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REVIEW ARTICLE

# The wide presence of fluorinated compounds in common chemical products and the environment: a review

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## Abstract

The C-F bonds, due to their many unique features, have been incorporated into numerous compounds in countless products and applications. These fluorinated compounds eventually are disposed of and released into the environment through different pathways. In this review, we analyzed the occurrence of these fluorinated compounds in seven types of products (i.e., refrigerants/propellants, aqueous film-forming foam, cosmetics, food packaging, agrochemicals, pharmaceuticals, coating materials) and discussed their fate in the environment. This is followed by describing the quantity of fluorinated compounds from each source based on available data. Total on- and off-site disposal or other releases of 536 fluorinated compounds in 2021 were analyzed using the data sourced from the U.S. EPA Toxics Release Inventory (TRI). Among the chemicals examined, chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) were the primary contributors in terms of total mass. Upon examining the seven sources of fluorinated compounds, it became evident that additional contributors are also responsible for the presence of organofluorine compounds in the environment. Although various toxic degradation products of fluorinated compounds could form in the environment, trifluoroacetic acid (TFA) was specifically highlighted in this review given the fact that it is a common dead-end degradation product of > 1 million chemicals. This paper ended with a discussion of several questions raised from this study. The path forward was elaborated as well for the purpose of protecting the environment and human health.

**Keywords** Fluorinated compounds · Chemical products · Per- and polyfluoroalkyl substances · Trifluoroacetic acid · Toxicity

## Introduction

C-F is one of the most robust covalent bonds with a high dissociation energy (up to 485 kJ $mol^{-1}$), short chemical bond length (1.35 Å), and strong dipole moment (1.41 D) due to the optimal orbital compatibility between carbon ($C^{\delta+}$) and fluorine ($F^{\delta-}$) and the extreme electronegativity of fluorine (O'Hagan 2008; Gillis et al. 2015; Kiel and Engesser 2015). As a result, fluorination of organic molecules usually improves their molecular stability. Inspired by such improvement, fluorinated compounds that contain one or more C-F bonds have been largely synthesized and applied in a variety of fields. The common fluorinated compounds that have been widely used in the past decades include fluorocarbons (refrigerants/propellants), fluoroelastomers (sealing/gasket materials), fluoropolymers (coating/lining materials), fluoroantimicrobials (medical products), fluoroacids (organic synthesis catalysts), and fluorinated surfactants (cleaning, lubrication, fire-fighting products) (Key et al. 1997; Lewandowski et al. 2006). The wide use and high physicochemical stability of fluorinated compounds unfortunately result in their ubiquitous occurrence in the environment, causing environmental health issues. Considering their persistent, bioaccumulative, and potentially harmful nature, it is important to monitor the levels of fluorinated compounds in the environment and to take steps to reduce the release of these compounds into the environment.

In this review, we aimed to provide an overview of the environmental occurrence of the most widely used

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fluorinated compounds in chemical products, such as refrigerants, propellants, aqueous film-forming foam, cosmetics, food packaging, agrochemicals, pharmaceuticals, and coating materials. The environmental fate of these compounds from each source was reviewed briefly as well. These are followed by discussing the quantity of these compounds disposed of and released to the environment based on available data in the US EPA's database. Since many of these compounds may share a common degradation end product, the toxicity of trifluoroacetic acid (TFA) was highlighted in this paper specifically. It needs to be noted that numerous degradation products, of which many could be highly toxic, could be formed from different fluorinated compounds. But it is not the intention of this review to cover the toxicity of these fluorine-containing compounds and their products through either biotic or abiotic degradation pathways. Finally, four lines of thoughts were raised and discussed based upon findings from this review. It is our sincere hope that this review will raise awareness of the presence of these compounds in every corner of our daily lives and that deep and broad awareness by all stakeholders will lead to actions and changes of agendas to protect the environment and human health.

## Occurrence of fluorinated compounds in chemical products and their fate in the environment

### Fluorinated compounds in refrigerants and propellants

Chlorofluorocarbons (CFCs) are commonly known by the DuPont brand name Freon and have been among the most useful fluorinated chemicals ever developed. CFCs have low toxicity, reactivity, and flammability and thus have been widely used as refrigerants, propellants, and solvents. CFCs are known to catalyze the conversion of ozone into $O_2$, thus contributing to ozone depletion in the upper atmosphere (Manzer 1990). Besides, CFCs can affect the climate as greenhouse gases due to their strong absorption in the spectral region of 7.8–15.3 μm by C-F and C–Cl bonds (Rothman et al. 2009). Thus, the manufacturing and use of CFCs have been phased out and banned under the Montreal Protocol, which was agreed upon on September 16, 1987. As a consequence, the atmospheric concentration of CFCs has declined over the last decades (Whitesides 2020; Young et al. 2021).

In response to the phase-out, CFCs have been replaced by hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs), leading to a dramatic increase in the atmospheric abundances of these compounds. Although HFCs do not contribute directly to ozone depletion, they have hundreds to thousands of times higher global warming potentials compared to $CO_2$ (Rigby et al. 2014; Hu et al. 2017). To address global climate change issues caused by HFCs, 197 countries agreed to phase down the production and consumption of HFCs under the Kigali Amendment to the Montreal Protocol on October 15, 2016. This agreement aims to reduce the global consumption and production of HFCs by more than 80% by 2047. Moreover, the U.S. EPA signed a final rule under the AIM Act in 2021 to decrease the use of HFCs in the USA by 85% over the next 15 years. Thus, reasonably, the atmospheric levels of HFCs are expected to continuously decrease with time.

In the atmosphere, HCFCs and HFCs (Berg et al. 2000) can interact with hydroxyl radicals, NO, and $O_2$ and be hydrolyzed to TFA ($CF_3COOH$) in water droplets (Ball and Wellington 1993; Franklin 1993; Kotamarthi et al. 1998). However, it was reported that there were unresolved sources contributing to the TFA in the atmosphere in 1999. This finding was based upon higher concentration of TFA than what could be from the CFC substitutes (Jordan and Frank 1999). At that time, in the major rivers in Germany, TFA was present at average concentrations of 140 ng/L. In rainwater collected from May 1995 to June 1996, the average TFA concentration was 120 ng/L, which was expected to be reached in 2010. Thermolysis or incineration of fluoropolymer wastes was assumed to be an important source of TFA while contributions from pesticides and fluorinated inhalation anesthetics were considered marginal.

In 2022, for surface water in Northern California, USA, it was reported that TFA concentrations increased by an average of sixfold over the intervening 23 years, which resulted in a median concentration of 180 ng/L (ranging between 21.3 and 2790 ng/L) (Cahill 2022). By comparing TFA concentrations in urban California vs. remote Alaska areas, the author excluded the source of TFA being solely from atmospheric oxidation of HFCs/HFOs and pointed to the existence of additional sources of TFA from urban areas. Pyrolysis of PTFE and pesticides were considered insignificant drivers of the observed TFA concentration. In China, it was disclosed that only 14% (ranging from 6 to 33%) of the TFA deposition was the result of HFC-134a oxidation (Wu et al. 2014). As shown below, numerous fluorinated compounds in other sources could contribute to the increasing presence of TFA in the environment.

### Fluorinated compounds in aqueous film-forming foam

Aqueous film-forming foam (AFFF) is a fire suppressant used to extinguish flammable liquid fires and is often used in chemical plants, flammable liquid storage and processing facilities, merchant operations, fire departments, firefighting training centers, aviation operations, and military facilities (Place and Field 2012; Conder et al.

2021). Per- and polyfluoroalkyl substances (PFAS) are widely used in AFFF as surfactants, which spread the foam to cool and suppress the fire (Houtz et al. 2013; Nickerson et al. 2020; Conder et al. 2021). Generally, PFAS can be divided into three categories: PFAS precursors, degradation intermediates, and degradation end products. PFAS precursors are polyfluorinated compounds. PFAS intermediates are products derived from PFAS precursors, while the end products are perfluoroalkyl acids (PFAAs) that are stable and generally considered as non-biodegradable compounds (Remde and Debus 1996; Ochoa-Herrera et al. 2016).

