Hazard assessment of fluorinated alternatives to long-chain perfluoroalkyl acids (PFAAs) and their precursors: Status quo, ongoing challenges and possible solutions

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ARTICLE INFO

Article history:
Received 17 October 2014
Received in revised form 13 November 2014
Accepted 18 November 2014
Available online xxxx

Keywords:
Short-chain perfluoralkyl acids
Perfluoroether carboxylic acids
Perfluoroether sulfonic acids
PBT assessment
Data gaps
Global contamination

ABSTRACT

Because of concerns over the impact of long-chain perfluoroalkyl acids (PFAAs) on humans and the environment, PFAAs and their precursors are being substituted by alternative substances including fluorinated alternatives that are structurally similar to the substances they replace. Using publicly accessible information, we aimed to identify the status quo of the hazard assessment of identified fluorinated alternatives, to analyze possible systemic shortcomings of the current industrial transition to alternative substances, and to outline possible solutions. Fluorinated alternatives, particularly short-chain PFAAs and perfluoroether carboxylic and sulfonic acids (PFECAs and PFESAs), possess high environmental stability and mobility implying that they have a high global contamination potential. In addition to their potential for causing global exposures, certain fluorinated alternatives have been identified as toxic and are thus likely to pose global risks to humans and the environment. Various factors, particularly the information asymmetry between industry and other stakeholders, have contributed to the current lack of knowledge about the risks posed by fluorinated alternatives. Available cases show that a non-fluorinated substitution strategy (employing either chemical or functionality substitutions) can be a possible long-term, sustainable solution and needs to be further developed and assessed.

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1. Introduction

Long-chain perfluoroalkyl acids (PFAAs) include perfluoroalkyl carboxylic acids (PFCAs, CnF2n+1-COOH) with ≥ 7 perfluorinated carbons and perfluorooalkane sulfonic acids (PFASs, CnF2n+1SO2-R) with ≥ 6 perfluorinated carbons (Buck et al., 2011). Several long-chain PFAAs, particularly perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), and their precursors derived from perfluoroalkane sulfonyl fluorides (PASFs; CnF2n+1SO2-R) and n:2 fluorotelomer raw materials (CnF2n+1 CH2CH2-R), have been used in various industrial and consumer applications for over 50 years, e.g., in the production of polytetrafluoroethylene (PTFE), hard metal plating, or surface treatment of textiles, carpets and papers (details on their production and use can be found in Armitage et al., 2009; Buck et al., 2011; OECD, 2013; Prevedouros et al., 2006; Wang et al., 2014a).

To date, long-chain PFAAs are recognized as global contaminants of high concern, after a decade of research that has shown their high persistence (P), bioaccumulation potential (B), toxicity (T) and ubiquitous distribution in the environment, biota and humans (evidence on their P, B, and T properties is reviewed by OECD (2013)). Driven by concerns about the undesired impacts on humans and the environment, actions to reduce the release of long-chain PFAAs and precursors have been taken by industry and regulators since 2000. Major manufacturers have voluntarily discontinued (3M, 2000a,b) or committed to discontinue the production of long-chain PFAAs and precursors (e.g., US EPA 2010/15 PFOA Stewardship Program; US EPA, 2006). Regulators have additionally enforced nationwide and/or international restrictions on the production and use of several long-chain PFAAs and their precursors. For example, PFOS and related substances based on perfluorooctane sulfonyl fluoride (POSF) were listed under Annex B (restriction of production and use) of the Stockholm Convention on Persistent Organic Pollutants in 2009. Recently, PFOA, its ammonium salt (APFO), and C11-C14 PFCAs were included in the Candidate List of Substances of Very High Concern for Authorisation under the European Chemicals Regulation, REACH (ECHA, 2013).

As a result of these industry and regulatory actions, an industrial transition is taking place to replace long-chain PFAAs and their precursors with other fluorinated and non-fluorinated chemicals (these replacements are referred to as alternatives hereafter). One might expect that the alternatives are less hazardous to the environment and humans than their predecessors. However, determining the hazards and risks of the various alternatives to long-chain PFAAs and their precursors is not
2. What are the known fluorinated alternatives?

