Environmental Science & Technology

Target and Nontarget Screening of PFAS in Biosolids, Composts, and Other Organic Waste Products for Land Application in France

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Cite This: https://doi.org/10.1021/acs.est.1c03697 **Read Online**

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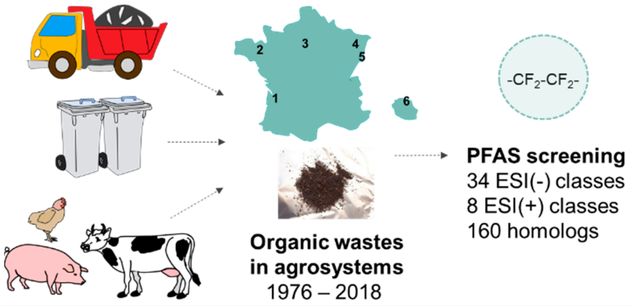

ABSTRACT: Zwitterionic, cationic, and anionic per- and polyfluoroalkyl substances (PFAS) are increasingly reported in terrestrial and aquatic environments, but their inputs to agricultural lands are not fully understood. Here, we characterized PFAS in 47 organic waste products (OWP) applied in agricultural fields of France, including historical and recent materials. Overall, 160 PFAS from 42 classes were detected from target screening and homologue-based nontarget screening. Target PFAS were low in agriculture-derived wastes such as pig slurry, poultry manure, or dairy cattle manure (median $\sum_{46}$PFAS: 0.66 μg/kg dry matter). Higher PFAS levels were reported in urban and industrial wastes, paper mill sludge, sewage sludge, or residual household waste composts (median $\sum_{46}$PFAS: 220 μg/kg). Historical municipal biosolids and composts (1976–1998) were dominated by perfluorooctanesulfonate (PFOS), *N*-ethyl perfluorooctanesulfonamido acetic acid (EtFOSAA), and cationic and zwitterionic electrochemical fluorination precursors to PFOS. Contemporaneous urban OWP (2009–2017) were rather dominated by zwitterionic fluorotelomers, which represented on average 55% of $\sum_{160}$PFAS (max: 97%). The fluorotelomer sulfonamidopropyl betaines (X:2 FTSA-PrB, median: 110 μg/kg, max: 1300 μg/kg) were the emerging class with the highest occurrence and prevalence in contemporary urban OWP. They were also detected as early as 1985. The study informs for the first time that urban sludges and composts can be a significant repository of zwitterionic and cationic PFAS.

KEYWORDS: *nontarget screening, Kendrick mass defect, cationic and zwitterionic PFAS, fluorotelomers, municipal biosolids, composts, agricultural wastes, temporal shift*

1. INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are a family of anthropogenic chemicals used extensively due to their unique surfactant properties and high thermal and chemical stability. As such, PFAS have been reported in a variety of specialty applications (e.g., fluoropolymer manufacture, aqueous film-forming foams (AFFFs) used in firefighting) and consumer products (e.g., coated paper and board for food packaging, cosmetics, and water-repellent clothing). Environmental research efforts accelerated since the 2000s after concerning reports on perfluorooctanesulfonate (PFOS; C8) and perfluorooctanoate (PFOA; C8) were published.[1] Of particular concern are the developmental toxicity, immunotoxicity, and hepatotoxicity of perfluoroalkyl acids (PFAAs).[1,2] Though PFOS, PFOA, and their homologues were the initial focus of research, the PFAS chemical diversity extends far beyond as demonstrated by recent discoveries of new classes.[3−5] Multiplatform approaches combining targeted and suspect-targeted screening confirmed that PFAAs represent a limited fraction of the estimated total PFAS in environmental samples.[6−8] Limited information is currently available regarding the toxicity and environmental fate of newly identified PFAS.

A large share of the total PFAS in any given sample may be composed of derivatives with nonfluorinated moieties, many of which could generate PFAAs during degradation. Well known examples of such precursors include classes having small head groups such as fluorotelomer sulfonates (X:2 FTSA), perfluoroalkyl sulfonamides, and related compounds. The infrequently monitored anionic, cationic, and zwitterionic PFAS with large nonfluorinated organic head groups can transform to the smaller, well-known precursors during environmental degradation, also leading to stable PFAAs.[9,10] Example classes include

Special Issue: Emerging Contaminants: Fluorinated Alternatives to Existing PFAS Compounds

Received: June 6, 2021
Revised: September 10, 2021
Accepted: September 22, 2021

telomerization-based fluorotelomer thioether propylamido dimethylethyl sulfonates and their sulfoxide/sulfone analogs,[6,11,12] fluorotelomer sulfonamidopropyl betaines,[13,14] and electrochemical fluorination (ECF)-based dimethylammoniopropyl and trimethylammoniopropyl perfluoroalkyl sulfonamides.[7,15]

The prevalence of these newly identified precursors may explain why PFAAs or degradation intermediates could increase along the treatment train of drinking water and wastewater.[16,17] A recent study evaluated PFAS following a simulated AFFF release within a wastewater treatment plant; aqueous concentrations of 6:2 FTSA increased 20 times in the wastewater influent 2 days after AFFF addition but 300 times in the effluent, presumably due to the transformation of unidentified precursors.[16] An increase over time of FOSA was also observed in biosolid-amended soil mesocosms, possibly reflecting the breakdown of unidentified precursors.[18] Unmonitored precursors also accounted for significant proportions of total PFAS via a persulfate oxidative assay in wastewater sludge,[16] landfill leachate from solid waste disposal facilities,[19] and organic solid waste composts.[20] Their chemical identities remain to be clarified. Achieving a detailed characterization of emerging PFAS may be compounded by analytical hurdles, including lack of certified standards. Enhanced extraction methods may also be required that differ from current-use methods.[7,21]

Recycling of organic-rich wastes in agriculture minimizes landfilling and incineration and allows organic matter and nutrient recycling. It can reduce the dependency on mineral fertilizers, thus lowering carbon footprints.[22,23] However, this valuable agronomic recycling is challenged by the putative introduction of contaminants.[24−27] Depending on the origin of raw materials, organic waste products (OWP) could constitute significant reservoirs for PFAS, allowing their re-entry to the environment via land application in agricultural fields.[28] Contamination of surface- and groundwaters used for drinking water production,[29] uptake by the edible crop fractions,[30] and contamination of cattle products[31] are related potential human exposure routes. For instance, Lindstrom et al. reported PFOS/PFOA exceeding EPA advisory levels (>70 ng/L) in water resources impacted by the repeated land application of PFAS-contaminated biosolids in Decatur, AL,[29] while Blaine et al. documented the bioaccumulation of PFAAs in crops grown in biosolids-amended soils or irrigated with reclaimed water.[32,33] The occurrence of PFAAs in sewage sludge has been previously investigated, for instance, in surveys from Australia[34] and the U.S.,[35] while data for precursors and emerging PFAS are still scarce. In particular, the contribution of newly identified zwitterionic, cationic, and anionic PFAS has not yet been quantified in biosolids. Only a few studies reported on the occurrence of historical PFAS (PFAAs) in urban composts,[20,36] while no previous study comprehensively evaluated PFAS in livestock manures.

