level**: **PU** = Public, **RE** = Restricted to a group of the specified Consortium, **PP** = Restricted to other program participants (including Commission Services), **CO**= Confidential, only for members of the Consortium (including the Commission Services)

Contents

1 Introduction

1.1 Background of the study

One of the specific objectives of MIDWOR-LIFE project is to evaluate the environmental impact of conventional and alternative DWORs[3] used by the textile sector.

Action B3 aims to study the **environmental impact of conventional and alternative DWOR finishing products** in the textile industry using **Life Cycle Assessment** (LCA) methodology. This LCA is based on the results obtained at Action B.1.2 (Industrial validation) where conventional and alternative DWORs have been compared in six pilot industries.

As this task is currently under development, only **partial results regarding the environmental impact of DWOR products** will be shown in this draft-deliverable, without including its application in a textile plant.

1.2 Life Cycle Assessment

On its *Communication on Integrated Product Policy* (COM (2003)302), the European Commission concluded that LCA is the best framework currently available for assessing the potential environmental impacts of products and processes.

LCA is a structured, comprehensive and internationally standardized method to quantify all relevant emissions and resources consumed by a product or a process, from raw material extraction through materials processing, manufacture, distribution, use, repair and maintenance, and disposal or recycling.

The goal of LCA is to compare the full range of environmental effects assignable to products and services by quantifying all inputs and outputs.

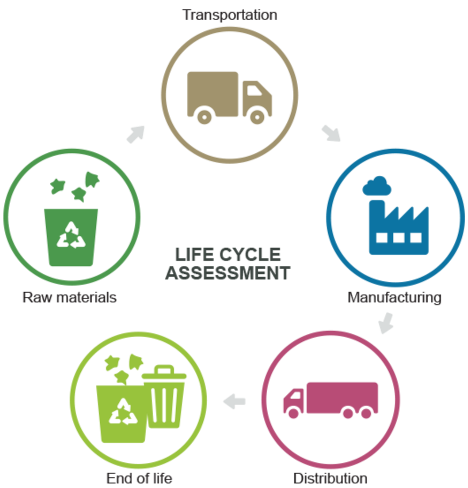

FIGURE 1. LIFE CYCLE ASSESMENT

LCA procedure is guided by two standards, ISO 14040 and 14044, which set the stages of this type of studies. According to these standards, LCA has four main stages:

[3] Durable Water and Oil Repellents

1) **Goal and Scope of the study:** In this initial stage, the objective of the LCA is defined, identifying the stages that will be included in the assessment, the boundaries of the study, and the functional unit (FU) which is the reference unit for the complete LCA. Other aspects regarding methodology of the LCA, such as the method selected for Impact Assessment, normalisation, weighting, etc. are defined also at this point.
2) **Life Cycle Inventory (LCI):** During this step, all imputes and outputs of the process are inventoried for each stage of the process/product to be evaluated, including raw matters, water, energy, land use, and any other materials. This stage is usually the most time-demanding task of the LCA and the most crucial for the accuracy of the assessment.
3) **Life Cycle Impact Assessment:** At this stage, all the system flows inventoried in the LCA are used to calculate the environmental impact over different categories, such global warming, human toxicity, water depletion…etc.
4) **Interpretation of Results and Reporting:** This last stage requires to analyse the results obtained from the LCA, verifying the achievement of the initial goal set for the assessment. In occasions results may show the need to perform changes in the definition, LCI or methodology of the study, in an iterative process until the objectives of the LCA are achieved.

FIGURE 2. STAGES OF A LCA. Source: paradigmsustain.com

2 Life Cycle Assessment of alternative DWORs

2.1 Goal and scope of the study

2.1.1 Objective of the study

The objective of this work is to **study and quantify the environmental impact of six different DWORs used by the textile industry**, including both **fluorinated** and **Fluorine-free** DWORs.

2.1.2 Functional Unit

The functional unit (FU) selected for the study is the production of **100m^2 of finished fabric,** ready to be shipped to the customers.