The use of PFAS in AFFF formulations has been linked to environmental contamination related to handling, storage, and usage (Rotander et al. 2015). Numerous studies have reported the occurrence of PFAS in soil, vadose zone, and groundwater samples collected from AFFF-impacted sites shown in Table 1 (Moody and Field 2000; Schultz et al. 2004; Kärrman et al. 2011; Backe et al. 2013; Houtz et al. 2013; Baduel et al. 2015; Filipovic et al. 2015; Kupryianchyk et al. 2016; Banzhaf et al. 2017; Dauchy et al. 2019; García et al. 2019; Martin et al. 2019; Bekele et al. 2020; Brusseau et al. 2020; Nickerson et al. 2020; Anderson 2021; Dasu et al. 2022). Once AFFF is released into the environment, PFAS precursors, which are the major chemicals in

**Table 1** Fluorinated compounds detected at AFFF-impacted sites

| Categories of samples | Sampling countries and locations | Analyzed fluorinated compounds | Concentrations in samples | References |
|---|---|---|---|---|
| Groundwater | U.S. Ellsworth Air Force Bases (AFB), SD | PFCAs, PFSAs, n:2 FTS, FHxSA | Σ13PFAS = 0.5–1478 μg/L | Houtz et al. 2013 |
| Soil | U.S. Ellsworth AFB, SD | PFCAs, PFSAs, n:2 FTS, FOSAs, FTSaAM | Σ15PFAS = 34–56,180 μg/kg | Houtz et al. 2013 |
| Sediment | U.S. Ellsworth AFB, SD | PFCAs, PFSAs, n:2 FTS, FOSAs, FTSaAM | Σ15PFAS = 383–2912 μg/kg | Houtz et al. 2013 |
| Groundwater | U.S. military bases | PFCAs, PFSAs, n:2 FTS | Σ19PFAS at site A = 0.198–513 μg/L<br>Σ19PFAS at site B = 122–1429 μg/L | Backe et al. 2013 |
| Groundwater | Canada, airports | PFCAs, PFSAs, n:2 FTS, n:2 FTCAs, n:2 FTUCAS, FOSA, FOSAA, FTAB, FTSaAM | Σ41PFAS at site A = 0.6–98 μg/<br>Σ41PFAS at site B = 0–5100 μg/L | Martin et al. 2019 |
| Groundwater | U.S. Naval Air Station, Fallon, NV; Tyndall AFB, FL; Wurtsmith AFB, MI | PFCAs, PFSAs, n:2 FTS | Σ11PFAS at Fallon = 0–8770 μg/L<br>Σ11PFAS at Tyndall = 1373–18,398 μg/L<br>Σ11PFAS at Wurtsmith = 0.9–419 μg/L | Schultz et al. 2004 |
| Groundwater | Europe, fire training area | PFCAs, PFSAs, n:2 FTS, n:2 FTCAs, n:2 FTUCAS, FOSA, FOSAA, FTAB, FTSaAM | Σ32PFAS = 0.3–8.3 μg/L | Dauchy et al. 2019 |
| Soil | Europe, fire training area | PFCAs, PFSAs, n:2 FTS, n:2 FTCAs, n:2 FTUCAS, FOSA, FOSAA, FTAB, FTSaAM | Σ32PFAS = 15–4300 μg/kg | Dauchy et al. 2019 |
| Concrete in an FTG | Australia, firefighting training ground (FTG) | PFCAs, PFSAs, n:2 FTS | Σ15PFAS = 877–244,294 μg/L | Baduel et al. 2015 |
| Groundwater | Sweden, military airport | PFCAs, PFSAs | ΣPFAS = 0.74–51 μg/L | Filipovic et al. 2015 |
| Surface water | Sweden, military airport | PFCAs, PFSAs | ΣPFAS = 0–0.08 μg/L | Filipovic et al. 2015 |
| Soil | Sweden, military airport | PFOA, PFOS | PFOA = 0.12–287 μg/kg<br>PFOA = 2.18–8520 μg/kg | Filipovic et al. 2015 |
| Soil | Norway, airports | PFCAs, PFSAs, n:2 FTS | Σ15PFAS at Kristiansand: 3600 μg/kg<br>Σ15PFAS at Evenes: 2400 μg/kg<br>Σ15PFAS at Bergen: 780 μg/kg | Kupryianchyk et al. 2016 |

AFFF, can be easily degraded into PFAS intermediates (Schultz et al. 2004; Houtz et al. 2013). These intermediates can then be transformed to PFAAs: (1) biotically due to aerobic or anaerobic biotransformation (Zhang et al. 2016, 2017) or (2) abiotically owing to the presence of ·OH or sulfate (SO4·-) radicals generated in reducing environments where Fe (II) and reduced DOM are present (Tong et al. 2016; Xiao et al. 2020). Such reducing environments include wetlands and soils during groundwater table fluctuation. As of now, most of the focus in the PFAS field has been on a few PFAAs with carbon chain length of equal to or larger than four. These attentions are in line with health advisory levels recommended by the US EPA and maximum contaminant levels (MCLs) established by different US states. None of the EPA and state regulatory agencies, however, has considered PFAAs with less than four carbon chains (e.g., C2-C3 ultrashort chain PFAS) (Liang 2022). Existing EPA methods specifically for PFAS, such as 537.1, 533 and Draft 1633 do not include ultrashort PFAS in the target list either.

However, it is known that ultrashort PFAS are degradation products of PFAS precursors and relatively long-chain PFAAs. It was reported that perfluorooctane sulfonamide (FOSA) was transformed to PFOA, perfluoroheptanoic acid (PFHpA), perfluorohexanoic acid (PFHxA), perfluoropentanoic acid (PFPeA), perfluorobutanoic acid (PFBA), PFPrA, and TFA by natural montmorillonite upon exposure to light (Lv et al. 2020). In anaerobic environment, pure and enrichment cultures of *Acidimicrobium* sp. strain A6 were reported to defluorinate PFOA and PFOS to C4-C7 products (Huang and Jaffé, 2019). The ultrashort PFAS were not analyzed in this biotransformation study; thus, it is unknown whether C2-C3 PFAS were also the degradation products. In groundwater samples from sites impacted by PFAS, perfluoro carboxylic acid (PFCA) concentrations ranged from 0.056 to 2.2 μg/L with TFA and PFOA being the predominant analytes (Janda et al. 2019a). In a soil core from a PFAS-polluted agricultural site, as revealed by oxidation by persulfate, the upper 40 cm was dominated by long-chain PFAS precursors. More than 40 cm below ground, precursors to C2-C4 PFAS were found to account for ~50% of the reaction products (Janda et al. 2019b). Thus, reasonably, ultrashort PFAS including TFA are expected to be prevalent in PFAS-contaminated sites where biotic and abiotic transformations are active. These potential natural transformations most likely will not happen as fast as those performed in laboratories. But considering the scale, over time, this process could lead to significant accumulation of ultra-short PFAS in the environment.

## Fluorinated compounds in cosmetic products

PFAS are commonly added to cosmetics to increase their durability and water resistance (Fujii et al. 2013; Schultes et al. 2018). Thus, high fluorine levels were frequently detected in cosmetic products advertised as “wear-resistant” to water and oils or “long-lasting” (Bui and Coleman-Nally 2017; Lam 2021; Richard 2021).

Table 2 shows the available studies focused on fluorinated compounds in cosmetics. To the best of our knowledge, the first study exploring the occurrence of PFAS in cosmetic products was published in 2013 (Fujii et al. 2013). Fifteen cosmetic products, including foundations and manicure products, were subject to targeted analysis for 9 PFCAs (C6–C14). PFHxA (up to 1100 ng/g), PFOA (up to 1700 ng/g), perfluorododecanoic acid (PFDoDA, up to 940 ng/g), and perfluorotetradecanoic acid (PFTeDA, up to 590 ng/g) were the major PFCAs detected in the tested samples. In a survey study focusing on cosmetic products available in Denmark, polytetrafluoroethylene (PTFE) was found in most products, followed by fluoroalcohol phosphates (C9–C15) (Brinch et al. 2018). The highest concentration of a single PFAS was 3340 ng/g for PFHxA in a foundation, while the highest concentration of ΣPFAS was 10,700 ng/g detected in a concealer.

