CHEM TRUST, CLIENTEARTH, EEB and IPEN 2nd submission to the REACH restriction: PFHxA, its salts and related substances

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The undersigning organisations would like to provide further comments to strengthen the restriction proposal on the following topics:

- **Threshold values.** For articles, the proposed threshold values should be replaced by a single value of the order of 1 µg/m2 of extractable substances in scope, or, alternatively 3 ppb. The exact value, however, should be derived by independent experts based on real data and using a transparent methodology. In the following, we explain and justify that such a threshold is both necessary for the effectiveness of the restriction and feasible with validated, broadly available analytical methods. We also refute claims by industry stakeholders that although there are methods that can register concentrations lower than the suggested limit values, they are not applicable to all matrices and cannot be accessed in practice by enforcement authorities.
- **Alternatives.** Many fluorine-free alternatives have been omitted in the dossier. We provide here (section 2) a list of substances and of cases of practical uses that should be considered.

- **Labelling.** Articles and mixtures for claimed essential uses benefitting from a derogation or a transition period under this restriction should be labelled; this way the purchaser can make an informed choice and proper waste management can be ensured.

1. The threshold values

In our contribution to the first phase of the public consultation, we have highlighted the lack of transparency in the dossier on how the proposed threshold value for PFHxA-related substances was derived; we proposed that such derivation is based on transparently reported data and a transparent assessment performed by independent experts.

We have also questioned the appropriateness of a threshold value expressed as a concentration (in ppb) and of the proposed value of 1000 ppb.

In the present submission, we provide more information on the purpose of the threshold value as well as considerations regarding practical enforcement using analytical methods.

1.1 Intentional use vs. contamination

The PFASs in the scope of this restriction can be present in articles because of intentional use, or because of contamination: this contamination, in turn, can originate in use of contaminated sources (such as contaminated water) or from process related contamination. The latter may arise when equipment is insufficiently cleaned between production batches, in a factory that uses different types of surface treatments, e.g. a C6-based treatment and a fluorine-free one.

The two types of unintentional contamination will result in very different types of fluorinated residues:

- Residues from contaminated water are dominated by soluble non-polymeric species present from environmental contamination; these may be PFHxA, PFOA and PFAS but will rarely include e.g. a side-chain fluorinated (meth)acrylic polymer. Switching water sources is not practical in most cases; however, concentrations of such contaminants are likely several orders of magnitude lower than those from process contamination or from intended uses.

- Residues from process contamination will be dominated by the molecular species present in the mixture used to treat the surface. This process-related contamination can be very strongly reduced by improved management processes and can be monitored analytically.

1.2 The purpose of the threshold value

The purpose of this value, as described by the dossier submitter, is to distinguish articles in which the substances in scope have been used with intention ("intentional use") or originate from poor industrial hygiene ("process contamination") from those where PFASs remain on surfaces due to use of polluted water.

The purpose of this value is not to detect the presence of PFASs in an article, which would depend on the limit of detection (LoD) of the analytical method used. The most sensitive techniques would detect any presence of fortuitous residues and would not serve the purpose of the restriction well.

The thresholds and analytical methods used to enforce a restriction must be simple and fast (to quickly test goods being put on the market) and reliable (to confirm whether or not goods caught in a test effectively breach the restriction). We explain a potential pragmatic concept in section 1.4. that would allow to distinguish intentional and unintentional use of PFHxA in articles while ensuring a higher level of protection to people and the environment.

1.3 Ratio or surface concentration

Most articles in the scope of this restriction are surface-treated articles: food contact paper, photographic film and textiles. Light wrapping papers have densities of the order of 50 g/m2, whereas a finished outdoor jacket or fabric for tents easily weighs 300 g/m2. The outer leather in outdoor shoes has densities around 2000 g/m2. The thickness of films necessary to impart repellent properties does not directly depend on the thickness of the substrate.

A heavy and a light substrate may have the same amount of surface treatment (in film thickness, or in mass per surface unit) to reach the same technical properties; however, their calculated overall concentrations (in ppb) will differ because of the type of the substrate. The same surface treatment may be banned under the restriction on a light substrate while being allowed on a heavier substrate – whereas environmental risks from both are likely similar. A metric describing surface concentration (e.g. in mg/m2) will more usefully capture the essence of a surface treatment.