Ever since 3M announced a global production phase-out of long-chain PFAs and precursors in 2000 (3M, 2000a,b), numerous efforts have been made to identify and assess fluorinated alternatives. For example, parties to the Stockholm Convention are encouraged to submit information on the alternatives to PFOS and related chemicals in open applications (UNEPC, 2012) and an update is scheduled for late 2014 (UNEPC, 2013a). Z. Wang et al. (2013) reviewed publicly accessible information on fluorinated alternatives and identified over 20 fluorinated alternatives used in various industry branches and consumer products. Known fluorinated alternatives can be categorized into two groups, namely [i] short-chain homologues of long-chain PFAs and their precursors and [ii] functionalized perfluoroalkylpolyethers (PFPEs), in particular perfluoroether carboxylic and sulfonic acids (PFECAs and PFESAs). In brief, the PFECAs and PFESAs are structurally similar to PFCAcs and PFPEs, with an acidic functional group attached to a per- or polyfluoroether chain instead of a perfluoroalkyl chain. The structural differences between known fluorinated alternatives and their precursors are illustrated in Table 1.

3. What are the hazards and potential impacts of the known fluorinated alternatives?

Some fluorinated alternatives (e.g., short-chain PFAs) have been shown to be less bioaccumulative (Conder et al., 2008) and toxic (Borg and Hakansson, 2012). However, our analysis of publicly accessible information reveals evidence that many known fluorinated alternatives may still possess hazardous properties (persistence, bioaccumulation potential, (eco)toxicity, and/or long-range transport potential) and thus may pose risks to humans and the environment. The ultimate transformation products of many fluorinated alternatives (e.g., perfluorobutane sulfonyle fluoride (PBSF) and 6:2 fluorotelomer-based substances) are short-chain PFAs and other substances such as COF₂, COF₂ is highly toxic (CDC, 2011), but is not considered as a perfluoroalkylated alkyl substance (PFAS; Buck et al., 2011); thus, it is not discussed here. Our discussion regarding the hazardous properties of alternatives focuses only on the PFAS-related, stable breakdown products (i.e., short-chain PFAs; PFPCs and PFESAs). The environmental and health-related profiles of these substances are summarized in Table 2; details on each aspect, including references, are provided in the subsections following the table.

3.1. Persistence

Short-chain PFAs are similarly persistent as their long-chain homologues (Parsons et al., 2008; Young and Mabury, 2010). Among PFECAs and PFESAs, there have been only limited studies on the biotic and abiotic degradability of three PFECAs and one PFESA. The insertion of oxygen atoms between perfluorinated chains to form a perfluoroether chain was intended to provide an attackable position, so that the perfluoroether chain might break down eventually into two or more short perfluorinated chains (Buck et al., 2011). Hori et al. (2009) reported that over 40 mol% of C₂F₆OC₂F₇SO₃⁻ and C₆F₁₅OC₂F₇SO₃⁻ were degraded after 6 h in subcritical water at 350 °C in the presence of oxygen (no reaction occurred below 300 °C), whereas almost no loss of C₆F₁₅SO₃⁻ occurred under the same conditions. The other experimental results, however, show that under environmentally relevant conditions perfluoroether chains are similarly resistant to abiotic (photolysis, reactions with OH radicals, and hydrolysis) and biotic degradation as the perfluoroalkyl chains (summarized in Table 3). Although more studies may be needed for a better mechanistic understanding, known PFECAs and PFESAs are likely to be highly persistent in the environment and not easily metabolized in biota.

Table 1

<table>
<thead>
<tr>
<th>Structural differences between long-chain PFAs (and their precursors) and identified fluorinated alternatives that are used to replace long-chain PFAs (and their precursors).</th>
</tr>
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<tbody>
<tr>
<td><strong>PFCA</strong></td>
</tr>
<tr>
<td><strong>Long-chain examples</strong></td>
</tr>
<tr>
<td>C₆F₁₃COOH (PFOA), C₈F₁₇COOH (PFNA)</td>
</tr>
<tr>
<td>C₆F₁₃COOH (PFPA)</td>
</tr>
<tr>
<td>C₆F₁₃COOH (PFHxNA)</td>
</tr>
<tr>
<td><strong>PFCAs</strong></td>
</tr>
<tr>
<td><strong>Long-chain examples</strong></td>
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<td>C₆F₁₃COOH (PFOA), C₈F₁₇COOH (PFNA)</td>
</tr>
<tr>
<td>C₆F₁₃COOH (PFPA)</td>
</tr>
<tr>
<td>C₆F₁₃COOH (PFHxNA)</td>
</tr>
</tbody>
</table>