In the present study, zwitterionic, cationic, and anionic PFAS (including PFAAs) were screened in historical and contemporaneous OWP used for land application in metropolitan France and Réunion Island. Forty-seven individual OWP samples were selected from six participating units within the French INRAE observatory SOERE-PRO.[37] The goals of this observatory are to investigate the agronomical effects of repeated applications of OWP in agriculture and related risks.[24−27,38] We chose representative OWP samples archived by the observatory, including livestock manures (raw or processed manure from poultry, pig, and dairy cattle livestock farming), urban OWP (sewage sludge composted or not, compost of municipal solid wastes and biowastes), and industrial wastes (paper sludge and ashes). A PFAS analytical workflow combining enhanced extraction methods, homologue-based nontargeted analysis with Kendrick mass defect filtering, and target/suspect-target screening was applied. To the best of our knowledge, this is the first comprehensive inventory of multiclass PFAS in various land-applied OWP. Profiling of solid urban wastes spanning 40 years (1976−2017) demonstrated temporal shifts in PFAS composition.

2. MATERIALS AND METHODS

2.1. Chemicals and Standards. Isotope-labeled internal standards were obtained from Wellington Laboratories (Guelph, ON, Canada). High-purity analytical standards of negative ion mode (ESI(−)) PFAS were procured from Wellington Laboratories (Guelph, ON, Canada), DuPont (Wilmington, DE), or Synquest Laboratories (Alachua, FL). Standards of cationic/zwitterionic PFAS were purchased from Wellington Laboratories (Guelph, ON, Canada) or custom-synthesized at the Fluobon Surfactant Institute (Beijing, China).[10] Light Water AFFF (3 M Lightwater, FC185F) and Arctic Foam AFFF (Solberg, 201AF, 1%) were also used to aid in compound identification. Further details on target analytes, internal standards, and other chemicals and materials are provided in Supporting Information (SI) Text S1 and Tables S1 and S2.

2.2. Sample Collections at INRAE-SOERE Experimental Sites. This study was conducted within the French observatory SOERE PRO and Cirad.[24,37,39] The observatory is a network of long-term field experiments (i.e., randomized block-devices), monitoring at the plot-scale the evolution of agro-systems receiving OWP.[24,39] Each field experiment is carried out since 1974 for the oldest one and is representative of regional OWP, crops and cultivated soils.

The studied OWP were sampled at the time of field application (just before spreading to the agricultural fields) for analysis of classical parameters and long-term storage for further potential analyses. A total amount of 15−20 kg fresh material was progressively taken from different points of the OWP pile intended for field application, so that the sample would be as representative as possible of the heterogeneity of the waste material. Three subsamples of about 1 kg each were then collected and used for analysis. Samples were stored at −20 °C for each site, except for EFELE and Couhins sites for which samples were stored at ambient temperature after drying at 40 °C. For PFAS analysis, archived samples were freeze-dried and aliquoted in 50 mL polypropylene falcon tubes (~40 mL per sample) prior shipping to the UdeM laboratory. Once received at the laboratory facilities, OWP samples were crushed with mortar and pestle and sieved (2 mm mesh) prior further preparation.

Samples of OWP were collected at six sites of the SOERE PRO network, including five sites in metropolitan France—La Bouzule (Nancy, Grand-Est), Couhins (Bordeaux, Nouvelle-Aquitaine), EFELE (Rennes, Bretagne), PROspective (Colmar, Grand-Est), QualiAgro (Feucherolles, Ile-de-France)—and the site of La Réunion (French Overseas, southwestern Indian Ocean). Couhins and La Bouzule are historical sites since the application of OWP stopped, respectively, in 1993 and 1996, whereas the other sites are still active.

Overall, 47 individual samples of OWP were targeted for this study (SI Tables S3−S6). Among urban OWP, municipal sewage sludge (SLU; $n = 10$) included both samples collected at historical SOERE PRO sites (year of collection: 1976−1998) and those from recent years collected at active sites (2009−2017). The other samples of urban OWP were collected from historical and active sites, including compost of green wastes and sewage sludge (C-GWS, $n = 6$, collected in 1996 and 2009−2017), compost of municipal biowastes (C-BIOW, $n = 4$, collected in 2009, 2011, 2013, and 2016), compost of residual municipal solid waste (C-MSW, $n = 3$, collected in 2011, 2013, and 2016), and digestate of urban wastes (DIG-UW, $n = 1$, collected in 2016). Note that C-BIOW refers to composts of greenwaste and the separately collected fermentable fraction of the municipal wastes, whereas C-MSW refers to composts made from the residual fraction of municipal solid wastes after separated collections of packaging, papers and cardboard, glass, and dangerous wastes. Twenty-one samples of livestock manure were sampled at active sites from 2011 to 2018, including farmyard manure of dairy cattle (FYM-DC, $n = 6$), pig slurry (PS, $n = 4$), poultry manure (PM, $n = 4$), compost of farmyard manure of dairy cattle (C-FYM-DC, n = 1), compost of farmyard manure of pigs (C-FYM-P, n = 3), and digestates of pig slurry (DIG-PS, n = 3). Two samples of OWP sourced from the industry were collected at La Bouzule historical site in 1996, paper sludge (PSLU, $n = 1$) and ashes (ASH, $n = 1$).

2.3. Quantitative Analysis of Target PFAS.

Full details on sample preparation and instrumental analysis are presented in SI Text S2 and Table S7. Surrogate internal standards were spiked to a sample dry weight of 0.1 g (for municipal wastewater sludge (SLU)) or 0.5 g (for other samples). Samples were submitted to ultrasound-assisted solvent extraction, followed by filtration through Supelclean ENVI-Carb cartridges (500 mg/6 mL). MeOH containing 10 mM NH_4OH was used as an extractant in the first two extraction cycles, whereas the third cycle used MeOH containing 100 mM CH_3COONH_4 for improved recovery of difficult-to-extract PFAS.[21,40] Extracts were analyzed by ultrahigh-performance liquid chromatography coupled to high-resolution mass spectrometry (UHPLC-HRMS Thermo Q-Exactive Orbitrap).[21,41]

2.4. Quality Assurance/Quality Control.

Method limits of detection, determination coefficients (R^2), instrumental accuracy, and intraday/interday precision are provided in SI Table S8. The accuracy of continued calibration verification (CCV) standards ranged between 81 and 121% (SI Table S9). Matrix spike-recovery experiments were performed on four types of organic solid waste samples, including dairy cattle manure, pig slurry, poultry litter, and organic waste compost (C-BIOW). Despite the high organic carbon content (4−42%), spike recoveries of the 46 target PFAS were between 75 and 113% (SI Table S10). In addition, the method trueness was verified upon extraction and analysis of a NIST standard reference material of domestic sludge (SRM 2781), in quintuplicate. For those PFAS with NIST reference values, accuracy was in the range of 81−130% (SI Table S11).