2.1.3 System Boundaries

Boundaries of the study have been set to focus the LCA into the finishing stage of a textile process, in a *gate-to-gate* approach (Figure 3). Thus, all the previous stages, such cotton cultivation, knitting, etc. will be out of the scope of the study. Also the further use of the finished fabrics or its final disposal at the end of its life will be out of the limits of the study.

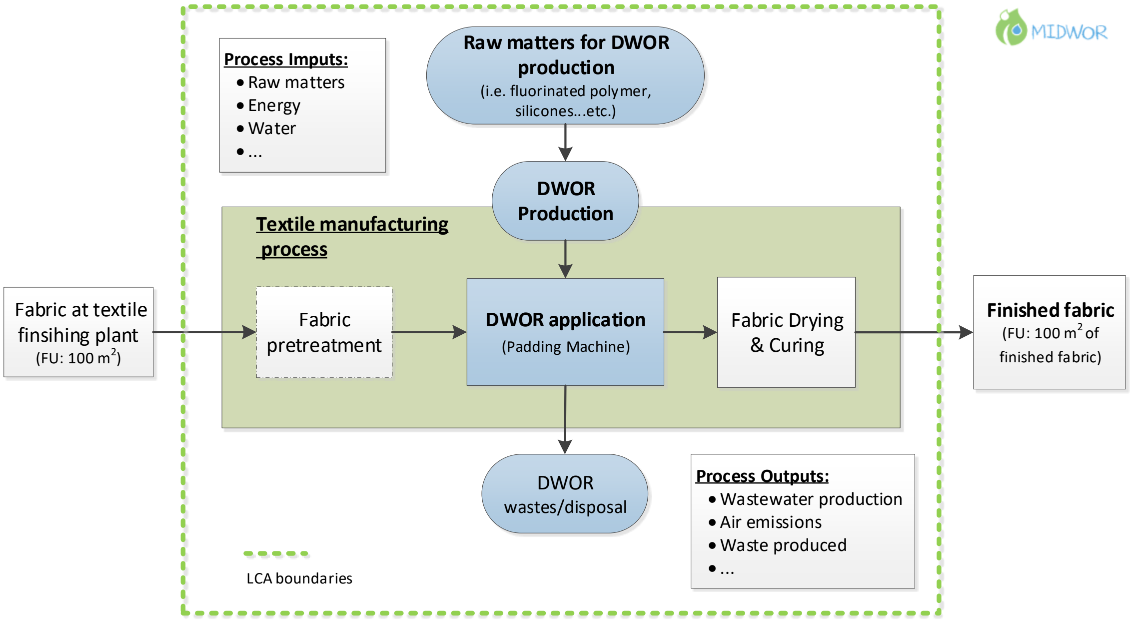

FIGURE 3. BOUNDARIES OF THE STUDY

As Figure 3 shows (blue flowchart), **DWOR production have been included in the LCA**, **covering all the stages of its life,** from the synthesis of its raw matters to its application in a textile factory and the disposal of wastes. This draft deliverable shows the results obtained from this part of the LCA.

Additionally, all flows related with the finishing process have been included, such raw matters, electricity, fuel consumption, water, compressed air, etc. and outputs such air emissions, wastewater, solid wastes, etc.

2.1.4 Assumptions

The following main assumptions have been taken, according with the information collected within the project:

