**Information Document accompanying**

**The Call for evidence supporting an analysis of restriction options for the PFAS group of substances (fluorinated substance(s))**

1. **Introduction**

The competent authorities of several member states, namely the Netherlands, Germany, Denmark, Sweden and Norway are planning to prepare an analysis of restriction options for the group of fluorinated substances subject to the description below (as defined under II.) since all these substances are considered to be persistent (see under III.) constituting an unacceptable risk to the environment and human health.

This call for evidence is intended to generate data and knowledge with regard to PFAS and their uses in order to decide on the initial chemical scope as well as use scope of a restriction proposal. The questionnaire further aims at understanding for which of the PFAS in scope chemical alternatives or technical replacements exist, voluntary measures or substitution processes etc. are ongoing. Based on that basic information appropriate options for a restriction proposal will be taken forward in the development of a REACH Annex XV Restriction Dossier.

1. **Proposal for the definition of PFAS considered to be in scope of the restriction**

As indicated by the name, per- and polyfluoroalkyl substances (PFASs) comprise a group of organic substances containing alkyl groups on which all or many of the hydrogen atoms have been replaced with fluorine as structural fragments. The most well-known PFASs contain fully fluorinated carbon chains (= alkyl chains) of various chain lengths attached to a functional group, like carboxylic or sulfonic acids. PFASs with only one perfluorinated carbon atom, like trifluoroacetic acid (TFA, CF3CO2H), carry the smallest possible structural unit required for a substance to be grouped in this class. Novel PFAS structures have been developed wherein new structure elements have been introduced, like other halogens (-Cl or -Br) or ether elements (-O-). Some of these PFASs contain no CF3-elements as there are other groups at the end of the alkyl chains, while they may contain several -CF2-units within their chemical structures. In any case, PFAS substances are persistent in the environment (resistant to degradation). Substances with a non-fluorinated part in addition to their PFAS-elements often degrade until they reach persistent PFAS degradation products.

Hence, as the scope of the current Call for Evidence have been selected:

**Substances that contain at least one aliphatic** **-CF2- or -CF3 element.**

The scope may be represented by the general structure formulas in Figure 1.



**Figure 1.** General structure formulas representing the scope of PFAS relevant for this Call for Evidence. R, R', R'' = any chemical group, n ≥ 0.

All substances covered by the scope are considered to contribute to the concentrations of persistent PFASs in the environment.

The length of the fluorinated alkyl chains in the structures in Figure 1 may be in the range of one carbon atom and upwards (linear or branched), while the groups R, R' and R'' may be any chemical groups or any combinations thereof, resulting in a large number of PFAS substances covered. Polymeric substances are also within the scope as long as they fulfil the indicated structure formulas, both backbone fluorinated and side-chain fluorinated polymers.

There are currently more than 4700 different PFAS substances on the market, and new PFASs are continuously developed. Due to the common feature of being persistent, all PFAS sub-groups are covered by the present investigation. Listed below are examples from a non-exhaustive list of substances and substance groups that are included.

*Non-exhaustive list of substances and substance groups:*

In the following, selected subgroups of PFASs are explained and exemplified. It is in general difficult to define non-ambiguous sub-categories for the whole class of PFASs due to their inherent complexity. Some PFAS substances may therefore belong to several of the groups indicated. The list below is a non-exhaustive list of PFASs and should be regarded as a help for the reader to understand the scope of the current investigation.

**R, R' and R''**

In the following, the groups R, R' and R'' may represent any chemical group or any combination thereof, including (but not limited to) hydrogen, linear and branched alkyl, olefinic, aromatic, alcohols (-OH), amines (-NH2), halogens (-F, -Cl, -Br, -I), esters (-CO2R), ethers (-O-), thiols (-SH), carboxylic acids (-CO2H), sulfonic acids (-SO3H), sulfinic acids (-SO2H), sulfones (-SO2R), phosphonic acids (-PO(OH)2), phosphinic acids (-PO(OH)), as well as their derivatives, including salt forms and polymers.

**Perfluoroalkyl substances**

Aliphatic substances for which all hydrogen atoms attached to carbon in the corresponding non-fluorinated substance have been replaced by fluorine atoms:

1. Perfluoroalkanes, linear and branched; CnF2n+2; n≥1

Examples:



1. Perfluorinated cycloalkanes; CnF2n; n≥3

Examples:



1. Aliphatic perfluoroalkyl substances, linear or branched; CnF2n+1-R,
R-CnF2n-R’; n≥1; R, R' as defined above
Examples:



This category includes many of the most well-known PFASs and subcategories, like carboxylic acids (PFCAs, e.g. TFA, PFBA, PFHxA, PFOA), sulfonic acids (PFSAs, e.g. triflic acid, PFBS, PFHxS, PFOS), sulfinic acids (-SO2H), phosphonic acids (-PO(OH)2), phosphinic acids (-PO(OH)), etc. Substances with more than one functional group attached to the perfluoroalkyl chain are also included.

1. Perfluorinated cyclic aliphatic substances; CnF2n-1-R, R-CnF2n-2-R’; n≥3; R, R' as defined above
Example:



This category includes in principle the same range of functionalities as the previous group. The only difference being that the perfluoroalkyl groups contains a cyclic structure.

1. Aliphatic perfluoroalkyl ethers, linear or branched, saturated or unsaturated;
R-CnF2n-O-CmF2m-R’; n, m ≥1; R, R' as defined above
Examples:



This category includes the full range of functionalities, including side-chain and backbone fluorinated polymers and polymers with perfluoroalkylether backbones.