PFCAs = perfluoroalkyl carboxylic acid, PFSA = perfluoroalkane sulfonic acid, PFAS = perfluoroalkane sulfonyle fluoride, FT = fluorotelomer, PFOA = perfluorooctanoic acid, PFNA = -perfluorononanoic acid, PFHxS = perfluorohexane sulfonic acid, PFOS = perfluorooctane sulfonic acid, PFOS = perfluorooctane sulfonyle fluoride, PFPA = perfluorobutanoic acid, PFHxNA = perfluorohexanoic acid, PFBS = perfluorobutane sulfonic acid, PBSF = perfluorobutane sulfonyle fluoride, PPE = perfluoroether, R = functional group, e.g., —OH.

The fluorinated chain with different lengths and/or shapes is highlighted in **bold** font; atoms other than fluorine attached on the fluorinated chain are highlighted in italic font. Text in parentheses represents the common terminology or commercial name.

Solvay, 2014; Solvay® from Solvay is being used for oil- and grease-resistant packaging to replace previous products such as PASF- and FT-based phosphate diesters (i.e., SAmPAPs and dipAPs). Its generic structure is unknown, but might be similar to the structure reported by Trier et al. (2011).
3.2. Bioaccumulation potential

Short-chain PFAAs are less bioaccumulative in animals and humans than the long-chain homologues (Conder et al., 2008; Z. Wang et al., 2013), but may show higher uptake into the leaves, stems and fruits of plants (Felizeter et al., 2012, 2014; Krippner et al., 2014). Among PFECAs and PFESAs, only serum elimination half-lives of two PFECAs (in rats and mice for GenX; in rats and humans for ADONA) were reported with limited experimental details provided (ECHA, 2014; EFSA, 2011a). The elimination half-lives of PFECAs were shorter than for PFOS and PFHxS, but the elimination was faster from rat and mouse serum than from human serum (Chang et al., 2012; Olsen et al., 2007; Sundström et al., 2012). Rather rapid elimination from rat and mouse serum cannot guarantee fast excretion from higher organisms and humans, [iii] The studies were often conducted with different dosing methods (oral vs. intravenous, single vs. repeated dose) and dosages; thus reported serum elimination half-lives cannot be directly compared between substances.

To establish a conclusive understanding of the bioaccumulation potential of known PFECAs and PFESAs, further studies are needed. Known PFECAs and PFESAs have similar physicochemical properties (high water solubility and air-water partition coefficient; within one order of magnitude range of the values for PFOA and PFOS) as long-chain PFAAs, based on a comparison of the non-dissociated forms of these acids (Gomis et al., 2014). This indicates that, like for PFOA, fish bioconcentration factors may not be the most relevant bioaccumulation metric for these substances (Vierke et al., 2012). The high water solubility might explain the effective excretion of PFOA by fish via gill permeation, facilitated by high water throughput (Vierke et al., 2012). The weight-of-evidence approach used to classify PFOA as bioaccumulative under REACH (by taking measured elevated levels in biota, information on the ability of the substance to biomagnify in the food chain, data from analysis of human body fluids and assessment of toxicokinetic behavior of the substance into consideration: Vierke et al., 2012; ECHA, 2013) may also be applied to PFECAs and PFESAs. We therefore recommend that terrestrial bioaccumulation studies for PFECAs and PFESAs using air-breathing animals be conducted and that biomagnification and trophic magnification factors (BMFs and TMFs) for terrestrial species and food webs, respectively, be derived. Additionally, concentrations in human body fluids as well as occurrence in endangered species and in vulnerable populations should be investigated. Since [i] the levels of these substances in the environment, biota and general population are likely low and challenging to quantify because they have not, to date, been used and released to the environment in large amounts and [ii] analytical standards are not readily available yet, development of alternative tests, e.g., laboratory-based terrestrial bioaccumulation experiments, is urgently needed. Another possibility is to conduct monitoring of terrestrial species close to obvious emission sources (e.g., manufacturing sites) where levels may be more easily detected. High-