In another study, 39 PFAS in 31 cosmetic products available on the Swedish market were analyzed using LC–MS/MS and combustion ion chromatography (CIC) (Schultes et al. 2018). The tested foundation and powder products contained 25 PFAS, which were mainly PFCAs and polyfluoroalkyl phosphate esters (PAPs) (Table 2). The tested powders had the highest total fluorine content (TF, 547–19,200 μg/g), followed by creams (0–11,100 μg/g) and foundations (326–3120 μg/g). For all samples, $\Sigma_{39}$PFAS only accounted for a small fraction of the TF implying the presence of unknown organic and/or inorganic fluorinated substances in tested cosmetic products. Similarly, Whitehead et al. (2021) screened a total of 231 cosmetic products purchased in the USA and Canada for TF analysis using particle-induced gamma-ray emission spectroscopy (PIGE), followed by targeted analysis of PFAS. Among the tested products, 63% of the foundations, 58% of the eye products, 55% of the lip products, and 47% of the mascaras had a high fluorine content over 0.384 μg F/cm$^2$. The concentration of $\Sigma_{53}$PFAS ranged from 22 ng/g in a mascara to 10,500 ng/g in a foundation. Fluorotelomer alcohols (FTOHs), methacrylates (FTMAs), and PAPs, which are PFCA precursors, were the most frequently detected PFAS and also contributed the most to $\Sigma_{53}$PFAS. The authors pointed out that only 8% of the 231 tested cosmetic products had PFAS listed as ingredients, highlighting the need for better government oversight and regulations of PFAS applications in cosmetics. More recently, Harris et al. (2022) further investigated the occurrence of PFAS in 38 cosmetics and personal care products available on the Canadian market. Their results indicated that all samples, including those that did not

**Table 2** Fluorinated compounds in cosmetic products

| Categories of cosmetic products | Sampling countries | Analyzed fluorinated compounds | Content in cosmetics | References |
|---|---|---|---|---|
| Foundations/manicure products | Japan | PFCAs (C6–C14) | $\Sigma_9$PFCAs: up to 5900 ng/g | Fujii et al. 2013 |
| Foundations/creams/powder/eyeliner/shaving foam/lotion | Denmark | PFAAs, PTFE, fluorotelomer sulfonate, C9-15 fluoroalcohol phosphate | ΣPFAS: up to 10,700 ng/g | Brinch et al. 2018 |
| Moisturizing creams/foundations/powders and eye shadows/eye pencil/shaving foams | Sweden | PFCAs, PAPs, and total fluorine | $\Sigma_{10}$PFCAs: up to 9220 ng/g in foundations; up to 679 ng/g in powder products<br>$\Sigma_{14}$PAPs: up to 471 µg/g in foundations; up to 282 ng/g in powder products<br>6:2/8:2 FTSA: up to 156 ng/g in foundations<br>Total fluorine: 547–19,200 µg/g in powders; 0–11,100 µg/g in creams; 326–3120 µg/g in foundations<br>Extractable organic fluorine: 0–55% of total fluorine | Schultes et al. 2018 |
| Lip, eye, face, eyebrow products/foundations/mascaras/concealers/miscellaneous | USA & Canada | 53 PFAS including PFAAs, FTOHs, FTMAs, PAPs, and total fluorine | $\Sigma_{53}$PFAS: up to 22 ng/g in mascaras; up to 10,500 ng/g in foundations<br>Average $\Sigma_{53}$PFAS: 264 ng/g; median $\Sigma_{53}$PFAS: 1050 ng/g<br>Total fluorine: ≥ 0.384 µg F/cm$^2$ in foundations, mascaras, and lip products | Whitehead et al. 2021 |
| Foundations/creams/concealer/moisturizer/hair oil/treatment mask/cleanser/lotion/shave foams/lip and eye products | Canada | PAPs, PFCAs, PFSAs, and FTSAs, and non-targeted analysis | Average ΣPAPs: 1,080,000 ng/g; median ΣPAPs: 299 ng/g<br>Average ΣPFCAs: 2760 ng/g; median ΣPFCAs: 111 ng/g<br>Average ΣPFSAs: 13.2 ng/g; median ΣPFSAs: 7.93 ng/g<br>Average ΣFTSAs: 4 ng/g; median ΣFTSAs: 0 ng/g<br>51 FTCAs and FTUCAs were found at low levels | Harris et al. 2022 |

list PFAS as ingredients, contained PFAS. PAPs predominantly and ubiquitously existed in the tested products. HRMS screening tests also showed the existence of numerous PFAS precursors at low levels in the tested samples.

Overall, high concentrations of PFAS (up to mg/kg or mg/L levels) were frequently detected in cosmetics, especially foundations and powder products, while these fluorinated compounds are usually not disclosed well in their ingredient lists. At this stage, it is unclear whether and how severe the PFAS in these products can affect users' health. What is clear is that all these PFAS, once washed off from the users, will eventually go to the wastewater streams and contribute to the PFAS load received by wastewater treatment facilities. At these facilities, during the biological wastewater treatment processes, such as activated sludge, some PFAS precursors will be degraded to PFAAs. The treated wastewater, once released from the facilities, will add PFAS to the receiving water bodies, either rivers, reservoirs, or lakes.

## Fluorinated compounds in food packaging materials

Food packaging materials, such as paper products usually contain coatings or additives with fluorinated compounds for oil and water resistance (Begley et al. 2005; Harada and Koizumi 2009). Therefore, the analysis of fluorinated compounds that could be released into the packed food is important for food safety (Table 3).

In the papers published by D'eon and Mabury (2007); D'eon et al. (2009), fluorinated compounds, such as PAPs in food contact paper, matched their profiles in human blood, raising the concern about human exposure to fluorinated compounds through indirect ingestion of chemicals applied to food packing materials. Such route has been proven by the relevant studies in the past 2 decades. For example, PFOA was detected in popcorn bags, hamburger wrappers, French fry boxes, and paper plates available on the U.S. market, with the highest concentration found in popcorn bags (up to 290 ng/g) (Begley et al. 2005, 2008). Sinclair et al. (2007) also found PFAS in popcorn containers at concentrations in the range of 0.5 – 6.0 ng/cm$^2$. 6:2 FTOH and 8:2 FTOH were even detected in the vapors released by microwaving popcorn bags at 223 ng/bag and 258 ng/bag, respectively. Microwavable popcorn bags of three different brands purchased in Spain contained significant levels of PFBA (291 ng/g), PFHxA (254.5), PFOA (51–198 ng/g), 6:2 FTCA (161.6 ng/g), and 6:2 FTUCA (114.4 ng/g) (Martínez-Moral and Tena 2012; Zabaleta et al. 2016). Zafeiraki et al. (2014) analyzed fluorinated compounds in similar materials available on the Greek market. Close to the previous reports, the tested microwavable popcorn bags had high levels of PFBA (275.84 ng/g), PFHxA (341.21 ng/g), and PFHpA (5.19 ng/g). The tested ice cream cups only contained PFHxA at 25.56 ng/g. In Thailand, PFOS and PFOA were detected in 34 samples of food packaging paper (Poothong et al. 2012). The highest concentration of PFOS was found in the fast-food container samples (92.48 ng/dm$^2$), while the highest concentration of PFOA was detected in the ice cream cup samples (16.91 ng/dm$^2$). In Germany, Still et al. (2013) disclosed that storage of butter in packaging coated with fluoropolymers increased the levels of PFAA and FTOH in the packed butter, leading to potential human exposure.

Besides PFAS targeted analysis, effort has been made to determine the unknown fluorinated compounds in food packaging materials. By using a Micromass QToF Ultima Global mass spectrometer, Trier et al. (2011) identified more than 115 molecular structures of polyfluorinated surfactants in industrial blends that were used to coat food paper and board packaging in the E.U., the USA, and China (Table 3). These PFAS precursors could then transform into PFAAs and migrate into the packed food, causing health issues to humans. Unfortunately, the concentrations of the identified fluorinated compounds were not presented clearly in this study. Similarly, through total oxidizable precursor (TOP) analysis, Chinthakindi et al. (2021) found that the majority of PFAS in the food packaging materials collected from NY, USA, was the group of unknown PFAS precursors. Schaider et al. (2017) measured TF in 407 food packaging materials collected from fast food restaurants throughout the USA and reported a TF content ranging from 16 to 800 nmol/cm$^2$ (304–15,200 ng/cm$^2$), which was higher than the TF concentration from the detected PFAS, implying that a significant portion of the TF in these samples could be inorganic fluorine, non-PFAS organofluorine compounds, or volatile PFAS that were not captured during the PFAS extraction process (Schaider et al. 2017). This is consistent with the results reported by Schultes et al. (2019), revealing large amounts of unidentified organofluorine compounds in food packaging products.