As an example, recent total organic fluorine (TOF) analyses on a selection of food packaging items shows that a moulded fibre takeaway box and a bakery paper bag have a similar TOF concentration in ppm or mg/kg (see Table 2[1], Independent Chip Shop sample: 750 mg/kg dw and

[1] Dinsmore, K., 2020. Forever chemicals in the food aisle. PFAS content of UK supermarket and takeaway food packaging. *Fidra report.*

Pret a Manger: 710 mg/kg dw). But when looking at surface concentration, the concentration of the moulded fibre box is 10 times higher than the paper bag (2290 µg/dm2 dw vs 271 µg/dm2 dw respectively), suggesting that the moulded fiber box had a higher amount of surface treatment than the paper bag. However, looking only at weight concentrations this would not have been evidenced as the moulded fibre box is heavier per area unit than the paper bag.

We recommend that the DS and ECHA's committees check and compare both avenues and conclude on the most appropriate metric, using data on concrete examples of surface-treated articles.

1.4 Total or extractable fluorine?

To quantify PFAS in different matrices, there are two main types of analytical techniques and which can in some cases be coupled:

- Total fluorine (TF) methods[2]: These methods are used to determine the total amount of fluorine atoms present in a material. They tend to be methods of high validity and accuracy, but they are not very sensitive. They generally inform quantitatively about the amount of fluorine present, but not about the exact nature of the substances (such as C6 or C8, carboxylic acid or amide). They are more expensive and some require apparatus that is not available in many analytical laboratories.
- Extractable fluorine (EF) methods: in these methods, "loose" molecules (i.e. those not linked to an insoluble molecule such as a polymer, or firmly embedded within a matrix) are extracted with a solvent and identified and quantified using certified standard samples. Equipment used is generally LC-MS/MS equipment available in many industrial and public laboratories and already used for restriction enforcement[3].

All fluorinated molecules at the surface of an article contribute to repellence, especially those covalently bound. In this sense, TF methods are the most relevant and they should be used to determine compliance with the restriction's terms. As noted above, the threshold value to be applied should be derived from transparently assessed data. Effective, but not necessarily fully representative, values for food contact materials ranged from 500 µg/g upwards, i.e. 500 000 ppb. Detection limits reported a few years ago for some of the reported techniques were of the order of a few thousand ppb; it may thus be assumed that with suitable validation and optimisation (e.g. of the size of the samples used) the proposed 1000 ppb and much lower concentrations could be

[2] A recent paper listing and comparing some of these methods: L. Schultes et al. (2019) Environ. Sci. Technol. Lett. 6 (2), 73-78.

[3] Identification and quantification of PFASs is complicated by the absence of a UV-active chromophore, limiting the use of simple HPLC without mass spectrometry. However, LC-MS techniques are already in use, e.g. in restriction 56. *See Compendium of analytical methods. Recommended by the Forum to check compliance with Reach annex xvii restrictions.* March 2016 Version 1.0

reliably measured according to the criteria of official guidance[4]. There has been fast progress in TF methods: Combustion Ion Chromatography is nowadays a common technique and it can be used reliably on virtually all matrices[5]. Its sensitivity is very high: concentrations as low as 0.05 µg F/kg (ca. 65-90 ppb of PFASs) are reported routinely by analytical specialist company Eurofins[6]. The advantages of the combination of TF and EF methods are also explained there.

Given the high cost and lower sensitivity and availability, TF methods can be usefully complemented with EF methods. Thanks to their simplicity and availability, EF methods can serve at least two purposes:

- Screening of articles being placed on the market. Enforcement authorities can relatively easily screen imported goods with such methods. Suspected non-compliant goods on the basis of EF could be subsequently double-checked using TF methods.
- Setting technical specifications for levels of process contaminations between importers and manufacturers of surface-treated articles (as in the example by the Fenix group cited below).

The content of extractable fluorine is obviously generally much lower than the total fluorine content, hence a threshold value on EF must be much lower than on TF. As we have requested in our 1st submission into the public consultation, such a value should be derived transparently and from good quality data.

Sensitivity of EF techniques is high and many different constituents can be quantified at the same time at concentrations at least as low as a few ppb as validated in the case of outdoor jackets[7]. Such techniques are also in use by outdoor companies that have phased out fluorinated water repellents, as in the case of Fenix Outdoor (brand holder for Fjällräven, Globetrotter and others). Their technical specifications[8] materials restrict PFCs to detection limits in textiles, following an EF method developed by commercial laboratory Eurofins. Detection limits for PFOA and PFOS have been stated as 5 ppb and 1 µg/m2 (ca. 3 ppb for many textile materials), respectively. Detection limits for the many other PFASs specified by Fenix are expected to be in a similar range. It should

4 *Methodology for recommending analytical methods to check compliance with REACH Annex XVII restrictions.* March 2016 Version 2.0.