A subset of the organic solid waste samples (six OWP tested, $n = 3$ per sample) with high PFAS content was selected to verify the residual PFAS amount from a second round of extraction cycles following the first three extraction cycles. The combined supernatants from the second round were kept separate from the primary extraction. The residual PFAS in secondary extraction were either nondetectable or <2.5% on average relative to the primary extraction (SI Table S12), confirming one round of extraction was sufficient.

2.5. Nontarget and Suspect Screening.

Select OWP samples of high target $\sum_{46}$PFAS (>200 μg/kg) were submitted to a new preparation and qualitative UHPLC-HRMS analysis (Orbitrap Q-Exactive). Data were acquired in scanning mode (full scan MS, range: m/z 150−1000, resolution setting of 70 000 fwhm at m/z 200), with separate acquisitions for negative and positive ionization modes.

Xcalibur raw files of select OWP were inputted pairwise with a procedural blank into XCMS Online (https://xcmsonline.scripps.edu) to eliminate the blank background. Further feature reduction using XCMS Online was performed using a signal intensity threshold of 1E4. The generated Excel data frame of peak lists (accurate m/z, retention time, and signal intensity) was subject to mass defect filtering[3,42] using an in-house script programmed with Anaconda (Python distribution). The measured mass from IUPAC mass scale was converted to Kendrick mass scale[43] and extracted peaks with CF_2-normalized mass defects of 0.85−1.0 or 0−0.15 were retained. Additional rules were adopted from the PFAS nontarget literature: the observation of ascending retention times for homologue series and the exclusion of dimers, adducts, and isotopes potentially corresponding to the same entity.[3,42] An automated library search (also programmed with Anaconda) was conducted within ±10 ppm by comparing m/z features to general PFAS Excel databases (the Norman Network PFAS Suspect List, available online at https://www.norman-network.com, the OECD's New Comprehensive Global Database for PFASs, available online at http://www.oecd.org/chemicalsafety/portal-perfluorinated-chemicals/) and lists for AFFF-derived PFAS from Barzen-Hanson et al.[3] and Nickerson et al.[7]

Tentative identity confirmation was conducted by reinjecting an aliquot using targeted MS/MS on the Orbitrap Q-Exactive. Select compounds among each class were inputted in the inclusion list with normalized collision energies tested at different levels. Spectrum elucidation was aided with literature[3,4,6] and in-silico prediction (Mass Frontier). The observation of consistent retention time patterns among homologous series and chromatographic peak shapes (e.g., presence of branched isomers for ECF-based PFAS) were the other factors considered. Identification confidence levels were assigned adapted from Schymanski's classification.[44] When the presence of homologues with ascending retention times was noted for a given class, this was marked with an asterisk (*). PFAS names/acronyms were referred according to a nomenclature table developed by Nickerson et al.[7]

The additional PFAS identified from nontarget screening were retrospectively inspected in the data files from the target analyses to get semiquantitative estimates (suspect screening). Suspect PFAS were matched with a reference calibrant (SI Table S13) and isotope-labeled internal standard (ILIS) of similar functional group and chain length, where possible, following the same methodology described in Mejia-Avendaño et al.[6]

2.6. Statistical Analyses.

Factorial analysis was performed with the R statistical software version 4.0.4 (R Core Team 2021, Vienna, Austria). The *FactoMineR*, *factoextra* (based on *ggplot2*), and *stats* R packages were used to conduct Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA; Ward's method).

3. RESULTS AND DISCUSSION

3.1. Detection of 42 PFAS Classes.

Overall, 42 PFAS classes (160 homologues) were detected with nontarget or suspect/target screening within the set Kendrick mass defect