In summary, known and unknown fluorinated compounds were frequently detected in food packaging materials. These compounds could leach to the packed food, leading to their ingestion by humans. The prevalence of fluorinated compounds in food packaging materials also hinted to their potentially significant contribution to environmental contamination during production and disposal. At present, in the USA, while some unsoiled food packaging materials are recycled and reused, the soiled counterparts are often composted or discarded at landfills. Both composting and landfilling, due to biological activities, can degrade some PFAS but will result in PFAS transfer from one place to another due to the use of the composted materials in gardening, agriculture, landscaping, etc. In terms of landfilling, the collected leachate, if not separately treated, will increase the loading of PFAS to centralized wastewater treatment facilities. Similar to cosmetic products, PFAS in these food

**Table 3** Fluorinated compounds in food packaging materials

| Categories of food packaging | Sampling countries | Analyzed fluorinated compounds | Content in food packaging materials | References |
|---|---|---|---|---|
| Microwave popcorn bags/hamburger wrappers/French fry boxes/paper plates | USA | PFOA | PFOA: up to 290 ng/g in popcorn bags | Begley et al. 2008; Begley et al. 2005 |
| Microwave popcorn bags | NY, USA | PFCAs (C5 – C12), FTOH | ΣPFAS: 0.5 – 6.0 ng/cm$^2$ | Sinclair et al. 2007 |
| Microwave popcorn bags | Spain | PFCAs, PFSAs | PFOA: 51–198 ng/g; ΣPFAS: 159–549 ng/g | Martínez-Moral and Tena 2012 |
| Microwave popcorn bags/pizza boxes/French fry wrappers/cinema popcorn boxes/muffin cups/milk bottles/coffee cups/ pre-cooked food wrappers | Spain | PFCAs, PAPs, FTCAs, FTUCA | In popcorn bags, PFBA: 291 ng/g, PFPeA: 20.5 ng/g, PFHxA: 254.5, PFHpA: 2 ng/g, 8:2 diPAP: 12.1 ng/g, 6:2 FTCA: 161.6 ng/g, 6:2 FTUCA: 114.4 ng/g, 5:3 FTCA: 24.6 ng/g | Zabaleta et al. 2016 |
| Microwave popcorn bags/ice cream cups/aluminum foil wrappers/baking paper materials/beverage cups | Greece | PFCAs, PFSAs | In popcorn bags, PFBA: 275.84 ng/g, PFHxA: 341.21 ng/g, PFHpA: 5.19 ng/g<br>In ice cream cups, PFHxA: 25.56 ng/g | Zafeiraki et al. 2014 |
| Instant food cups/microwave popcorn bags/beverage cups/ice cream cups/fast-food containers/dessert containers/baking paper | Thailand | PFOA, PFOS | Average PFOS: 8.57 ng/dm$^2$; Average PFOA: 5.03 ng/dm$^2$<br>Highest PFOS: 92.48 ng/dm$^2$ in fast-food containers<br>Highest PFOA: 16.91 ng/dm$^2$ in ice cream cups | Poothong et al. 2012 |
| Butter wraps | Germany | PFCAs (C4 – C12), FTOH | PFCAs: 1–8 ng/g; FTOH: 0.9–2.6 μg/g | Still et al. 2013 |
| Food packaging coating blends/food packaging paper and board materials | EU, USA, China | Identified over 115 structures, including PFOSA, PAPs, fluoroethoxylates, fluoroacrylates, fluoroamino acids, fluorosulfonamide phosphates, and fluorothio acids | – | Trier et al. 2011 |
| Food packaging materials (407 samples) | USA | PFCAs, PFSAs, FTSs, PAPs, polyfluorinated ethers, total fluorine (PIGE) | Total fluorine: 304–15,200 ng/cm$^2$, equivalent to ~60 μg/g in wrappers; ~14 μg/g in paperboard in 33% of the tested products | Schaider et al. 2017 |
| Microwave popcorn bags/French fry bags | Sweden | PFCAs, PFSAs, FTSAs, FOSAA, Me-FOSAA, FPrPA, FPePA, PHpPA, PAPs, total fluorine (PIGE, CIC, INAA) | Σ44PFAS: 23.9–2220 pg/cm$^2$ | Schultes et al. 2019 |
| Plastic food packaging/pet food packaging materials | NY, USA | PFCAs (C4–C12), PFSAs (C4–C12), total PFAS precursors | In plastic food packaging: $\Sigma_9$PFCA, 1.28 ng/g; total PFAS precursors, 10.52 ng/g<br>In pet food packaging: $\Sigma_9$PFCA, 0.89 ng/g; total PFAS precursors, 4.82 ng/g | Chinthakindi et al. 2021 |

packaging materials will be spread to other environments through the discharge of treated wastewater.

## Fluorinated compounds in agrochemicals

Currently, fluorinated compounds are widely used in agrochemicals, including herbicides, fungicides, insecticides, acaricide, rodenticides, molluscicides, nematicides, fertilizers, and soil conditioners. Fluorination of aromatic and aliphatic molecules may lead to distinct changes in physicochemical properties of organic compounds (Linclau et al. 2016; O'Hagan and Young 2016). In agrochemicals, fluorine substitution mostly occurs in the aromatic scaffolds, and the most common fluorine-containing groups of agrochemicals are aromatic fluorine and aromatic trifluoromethyl (Theodoridis 2006). The fluorination of aromatic scaffolds enables the fine-tuning of agrochemicals' in vivo stability, lipophilicity, and stereochemical behavior (Alexandrino et al. 2022). These compounds would then have promoted hydrophobic interactions, higher membrane permeability, and stronger protein binding. The modulation of these attributes brings favorable properties to agrochemicals, such as high selectivity and specificity, quick action, and prolonged residual activity (Jeschke 2004).

So far, over 1200 agrochemicals, including discontinued products, are registered and used worldwide. Ogawa et al. (2020) evaluated the contribution of fluorinated compounds to agrochemicals and established a database containing 424 fluorinated agrochemicals based on the available literature (Fig. 1A–C). Among these chemicals, 40% were herbicides, followed by insecticides (25%), fungicides (17%), acaricides (9%), and other compounds. Another survey on agrochemicals reported that around 25% of licensed herbicides contain at least one fluorine atom, most often present as aryl-F, aryl-$CF_3$, and aryl-$OCF_3$ substituents (McDougall 2006).

It is known that four insecticides, sulfluramid, flursulamid, LPOS, and SIOC-I-013 have linear per-fluoroalkyl structures, resembling PFAS (Ogawa et al. 2020). Very recently, in 6 of the 10 insecticide formulations studied, PFOS was found with concentrations ranging from 3.92 to 19.2 mg/kg (Lasee et al. 2022). Several additional PFAS were also detected in soil and plant samples collected at a site in the USA where the insecticide was used, with PFOS being the most prominent. In addition to the targeted 24, several suspected PFAS were observed in 7 of the 10 samples by suspect screening. Given the high PFOS concentration revealed in the insecticides, this study raised a series of questions warranting further investigations. For example, are PFAS present in all agrochemicals? If yes, what kind of PFAS and what are their concentrations? What are the fates of these PFAS once they are applied to agricultural fields?