### Table 3
Summary of experimental results on the degradability of PFECAs and PFESAs.

<table>
<thead>
<tr>
<th>Structure</th>
<th>CAS no.</th>
<th>Photolysis</th>
<th>OH reaction</th>
<th>Hydrolysis</th>
<th>Biodegradation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF₃OC₂F₄OCF₂COO⁻ (ADONA)</td>
<td>958445-44-8</td>
<td>N.A.</td>
<td>N.A.</td>
<td>0% after 5 days (OECD 111)</td>
<td>Not readily (OECD 301B)</td>
</tr>
<tr>
<td>CF₃OC₂F₄OCF₂COO⁻ (GenX)</td>
<td>62037-80-3</td>
<td>N.A.</td>
<td>N.A.</td>
<td>0% after 5 days (OECD 111)</td>
<td>Not readily (OECD 301B)</td>
</tr>
<tr>
<td>CF₃OC₂F₄OCF₂COO⁻ (EEA)</td>
<td>151772-58-6</td>
<td>N.A.</td>
<td>N.A.</td>
<td>0% after 5 days (OECD 111)</td>
<td>Not readily (OECD 301B)</td>
</tr>
<tr>
<td>CF₃OC₂F₄OCF₂COO⁻ (ADONA)</td>
<td>908020-52-0</td>
<td>0% with UV-VISIBLE light</td>
<td>1.90-4.27%</td>
<td>(Almost) 0%</td>
<td>N.A.</td>
</tr>
<tr>
<td>CF₃OC₂F₄OCF₂COO⁻ (EEA)</td>
<td>151772-59-7</td>
<td>N.A.</td>
<td>N.A.</td>
<td>(Almost) 0%</td>
<td>N.A.</td>
</tr>
<tr>
<td>CF₃OC₂F₄OCF₂COO⁻ (F-55B)</td>
<td>73606-19-6</td>
<td>0% after 2 h irradiation</td>
<td>&lt;5% after 2 h in a UV/H₂O₂ system</td>
<td>N.A.</td>
<td>Not readily (OECD 301D)</td>
</tr>
</tbody>
</table>

N.A. = not available.

- **a** Gordon (2011); no details on the empirical studies were given.
- **b** Hori et al. (2008a); tested in hot water at 80 °C for 6 h; 0 mol% loss of CF₃OC₂F₄OCF₂COO⁻, 1.5 mol% loss of CF₃OC₂F₄OCF₂COO⁻ (with 0.02 mol% formation of F⁻) and 1.6 mol% loss of CF₃OC₂F₄OCF₂COO⁻ (with 0.04 mol% formation of F⁻) were reported, respectively.
- **c** Hori et al. (2012); tested in water maintained at 28 °C with 10 mM S₂O₈⁻ for 24 h; 1.5 mol% loss of CF₃OC₂F₄OCF₂COO⁻ with no formation of F⁻ was reported.
- **d** Hori et al. (2008b); the UV absorption spectrum of the compound is below 230 nm, which is in the UV-C range; the reaction with OH-radicals was tested by UV-visible irradiation (wavelengths >290 nm) in the presence of H₂O₂ (1 M) and by treatment with Fenton’s reagent (1 M H₂O₂ + 5.01 mM Fe²⁺) at pH = 1.7 at 25 °C for 12 h.
- **e** S. Wang et al. (2013); the UV light spectrum in the photolysis study and the H₂O₂ content in the OH reaction study were not reported; with reaction; with O₂ and H₂O₂ was tested, where only limited degradation was observed.
resolution mass spectrometry can be used to identify fluorinated alternatives near to sources and, in the absence of analytical standards, provide semi-quantitative information on levels. Until these studies have been conducted, the possibility that known PFECAs and PFESAs are bioaccumulative cannot be ruled out.