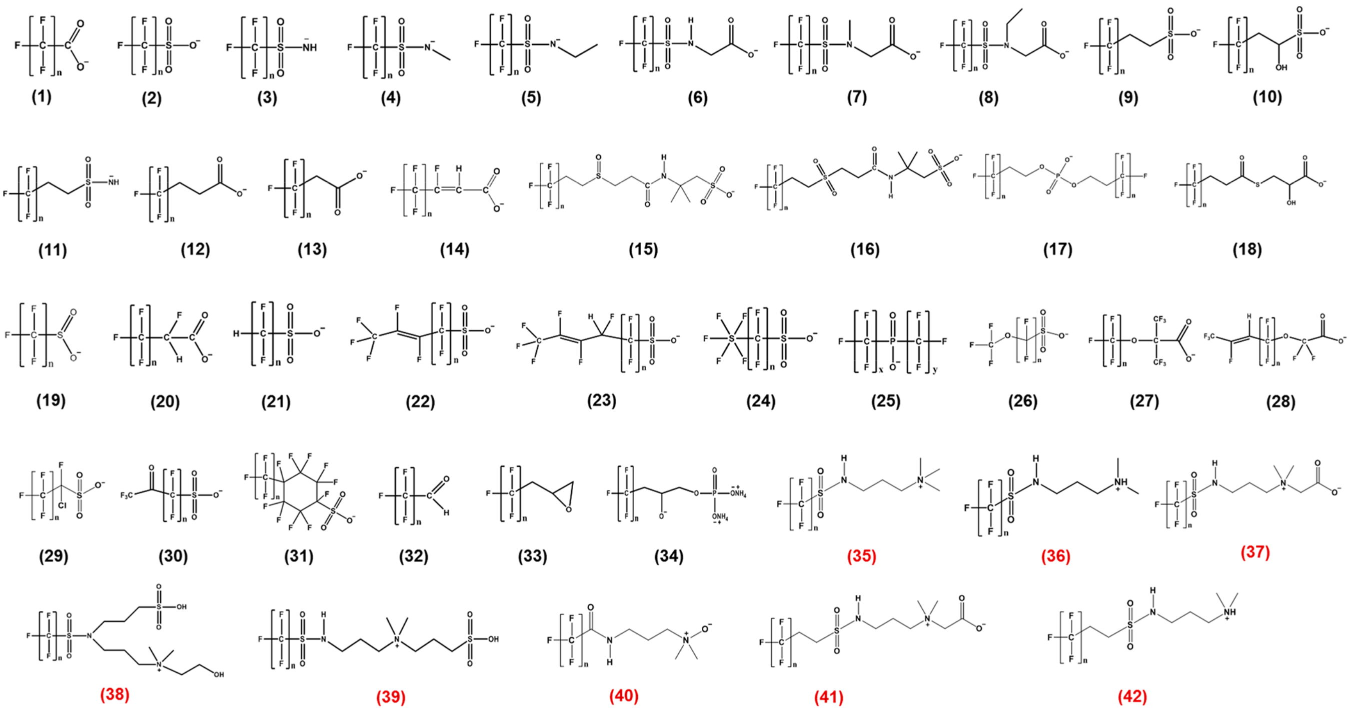

Figure 1. Structures of the 42 PFAS classes detected across OWP samples. ESI(+) classes are highlighted in red font. Class acronyms: (1) PFCA; (2) PFSA; (3) FASA; (4) MeFASA; (5) EtFASA; (6) FASAA; (7) MeFASAA; (8) EtFASAA; (9) X:2 FTSA; (10) X:2 HO-FTSA; (11) X:2 FTSA-PrA; (12) X:3 FTCA; (13) X:2 FTCA; (14) X:2 FTUCA; (15) X:2 FTSAS-sulfinyl; (16) X:2 FTSAS-sulfonyl; (17) X:2 diPAP; (18) X:3 keto-FTTh−OH-PrAcid; (19) PFASi; (20) H-PFCA; (21) H-PFSA; (22) U-PFSA; (23) H−U−PFSA; (24) F5S-PFSA; (25) X:Y PhiA; (26) O-PFSA; (27) O-PFCA; (28) O−U−H-PFCA; (29) Cl-PFSA; (30) Keto-PFSA; (31) PFEtCHxS; (32) PFAAl; (33) PFA-oxirane; (34) diammonium-PAPs; (35) TAmPr-FASA; (36) AmPr-FASA; (37) CMeAmPr-FASA; (38) EtOH-AmPr-FASAPrS; (39) SPAmPr-FASA; (40) OAmPr-FAAd; (41) X:2 FTSA-PrB; (42) X:2 FTSA-PrDiMeAn.

range (Figure 1). Most of the detected classes correspond to negative ion mode PFAS (ESI(−)) in contrast to fewer hits for the positive ion mode (ESI(+)). Figure 2 provides an example CF_2-adjusted KMD plot for ESI(−) data and illustrates the identification of a sulfonate derivative previously discovered in ECF products.[3] Illustrative MS/MS fragment ion spectra are also compiled in SI Figure S2 for key PFAS classes. Further details on measured exact m/z, molecular formulas, and exact mass accuracy are compiled in SI Table S13.

Of the 47 screened waste products, 43 (91%) presented detections of at least one PFAS, and up to 113 PFAS were detected in a single OWP sample. Livestock manures presented a relatively low number of detected homologues per sample (on average four PFAS detected, range: 0−15 PFAS) compared to wastes of urban origin (on average 39 PFAS, range: 7−113 PFAS). Overall detection frequencies (n = 47) of the 160 detected PFAS are summarized in SI Table S14. The following subsections discuss the detections of the 42 PFAS classes, grouped into seven superclasses:[45] (1) PFCAs (−); (2) PFSAs (−); (3) ECF-sulfonamides (−); (4) fluorotelomers (−); (5) miscellaneous (−); (6) ECF (+); (7) fluorotelomers (+).

PFCAs (−). Up to 17 PFCAs (Class 1, C3−C19) were detected in OWP, with PFOA the most frequent (overall detection rate of 68.1%). PFCAs of chains longer than C16 have been infrequently reported.[46]

PFSAs (−). Up to 15 PFSAs (Class 2, C3−C17) were detected in OWP, with PFOS and PFHxS the most recurrently detected homologues (72.3% and 59.6%, respectively). This is one of the first reports of C13−C17 PFSA in environmental samples.

ECF-Sulfonamides (−). ECF-sulfonamides (PFSA precursors) were detected in urban-sourced wastes and paper mill sludge. Detected compounds included perfluoroalkyl sulfonamides (Class 3, C3−C6,C8) and *N*-alkylated sulfonamides (Classes 4−5: Me/EtFOSA). Perfluoroalkyl sulfonamide acetates and *N*-alkyl derivatives (Classes 6−8) were also identified at high confidence levels (1*-2*), with the C8 homologues presenting the highest detection rates (e.g., EtFOSAA: 51.1%).

Fluorotelomers (−). ESI(−) fluorotelomers with detection rates higher than 30% included 6:2 FTSA (44.7%), 8:2 FTSA (36.2%), and 6:2 diPAP (34.0%). Fluorotelomer sulfonates were reported over an extensive breadth of chain lengths (Class 9, 4:2 to 16:2 FTSA), mostly in urban OWP. Hydroxy fluorotelomer sulfonates were previously discovered in AFFF-impacted groundwater[3] and were also detected through nontarget screening in the present study (Class 10, 6:2 to 14:2 HO-FTSA). Fluorotelomer sulfonamides (Class 11, 6:2, 8:2, and 10:2 FTSA-PrA) were identified through suspect screening in some urban waste composts (C-GWS and C-MSW but not in C-BIOW), with two main MS/MS fragment ions (SI Figure S2-j). X:3 acids (Class 12, 5:3 to 11:3 analogs) were identified in urban OWP, with two characteristic MS/MS fragment ions (SI Figure S2-k,l). Other anionic fluorotelomers (Classes 13−17) identified in organic urban waste samples included X:2 FTCAs, X:2 FTUCAs, sulfinyl and sulfonyl analogs of a fluorotelomer thioether sulfonate (6:2 FTSO-PrAdDiMePrS and 6:2 FTSO2-PrAdDiMeEtS, respectively), and 6:2 diPAP. A tentative candidate class for the low-intensity peaks at m/z 558.967 (RT 6.36 min) and m/z 658.960 (RT 7.28 min) is the X:3 ketone fluorotelomer thia hydroxy propanoic acids (Class 18, 7:3 and 9:3 analogs). Based on observations for a shorter-chain

