



# A modeling assessment of the physicochemical properties and environmental fate of emerging and novel per- and polyfluoroalkyl substances



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## HIGHLIGHTS

- COSMOtherm and SPARC are used to estimate physicochemical properties.
- The properties of PFECAs and PFESAs are similar to PFCAs and PFASs, respectively.
- The OECD Tool is used to estimate the environmental fate.
- Many fluorinated alternatives have similar environmental fate to legacy PFASs.
- Urgently needed experimental studies are highlighted.

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## ABSTRACT

Long-chain perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFASs) are persistent, bioaccumulative, and toxic contaminants that are globally present in the environment, wildlife and humans. Phase-out actions and use restrictions to reduce the environmental release of long-chain PFCAs, PFASs and their precursors have been taken since 2000. In particular, long-chain poly- and perfluoroalkyl substances (PFASs) are being replaced with shorter-chain homologues or other fluorinated or non-fluorinated alternatives. A key question is: are these alternatives, particularly the structurally similar fluorinated alternatives, less hazardous to humans and the environment than the substances they replace? Several fluorinated alternatives including perfluoroether carboxylic acids (PFECAs) and perfluoroether sulfonic acids (PFESAs) have been recently identified. However, the scarcity of experimental data prevents hazard and risk assessments for these substances. In this study, we use state-of-the-art in silico tools to estimate key properties of these newly identified fluorinated alternatives. [i] COSMOtherm and SPARC are used to estimate physicochemical properties. The US EPA EPISuite software package is used to predict degradation half-lives in air, water and soil. [ii] In combination with estimated chemical properties, a fugacity-based multimedia mass-balance unit-world model – the OECD Overall Persistence ( $P_{OV}$ ) and Long-Range Transport Potential (LRTP) Screening Tool – is used to assess the likely environmental fate of these alternatives. Even though the fluorinated alternatives contain some structural differences, their physicochemical properties are not significantly different from those of their predecessors. Furthermore, most of the alternatives are estimated to be similarly persistent and mobile in the environment as the long-chain PFASs. The models therefore predict that the fluorinated alternatives will become globally distributed in the environment similar to their predecessors. Although such in silico methods are coupled with uncertainties, this preliminary assessment provides enough cause for concern to warrant experimental work to better determine the properties of these fluorinated alternatives.

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## 1. Introduction

In the last decade, perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFASs) were recognized as

persistent (Remde and Debus, 1996; Key et al., 1998) and those with “long” perfluoroalkyl chains were shown to be bioaccumulative (Houde et al., 2006) and toxic (Kennedy et al., 2004; Borg et al., 2013). Our definition of “long” chain refers to PFCAs with 7 or more fluorinated carbons (including PFOA, which is designated as bioaccumulative under REACH; ECHA, 2013) and their precursors as well as PFASs with 6 or more fluorinated carbons and their precursors (Buck et al. 2011).

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Long-chain PFCAs and PFSAs are globally present, including in the abiotic environment (Yamashita et al., 2005; Young et al., 2007) and wildlife (Kannan et al., 2002) in remote regions, indicating the long-range transport potential of these substances. Furthermore, humans in industrialized countries contain relatively high levels of long-chain PFCAs and PFSAs in their serum (Kannan et al., 2004; Olsen et al., 2003), suggested to be due to the historical presence of these substances and their precursors in a wide range of consumer products (Vestergren and Cousins, 2009). Due to concern regarding their hazardous properties, there have been a number of actions by industry and regulatory authorities to reduce the environmental release of long-chain PFCAs, PFSAs and their precursors. In the period 2000–2002, 3M phased out its global production of perfluorooctane sulfonic acid (PFOS) and related chemicals derived from perfluorooctane sulfonyl fluoride (POSF, C<sub>8</sub>; i.e., POSF-based chemicals) and replaced their use in certain key products with perfluorobutane sulfonyl fluoride (PBSF, C<sub>4</sub>)-based chemicals. In 2009, PFOS and related POSF-based chemicals were added to Annex B (restriction of production and use) of the Stockholm Convention on Persistent Organic Pollutants (UNEP, 2009). Similar actions have also taken place for perfluorooctanoic acid (PFOA) and other long-chain PFCA homologues. For example, the US Environmental Protection Agency (US EPA) and eight major global fluoropolymer and fluorotelomer manufacturers have agreed to work toward the elimination of long-chain PFCAs and their precursors from point-source emissions and products by 2015 (US EPA, 2006). In addition, PFOA and its ammonium salt (APFO) as well as C<sub>11</sub>–C<sub>14</sub> PFCAs have been listed in the Candidate List of Substances of Very High Concern under the European chemicals regulation, REACH (ECHA, 2013).