3.3. (Eco)toxicity

In most cases, e.g. hepatotoxicity and reproductive toxicity, short-chain PFAAs are less toxic than long-chain homologues (Borg and Hakansson, 2012 and the references therein; Daikin, 2014). However, PFHxS is reported to be more acutely toxic (3–5 times) to three aquatic species than PFOA (Asahi, 2006). The cause of this variability in species sensitivity was not elucidated. It is unclear whether the current standard tests cover all relevant (eco)toxicological aspects of short-chain PFAAs, at least for PFHxS. For PFOS, only one 96-h study is available, reporting that F-53B has a similar toxicity to zebrafish (LC50 = 15.5 mg/L) as PFOS (LC50 = 17 mg/L; S. Wang et al., 2013). Extensive toxicological profiles of two PFECAs (GenX and ADONA) have been reported, including acute toxicity, eye and skin irritation, dermal sensitization, genotoxicity, repeated-dose toxicity, and developmental toxicity (ECHA, 2014; Gordon, 2011), whereas for two other PFECAs only a few endpoints were reported (EFSA, 2010, 2011b). Most notably, ADONA and GENX were shown to cause liver damage in (at least) male rats or mice under repeated low exposure (<10 mg/kg/day); ADONA was also shown to be a PPARα agonist in male rats (ECHA, 2014; Gordon, 2011). In addition, another unknown PFeca (but structurally similar to CF3-O(CF2)3CF=(CF2)O)2CF2COO−) was reported to cause increases in liver weight in rats, but experimental details including the levels of exposure were not reported (Johnston et al., 1996a,b). Furthermore, GenX has been suggested by its producer to be classified as STOT Rep. 2 H373 in accordance with Regulation (EC) No. 1272/2008 (this refers to "specific target organ toxicity", i.e. the chemical may cause damage to organs through prolonged or repeated exposure; ECHA, 2014), by which it would fulfill the toxicity criteria in Annex XIII of REACH (ECHA, 2008). After considering the knowledge that PFOA has been classified as a toxic substance under REACH due to its high hepatotoxicity under repeated exposure (STOT Rep. Exp. 1 H372) and is a PPARα agonist (ECHA, 2011), it seems reasonable to conclude that the modification of the molecular structure by inserting oxygen between perfluoroalkyl chains has little or no influence on the mode-of-action, but only alters the levels of toxicity. Thus, based on their structural similarity, the other known PFECAs may well have the same (or a similar) mode-of-action as the tested PFECAs and PFOA and may fulfill the toxicity criteria under REACH. This question needs to be clarified urgently.

3.4. Long-range transport potential

In comparison to the long-chain homologues, due to their higher solubility in water and lower sorption to solids, short-chain PFAAs are more mobile in soil and sediment, which leads to higher mobility in the environment (Venkatesan and Halden, 2014; Vierke et al., 2014). PFECAs and PFESAs are expected to be highly persistent (see Section 3.1. Persistence above) and have physicochemical properties (e.g. high water solubility and low PCt) similar to those of PFCS and PFASs. They are thus likely to have similarly high long-range transport potential in water (Gomes et al., 2014). To date, no evidence of the presence of PFECAs and PFESAs in remote regions has been reported, which is likely due to a combination of factors: [i] the amounts historically emitted are likely to be low because some of these substances have either only recently been used commercially (in the case of many PFECAs) or been used in rather small amounts (in the case of PFESAs); [ii] contrary to PFCS and PFASs, there are no known (semi-)volatile precursors to PFECAs and PFESAs, although they could potentially exist; [iii] there is a time lag between emissions and the resulting contamination in remote regions, the length of which depends on the transport pathways (e.g. via air or seawater, and whether precursors are involved; Scheringer et al., 2009; Young et al., 2007); and [iv] no sensitive analytical techniques are readily available for PFECAs and PFESAs, which is partly due to the lack of availability of analytical standards.

3.5. Summary on hazardous properties

We observe that a fair amount of information on certain fluorinated alternatives is publicly available, which is, however, scattered over numerous documents. Overall, the current publicly accessible data are not conclusive to evaluate the hazardous properties of known fluorinated alternatives. In particular, there is a dearth of information on the bioaccumulation of PFECAs and PFESAs as well as an incomplete understanding of the (eco)toxicity of short-chain PFAAs, PFECAs and PFESAs. Thus, they may currently be considered as safe alternatives under existing chemical regulations, but the limited information does reveal evidence that many fluorinated alternatives may well still be problematic, in particular: [i] short-chain PFAAs, PFECAs and PFESAs are highly persistent and mobile in the environment; [ii] known PFECAs have likely the same or a similar toxic mode-of-action as