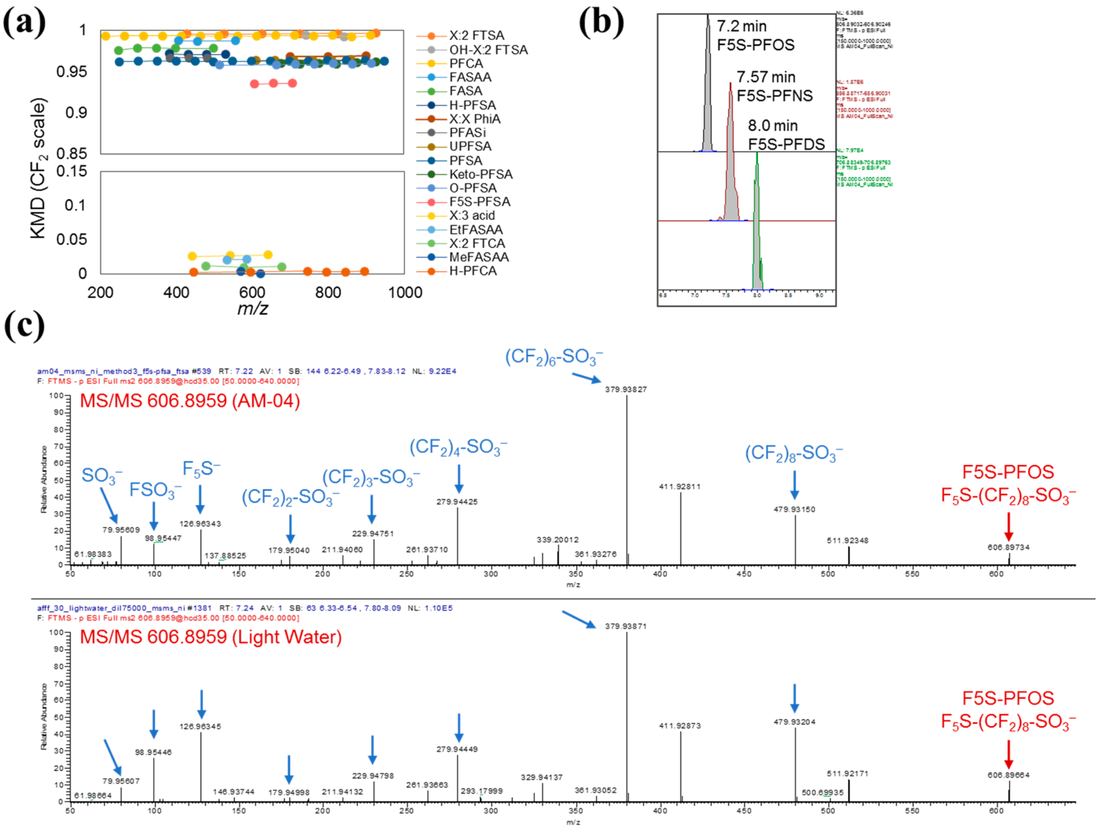

Figure 2. CF$_2$-normalized Kendrick mass defect plot (2a) for ESI(−) data in a compost of green wastes and sewage sludge and identification of a series of pentafluorosulfide perfluoroalkanesulfonates (F5S-PFSA) previously discovered by Barzen-Hanson et al.[3] Ascending retention times with increasing perfluoroalkyl chain length shown in full scan LC-HRMS chromatograms of C8, C9, and C10 homologues (2b) together with high-resolution MS/MS spectra of F5S-PFOS (2c) in sample AM-04 (C-GWS from La Bouzule) and reference Light Water AFFF supported identification at confidence level 1*.

analog (5:3 keto-FTTh−OH-PrAcid),[47] these may be biotransformation conjugates of 7:3 and 9:3 acids.

Miscellaneous (−). Perfluoroalkyl sulfinates (Class 19, C6−C8, C10 homologues) were detected in paper sludge, sewage sludge, and urban composts, with PFOSi the dominant homologue.

A series of long-chain hydrido-PFCA homologues (Class 20, C9−C20) was detected in sewage sludge and related composts with ascending retention times from H-perfluorononanoate (C9, 5.33 min) to H-perfluoroeicosanoate (C20, 9.32 min). H-PFCAs were previously evidenced in the wastewater of fluorochemical manufactures (C5−C16)[48] and municipal wastewater treatment plants (WWTPs) (C2−C8) in China.[49] Short-chain H-PFCAs were also recently reported in wastewater from electronics fabrication facilities.[50]

Hydrido-PFSAs (Class 21, C6−C9 homologues) were identified in sewage sludge and related composts, with chromatographic retention times and MS/MS fragment ion spectra matching those acquired for Light Water AFFF (SI Figure S2-b). H-PFSAs of diverse chain lengths (C3−C10) were recently reported in Chinese municipal WWTP effluents.[49] U-PFSA (Class 22) and hydrido-U-PFSA (Class 23) were also detected, mostly in urban OWP.

Pentafluorosulfide perfluoroalkanesulfonates (Class 24, C8−C10) were identified in sewage sludge and urban composts, based on matching retention times with the reference Light Water AFFF and the observation of up to 8 characteristic MS/MS fragment ions (Figure 2 and SI Figure S2-d). F5S-PFSAs (C3−C9) were discovered by Barzen-Hanson et al. in ECF products, including a 3 M PFOS-based industrial surfactant (3 M Fluorad FC-95, a wetting agent used in the chemical milling of metals), and five of six tested 3 M AFFFs.[3] F5S-PFSAs (C6−C9) were recently reported in rivers discharging into Bohai Bay, China,[51] and AFFF-impacted soil at a former U.S. Air Force Base.[52] To the best of our knowledge, this is the first report of F5S-PFSAs in European samples.

Nontarget screening highlighted high-intensity signals of m/z 700.923, 800.918, and 900.912 (Class 25), especially in sewage sludge and related composts (C-GWS), as well as in paper mill sludge. Automated database search returned bisperfluoroalkyl phosphinic acids as a potential match (6:6, 6:8, and 8:8 PhiA) with three characteristic fragment ions (SI Figure S2-o). The X:Y PhiA were recently reported in biosolid samples from Australia.[53]

Miscellaneous ESI(−) classes also included ether-PFAS (Classes 26−28), PFSAs with chlorine or ketone substituents (29−30), and other classes (31−34) detected in some sewage sludge and urban-sourced composts. Two perfluoroalkyl heterocyclic compounds preregistered under REACH, 1H,1H-perfluoroisotridecanyl oxirane (C13, CAS 54009−78−8) and 1H,1H-perfluoroisopentadecanyl oxirane (C15, CAS 54009−77−7), were identified by nontarget screening (Class 33). Their respective retention times of 8.7 and 9.15 min are bracketed by those of PFTeDA-PFOcDA (8.3−9.4 min), consistent with their long perfluoroalkyl chains. These fluorinated epoxides may be related to processes requiring low surface tension films or