- DWOR composition have been obtained from the safety data sheets (SDS) provided by distributors or manufacturers. Composition of DWORs used at industrial validation have been used as primary source and, when necessary, they have been complemented by data from SDS from equivalent products, patents or peer-reviewed journals.
- It has been assumed that DWORs are produced as a formulation of different chemical compounds. These substances have been included using Ecoinvent database. Unknown compounds or those not present in Ecoinvent database have been included in the inventory using the generic compounds (organic and inorganic) present in the database.
- Fluorinated DWOR production includes a fluorinated copolymer as base of its composition. This polymer has been obtained by telomerisation from tetrafluoroethylene, as it is the most common process at present [1], [2].
- DWOR synthesis takes place in South-East Asia, unless otherwise stated. Products are first shipped by sea to Europe (*Transport, freight, sea, transoceanic ship*: 14.000 km) and then by road (*Transport, freight, lorry 16-32 metric ton, EURO5*; 1.000 km).
- Electricity used in the formulation process is estimated in 1.5 kWh/t produced. Energy required for synthesis of each raw matter used is considered on each compound. When included, electricity have been considered as *medium voltage using the European energetic mix*.
- Heat used in formulation of DWORs have been estimated in 3 m^3 of Natura Gas per ton of DWOR produced (111 MJ/t).Additionally, heat required for the synthesis of each raw matter is already included on each compound from Ecoinvent database.
- As a global procedure, emissions have been estimated using the *"Default worst-case release factors"* indicated in the Appendix A.16-1 of the ECHA report *Guidance on information requirements and chemical safety assessment* [3].

2.1.5 Limitations

The main limitation observed during the development of the study was the lack of information regarding the composition of the different DWORs and its production process. This lack of information have been overcome by using data from peer-review journals and technical bibliography regarding finishing products.

2.1.6 Impact assessment Method

The method used to determine the environmental impact of the DWORs was **ILCD 2011+.** This method, developed by the European Platform of LCA and the Institute for Environment and Sustainability [4], combines different impact categories from several globally accepted methods (USEtox, ReCiPe, IPCC, etc.) based on the reliability and consistency of its results. It includes 16 impact categories (Table 1), embracing a wide range of fields (atmosphere, climate change, water bodies, soil, human health, etc.).

TABLE 1. ILCD2011+ IMPACT CATEGORIES

Impact Categories	Unit
Climate change	kg CO_2 eq
Ozone depletion	kg CFC-11 eq
Human toxicity, non-cancer effects	CTU_h
Human toxicity, cancer effects	CTU_h
Particulate matter	kg $PM_{2.5}$ eq
Ionizing radiation HH	kBq U_{235} eq
Ionizing radiation E (interim)	CTUe
Photochemical ozone formation	kg NMVOC eq
Acidification	molc H^+ eq
Terrestrial eutrophication	molc N eq
Freshwater eutrophication	kg P eq
Marine eutrophication	kg N eq
Freshwater ecotoxicity	CTUe
Land use	kg C deficit
Water resource depletion	m^3 water eq
Mineral, fossil & ren resource depletion	kg Sb eq

2.1.6.1 Inclusion of perfluorocarbon substances

Impact assessment methods includes a large set of substances with assigned Characterisation Factors (CF) for each Impact Category. These CF can be considered as factors used to convert the flows, previously quantified in the LCI, into environmental impacts for each category. Thus, if a substance is not included in a method, is not taken into account in the environmental Impact.

Nor the selected method for this LCA (ILCD 2011+) or any of the most common methods, such ReCiPe, USETox, CML, etc includes PFOA, PFOS or any substance related with the use of perfluorinated substances. Thus, it is necessary to include these new substances in order to reflect the environmental impact of DWORs properly.

Six new DWOR related substances have been included in the ILCD2011+ method, and Characterisation Factors (CF) have been assigned from Roos et al.[5]:

- Perfluoro-1-hexanol (4:2 FTOH) & Perfluorodecylacrylate (8:2 FTA)
- Perfluorobutane sulfonic acid (PFBS)
- Perfluorohexanoic acid (PFHxA) & Perfluorooctanoic acid (PFOA)
- Polydimethyl siloxane PDMS

According with the properties and environmental fate reported for these substances, **three Impact categories have been selected**, based on its environmental behaviour reported in literature:

- Human toxicity, Cancer effects,
- Human toxicity, non-cancer effects
- Freshwater ecotoxicity

2.1.6.2 Normalisation

According to ISO 14044 normalisation, in the context of Life Cycle Assessment (LCA), is an optional step of Life Cycle Impact Assessment (LCIA) which allows the practitioner to express results after the characterisation step using a common reference impact [6].