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Table 4

<table>
<thead>
<tr>
<th></th>
<th>Rats</th>
<th>Mice</th>
<th>Humans</th>
</tr>
</thead>
<tbody>
<tr>
<td>GenX (F)</td>
<td>&lt;12 h</td>
<td>Oral 30 ppm</td>
<td>–</td>
</tr>
<tr>
<td>GenX (M)</td>
<td>&lt;12 h</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>ADONA (M)</td>
<td>44 h</td>
<td>5-mm oralP</td>
<td>–</td>
</tr>
<tr>
<td>PFBA (F)</td>
<td>1 h</td>
<td>IV 30 ppm</td>
<td>2 h</td>
</tr>
<tr>
<td>PFBA (M)</td>
<td>5 h</td>
<td>9 h</td>
<td>13 ± 5 h</td>
</tr>
<tr>
<td>PFHxA (F)</td>
<td>0.4 h</td>
<td>IV 10 ppm</td>
<td>1.2 h</td>
</tr>
<tr>
<td>PFHxA (M)</td>
<td>1 h</td>
<td>2.4 h</td>
<td>–</td>
</tr>
<tr>
<td>PFOS (F)</td>
<td>2 h</td>
<td>IV 20 ppm</td>
<td>–</td>
</tr>
<tr>
<td>PFOS (M)</td>
<td>6 days</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>PFOS (all)</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>PFOS (all)</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>PFOS (all)</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Notes: a) similar to those of PFCAs and PFSAs, b) STOT g 1, c) STOT g 2, d) STOT g 3, e) STOT g 4, f) STOT g 5, g) STOT g 6, h) STOT g 7, i) STOT g 8, j) STOT g 9, k) STOT g 10, l) STOT g 11, m) STOT g 12, n) STOT g 13, o) STOT g 14, p) STOT g 15, q) STOT g 16, r) STOT g 17, s) STOT g 18, t) STOT g 19, u) STOT g 20, v) STOT g 21, w) STOT g 22, x) STOT g 23, y) STOT g 24, z) STOT g 25, A) STOT g 26, B) STOT g 27, C) STOT g 28, D) STOT g 29, E) STOT g 30, F) STOT g 31, G) STOT g 32, H) STOT g 33, I) STOT g 34, J) STOT g 35, K) STOT g 36, L) STOT g 37, M) STOT g 38, N) STOT g 39, O) STOT g 40, P) STOT g 41, Q) STOT g 42, R) STOT g 43, S) STOT g 44, T) STOT g 45, U) STOT g 46, V) STOT g 47, W) STOT g 48, X) STOT g 49, Y) STOT g 50, Z) STOT g 51.
PFOA and one PFECA fulfills the criterion for being classified as toxic under REACH.

3.6. Assessment of risks, now and in the future

There are studies showing on-going releases of fluorinated alternatives into the environment (e.g., for PFCEs, see BalIU, 2010a,b and Strynar et al., 2012; for PFSAs, see S. Wang et al., 2013; for short-chain PFCAs and PFSAs, see Dauchy et al., 2012 and Möller et al., 2010; for 6:2 FTOH, see Gawor et al., 2014). Because of on-going (increasing) emissions and high persistence, short-chain PFAAs, PFCAs and PFSAs are accumulating in the environment, which will lead to increasing exposure to these substances over time. This has already been observed for some short-chain PFAAs in environmental and human matrices in different regions (Ahrens, 2011; Glynn et al., 2012; Kirchgeorg et al., 2013; Zhou et al., 2013, 2014). From the principle of chemical risk assessment (i.e., risk ratio = exposure level / no-effect threshold), it follows that the environmental and human-health risks posed by these fluorinated alternatives are growing over time with direct proportionality to the increasing exposure, even though the current levels of these substances in the environment and biota and their corresponding risks might still be low.

It should be noted that emissions of fluorinated alternatives, in particular short-chain PFAAs, do not only occur during the life-cycle of these substances, but may also originate from transformation of (often overlooked) precursors including side-chain fluorinated polymers, hydrofluorocarbons and hydrofluoroethers (Prevedouros et al., 2006; Wang et al., 2014a,b). Some of these (overlooked) precursors have been in use for decades and significant reservoirs of them might have built up in the environment (Wang et al., 2014b). Thus, the actual exposure of, and risks associated with, these fluorinated alternatives may well be higher than indicated by their current production, uses, emissions, and measured environmental levels.