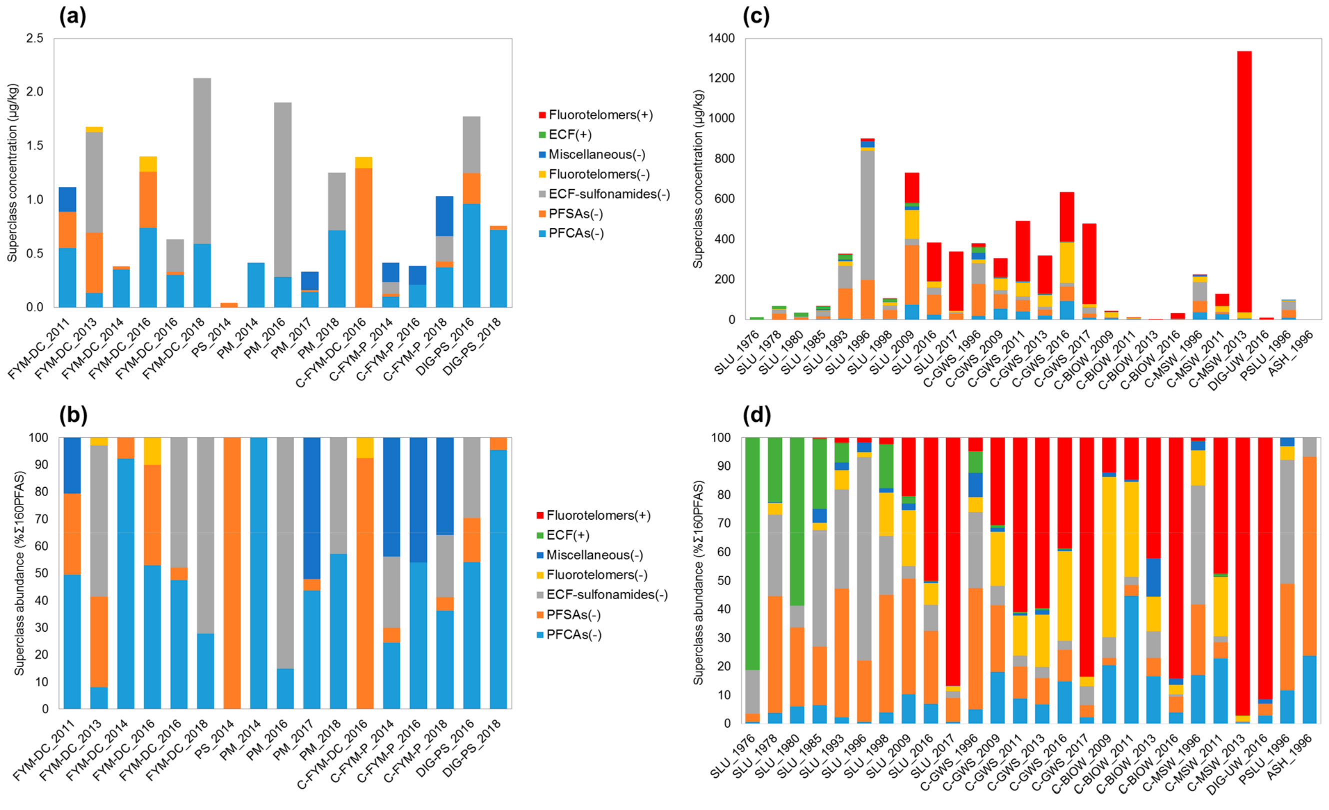

Figure 3. Contribution of the 7 PFAS superclasses (Σsuperclass) in the organic waste products in terms of concentration levels (µg/kg dry weight; top) and the relative contribution (%) of each superclass to the overall summed PFAS (bottom). Left panels correspond to agricultural OWP (3*a*/3b) and right panels to urban/industrial OWP (3*c*/3d). Note the vastly different scales of concentration levels between agricultural and urban OWP. The four agricultural OWP samples without any detected PFAS (i.e., three samples of pig slurry and one sample of digestate of pig slurry) are not shown in this figure.

used as synthesis intermediates in the preparation of perfluorinated/perfluoropoly ethers.[54] The diammonium adducts of two mono-PAPs (Class 34), nocosafluoro-2-hydroxyheptadecyl phosphate (C14, CAS 94200−48−3) and hentriacontafluoro-2-hydroxyheptadecyl phosphate (C15, CAS 94200−52−9), were identified within 5 ppm of their theoretical exact mass (RT of 8.6 and 8.8 min, respectively). Despite the agreement between the observed and theoretical ^{13}C monoisotopic mass abundance, these are tentative candidates and not confirmed structures; mono-PAPs are also known to present analytical challenges.[55]

ECF (+). Two quaternary ammonium derivatives (Class 35), T-AmPr-FHxSA (PFHxSAmS) and T-AmPr-FOSA (PFOSAmS), were identified in more than 20% of samples overall, particularly in sewage sludge and related composts (C-GWS). A possible isomeric class is X:2 FTSA-Pr-MeAn, which was discarded based on LC-MS evidence (SI Figure S2-p): (1) the close match in retention times and MS/MS fragmentation in the compost of urban sludge and T-AmPr-FASA reference standards, and (2) the similar chromatographic shape compared with a Fluobon standard showing both branched (minor) and linear (major) T-AmPr-FOSA, characteristic of ECF chemistry. Two tertiary amine homologues (Class 36), used as synthesis intermediates[10] of zwitterionic PFAS and discovered in 3 M and Angus Fire AFFFs,[4,56] were identified in sewage sludge (SI Figure S2-q): *N*-dimethylammoniopropyl perfluorohexane sulfonamide (AmPr-FHxSA) and perfluorooctane sulfonamide (AmPr-FOSA). A betaine derivative of perfluorooctane sulfonamide (Class 37), CMeAmPr-FOSA (PFOSB), was identified through target screening with characteristic fragment ions at *m/z* 58.065 ($(CH_3)_2N = CH_2^+$) and *m/z* 104.071 (betaine fragment: $[(CH_3)_2NHCH_2COOH)]^+$) and branched +linear peaks indicative of ECF chemistry (SI Figure S2-r). T-AmPr-FASAs, AmPr-FASAs, and C-MeAmPr-FOSA were recently reported in AFFF-impacted environments in Canada,[6] France,[41] and China.[15] This is the first report of these compounds in organic waste products.

A perfluorooctane sulfonamide derivative with sulfonate and alcohol terminal moieties discovered by Barzen-Hanson et al.,[3] EtOH-AmPr-FOSAPrS (Class 38, also referred as N-HOEAmP-FOSAPS), was detected in sewage sludge and related composts (C-GWS), within 2 ppm of its theoretical exact mass. The ^{13}C monoisotopic mass abundance (21.9%) nearly matched the theoretical isotopic distribution (22.4%), supporting 18 carbon atoms in the compound structure. Its retention time (6.2 min) was also comparable with those of C8 ESI(+) compounds with available Fluobon standards. A perfluorohexane sulfonamide derivative also discovered by Barzen-Hanson et al.,[3] *N*-sulfopropyl dimethylammoniopropyl perfluorohexane sulfonamide (Class 39, SPAmPr-FHxSA or N-SPAmP-FHxSA), was detected in composted wastes. Both ESI(+) and ESI(−) signals are present at 5.24 min, within 1.9−2.5 ppm of their theoretical exact masses.

A fluorinated amine oxide derivative (Class 40) referred in AFFF patents,[57] *N*-oxide dimethylammoniopropyl perfluorooctaneamide (OAmPr-FOAd or PFOANO), was identified for the first time in municipal biosolids and related composts (C-GWS).

Table 1. Major PFAS Classes Reported in Urban/Industrial Waste Products Screened in the Present Study ($n = 26$), Ranked by Maximum Observed Summed Concentration ($\sum$class)[a]