For this LCA, normalization have been carried out using the factors corresponding to EC-JRC Global (Table 2), which corresponds to the average emissions per person in the UE27 for each Impact Categories.

TABLE 2. NORMALISATION FACTORS EC-JRC GLOBAL

ILCD Impact Category	Unit	Factor
Climate change	kg CO_2 eq.	7,07E+03
Ozone depletion	kg CFC-11 eq.	1,22E-02
Human toxicity, cancer effects	CTUh	1,24E-05
Human toxicity, non-cancer effects	CTUh	1,55E-04
Particulate matter/Respiratory inorganics	kg $PM_{2.5}$ eq.	5,07E+00
Ionizing radiation, human health	kBq U_{235} eq. (to air)	2,41E+02
Photochemical ozone formation, human health	kg NMVOC eq.	4,53E+01
Acidification	mol H^+ eq.	5,61E+01
Eutrophication terrestrial	mol N eq.	1,64E+02
Eutrophication freshwater	kg P eq.	6,54E+00
Eutrophication marine	kg N eq.	3,04E+01
Land use	kg C deficit	5,20E+06
Ecotoxicity freshwater	CTUe	3,74E+03

Resource depletion water	m^3 water eq.	6,89E+01
Resource depletion, mineral, fossils and renewables	kg Sb eq.	1,93E-01

2.1.7 Software and databases used

This LCA have been developed using the software Simapro 8.5 and the database Ecoinvent 3.4.

2.2 Inventory analysis for DWORs

This section describes briefly the inventory used for the development of the LCA. Final inventory with the flows considered for each unit of the LCA will be included in the final version of the deliverable.

2.2.1 Fluorinated DWORs (C8-C6)

2.2.1.1 C8-DWOR synthesis

Production of C8 DWORs have been modelled into two stages, the synthesis of a long-chain perfluorinated polymer, and the further production of the DWOR using this perfluorinated polymer as one of its constituents.

Long-Chain perfluorinated polymer

Due to the inability to collect real manufacturing data from PFC production, the process included in the present LCA "Production of perfluorinated polymers" has been modelled using data available from peer-reviewed journals and reports from ECHA and OECD.

- Telomerisation reaction is expected to have a yield of 80%, and its main constituents are tetrafluoroethylene (85.8%) and Iodine pentafluoride [7].
- Emissions to the environment are estimated using the "Default worst-case release factors" scenario values for the manufacture of a substance; Air 5%, Water (before WWTP) 6%, and soil (0.01%) [3].
- Both water and gas emissions are treated with an installation efficiency of 85% for all emissions but perfluorinated substances. According to the fate of perfluorinated compounds in water treatment systems, no degradation have been considered for PFOA and perfluorodecyl acrylate [8], [9]
- Waste production have been estimated as an average value of 0.125 kg per kg of perfluorinated compound produced. Based on Paul et al.[10] most of the wastes are produced in a solid form and disposed through incineration, 33% are sent to a hazardous waste landfill and another 4% to non-hazardous landfills.

C8-DWOR based on Repellan KFC-N

Production of C8-DWOR have been considered as a formulation into a mixture of different chemical compounds, including the LC-Perfluorinated polymer.

- Production of the C8-DWOR takes place in China, and is transported to Europe by sea (14000 km) and road (1000 km).
- An estimated energy consumption of the mixture process is estimated in 1.5 kWh/t and 3 m3 of natural gas for thermal purposes/steam production.
- Emissions to the environment were estimated using the "Default worst-case release factors" scenario values for the formulation into a mixture; Air 2.5%, Water (before WWTP) 2.5%, and soil (0.01%) [3].
- Composition of C8-DWOR is based in Repellan KFC-N and other LC-DWORs:
  - Fluorinated Acrylic Copolymer: 30%
  - Glycols: 15%
  - Citric acid: 3%
  - Ethoxylated alcohol (emulsifier): 1%

2.2.2 C6 DWOR

Production of C6-DWOR follows the same scheme than C8-DWOR. In first place, a short chain fluorinated polymer is obtained by telomerisation. This compound is used in the production of the short-chained DWOR according with the composition of the product.