Due to the high persistence and environmental mobility of these fluorinated alternatives (and their precursors), even if emissions cease in the future, it will take decades to centuries to reverse the global contamination of short-chain PFAAs, PFCAs and PFSAs (Stephenson, 1977; Scheringer, 2002). Following the precautionary principle, it has been argued that it is irresponsible to release chemicals into the environment that will cause irreversible, planetary contamination (Scheringer, 2002; Persson et al., 2013) unless one is certain that such chemicals are benign to the environment and humans. In addition to their low environmental reversibility, it may be challenging to remove these substances from food (Vestergren and Cousins, 2013 and the references therein) and drinking water (Rahman et al., 2014 and the references therein), which have been identified as the major exposure pathways of long-chain PFAAs for the general population (Vestergren and Cousins, 2013).

Hence, there is an urgent need to overcome the current lack of knowledge and awareness concerning the increasing risks of these fluorinated alternatives, so that risk reduction measures can be taken early enough.

4. What are the reasons for the scarcity of publicly accessible data on fluorinated alternatives?

Importantly, the current data scarcity in the public domain might be rather factitious, i.e., certain information has been generated, but not been made publicly available. Many alternatives have been studied and commercialized by the manufacturing industry many years previously. Already back in the 1980s or earlier, short-chain PFAAs and related chemicals were produced or imported in the United States (US EPA, 2013; Wang et al., 2014b). Similarly, the two PFSAs used as alternatives to PFOS in hard chrome plating were used in China already in the 1970s (S. Wang et al., 2013). In addition, physicochemical properties of various PFCAs have been extensively studied since the 1970s and multiple mixtures of PFCAs have been used since the 1980s or earlier (Sianesi et al., 1973; Caporiccio et al., 1984; Chittofrati et al., 1989; Doan et al., 1997; Kasai, 1995; Mele et al., 2004; Monduzzi et al., 1994; Tomasić et al., 1995; Visca and Lenti, 1997; Würtz et al., 2001). Some of the early PFCAs are longer-chain homologues or structurally similar to the current PFCAs that are used to replace PFOA in the fluoropolymer production. Therefore, it is likely that there are more data regarding the production, use, emissions and (hazardous) properties, as also pointed out by industry in several studies (Asahi, 2006; Gordon, 2011; Johnston et al., 1996a,b; FluoroCouncil, 2014). Two factors may have contributed to this information asymmetry between industry and other stakeholders: [i] the information asymmetry is legitimate under current regulations; and [ii] there is a lack of incentive systems to encourage the industry to share more data.

In the United States (US), manufacturers of fluorinated alternatives (polymeric or non-polymeric) are obliged to submit certain data regarding the fate, bioaccumulation and toxicity of the substances to the US Environmental Protection Agency; however, this information can be claimed as confidential business information (CBI) and concealed from the public (US EPA, 2012). In the European Union (EU), the data requirements are associated with the substance type and its production volume. For example, several PFCAs are considered as polymers (Buck et al., 2011) and thus exempted from registration and evaluation under REACH (ECHA, 2012). Furthermore, a single long-chain substance in a specific application is replaced by mixtures or combinations of several alternatives (examples see Z. Wang et al., 2013); this results in smaller amounts of individual alternatives being used than was the case for the predecessors and possibly lower data requirements for individual alternatives. For instance, less than 100 tonnes per annum of GenX are used by DuPont in the EU (ECHA, 2014); thus, no data regarding its bioaccumulative potential is required under REACH (ECHA, 2006), although larger amounts of GenX might be used in DuPont’s fluoropolymer production in other regions (deduced from estimates of DuPont’s global production capacities of relevant fluoropolymers; Kalin et al., 2012). Also, the companies are eligible to claim safety data covered by REACH Article 119(2) as a trade secret and are not obliged to release them to the public.