class	superclass	max. $\sum$class (rank/42)	detection rate (rank/42)	dominant homologues
X:2 FTSA-PrB	fluorotelomer(+)	1300 μg/kg (1)	81% (4)	6:2 FTSA-PrB (FTAB)
EtFASAA	ECF sulfonamide(−)	580 μg/kg (2)	88% (3)	EtFOSAA
PFSA	PFAAs(−)	300 μg/kg (3)	100% (1)	PFHxS, PFOS
X:3 acid	fluorotelomer(−)	150 μg/kg (4)	58% (10)	7:3 acid, 9:3 acid
PFCA	PFAAs(−)	94 μg/kg (5)	100% (1)	PFHxA, PFOA, PFDA, PFDoA
MeFASAA	ECF sulfonamide(−)	43 μg/kg (6)	69% (7)	MeFOSAA
X:2 FTSA-PrDiMeAn	fluorotelomer(+)	39 μg/kg (7)	35% (17)	6:2 FTSA-PrDiMeAn
X:2 FTSA	fluorotelomer(−)	38 μg/kg (8)	73% (6)	6:2 FTSA, 8:2 FTSA, 10:2 FTSA
X:Y PhiA	miscellaneous(−)	23 μg/kg (9)	77% (5)	6:8 PhiA, 8:8 PhiA
TAmPr-FASA	ECF(+)	18 μg/kg (10)	62% (8)	TAmPr-FOSA (PFOSAmS)
X:2 FTCA	fluorotelomer(−)	17 μg/kg (11)	19% (25)	8:2 FTCA
X:3 keto-FTTh−OH-PrAcid	fluorotelomer(−)	11 μg/kg (12)	15% (29)	7:3 keto-FTTh−OH-PrAcid
HO-X:2 FTSA	fluorotelomer(−)	8.4 μg/kg (13)	35% (17)	HO-12:2 FTSA
CMeAmPr-FASA	ECF(+)	8.2 μg/kg (14)	12% (32)	CMeAmPr-FOSA (PFOSB)
FASA	ECF sulfonamide(−)	7.6 μg/kg (15)	50% (11)	FHxSA, FOSA
X:2 diPAP	fluorotelomer(−)	7.6 μg/kg (16)	62% (8)	6:2 diPAP
F5S-PFSA	miscellaneous(−)	6.6 μg/kg (17)	23% (23)	F5S-PFOS
AmPr-FASA	ECF(+)	6.6 μg/kg (18)	31% (20)	AmPr-FOSA (PFOSAm)
FASAA	ECF sulfonamide(−)	6.3 μg/kg (19)	46% (12)	FHxSAA, FOSAA
U-PFSA	miscellaneous(−)	5.9 μg/kg (20)	42% (14)	U-PFDS, U-PFUnS

[a] Corresponding superclass (and ESI detection mode), detection rate ($\sum$class), and representative dominant homologs are also included.

Fluorotelomers (+). The 6:2 FTSA-PrB (also known as 6:2 FTAB) was identified at level 1* in a wide range of urban-sourced products (sewage sludge, C-BIOW, C-GWS, and C-MSW). The overall detection rate of 6:2 FTSA-PrB was 44.7% (n = 47 OWP). Five additional homologues (Class 41) were detected at level 1* through nontarget/suspect screening (4:2, 8:2, 10:2, 12:2, and 14:2 FTSA-PrB). Their chromatographic retention time, peak shapes, and characteristic MS/MS fragments matched those of the reference Arctic Foam AFFF (SI Figure S2-t) and agreed with literature spectrum data.[4,6] The homologues present at the highest abundance were also detected in ESI(−) mode through nontarget screening, consistent with observations by D'Agostino & Mabury.[4] Though the X:2 FTSA-PrB appeared in patents dating back to the 1970s,[58] the class was not formally identified until recently.[56] Since its discovery in AFFF-impacted groundwater,[59] 6:2 FTSA-PrB has been increasingly reported in environmental samples as reviewed by Xiao.[60] This is the first report of X:2 FTSA-PrB in organic waste products.

Fluorotelomer sulfonamidopropyl dimethylamines (Class 42) were detected at level 2a* (6:2, 8:2, and 10:2 FTSA-PrDiMeAn) in SLU and urban-sourced composts, and may be synthesis intermediates/by products of X:2 FTSA-PrB.[4,56]

3.2. PFAS Levels in Organic Waste Products.

3.2.1. Summed PFAS.

Overall, the summed PFAS (Σ_{160}PFAS) ranged from below the detection limit (LOD range of 0.005−0.25 μg/kg, SI Table S8) to 1330 μg/kg. Concentrations of 160 PFAS x 47 OWP are provided as a supporting Excel file.

Agricultural wastes displayed consistently lower $\sum_{160}$PFAS (average: 0.81 μg/kg; median: 0.63 μg/kg) compared to urban-sourced OWP $\sum_{160}$PFAS (average: 307 μg/kg; median: 265 μg/kg) (see also Figure 3a and SI Figure S3). In urban wastes, $\sum_{160}$PFAS generally ranked as follows: municipal sewage sludge and related compost ∼ compost of residual domestic wastes ≫ compost of municipal biowastes > digestate of urban wastes. Considering the industrial wastes available for analysis, the historical sample of paper mill sludge (PSLU) presented an intermediate $\sum_{160}$PFAS (100 μg/kg), while the combusted waste (ASH) presented very low $\sum_{160}$PFAS (lower than 0.5 μg/kg).

The contamination of livestock effluents was relatively well explained by a classical list of analytes including PFOS/PFOA and commonly targeted PFAAs (64% of $\sum_{160}$PFAS) or by targeted PFAAs together with common negative ion mode precursors (86% of $\sum_{160}$PFAS). In urban wastes, in contrast, the sum of targeted PFAAs represented a limited proportion of the summed PFAS (on average 27% of $\sum_{160}$PFAS). This implies that monitoring only the historical PFAS could lead to dramatic underestimation of the summed PFAS, especially in urban wastes. As the comparison is only made to summed detected PFAS, and not stricto sensu to total PFAS, the magnitude of the underestimation may be even higher than discussed here.

A composted residual municipal solid waste (C-MSW, QualiAgro site; Year: 2013) presented the highest $\sum_{160}$PFAS across waste samples (1330 μg/kg) and can be used to illustrate the potentially vast underestimation of $\sum$PFAS based on differing analyte lists (SI Figure S4). Targeting the common suite of PFAAs (i.e., two classes) would have implied a 160-fold underestimation, while adding in common ESI(−) precursors would still imply a 40-fold underestimation. This, along with recent observations at Canadian and U.S. sites,[6,7] emphasizes the need to include zwitterionic and cationic homologues more systematically in PFAS characterization efforts.

3.2.2. PFAS Superclasses.

Figure 3 illustrates the prevalence of different superclasses[45] among OWP samples with detectable PFAS levels (n = 43), arranged per sample type (see also SI Table S15 and Text S3). In agricultural wastes (Figure 3a,b), only negative ion mode PFAS were detected, and the dominant superclasses were PFCAs, PFSAs, and ESI(−) ECF-sulfonamides (averaged contributions of 45%, 20%, and 22% of the summed PFAS, respectively).

The urban wastes showed distinct superclasses according to year (Figure 3c,d). The pre-2002 samples had PFSAs, ESI(−) ECF-sulfonamides, and ESI(+) ECF precursors (mainly ECF-