- In this case, emissions considered for both C6-DWOR and Short-Chain fluoroacrylate polymer were estimated to be in form of a short-chain related compounds such Perfluorohexanoic acid (PFHxA).
- Composition of C6-DWOR were based in Repellan TC-6 from Pulcra Chemicals and Phobol CP from Huntsman:
  - Partially Fluorinated Acrylic Copolymer: 30%
  - Poly(oxy-1,2-ethanediyl), .alpha.-isodecyl-.omega.-hydroxy: 3%
  - Citric acid: 3%

2.2.3 Perfluorosilicone

Perfluorosilicone inventory is based on the composition reported for UNIDINE TG-5601. This compound includes a short-chain fluorinated co-polymer in its formulation.

- In the present LCA, it was considered the same co-polymer than for the C6-compound.
- Emissions for this DWOR were considered in form of PFHxA and polydimethyl siloxane (PDMS) related compounds [11], [12].
- Composition considered for this perfluorosilicone was:
  - Fluoralkyl acrylate copolymer + emulsifier: 30%
  - [(Methylenethylen)bis(oxy)]dipropanol: 5-10 %
  - Water: 60%

2.2.4 Silicone

Silicone is based in DRYOL S600 produced by PROTEX. Production takes place in Asia and is shipped to Europe by sea and road, as detailed for other compounds.

- Emissions have been considered in form of PDMS and derivatives, such silanols (dimethylsilanediol and trimethylsilanol).
- Main composition reported for this compound is:
    - Silicone emulsion: 56%
    - Ethoxylated alcohol: 40%
    - Minor chemical compounds: <3%

2.2.5 Dendrimer

Dendrimer is based in RUCODRY ECO PLUS. According to its safety data sheet (SDS), it is a hyperbranched polymer with the following composition:

- Functionalized polymer 15%
- Propane-1,2-diol 5%
- Other chemical compounds 10%

2.2.6 Paraffin

Paraffin is based in Polyguard BD 7300 from Polysystec. Is provided in a 120 kg drum and produced in south-east Asia. Composition considered for this substance according to its SDS is:

- Composition considered is 80% paraffin wax
- Cationic ethoxylated derivative (2.5%)
- Other chemical compounds (inorganic) 10%

2.3 Results and Discussion

2.3.1 Impact of DWOR production process

As a preliminary output of Action B3, results regarding the production of DWORs have been obtained. These results corresponds to the production of **1 kg of DWOR** at the gate of the distributor in Europe.

Figure 4 shows the impact of each DWOR for the 6 main categories of impact, which accounts for nearly the 98% of the total impact of each. These results are expressed in normalised values and in percentage of the one with highest value.

Results show than Fluorine-based DWORs presents a higher environmental impact in nearly all categories analysed**. C8-DWOR** shows the highest impact over human toxicity, in a range about 10 times higher than the other DWORs, including **C6- DWOR** and **Fluorine-free**. Only in these two categories related with human toxicity (cancer and non-cancer effects), a clear difference between C8 and C6 can be appreciate, as both compounds presents nearly the same impact for the remaining 4 main categories showed in the figure.

As could be expected by its characteristics, **perfluorosilicone** presents a lower environmental impact than C8 and C6 DWORs, but a higher impact than other Fluorine-free alternatives.