In our opinion, the main reason preventing industry from sharing more data than requested is that there is little incentive for companies to do so. First, the costs to commercially develop a chemical product and conduct safety tests for relevant endpoints are high, e.g., multigenerational rat studies can cost up to €2 million per chemical (Gilbert, 2011). Thus, it is logical for a company to protect its own intellectual properties so that competitors cannot easily copy the products and/or skip the essential testing procedures (Robert Buck from DuPont, personal communication). Second, in some cases, particularly where the chemicals are potentially problematic for human health and the environment but highly profitable, companies might even benefit from not sharing data; because only when their information is made available the hazards and risks can be characterized and, if needed, measures to restrict production and emissions can be taken (see Lewis, 2005, 2006, 2007 for an example for PFOA). Third, often there is no direct benefit for companies to share information, even if the information is neutral to the companies’ interests, e.g., data on some discontinued substances that may help scientists to develop better quantitative structure–activity relationships for certain endpoints.

This inaction might be justifiable on the company level for its own existence, but is not justifiable for society as a whole because substantial societal costs may be incurred (UNEP, 2013b), including [i] the costs of publicly financed research and consultancy on the exposure and effects of fluorinated alternatives that might be repetitive in some cases; and [ii] the costs to reduce and minimize the environmental and human exposures when risks associated with fluorinated alternatives are recognized. In the past, there have been cases where companies were fined for the damages caused by their inactions (see Janofsky, 2005 for an example for PFOA). However, it is challenging to uncover and estimate the
total costs of industry inaction on society as a whole (UNEPA, 2013b) and not all costs can be easily monetized and quantified, such as the loss of resources, endangered species and human life years. Hence, a mechanism that encourages the manufacturing industry to share information and ensures an effective information exchange among stakeholders is urgently needed.

5. Implications for the future practice of the industrial transition to alternatives

In addition to the current dearth of data in the public domain, there are also more general problems with the transition strategy for alternative products adopted by industry. Not only do the current practices of major manufacturers largely rely on chemical replacements with structurally similar (sometimes also long-used) fluorinated substances as shown in Table 1, but also the development of the next generation(s) of replacements in the foreseeable future might still use the same concept by slightly modifying the currently used fluorinated alternatives. For example, DuPont developed fluorotelomer-like sulfonates and derivatives as possible alternatives to the current 6:2 fluorotelomer-based substances, in which ether oxygen (–O–) or methylene (–CH₂–) linkages are inserted between perfluoroalkyl chains (e.g., C₆F₃OCF₂CF₂CH₂SO₃H and C₆F₅CH₂CF₂CH₂SO₃H) (Peng and Hung, 2012; Coope et al., 2014). Although the non-fluorinated part of these structures may undergo (bio)degradation, the transformation products are still likely to be the environmentally stable PFCAs (considering the stability of perfluoroether chain as discussed above) or short-chain PFCAs (as observed by Arakaki et al., 2010). Therefore, we believe that although this type of industrial practice (of incrementally modifying the molecular structure of long-used substances) may cap the risks of long-chain PFCAs (Wang et al., 2014b), it will also result in the increase of risks caused by many fluorinated alternatives, particularly short-chain PFAAs, PFCAs and PFSAs.

We therefore believe that a non-fluorinated replacement strategy should be pursued. It is challenging to develop non-fluorinated alternatives that offer similar technical performance because of the unique properties of the carbon-fluorine bond. To date, there have been some technological developments of non-fluorinated alternatives (OECO, 2013). For example, non-fluorinated water-repellent textile finishes that are based on high-molecular weight and highly branched polymers known as dendrimers have been commercialized (Rudolf Group, 2014). In addition, Milani et al. (2013) showed the potential of using naturally occurring surfactants, hydrophobins, in emulsion polymerization of fluoropolymers. Alternatively, substitutions can go beyond chemical replacement, i.e., they can also be systematic changes in industrial processes (Hansson et al., 2011). For example, PFOS is no longer essential in decorative chrome finishers that are based on high-molecular weight and highly fluorinated water-repellent substances, in which ether oxygen (–O–) linkages are inserted between perfluoroalkyl and polyfluoropolyether surfactants. J. Colloid Interface Sci. 98, 202–209.


Acknowledgment

Funding by the Swiss Federal Office for the Environment (FOEN) is gratefully acknowledged. We gratefully thank the anonymous reviewers for their constructive comments and suggestions.

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