Fluorinated agrichemicals can be degraded biotically and abiotically in the environment (Aislabie and Lloyd-Jones 1995; Ikehata and El-Din 2006). It was reported that aryl F and heteroaromatic F groups in several pesticides are more

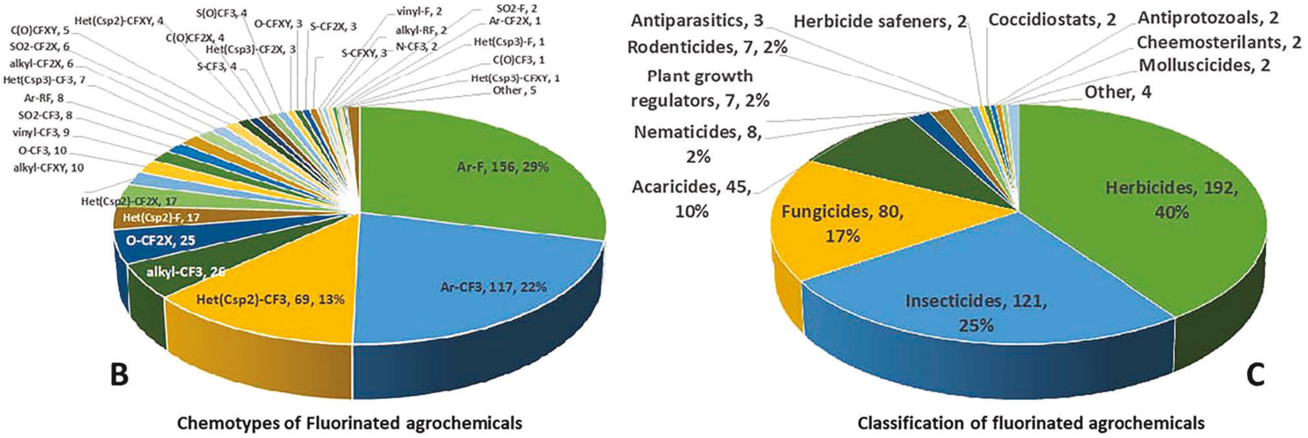


**Fig. 1** **A** Contributions of fluorinated compounds to agrochemicals (Ogawa et al. 2020). **B** Chemotype distribution and **C** classification of 424 identified fluorinated agrochemicals (Ogawa et al. 2020)

easily destroyed by photolysis than aliphatic and heteroaromatic $CF_3$, forming fluoride as the major end-product. Upon photo exposure, the presence of $CF_3$ and $CF_2$ groups leads to the formation of TFA and difluoroacetate, respectively. Thus, fluorinated agrichemicals are a source of fluoroacetic acids in the aquatic environments (Bhat et al. 2022).

## Fluorinated compounds in pharmaceuticals

Similar to agrochemicals, fluorinated pharmaceuticals (fluoro-pharmaceuticals) have improved bioavailability, metabolic stability, and chemical reactivity due to fluorine substituents (Linclau et al. 2016; O'Hagan and Young 2016). In general, fluorine induces bond polarization to the fluorinated compounds, affecting their lipophilicity and p$K_a$ values (Isanbor and O'Hagan 2006). The strong inductive electron withdrawal of fluorine can also enhance the acidity of the nearby acidic groups (e.g., alcoholic groups, phenolic OH groups) and reduce the basicity of nearby amino groups. This modulation of acidity and basicity resulted in lower p$K_a$ values and higher bioavailability of pharmaceuticals. Fluorine substituents, such as $CF_3$, S-$CF_3$, and O-$CF_3$ groups, could also effectively improve the lipophilicity of fluoro-pharmaceuticals, further influencing pharmaceuticals' binding affinity and bioavailability (Muller et al. 2007; Zhou et al. 2016). Moreover, the high strength of C-F bond increases the metabolic stability of fluoro-pharmaceuticals.

In 2018 and 2019, over 43% of newly approved pharmaceuticals by the U.S. FDA were fluoro-pharmaceuticals (Jarvis 2019, 2020). In 2020, there were 14 fluoro-pharmaceuticals approved by the U.S. FDA, and most of them feature aromatic fluorine (Ar-F) (11 compounds). So far, more than 300 fluoro-pharmaceuticals have been approved and/or registered globally, accounting for ~ 20% of the commercial pharmaceuticals (Fig. 2) (Inoue et al. 2020). Most fluoro-pharmaceuticals contain Ar-F, alkyl-CR-F, and Ar-$CF_3$, while some products contain heterocyclic fluorine (Het-F). Overall, fluoro-pharmaceuticals are already making a

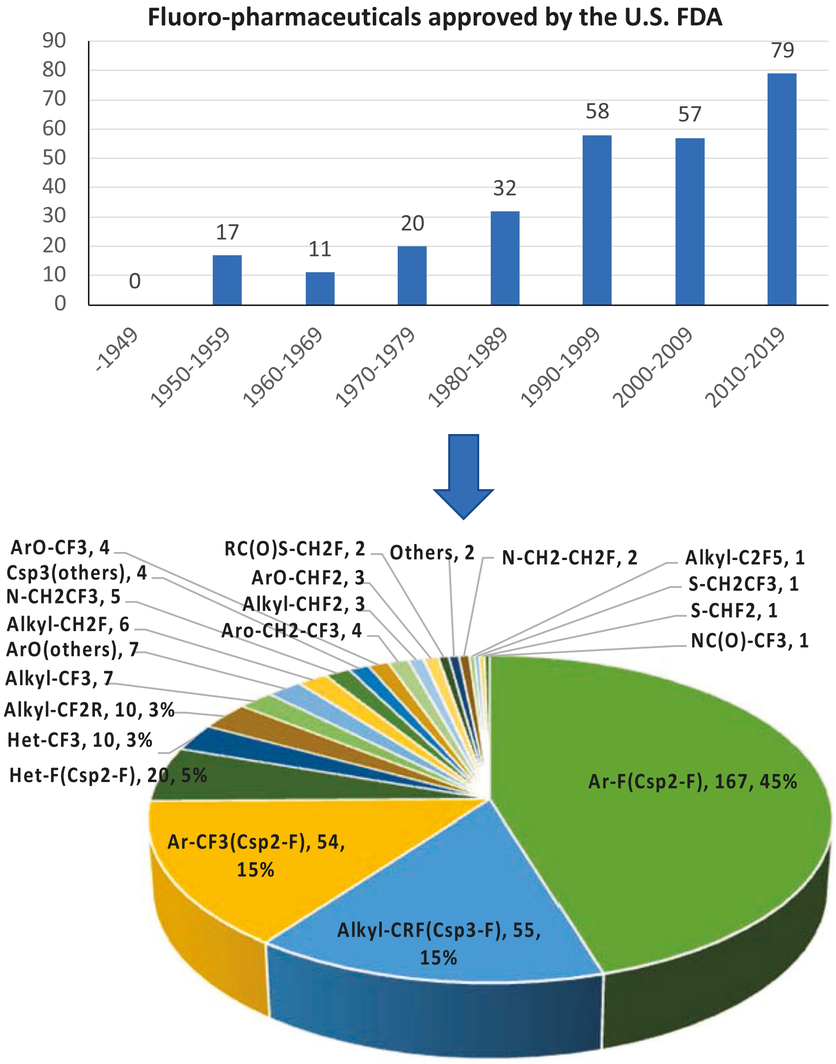


**Fig. 2** Numbers of fluoro-pharmaceuticals approved by the U.S. Food and Drug Administration through the end of 2019 (Johnson et al. 2020) and chemotype distribution of 369 fluorinated compounds used in pharmaceuticals (Inoue et al. 2020)

notable impact on medicinal chemistry, pharmaceutical, and chemical industries.

Pharmaceuticals, once taken by a human being, will undergo metabolism to a certain degree. Eventually, the drugs and their metabolites are excreted in urine and/or feces, hence entering municipal wastewater treatment plants (WWTPs) (Carlsson et al. 2006). Thus, occurrence of pharmaceuticals including those fluorinated ones in the environment is a growing concern globally. For example, a review article about the detection of 118 pharmaceuticals in raw and treated urban wastewater showed that the investigated pharmaceuticals were usually present in raw influent at $10^{-3}$–$10^{2}$ µg/L (Verlicchi et al. 2012).

A few fluorinated pharmaceuticals were reported to be biodegradable. For instance, the anti-depressant drug, fluoxetine with annual sales in the billions of dollars, can be degraded by common environmental bacteria to TFA and fluoride ion (Khan and Murphy 2021). The trifluoromethyl phenyl group that is present in a large number of drugs, such as Prozac and Celecoxib, is degradable by an isolated bacterial strain, *Rhodococcus* sp. 065240. TFA is the final degradation product (Yano et al. 2015). Thus, it is reasonable to expect that some of the fluorinated drugs are transformed by bacteria and fungi (Murphy 2016) once they are released into wastewater and during the process of wastewater treatment at WWTPs. The remaining drugs and their associated metabolites will then be discharged into the receiving environment where they may persist or be further degraded. While significant amount of research has been dedicated to pharmaceuticals in general, especially common drugs, (2009; Letsinger et al. 2019), research specifically targeting fluorinated drugs is relatively rare. In light of their increased production and use, the environmental fate of these compounds deserves to be understood better.