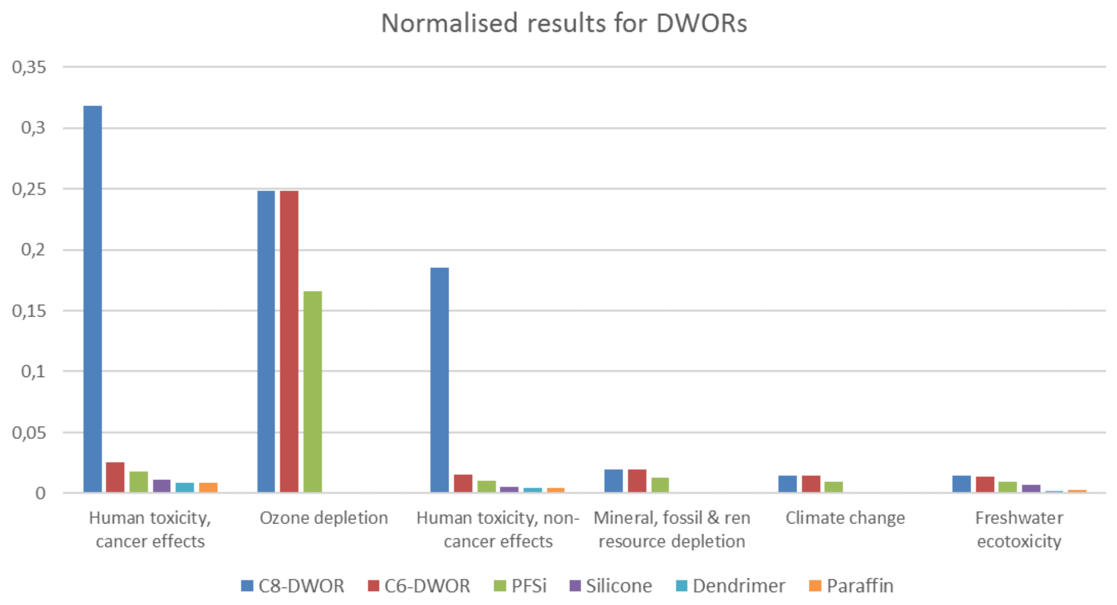

FIGURE 4. NORMALISED RESULTS FOR THE PRODUCTION OF 1 KG OF EACH DWOR

A better perspective of the difference between the 6 DWORs evaluated can be observed in Figure 5, where the impact of each product is presented in an accumulative way in total impact units.

As mentioned before, **C8-DWOR presents the highest environmental impact** of all DWORs evaluated. This impact is over 2 fold greater than the equivalent C6-based DWOR, and over 3 times when it is compared with the perfluorosilicone. Human toxicity and ozone depletion are the main contributors to this total impact.

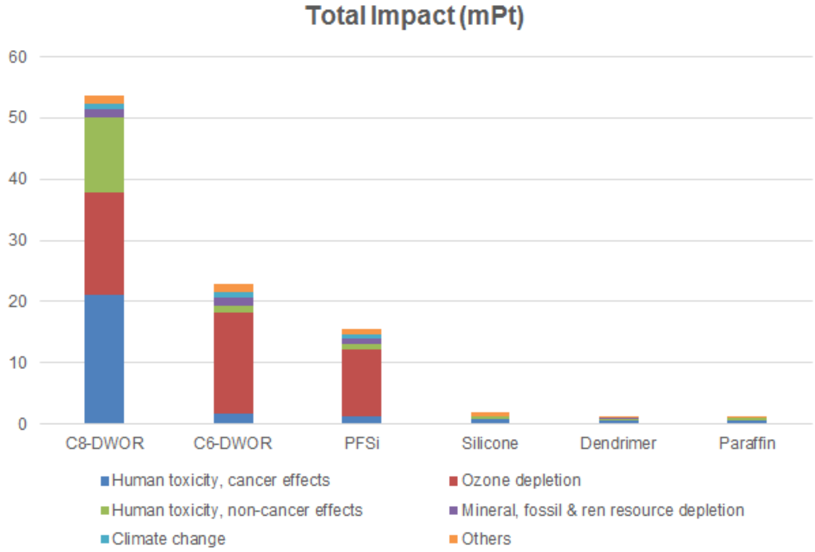

FIGURE 5. TOTAL IMPACT FOR THE PRODUCTION OF 1 KG OF EACH DWOR

Fluorine-free alternatives presents a much lower impact, ranging 30-40 times lower than a C8-based DWOR in global terms. **Paraffin** and **Dendrimer** showed nearly the same impact, while **Silicone** presents a slightly higher total impact. However, uncertainty regarding the formulation and origin of the DWORs does not allow to extract a reliable conclusions between these 3 DWORs.