5 The Australian National Environmental Management Plan for PFASs (current version: January 2020) recognises CIC as "the most common [TF] method available" and recommends it for determination of total organic fluorine in waste (p. 87). A method that can be used on a matrix as ill-defined as waste can be used on any commonly encountered substrate.

6 The list and descriptions of analytical tests by Eurofins are available here: https://cdnmedia.eurofins.com/apac/media/604346/analytical-method-summaries_jan-2020.pdf

7 C. Gremmel, T. Frömel, T.P. Knepper (2016). Systematic determination of perfluoroalkyl and polyfluoroalkyl substances (PFASs) in outdoor jackets. Chemosphere 160, 173-180.

8 See sections 7.2.25-27 and Appendix 7 in: FENIX OUTDOOR Chemical Guideline and Restricted Substances List(RSL). 2018

be noted that these are LoDs obtained by routine methods from commercial laboratories and as such could be easily applied by many companies and border enforcement agencies.

As demonstrated in the literature, more sophisticated equipment and methods can drive down LoD and LoQ to even lower values than a few ppb - the essence of these data is to show that the 1000 ppb limit proposed by the dossier submitter:

- Is not based on data differentiating intentional and non-intentional uses;
- Does not reflect widely used and available analytical techniques;
- And therefore does not serve the purpose of this restriction.

1.5 Sensitivity and validity of different techniques

Identifying and reliably quantifying PFASs (hence also those in scope of this restriction) is not a sinecure. PFASs lack the analytical signatures that would allow for easy recognition of the F11C5-C(O)O- moiety in PFHxA or the F13C6-CH2-CH2- in the 6:2 fluorotelomer substances: no simple flame test (as for chloro and bromo derivatives), low volatility and solubility for covalently bound entities (hampering GCMS, HPLC and LC-MS methods), no UV-vis chromophore, no presence of atomic ions (for adsorption spectra or ion chromatography), no specific isotopic signature for mass spectrometry.

Simple soluble species like the PFHxA anion itself can be detected reliably in drinking water down to 0.002 ppb, as stated e.g. in appendix E.1 of the Annex to the Annex XV dossier. However, the appendix does little to look at the analytical techniques available and able to serve the purpose of this restriction, as most of the promising techniques are not mentioned there.

Detection of specific PFASs in articles and mixtures does not reach these levels of sensitivity, yet proven and validated LoDs and LoQs are as low as several ppb - at least two orders of magnitude lower than the proposed thresholds of 25 ppb (PFHxA and its salts) and 1000 ppb for the sum of the other substances in scope. As noted above, TOF-CIC can be used to report concentrations as low as the order of 65-90 ppb, and with extraction methods, single PFASs methods can be quantified to concentrations down to 5 ppb. This is routinely done by co-elution and co-injection of known concentrations of isotopically labelled PFASs in LC-MS.

Although esp. TOF-CIC is used much more often on samples such as soil, water or living tissue rather than on textiles, photographic films or PPE, when a new matrix is introduced for the first time, validation for this matrix can be performed rapidly by anyone skilled in the technique. Overall, both methodologies can be validly applied to many different matrices after limited analytical checks and calibrations:

- In TF methods such as TOF-CIC, this is achieved thanks to the high and controlled combustion temperatures, which decompose any organic (natural or artificial, as well as many inorganic) matrices and thereby liberate all PFAS-related fluorine contained therein. Corrections for inorganic fluorine (e.g. fluoride or hexafluorophosphate) are routinely made. For this reason, TOF-CIC results are highly matrix-independent and they do not overestimate fluorine content – which would lead to undesirable false positives.
- Extraction methods, on the other hand, are also robust with respect to the matrix used: PFAS are mostly present at the surface, and the organic solvents used generally swell the matrix and ensure mobility of the extractable, unbound species. Also here, any non-extracted PFAS, if ever, would not lead to an over-estimation (and thus to false positives) of the true extractable PFAS content. Also, given the stable nature of most PFASs and the chemically and toxicologically meaningful use of the concept of related substances in this proposal, specific PFAS detected and quantified would not lead to any false indictment of an article or its seller.

1.6 Proposal for an enforcement strategy

Claims that appropriate methods are not available or not validated are rife, but mostly unspecific. We urge the dossier submitter and ECHA's committees to rely on the opinion of independent experts in the topic and to request specification when allegations are made. The peer-reviewed literature actually suggests that such claims are false. We recommend a recent review (including many references) on available analytical methods, including their suitability for identification and quantification, as well as sensitivity (LoD) [9].

Proper validation of tests is paramount for decent enforcement of a restriction. ECHA's guidance on analytical methods provides a practical framework for validation: where validation of sufficient quality is demonstrably not available yet, a programme to ascertain proper validation should be set up.