## Fluorinated compounds in coating materials

Fluorinated polymers have unique properties including low surface energies, high insulating capabilities, low permeability to gases, and high resistance to water, oils, chemicals, UV radiation, etc. (Imae 2003). These properties make fluorinated polymers excellent coating materials that are highly durable and weatherable. Thus, fluorinated polymers, such as polytetrafluoroethylene (PTFE or Teflon), fluorinated ethylene propylene (FEP), ethylene tetrafluoroethylene copolymer (ETFE), polyvinylfluroide (PVF), polyvinylidene fluoride (PVDF), and fluoroethylene vinyl ether (FEVE), are widely used in many coating formulations applied in architectural buildings, structural steel, composite structures, renewable energy infrastructure, bridges, walkways, and sculptures.

Due to the increasing demand, the global fluoropolymer market was valued at 4.7 billion € in 2015 and is expected to reach 7.8 billion € by 2022 with a compound annual growth rate of 7.7% from 2016 to 2022 (Martinelli and Nikel 2019). The increasing demand for fluoropolymers is not only driven by continued expansion in the construction market, but also due to strong growth in emerging markets such as photovoltaic modules and advanced batteries for electric vehicles (Ameduri 2020).

Although fluorinated polymeric coatings are designed to have prolonged life cycles, their manufacturing process could lead to the release of fluorinated compounds to the environment. For example, Wang et al. (2014) found that fluoropolymer facilities were associated with PFAA contamination. The concentration of ΣPFAAs was up to 5068.97 ng/L near the PTFE production facilities in the South Bohai coastal region. The estimated mass flux of PFAAs in rivers to the Bohai Sea was 4961.9 kg/year. Song et al. (2018) also analyzed water and sediment samples in a river receiving water discharge from one of the major fluoropolymer manufacturing facilities in China. A total of 42 PFAS, including tetramer acid of hexafluoropropylene oxide (HFPO-TeA) and C9–C14 per- or polyfluoroalkyl ether carboxylic acids (PFECAs), were detected. No measurable degradation of C3-C9 perfluorinated compounds was found when they were transported unimpededly with the bulk water flow. In the USA, PFOA and its alternative, GenX, were detected in water and soil samples collected from the upstream and downwind of a fluoropolymer production facility (Galloway et al. 2020). The concentration of PFOA was higher than 1000 ng/L at 13 sample sites within an 8 km radius of the facility, while the concentration of GenX was over 100 ng/L in surface water up to 6.4 km north of the facility.

In addition to PFAS used during and released from the manufacturing of the fluoropolymers, disposal of the spent or used polymers has raised serious concerns. In light of limited options for their recycling from consumer articles (Lohmann et al. 2020), thermal treatment has been commonly adopted. In one study, thermolysis of three polymers, poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), poly (vinylidene fluoride-co-chlorotrifluoroethylene) (PVDF-CTFE), and PTFE, yielded TFA at 1.2%, 0.9%, and 0.3%, respectively, when the polymers were heated to 500 °C and above (Cui et al. 2019). More than 20 years ago, thermolysis of fluoropolymers in industrial and consumer high-temperature applications (ovens, non-stick cooking utensils, and combustion engines) was believed to be a significant source of TFA in urban rainwater based on estimation of Toronto (Ellis et al. 2001). In addition to TFA, a wide range of short-chain fluorochemicals have been formed during the polymer combustion process. For example, thermal decomposition of polychlorotrifluoroethylene (PCTFE) led to the formation of 29 perhalogenated carboxylic acid groups and 21 chlorine/fluorine substituted polycyclic aromatic hydrocarbon groups (Myers et al. 2014).

## Disposal and releases of fluorinated compounds in the USA

The U.S. EPA tracks toxic chemicals that may pose a threat to human health and the environment through its Toxics Release Inventory (TRI) program. To collect data and establish corresponding databases, the U.S. EPA requires certain industrial and federal facilities to report the releases of toxic chemicals, as well as their management of these chemicals through recycling, combustion for the purpose of energy recovery, and treatment. According to the latest 2021 dataset, 48 fluorinated compounds were disposed of (on- and off-site) or released to the environment in the USA (Table 4). The annual amount of disposed/released fluorinated compounds in 2021 was 974,765 kg. Among these chemicals, CFC and HCFC chemicals, especially chlorodifluoromethane (HCFC-22), contributed the most (752,283 kg) in terms of the total mass.

The amount of vinyl fluoride and tetrafluoroethylene, which are usually used as precursors to manufacture fluoropolymers, was 59,429 kg and 50,522 kg, respectively, in 2021. Besides, multiple PFAS chemicals were included in the database. The 2021 TRI factsheet for PFAS chemicals showed that 44 facilities reported their handling of these compounds (Fig. 3). In total, 0.59 million kg of PFAS waste were managed through recycling (64%), treatment (26%), energy recovery (1%), and disposal/releases (8%) in that year. According to the TRI data, 377,389 kg of PFAS was recycled. However, the approaches/methods for PFAS recycling were not clearly reported by the managing facilities or the U.S. EPA. Focusing on PFAS disposal/releases, the total mass in 2021 was 49,124 kg, which is 4.5 times greater than that in 2020 (10,886 kg). The majority of the released PFAS chemicals in 2021 went to land (71%), followed by off-site disposal/other releases (27%). Releases to land include disposal of PFAS waste in landfills, land application to agricultural soil, and other land disposal methods (such as surface impoundments in uncovered holding areas, waste piles, and spills/leaks to land).

It is worth noting that there were still 336 kg and 635 kg of PFAS chemicals directly discharged into water and air, respectively, causing PFAS pollution in the environment. In 2022, EPA issued interim updated drinking water health advisories for the two most widely detected PFAS chemicals, PFOA and PFOS, at 0.004 ng/L and 0.02 ng/L, respectively. At the same time, EPA also issued final health advisories for perfluorobutane sulfonic acid (PFBS, 2000 ng/L) and hexafluoropropylene oxide dimer acid and its ammonium salt (GenX, 10 ng/L). From the TRI database, the mass of disposed/released PFOA, PFOS, and GenX in 2021 was 132 kg, 10,573 kg, and 6559 kg, respectively. Although most applications of PFOA and PFOS were voluntarily phased out by U.S. manufacturers, there are a limited number of ongoing uses. The major sources of PFOA, PFOS, PFBS, and GenX in the USA in 2021 were reported to be industrial gas manufacturing facilities, plastics material and resin manufacturing facilities, laminated/unlaminated plastics plate, sheet, and shape manufacturing facilities, hazardous waste treatment and disposal facilities, military facilities, solid waste combustors and incinerators, petroleum bulk stations and terminals, surface active agent manufacturing facilities, abrasive product manufacturing facilities, paint and coating manufacturing facilities, and cement manufacturing facilities.

Overall, the available databases from the U.S. EPA provide valuable information for assessing environmental risks caused by fluorinated compounds, but it is important to note that not all fluorinated chemicals are subject to reporting under the TRI program, and the data may not reflect the full extent of their production, use, and releases to the environment in the USA For instance, only two fluorinated agrochemicals (i.e., oxyfluorfen, acifluorfen) and one pharmaceutical (i.e., fluorouracil) were reported and included in the TRI list. There is still a huge knowledge gap on the releases of fluorinated compounds from food packaging, cosmetic, agrochemical, and pharmaceutical industries.

## Perspective and outlook

According to the literature examined, it was commonly believed prior to 2010 that agrochemicals, anesthetics, and fluoropolymers, in addition to CFC substitutes, constituted the primary and distinct categories that release fluorine-containing anthropogenic organic compounds to the environment. Here, through reviewing the seven sources of fluorinated compounds, it became clear that there are a great many sources contributing to the load of organofluorine-containing compounds including TFA in the environment.