1. Perfluoroalkyl amines; N(CnF2n+1)(CmF2m+1)(CxF2x+1); n, m, x ≥1

Example:



**Polyfluoroalkyl substances**

Substances containing at least one aliphatic group wherein several but not all of the hydrogen atoms attached to carbon have been replaced by fluorine in such a way that they carry at least one -CF2- or -CF3 element.

1. Aliphatic polyfluorinated substances, linear or branched, cyclic, saturated or unsaturated; R-CnF2n-R’ or R-CnF2n-xHx-R’; n, x ≥1; R, R' as defined above

Examples:


This category includes a broad range of different substances. It is similar to group 3 above, but in addition to the per- or polyfluoroalkyl units, the substances may also contain non-fluorinated fragments. In principle, about any possible chemical group can be attached to a perfluoroalkyl chain. This category includes e.g. fluorotelomer substances (n : 1 and n : 2) and their derivatives, semi-fluorinated alkyl substances, hydrofluorocarbons and hydrofluoroolefins (used in refrigerants), substances with perfluoroalkyl groups attached to aromatics, PFCA- and PFSA-derivatives (usually prepared via the corresponding alkanoyl fluoride or sulfonyl fluoride substances), and side-chain fluorinated polymers, etc.

1. Aliphatic polyfluorinated ethers, linear or branched, saturated or unsaturated; R-CnF2n-xHx-O-CmF2m-yHy-R’; m, n, x, y ≥1; R, R' as defined above

Examples:


This category includes some of the more novel PFAS substances developed to replace substances like PFOA and PFOS. However, the new alternatives also tend to be persistent or degrade to persistent PFASs in the environment.

1. Hydrofluoroethers; R-CnF2n-O-CmH2m-R’; n, m ≥1; R, R’ as defined above, including side-chain fluorinated polymers

Example:



1. Fluoropolymers, polymers with a poly- or perfluorinated backbone

Example:



This category includes a range of different polymers prepared from different monomers or mixtures of monomers, including homopolymers from the following monomers: CF2=CF2 (PTFE); CF2=CH2 (PVDF); CF2=CFCl (PCTFE); and co-polymers from the following monomer combinations: CF2=CF2 + CF2=CF–O–CnF2n+1 (PFA); CF2=CF2 + CF2=CF–CF3 (FEP); CF2=CF2 + CH2=CH2 (ETFE); CF2=CF2 + CF2=CF–CF3 + CF2=CH2 (THV), etc. Perfluoropolyethers (PFPEs) with a polymer backbone of repeating units of -CnF2n-O-CmF2m- are included in this group.

1. Side-chain fluorinated polymers

Example:



The side-chain fluorinated polymers include a range of different polymers based on standard polymer chemistry with different per- or polyfluorinated side-chains attached to the polymer backbone. Examples include acrylate based polymer backbones with fluorotelomer side-chains (like above) and similar solutions based on urethane linkages of the side-chains to the backbone.

**Differentiation between fluoropolymers and side-chain fluorinated polymers**

Large quantities of the low molecular PFASs are used to produce targetly designed polymers. In general, these polymers belong to two different polymer classes: fluoropolymers and side-chain fluorinated polymers (SFPs). Fluoropolymers, such as polytetrafluoroethylene (PTFE), have a carbon-only polymer backbone where fluorine is directly attached to the backbone carbon atoms. SFPs consist of a non-fluorinated polymer backbone with fluorinated side-chains. Non-fluorinated side-chains can be present as well. The fluorinated side-chain is typically composed of a terminal perfluoroalkyl moiety, a spacer and a linker (Buck et al., 2011; Henry et al., 2018).

1. **Considerations related to persistence for all PFAS in scope**

The carbon-fluorine bonds are one of the strongest chemical bonds in organic chemistry. This means substances containing this chemical bond resist degradation when used and also in the environment. All PFASs subject to the description above (as defined in Section II.) are, or ultimately transform into, persistent substances. Perfluorinated chemicals are thermally, chemically and biologically highly inert. Due to the very strong carbon-fluorine bound, these substances can resist degradation by acids, bases, oxidants, reductants, photolytic processes, microbes and metabolic processes (Parsons et al., 2008; Schultz et al., 2003; Siegemund et al., 2000).

Persistent substances are substances that fulfil the P/vP-criteria according to REACH Annex XIII.

Relevant are these fluorinated substances, which are emitted into the environment (during all life cycle stages) and are not able to degrade under environmental conditions.

1. **Stakeholders, addressees of the questionnaire**

Manufacturer: means any natural or legal person established within the Community who manufactures PFAS, PFAS-containing mixture or article within the Community;

Importer: means any natural or legal person established within the Community who is responsible for the import of PFAS, PFAS-containing mixture or article which is the physical introduction into the customs territory of the Community

Distributor: means any natural or legal person established within the Community who only stores and places on the market PFAS, on its own or in a preparation/mixture or article, for third parties

Downstream user: means any natural or legal person established within the Community, other than the manufacturer or the importer, who uses PFAS, either on its own or in a preparation/mixture or article, in the course of his industrial or professional activities. A distributor or a consumer is not a downstream user.

1. **References**

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1. **Abbreviations**

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| PFBA | perfluorobutanoic acid, C4-PFCA |
| PFBS | perfluorobutansulfonic acid |
| PFCA | perfluoroalkyl carboxylic acid/ perflouroalkyl carboxylate |
| PFHxA | perfluorohexanoic acid, C6-PFCA |
| PFHxS | perfluorohexasulfonic acid |
| PFOA | perfluorooctanoic acid, C8-PFCA |
| PFOS | perfluorooctansulfonic acid |
| PFSA | perfluoroalkyl sulfonic acid |
| TFA | trifluoroacetic acid |