A common feature of all the above actions is an on-going industrial transition to replace long-chain PFCAs, PFSAs and their precursors with alternatives, particularly other poly- and perfluoroalkyl substances (PFASs) such as shorter-chain homologues and functionalized perfluoropolyethers (PFPEs) in applications where extremely low surface tension and/or durable oil- and water-repellency is needed (Holt, 2011). Although the identity of fluorinated substances used in industrial processes and consumer products is often claimed as “confidential business information” (CBI) by the manufacturers, a number of fluorinated alternatives used in different industrial branches and consumer products were identified by Wang et al. (2013). A key question is: are these fluorinated alternatives less hazardous for humans and the environment than their predecessors? There have been other historical examples showing the problems associated with removing a chemical from the market and replacing it with other structurally similar chemicals from the same class of substances (Strempel et al., 2012; Goldstein et al., 2013). Wang et al. (2013) reviewed available knowledge on the identified fluorinated alternatives and highlighted the scarcity of information on their production volumes, emissions, (bio) degradability, bioaccumulative potential and (eco)toxicity. Conducting experiments to generate missing data for all these fluorinated alternatives is expensive and time-consuming. However, a preliminary assessment using *in silico* methods including quantitative structure–property/activity relationships (QSPRs/QSARs) can provide valuable insights and help to prioritize future research needs (Strempel et al., 2012, Gawor and Wania, 2013; Howard and Muir, 2010).

The aim of this work is to provide a preliminary assessment of emerging and novel fluorinated alternatives with state-of-the-art *in silico* tools. We use the terminology of “emerging” and “novel” that has previously been applied to brominated flame retardants (Bergman et al., 2012). Emerging fluorinated alternatives are defined as alternatives have been recently identified in the environment, wildlife, food or humans (e.g. Adona). Most of the alternatives included in this study are novel alternatives, i.e. those are known to be present in manufacturing processes, materials and products but have not yet been identified in environmental samples, wildlife, food or humans. First, COSMOtherm and SPARC are used to predict physicochemical properties and EPISuite is used to predict degradation half-lives in air, water and soil.

COSMOtherm and SPARC were previously used to estimate the physicochemical properties of long-chain PFASs, including partition coefficients (Arp et al., 2006; Wang et al., 2011) and acid dissociation constants (pK<sub>a</sub>s) (Goss, 2008). The US EPA EPISuite software package is a well-established QSPR/QSAR tool used to estimate physicochemical properties and degradation half-lives in hazard assessments (Strempel et al., 2012; Zarfl et al., 2012). It has, however, been shown to be inaccurate for estimating the physicochemical properties of PFASs (Arp et al., 2006) and is therefore only used here for estimating the environmental degradation half-lives. The structural differences of the fluorinated alternatives and their estimated physicochemical properties are analyzed to provide insights into the impact of structural changes on physicochemical properties. Second, based on the estimated physicochemical properties and degradation half-lives, the environmental fate of the fluorinated alternatives, more specifically the overall persistence (P<sub>OV</sub>) and long-range transport potential (L RTP), is assessed by using the OECD Overall Persistence and Long-Range Transport Potential Screening Tool (hereafter “the OECD Tool”). The OECD Tool was developed as a “consensus model” combining the essential aspects of nine multimedia fate and transport models (Wegmann et al., 2009). It should be noted that this study focuses on the physicochemical properties and possible environmental fate (POV and L RTP) of the selected fluorinated alternatives. The prediction of bioaccumulation potential (B) and (eco)toxicity (T) is not included in this study because there is a lack of mechanistic understanding about the possible oleo- and proteinophilic bioaccumulation behavior as well as the toxic mode-of-action of these fluorinated alternatives. However, a discussion of possible strategies for assessing B is included in the Discussion section.

## 2. Methods

### 2.1. Selected fluorinated alternatives

A total of 16 emerging and novel fluorinated alternatives were investigated, including five perfluoroether carboxylic acids (PFECAs) and two perfluoroether sulfonic acids (PFESAs) identified by Wang et al. (2013) and for which the chemical structures were known (see Table 1). The selection of the fluorinated alternatives for this study was limited by the large amount of unknown fluorinated chemical structures in the products identified by Wang et al. (2013). Furthermore, some fluorinated alternatives (namely “CF<sub>2</sub>=CFOCF<sub>2</sub>CF(CF<sub>3</sub>)CF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F (CAS no. 16090-14-5) and CF<sub>3</sub>OCF(CF<sub>3</sub>)COF”) were not considered due to their use in closed industrial processes. These substances are likely used as intermediates to produce monomers for certain polymer. they are not expected to be present in significant quantities in the environment because they are chemically bound on the polymers resulting in a limited fraction of them in industrial waste streams (US EPA, 2012). The plausible degradation products of two alternatives were, on the other hand, included in the analysis, since they could possibly be long-lived chemicals and more toxic than their parent compounds, as observed for other contaminants (Farré et al., 2008).

The 16 fluorinated alternatives and 6 degradation products were divided into four groups: 1) fluorinated alternatives replacing PFOA; 2) fluorinated alternatives replacing PFOS; 3) fluorinated alternatives replacing 8:2 fluorotelomer alcohol (8:2 FTOH); and 4) fluorinated alternatives replacing certain POSF- and/or fluorotelomer-based substances.

For practical purposes, each compound was renamed with a specific abbreviation (based on its acronym, commercial name, etc.) as indicated in Table 1 and will be referred to by this abbreviation throughout the paper.

### 2.2. Estimation of physicochemical properties

For fluorinated alternatives and their predecessors (PFOA, PFOS and 8:2 FTOH), physicochemical properties were predicted using

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