

EEB CONTRIBUTION TO CALL FOR EVIDENCE SUPPORTING AN ANALYSIS OF RESTRICTION OPTIONS FOR PFAS

31 July 2020

Lessons learnt from previous PFAS restrictions and the high political support for a broad restriction of PFAS at EU and national levels set the scene for putting forward a protective restriction proposal. Public pressure is also strong after areas and people have been affected by PFAS pollution in the EU. NGOs have campaigned to raise awareness on the issue, and the recent *Dark Waters* movie has shed the light on the PFAS issue, also impacting the US. With this process, the EU will be watched around the world on its handling of the PFAS restriction. Robust science needs to feed into the decision making, and regulatory guarantees must be fully used (such as the use of the precautionary principle throughout the whole process, consideration for the international law concept of essential uses, the principle of reduction of pollution at source) to propose a restriction that protects human health and the environment as foreseen in the REACH regulation (recital 87).

The EEB thanks the national authorities of Germany, the Netherlands, Norway, Sweden and Denmark for considering a broad restriction proposal for PFAS. In this submission, we provide information on uses and on the issue of threshold values.

Information on uses

ad V. Questions - Section A - Specific Uses: Lubricants and greases

Fluorinated or fully fluorinated solvents are omitted from the questionnaire, but they fulfil the definition of PFAS as used in this restriction proposal. As they are commercially sold as solvents to remove lubricants and greases, we submitted the information below in section V.

- PF-NMM (perfluorinated *N*-methylmorpholine) is produced by 3M and sold as PF-5052 as a solvent to remove fluorinated greases and lubricants. It is registered under REACH for the tonnage band 100-1000 t/y; EC 206-841-1, CAS 382-28-5. A related substance (mixture of PF-*N*-isopropyl morpholine and PF-*N*-*n*-propyl morpholine) is registered 100-1000 t/y as EC 473-390-7 (see attached TDS).

ad V. Questions - Section A - Specific Uses: F-gases (PFC, HFE, HFC/HFO, HCFC/HCFO) and refrigerants

A use not considered in the questionnaire is as a propellant gas, whereas such uses lead – by definition – to all but complete release of the PFAS into the environment.

Applications that do not fit any section of the questionnaire:

- **Flame retardant for polycarbonate:** PFBS-K (EC 249-616-3) is marketed by 3M as a flame retardant for clear polycarbonate under the commercial name FR-2025. The fluorinated tails of the substance will “stick out” of the polymer matrix, the hydrophilic heads being anchored in the surface. Thereby a molecular layer of non-combustible material is created. Articles may release PFAS during service life and at the waste treatment stage (see attached TDS).
- **Cover gas** for magnesium casting and heat transfer fluid: PF-isopropylethylketone (EC 436-710-6), a low-boiling perfluorinated solvent is used to provide an inert gas blanket over magnesium casting operations. The registered tonnage bands indicate high volume uses. It is marketed by 3M as Novec 612 (as cover gas) and Novec 649 (as a heat transfer fluid), as well as by other registrants (see attached TDS).

Threshold values

1.1. Process for deriving the threshold

Former restriction proposals on PFOA, PFHxS, PFHxA have established or proposed threshold values of 25/ 1000 ppb (for example 25 ppb for the sum of PFHxA and its salts or 1000 ppb for the sum of PFHxA- related substances) although the dossier submitters and the opinions from the RAC and SEAC Committees did not reveal how these values were derived, and in what way they would best serve the purpose of the restrictions (addressing an unacceptable risk, Reach Art. 68(1), or indeed the higher-level conclusions of the Council of the EU of June 2019 (“to eliminate all non-essential uses of PFAS”).

For the present restriction proposal, EEB urges the national and European authorities to adopt an evidence-based approach, and to document the findings transparently. Independent experts (i.e. highly knowledgeable people without any conflict of interest) should assess data needs, all relevant data and their documentation.

Experience from earlier restriction proposals shows that such scientific and objective approaches are the exception rather than the rule. In the following, we submit some examples of comments already provided in earlier public consultations.

For example, information in section 2.4 of the Annex XV dossier of the PFHxA restriction unspecifically calls the limit value of 1000 “feasible” and points to Annex G, the results of the stakeholder consultation. It uses a false alternatives fallacy (“*threshold of zero [...] most effective, [...] [but] not feasible and enforceable (e.g. due to detection limits)*”).

This casts doubt on whether this value was derived specifically for the chemicals under consideration in this restriction proposal or has been re-used from previous restrictions of other PFAS (Eg. PFOA, PFHxS).

Furthermore, Annex G of the PFHxA dossier reveals that the stakeholder consultation included *"companies as well as associations"* (Annex to the dossier, p. 214). This casts further doubt on the justification of this value:

the stakeholder group did not include independent experts.