3 Conclusions

Preliminary results regarding the production of the 6 DWORs included in the LCA of the project allows to extract the following conclusions:

- Fluorinated DWORs presents a clearly higher environmental impact compared with fluorine-free alternatives.
- Human toxicity and ozone depletion are the main environmental categories affected by fluorinated DWORs. Impact of these compounds can be attributed mainly to the synthesis of the perfluorinated polymer and the release of compounds such PFOA, PFHxA, to the environment.
- As expected, perfluorosilicone presents the lowest impact among the fluorine-based DWORs, due to the low amount of this compound present in its composition.
- Fluorine-free DWORs present a clearly lower impact in almost every category studied in the LCA. Total impact of these compounds can be estimated in 30-40 times lower than the C8-DWOR used as reference.
- Uncertainty regarding the composition of the different Fluorine-free DWORs evaluated does not allow to extract conclusions between these 3 compounds.

4 Bibliography

[1] L. Vierke, C. Staude, A. Biegel-Engler, W. Drost, y C. Schulte, «Perfluorooctanoic acid (PFOA)—main concerns and regulatory developments in Europe from an environmental point of view», *Env. Sci Eur*, vol. 24, n.º 1, pp. 1–11, 2012.

[2] C. Lassen *et al.*, «Survey of PFOS, PFOA and other perfluoroalkyl and polyfluoroalkyl substances», The Danish Environmental Protection Agency, Copenhagen K, 2013.

[3] ECHA, «Chapter R.16 : environmental exposure assessment», en *Guidance on information requirements and chemical safety assessment*, European Chemical Agency, 2016.

[4] European Commission, Joint Research Centre, y Institute for Environment and Sustainability, *International reference life cycle data system (ILCD) Handbook: Recomendations for Life Cycle Assessment in the European context*. Luxembourg: Publications Office, 2011.

[5] S. Roos, H. Holmquist, C. Jönsson, y R. Arvidsson, «USEtox characterisation factors for textile chemicals based on a transparent data source selection strategy», *Int. J. Life Cycle Assess.*, pp. 1-14, jun. 2017.

[6] L. Benini *et al.*, *Normalisation method and data for environmental footprints*. Luxembourg: Publications Office, 2014.

[7] E. Kissa, *Fluorinated Surfactants and Repellents, Second Edition,*. CRC Press, 2001.

[8] Z. Liu *et al.*, «Pollution pathways and release estimation of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) in central and eastern China», *Sci. Total Environ.*, vol. 580, n.º Supplement C, pp. 1247-1256, feb. 2017.

[9] M. Clara, S. Scharf, S. Weiss, O. Gans, y C. Scheffknecht, «Emissions of perfluorinated alkylated substances (PFAS) from point sources—identification of relevant branches», *Water Sci. Technol.*, vol. 58, n.º 1, p. 59, jul. 2008.

[10] A. G. Paul, K. C. Jones, y A. J. Sweetman, «A First Global Production, Emission, And Environmental Inventory For Perfluorooctane Sulfonate», *Environ. Sci. Technol.*, vol. 43, n.º 2, pp. 386-392, ene. 2009.

[11] H. Holmquist, S. Schellenberger, I. van der Veen, G. M. Peters, P. E. G. Leonards, y I. T. Cousins, «Properties, performance and associated hazards of state-of-the-art durable water repellent (DWR) chemistry for textile finishing», *Environ. Int.*, vol. 91, pp. 251-264, may 2016.

[12] D. Graiver, K. W. Farminer, y R. Narayan, «A Review of the Fate and Effects of Silicones in the Environment», *J. Polym. Environ.*, vol. 11, n.º 4, pp. 129-136, oct. 2003.