2 The analysis of alternatives

2.1 Manufacture of fluoropolymers

Cf. section 2.5.1.1 of the Annex XV report, p. 47.

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[9] A. Koch et al. (2020) Towards a comprehensive analytical workflow for the chemical characterisation of organofluorine in consumer products and environmental samples. Trends in Analytical Chemistry 123, 115423

The SEAC draft opinion (p. 22) wisely questions the validity of this. The 1st NGO submission into the Public Consultation mentions this, as well as the likely possibility that fluorosurfactants can be dispensed with.

2.2 Textiles

Cf. section 2.5.1.2 of the Annex XV report, p. 49.

Textiles may be used:

- in amateur or professional uses,
- as PPE or not as PPE,
- for water or oil repellency, or both
- with durable (i.e. life-time) repellence or not.

Whenever it is claimed that PFAS in scope cannot be replaced, the precise uses this applies to should be clarified. Generic terms like "textiles" are often not specific enough – the result of vague terminology is that successful phaseout of fluorinated surface treatments by substantial industrial sectors are overlooked. We provide more details here on the sector of outdoor textiles, which has booked many successes and successfully implemented fluorine-free surface treatments. We urge the authorities not to weaken an ambitious and necessary restriction proposal by adding transition periods or exemptions for uses that have largely disappeared from the market.

2.2.1 Water repellency only: evidence from suppliers

Whenever only water repellency is required, many alternatives exist and performance is equivalent to C6- PFASs. A recent preliminary report identified more than forty of them[10]. Many of them have been on the market for several years, often by the important players on the market providing PFAS-based repellents:

- Archroma has marketed its Smartrepel® Hydro since 2015 as a "positive alternative" and of "a level of performance […] similar to C6-based solutions", based on standardised test data[11]. Water repellency is "exceptional, durable"[12]; oil repellency is obviously not claimed.
- Rudolf's Bionic-Finish® Eco has been on the market for more than 10 years and has been praised for not "compromise[ing] on functionality and performance" by downstream user

10 Amec Foster Wheeler 2020, The use of per- and polyfluoroalkyl substances (PFAS) and fluorine-free alternatives in textiles, upholstery, leather, apparel, and carpets. Presentation slides state the number of 40-45. Older lists of such products can be found on p. 20 of this DK EPA report.

11 Archroma's press release of 19/03/2020.

12 Archroma's website.

Sympatex[13]. Rudolf have marketed a Ruco®-Dry Eco Plus, since 2015 as an improvement on their first- generation product allowing for the "sensible and sustainable withdrawal from fluorine chemistry"[14]. The portfolio is complemented with fluorine-free polysiloxanes such as ®RUCO 1410.

- Maflon describes both their PFAS-based Hexafor® products as their fluorine-free Hydrosin® NF series as imparting "excellent [and] durable water repellency", and stain release[15].

- Daikin's fluorine-free Unidyne XF series has been on the market for a few years: it boasts the highest possible rating for water repellency[16] and excellent washing machine durability, and these products are "now widely used throughout the global textiles industry"[17].

This list of major players' broadly applicable fluorine-free DWR products is complemented with products by several other companies. Although the above descriptions have a slight marketing tinge, this information should be taken seriously as long as no data to the contrary are made available. Also here, an assessment by independent experts would serve the purpose of the restriction.

More examples of commercially available alternatives can be found on ChemSec's Marketplace website.

2.2.2 Water repellency only: evidence from users

Another way to assess suitability and market penetration of fluorine-free surface treatments for water repellency is to consider cases of textile companies having phased out perfluorinated chemicals.

According to a report[18] by outdoor and sportswear associations from Germany, the EU and the US, many brands were "currently [before or in 2014] sourcing alternative technologies to replace PFC-based DWRs". The report clarifies that "fluorine-free finishes do represent a drop in performance but can usually be considered acceptable in all but the harshest conditions". The report gives a list of major outdoor wear manufacturers who had already phased-out fluorine-containing treatments, or who had committed to do so by 2015 or 2020.

A few examples, which generally also count for non-garment articles such as tents or bags:

- Fjällräven committed to elimination of fluorinated chemicals by 2015. The 2018 sourcing guideline[19] of Fenix, Fjällräven's mother company, explicitly forbids the use of PFCs in textile, leather, accessories and packaging.

- Several years ago, Haglöfs committed to be fluorocarbon-free by 2020 and have currently reached 95% of their goal[20].

13 Rudolf's website.
14 Rudolf's website.
15 Maflon's website.
16 Daikin's website.
17 Daikin's website.
18 BSI, EOG and Outdoor Industry Association, available here.
19 Available here, section 7.2.27.
20 Haglöfs website.