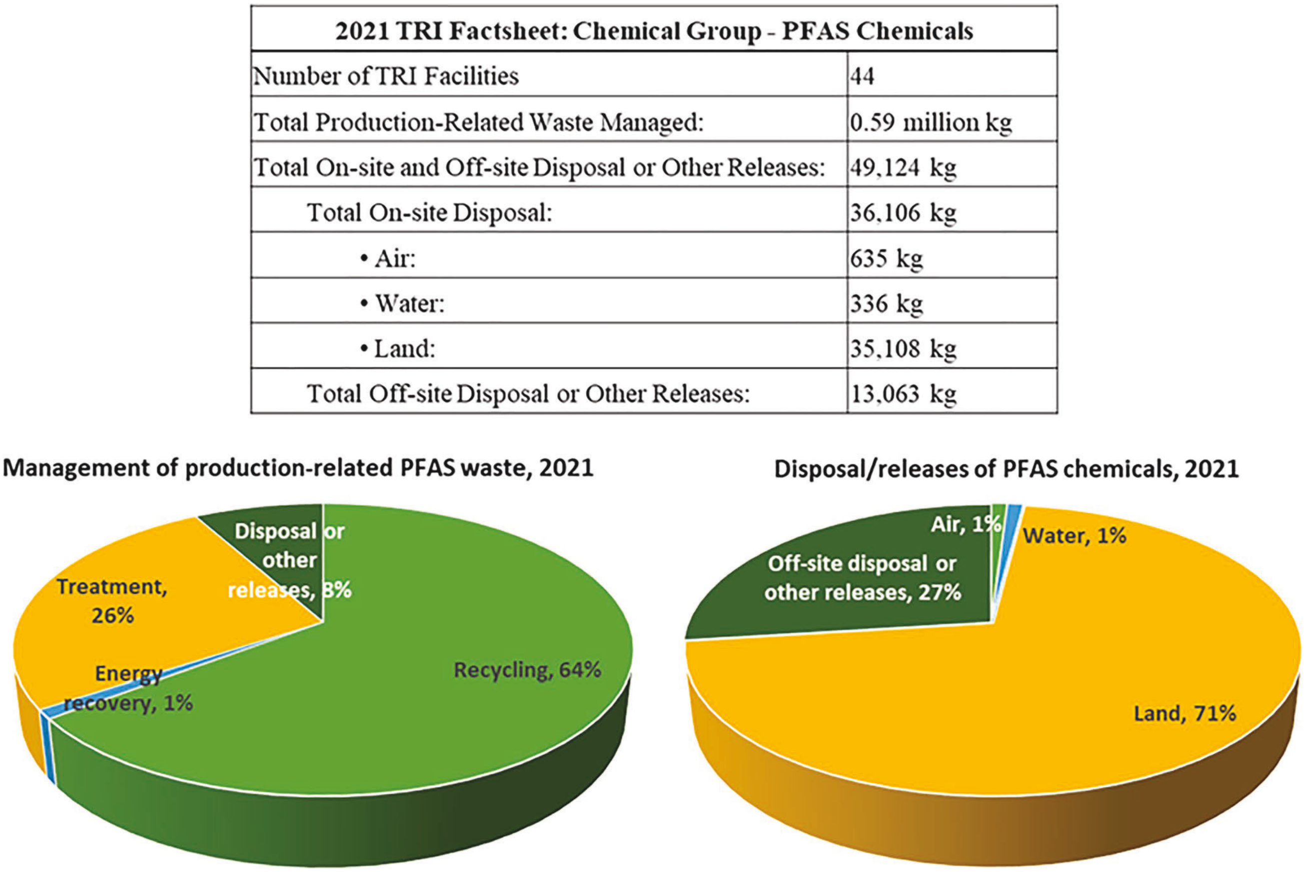
Specific to TFA, it is estimated that this compound could be a potential environmental breakdown product of > 1 million chemicals (Solomon et al. 2016). In rat's body, the $LD_{50}$ of TFA has been reported between > 400 and > 5000 mg/kg (Airaksinen and Tammisto 1968; Blake et al. 1969; Rosenberg and Wahlström, 1971). When pregnant mice were injected with TFA at 34 mg/kg of body weight for one hour, TFA was found to accumulate in amniotic fluid than in the plasma of the mother (Ghantous et al. 1986). Thus, TFA might have fetal toxicity. In the environment, TFA as an acid or salt has low to moderate toxicity to a wide range of organisms (Solomon et al. 2016). At present aquatic environmental levels, TFA is

**Table 4** Total on- and off-site disposal or other releases of fluorinated compounds in 2021 based on the U.S. EPA Toxics Release Inventory (TRI)

| Fluorinated compounds | Categories | Total on- and off-site disposal or other releases (kg) |
|---|---|---|
| Chlorodifluoromethane (HCFC-22) | CFC/HCFC | 464710.47 |
| Trichlorofluoromethane (CFC-11) | CFC/HCFC | 95037.81 |
| Vinyl fluoride | Precursor to fluoropolymers | 59428.54 |
| 1-Chloro-1,1-difluoroethane (HCFC-142b) | Refrigerant | 54667.72 |
| Tetrafluoroethylene | Precursor to fluoropolymers | 50521.98 |
| 1,2-Dichloro-1,1,2-trifluoroethane (HCFC-123a) | CFC/HCFC | 44661.38 |
| 2-Chloro-1,1,1,2-tetrafluoroethane (HCFC-124) | CFC/HCFC | 42115.18 |
| Dichlorotetrafluoroethane (CFC-114) | CFC/HCFC | 35839.04 |
| 2,2-Dichloro-1,1,1-trifluoroethane (HCFC-123) | CFC/HCFC | 18115.51 |
| Dichlorodifluoromethane (CFC-12) | CFC/HCFC | 15867.61 |
| Thiols, C8-20, γ-ω-perfluoro, telomers with acrylamide | PFAS | 12246.98 |
| 1-Propanesulfonic acid, 2-methyl-, 2-[[1-oxo-3-[(γ-ω-perfluoro-C4-16-alkyl)thio]propyl]amino] derivs., sodium salts | PFAS | 10886.21 |
| 1,2-Dichloro-1,1-difluoroethane (HCFC-132b) | CFC/HCFC | 10351.88 |
| 2-Chloro-1,1,1-trifluoroethane (HCFC-133a) | CFC/HCFC | 9220.66 |
| 1,1,1,2-Tetrachloro-2-fluoroethane (HCFC-121a) | CFC/HCFC | 8085.28 |
| Perfluorooctane sulfonic acid | PFAS | 7397.38 |
| Bromotrifluoromethane (Halon 1301) | Firefighting | 6319.90 |
| Hexafluoropropylene oxide dimer acid | PFAS | 6187.48 |
| Potassium perfluorooctanesulfonate | PFAS | 3175.23 |
| Perfluorooctyl iodide | PFAS | 2683.19 |
| 1,1-Dichloro-1-fluoroethane (HCFC-141b) | CFC/HCFC | 2639.50 |
| Monochloropentafluoroethane (CFC-115) | CFC/HCFC | 2319.64 |
| Oxyfluorfen | Agrochemical | 2260.43 |
| 1-Chloro-1,1,2,2-tetrafluoroethane (HCFC-124a) | CFC/HCFC | 1689.12 |
| Bromochlorodifluoromethane (Halon 1211) | CFC/HCFC | 1578.50 |
| 1-Propanaminium, 2-hydroxy-N,N,N-trimethyl-, 3-[(γ-ω-perfluoro-C6-20-alkyl)thio] derivs., chlorides | PFAS | 1360.78 |
| 1-Propanaminium, 3-amino-N-(carboxymethyl)-N,N-dimethyl-, N-[2-[(γ-ω-perfluoro-C4-20-alkyl)thio]acetyl] derivs., inner salts | PFAS | 1360.78 |
| Poly(oxy-1,2-ethanediyl), α-[2-[ethyl[(heptadecafluorooctyl)sulfonyl]amino]ethyl]-ω-hydroxy- | PFAS | 1303.62 |
| 3-Chloro-1,1,1-trifluoropropane (HCFC-253fb) | CFC/HCFC | 1039.46 |
| Dichlorofluoromethane (HCFC-21) | CFC/HCFC | 589.67 |
| Hexafluoropropylene oxide dimer acid ammonium salt | PFAS | 371.93 |
| Chromium(III) perfluorooctanoate | PFAS | 340.19 |
| Perfluorohexanesulfonic acid | PFAS | 226.80 |
| Perfluorooctanoic acid | PFAS | 132.38 |
| Dibromotetrafluoroethane | Firefighting | 5.44 |
| Acifluorfen, sodium salt | Agrochemical | 4.63 |
| Poly(difluoromethylene), α,α’-[phosphinicobis(oxy-2,1-ethanediyl)]bis[ω-fluoro-, ammonium salt | PFAS | 4.54 |
| Poly(difluoromethylene), α-fluoro-ω-[2-(phosphonooxy)ethyl]-, diammonium salt | PFAS | 4.54 |
| Siloxanes and silicones, (3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)oxy Me, hydroxy Me, Me octyl, ethers with polyethylene glycol mono-Me ether | PFAS | 4.54 |
| Ethanol, 2,2′-iminobis-, compd. with α-fluoro-ω-[2-(phosphonooxy)ethyl]poly(difluoromethylene) (2:1) | PFAS | 3.47 |
| Ethanol, 2,2′-iminobis-, compd. with α,α’-[phosphinicobis(oxy-2,1-ethanediyl)]bis[ω-fluoropoly(difluoromethylene)] (1:1) | PFAS | 1.67 |