- Information in scientific and technical literature seems excluded.
- Information from the stakeholder consultation is not included. It is unclear whether the consulted stakeholders were asked *"whether a threshold of 1000 ppb is feasible"* (although it is not clear what *"feasible"* means) or to communicate effective concentrations of the substances in scope in products (esp. mixtures and articles).
- No *ad-hoc* analyses were carried out. With modern analytical tools, it would have been proportionate to determine relevant levels of PFASs in currently existing products, especially in those giving rise to high release potential.

We believe that the restriction proposal should include a transparent justification on the data and scientific justification for deriving the proposed threshold in order to avoid repeating such shortcomings.

1.2. Regarding the outcome

The figure of 1000 ppb (i.e. 1 ppm) may appear low and therefore effective at first sight. However, the threshold must take into account the specific properties, uses and releases of PFAS to avoid a meaningless restriction that would not force a major shift towards safer alternatives in order to protect human health and the environment. When those elements are taken into account, the logical conclusion is that this limit should be significantly lower by several orders of magnitude.

Many applications, especially in articles, are surface treatments with high release potential. These surface treatments are applied as thin layers to thicker substrates and as such represent only a small part of the total mass. Even on light substrates, such as an outdoor jacket, scientific results and a back-of-the-envelope calculation show that the value of 1000 ppb is too high to force companies to

change their current practice by substituting or meaningfully reduce the use of the substances concerned. A more justifiable threshold based on available data and information would be 2 ppb (according to evidence we further detail in the next paragraphs). In any case, the final threshold should be derived on the basis of information consolidated by experts devoid of any conflict of interest, using a fully transparent approach.

Alternatively, a concentration threshold may be derived for the relevant layers of the treated materials. Surface treatments are by definition 1) non-uniformly distributed and 2) present in the outer layers of the material. Therefore a concentration threshold on the surface (e.g. the top 5 μm) would be more meaningful, while also simplifying material sampling and sample preparation.

A study by Gremmel et al. [2] analysed extractable contents of fluorotelomer alcohol moieties (6:2, 8:2 and 10:2) in fifteen outdoor jackets (of which one being PPE). Fourteen of the jackets had total extractable fluorotelomer concentrations well below 1000 ppb, ranging as low as ca. 10 ppb! As the value in the paper are expressed in $\mu\text{g}/\text{m}^2$, a more useful metric for surface treatments, we converted them to ppb, assuming a weight of 450 g per jacket and a surface area of 1.4 m^2 , based on real measurements. It should be noted that most of the jackets in the Gremmel study were coated with 8:2 chemistry rather than the 6:2 chemistry in scope here; this may make a subtle difference. More importantly, the discrepancy among the studied jackets, and between real values and this dossiers' assumptions, by more than two orders of magnitude demonstrates:

- That the 1000 ppb threshold is very likely wrongly derived (even a "most-plausible-case" scenario of an outdoor jacket, as a rather light item).
- That available scientific literature provides evidence to support a much lower threshold.
- That many manufacturers, at least 10 years ago, had poor process control and used either excessive amounts (up to 100-fold between the jackets with the highest and the lowest extractable FTOH concentrations in articles of the same function), or inefficient types of treatment. Regarding SEAC's prerogatives, this suggests that the cost of PFAS is likely so minor in the total cost of articles that manufacturers do not even try to optimise it – this situation is unlikely to have changed since then.

Furthermore, a recent study by I van der Veen et al. [3] showed that the concentration may increase during the use. Increased concentrations of several PFAS (including PFHxA) in textiles were observed after weathering. Concentrations of PFHxA increased after weathering in 8 out of the 13 samples as much as two orders of magnitude, surpassing by far the proposed limit value of 25 ppb. The study

highlights that the increase in concentrations of PFASs due to weather conditions might not only have an environmental impact, but also a health impact as the use in outdoor clothing may also form a direct exposure route to humans, since there is dermal contact with the textiles. In order to take into account the fact that the amount of PFHxA tested on the shelf might not reflect the value in real life a conservative threshold should be established.

For articles, we propose a single value of the order of 1 µg/m² of extractable substances in scope, or, alternatively 2-3 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. Industry's claim, 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, has not been justified.

1.3. Intentional use vs. contamination

PFAS 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. The EEB believes that these residues should be considered for the restriction process.

1.4 The purpose of the threshold value

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The purpose of this value 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 1.6 that would allow to distinguish intentional and unintentional use of PFAS in articles while ensuring a higher level of protection to people and the environment

1.5 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, Independent Chip Shop sample: 750 mg/kg dw and 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 wouldn't have been evidenced as the moulded fibre box is heavier than the paper bag.

We recommend that the DS checks and compares both avenues and conclude on the most appropriate metric, using data on concrete examples of surface-treated articles.

1.6 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:** 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 expensive and require apparatus that is not available in most 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.

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 materials¹ 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 reliably measured according to the criteria of official guidance. 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. 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. The advantages of the combination of TF and EF methods are also explained there.

However, 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.

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 stated above, 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 by both academic and commercial laboratories.

1.7 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.

1.8 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 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). 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.

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