- Jack Wolfskin committed to phasing out PFCs by 2020 and reached their goal for all clothing and bags by summer 2019[21]. Deuter's product range has been PFC-free since 2018[22].
- Companies such as The North Face, Deuter and Vaude[23] are planning to phase out all fluorinated DWRs in 2020 and currently appear to be on track.

2.2.3 Repellency of substances other than water

In these rarer cases, non-fluorinated substances that meet the product requirements (to be distinguished from any customer specifications) are likely not available for all uses. In this scenario, several aspects must be addressed:

- Whether the use foreseen is essential or not[24]; for truly essential uses a derogation should be agreed.
- Whether the user has adequate information on the presence of PFAS and proper disposal options (i.e. product labelling).

The above-cited report (footnote 14) clarifies (p. 19) that "oil, dirt and soil repellency are not considered essential for sports/outdoor fabrics", and that "dirt/soil repellency was the least important property in a DWR treated garment".

2.3 Fire fighting foams

Cf. section 2.5.1.3 of the Annex XV report, p. 52. describes available alternatives to fire fighting foams containing PFHxA. It mentions that alternatives are available already for almost all uses and identifies two uses where they consider that temporary derogations are necessary: certain uses in the petrochemical industry and for certain uses in defence applications.

2.3.1 For large storage tanks

The Annex XV dossiers proposes (section 4, p. 80) a 12-year exemption for large storage tanks.

Two recent reports from IPEN[25] and from the European Commission and ECHA[26] include information on available alternatives and the experience of Equinor, a large petrochemical

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21 Jack Wolfskin website.

22 Deuter's website.

23 The North Face website, Vaude website.

24 A thorough independent assessment based on the authoritative definition of essentiality from the Montreal protocol is provided in I.T. Cousins et al. (2019), *Environ. Sci.: Processes Impacts*, 21, 1803

25 IPEN 2019/Stockholm Convention COP-9 White Paper, The Global PFAS Problem: Fluorine-Free Alternatives As Solutions. https://ipen.org/sites/default/files/documents/global_pfas_exec-sum_en.pdf

26 European Commission DG Environment / European Chemicals Agency (ECHA)The use of PFAS and fluorine-free alternatives in fire-fighting foamsFinal reportSpecific contracts No 7.0203/2018/791749/ENV.B.2 and ECHA/2018/561 https://echa.europa.eu/documents/10162/28801697/pfas_flourine-free_alternatives_fire_fighting_en.pdf/d5b24e2a-d027-0168-cdd8-f723c675fa98

company in Norway that has successfully substituted AFFF in its offshore and onshore facilities and operations, including storage facilities. They state “We have investigated and verified all aspects of the fluorine-free foam (F3) used, RF1-AG, with respect to operational firefighting efficiency, health and safety, freeze protection, aging, etc. We regard the new fluorine-free foam as a fully acceptable and even better replacement for AFFF” (IPEN,2019 p 64).

2.3.2 For defence applications

The Annex XV dossiers proposes (section 4, p. 80) an exemption for defence uses that is subjected to an annual report and revision clause.

The European Commission and ECHA report concludes “Alternatives are less well established in the military sector, but it has been indicated by stakeholders that alternatives are considered to be feasible, although not many have yet been certified or implemented by users. The military applications are similar to those seen in airports and municipal fire brigades and the foams used are, after the necessary testing and adjustment of equipment, considered to be useful for military applications as well”.

Also, a report by IPEN on fluorine-free fire fighting foam (F3) alternatives AFFF[27] describes how some European military users including the Danish and Norwegian Armed forces have moved to F3 foams, with the Royal Danish Air Force transitioning to F3 foams several years ago.

2.4 Chrome Plating

Cf. section 2.5.1.8 of the Annex XV report, p. 63.

The report conclusions on the alternatives for fluorinated surfactants in chrome plating (even the Cr(VI)- based hard chrome plating) are vague and appear to give equal credit to those who claim that satisfactory alternatives are not available and to those who report success.

The cited UNEP report[28] states in point 145 that “non-fluorinated alternatives for hard metal plating […] available on the European market […] appear functional with some slight process changes.

27 IPEN 2018/POPRC-14, White paper, Fluorine-free firefighting foams (3F) – Viable alternatives to fluorinated aqueous film-forming foams (AFFF). https://ipen.org/sites/default/files/documents/IPEN_F3_Position_Paper_POPRC-14_12September2018d.pdf

28 UNEP/POPS/POPRC.12/INF/15/Rev.1, available here.