**Table 4** (continued)

| Fluorinated compounds | Categories | Total on- and off-site disposal or other releases (kg) |
|---|---|---|
| Sodium fluoroacetate | Agrochemical | 1.36 |
| 2-Propenoic acid, esters, 2-methyl-, dodecyl ester, polymer with α-fluoro-ω-[2-[(2-methyl-1-oxo-2-propen-1-yl)oxy]ethyl]poly(difluoromethylene) | PFAS | 0.45 |
| 1-Octanesulfonamide, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-N-methyl- | PFAS | 0.36 |
| 2-Propenoic acid, butyl ester, telomer with 2-[[(heptadecafluorooctyl)sulfonyl]methylamino]ethyl… | PFAS | 0.19 |
| Fluorouracil | Pharmaceutical | 0.09 |
| Poly(oxy-1,2-ethanediyl), α-hydro-ω-hydroxy-, ether with α-fluoro-ω-(2-hydroxyethyl) poly(difluoromethylene) (1:1) | Precursor to agrochemicals/ pharmaceuticals | 0.05 |
| Ethanaminium, N,N,N-triethyl-, salt with 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-1-octanesulfonic acid (1:1) | PFAS | 0.03 |



| 2021 TRI Factsheet: Chemical Group - PFAS Chemicals | |
|---|---|
| Number of TRI Facilities | 44 |
| Total Production-Related Waste Managed: | 0.59 million kg |
| Total On-site and Off-site Disposal or Other Releases: | 49,124 kg |
| Total On-site Disposal: | 36,106 kg |
| • Air: | 635 kg |
| • Water: | 336 kg |
| • Land: | 35,108 kg |
| Total Off-site Disposal or Other Releases: | 13,063 kg |

**Fig. 3** Management of production-related PFAS waste listed in the U.S. EPA Toxics Release Inventory (TRI) in 2021

not shown to be acutely toxic according to short-term terrestrial ecotoxicological tests (Jordan and Frank 1999). TFA concentration of 0.10 mg/L is regarded as safe for the aquatic ecosystem (Berends et al. 1999). Nevertheless, for higher terrestrial plants, such as trees and in particular conifers, enrichment in leaf or needle tissue by a factor of $10^3$ within a year relative to rain and surface waters has been observed, calling for detailed studies of potential long-term effects. More importantly, given the possibility of TFA entering the food chain through plant uptake, its accumulative nature in the environment, and the ever-increasing chemicals and products that can be broken down into TFA, TFA's concentration in the environment needs to be monitored continuously. Fortunately, TFA at its current level in the environment does not pose an immediate danger and threat to public health. But this does not guarantee that TFA will never reach a point that is toxic to the ecosystem. In addition, the use of PFAS in numerous products has led to detection of extremely toxic chemicals in the environment and humans (Backe et al. 2013; Ahrens and Bundschuh 2014; De Silva et al. 2021; Panieri et al. 2022), which is why maximum contaminant level (MCL) for a few PFAS has been legalized in several US states and proposed by the US EPA in March of 2023. To protect public health and the environment, a few thoughts deserve to be pondered upon.

First, as discussed above, numerous PFAS have been used in consumer products, like clothing, cookware, furniture, carpet, and cosmetic products. At present, even if PFAS are used in these products, they are invisible to consumers. Shall manufacturers be required to disclose such information in their list of ingredients and materials? If yes, then consumers at least can have the opportunity to choose what they would like to buy and use.

Second, as analyzed above, a lot of fluorinated compounds in consumer products, pharmaceuticals, etc. will eventually enter the wastewater treatment facilities where they may bind to sewage sludge or be released to receiving environmental bodies. At this stage, these chemicals are not regulated by the U.S. EPA. The state of Maine in the USA, however, has set upper limits of PFOA (2.5 μg/kg), PFOS (5.2 μg/kg), and PFBS (1900 μg/kg) for beneficial use of solid wastes. A few countries, such as Denmark, Germany, the Netherlands, Sweden, and Australia had set PFAS limits in soils (Hall et al. 2020). As a result of Maine's regulation, sludge and biosolids in this state can no longer be land applied. The local governments that operate and maintain the wastewater treatment facilities are forced to find other ways to dispose of their sludge. Aside from financial burdens, this adds significant constraints to these facilities as they face the challenges of operating an infrastructure that could be well over 100 years old. In addition, to the best of our knowledge, there are no suitable technologies that can destroy PFAS in sewage sludge (Zhang and Liang 2021; Zhang et al. 2022a, 2022b). Therefore, facilities subject to regulations regarding PFAS in sludge ship their waste to other locations for disposal through landfill or incineration. This approach, however, does not solve the PFAS problem at all. It is reasonable and, in many cases, needed to regulate PFAS in sludge to protect the environment and human health. The question is: who should pay for all added or extra costs related to PFAS treatment? At present, in villages and cities in the USA, residents within a city limit are ratepayers for the water and sewer systems. With the expected increasing cost for handling PFAS-related issues, should all expenses be piled onto the taxpayers? What is the role of the manufacturers who use PFAS in their products? How much do they need to contribute to solving the PFAS problem globally?

Third, as discussed above, fluorinated compounds in each field are used due to many justifiable reasons. Although the inclusion of C-F bonds brings numerous positive properties to a certain compound or material, the question is: can we develop other chemicals and products that have similar properties but without the negative environmental consequences? Finding, developing, and evaluating non-PFAS-containing firefighting foam have been ongoing for several years (Dubocq et al. 2019; Ross et al. 2021; Dahlbom et al. 2022; Wu et al. 2022; Yu et al. 2022). Although the progress is not fast, it is a plausible approach to move forward. Similar efforts should be attempted to develop green and non-fluorine-containing compounds for other applications, like consumer products, coating materials, and pharmaceuticals as reviewed above.

Fourth, due to limited data in EPA's TRI program, it is not possible to calculate the mass input of fluorinated compounds to the environment from each source. As a consequence, the total burden of fluorinated compounds added to the environment is unknown at this point. To know this clearly, manufacturers who use these compounds must disclose and report their data to EPA. Only when all relevant data are out there in the light, a better picture of these compounds in the local, national, and global environment can be obtained. Such information will then enable the scientific community to calculate the loads of these chemicals to different environmental matrices and predict what will happen in the near, midterm, and long-term future. Such knowledge and predictions cannot take place without the seamless collaborations among government agencies, industries, and academia.

**Author contribution** Weilan Zhang: investigation, validation, formal analysis, and writing—original draft.

Yanna Liang: conceptualization, supervision, and writing—review and editing.

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**Data availability** The authors have no data availability related matters to declare.

## Declarations

**Ethical approval** This research does not involve human participants and/or animals.

**Consent to participate** Informed consent was obtained from all individual participants included in the study.

**Consent for publication** The participant has consented to the submission of the case report to the journal.

**Competing interests** The authors declare no competing interests.

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