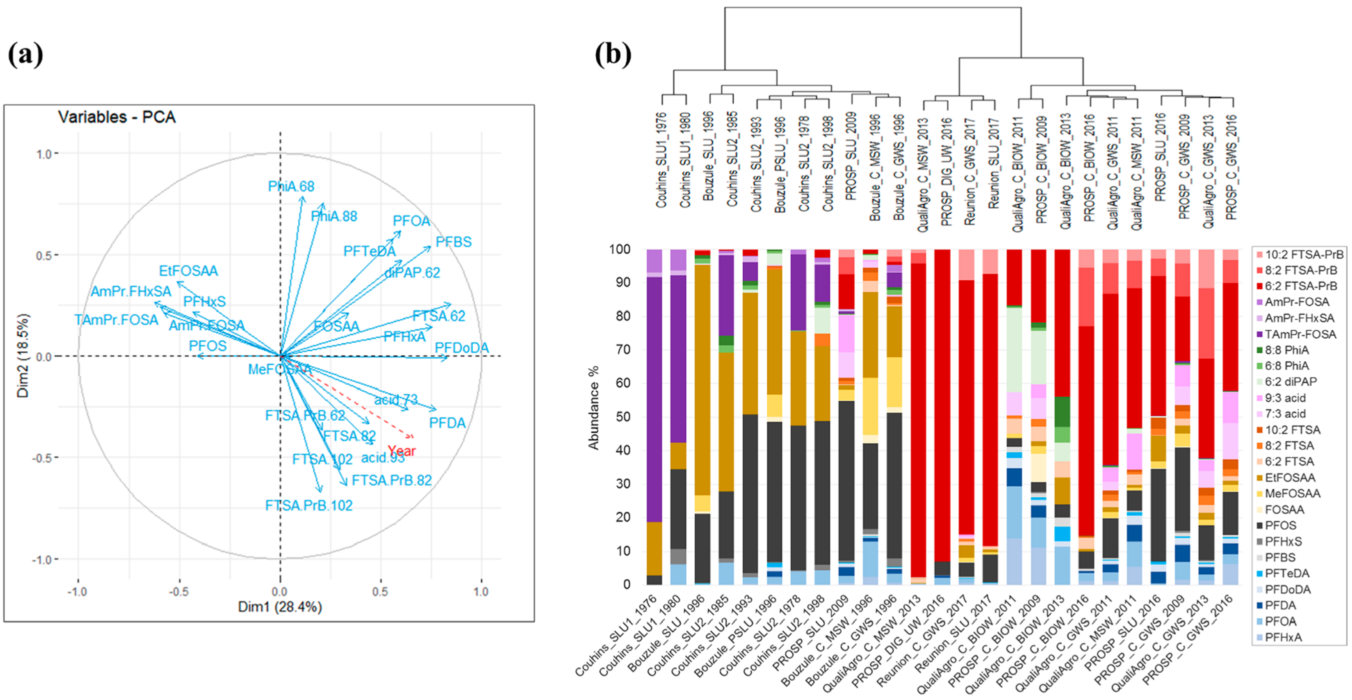

Figure 4. Factorial analysis on relative abundance profiles of 25 characteristic PFAS homologues (individual PFAS) in urban/industrial organic waste products, including principal component analysis (PCA) loading plot of variables (chemicals) with sample year (1976−2017) as additional numeric explanatory variable (4a) and Ward's hierarchical cluster analysis among individuals (samples) with corresponding PFAS abundance profiles (4b).

sulfonamides (+)) as dominant superclasses (on average, 30%, 32%, and 24% of the summed PFAS, respectively), while the more recent samples (2009−2017) were often dominated by ESI(+) fluorotelomers (averaged contribution to the summed PFAS: 55%; max. 97%). The urban wastes from the PROspective site (2009−2016) presented an intermediate profile, with dominant contributions of PFSAs, ESI(−) fluorotelomers, and ESI(+) fluorotelomers.

3.2.3. *Major PFAS Classes.*

Only a few PFAS classes were found in agricultural OWP (SI Table S16). The most frequently detected classes were the PFCAs and PFSAs (overall detection rates of 71% and 57%, respectively). The mean PFAA abundance profile in agricultural OWP was markedly different from that of other waste types, with a clear dominance of PFBA (C4; 61% of $\sum$PFAA). The C6 and C8 PFAAs made most of the remaining contributions (PFOS: 16%, PFHxS: 8.9%, PFOA: 6.8%, PFHxA: 4.6%).

Table 1 summarizes the major PFAS classes (and dominant homologues) in urban/industrial wastes (n = 26), arranged according to the maximum observed concentration. Historically monitored PFAAs ranked first in terms of detection rates but not in terms of maximum summed concentrations compared to other classes ($\sum$PFSA: rank 3/42; $\sum$PFCA: rank 5/42). The PFOS concentration range in municipal sewage sludge from the present study (0.4−284 μg/kg; n = 10) is low to intermediate compared to data from the literature, including biosolids from 16 WWTPs in Australia (year: 2014; concentration: 11−370 μg/kg),[34] sewage sludge from 32 U.S. states (2011; 308−618 μg/kg),[35] sewage sludge from 43 WWTPs in the Czech Republic (2018−2019; 5−933 μg/kg),[61] and biosolids from 12 WWTPs in Shanghai, Guangzhou, and Dalian, China (2011; 0.5−19.8 μg/kg).[62] We observed a maximum PFOA level of 13 μg/kg in a municipal sludge of 2009. This is one to 2 orders of magnitude lower than maximum levels reported in WWTP sludge from the U.S. (68−70 μg/kg) and China (158 μg/kg),[28,35,62] which historically hosted production and use of PFOA by major manufacturers.[63] The other major ESI(−) classes in urban/industrial wastes included various types of ECF-sulfonamide precursors (especially Me/EtFOSAA), X:3 fluorotelomer carboxylates, and X:2 fluorotelomer sulfonates (Table 1). Composting the sewage sludge marginally impacted the levels of PFSAs but led to increased levels of PFCAs compared to unprocessed sludge, especially in recent samples. This may be due to the enhanced degradation of fluorotelomers under composting conditions.[20]

Of the 20 classes listed in Table 1, five correspond to ESI(+) PFAS. The X:2 FTSA-PrB ranked first in terms of maximum concentration (1300 μg/kg) and 4/42 in terms of occurrence (detection rate of 81% across the 26 urban/industrial OWP). Other ESI(+) classes with concentrations surpassing 10 μg/kg included the X:2 FTSA-PrDiMeAn (max. 39 μg/kg) and TAmPr-FASA (max. 18 μg/kg).

3.3. Trends Related to Urban/Industrial Waste Products.

The archived urban/industrial OWP extended from 1976 to 2017, allowing the investigation of systematic trends according to product type and year. Multifactorial analyses were conducted on PFAS relative abundance profiles considering major homologues (Figure 4).

The PCA correlation circle (loading plot) discriminated three main groups of PFAS (Figure 4a). Vectors of PFHxS, PFOS, EtFOSAA, and ESI(+) sulfonamide precursors (AmPr-FHxSA, AmPr-FOSA, and TAmPr-FOSA) were correlated to one another but opposed with the additional explanatory variable "year" (numeric). This is expected, as a major source of these historical PFAS is the ECF-based products, which have been gradually restricted or eliminated from use or commerce since 2002 after a steep increase over the 1970−1990 period.[64,65] Regardless of sample subtype, the pre-2000 urban OWP (Bouzule, Couhins) were also grouped within a common supercluster by hierarchical clustering (Figure 4b) and were

https://doi.org/10.1021/acs.est.1c03697

characterized by a high prevalence of PFOS and two of its precursors, EtFOSAA and TAmPr-FOSA (PFOSAmS).

ESI(+) fluorotelomers were in the opposing quadrant to historical PFAS, the near 180° opposition suggesting a strong negative correlation (Figure 4a). The fluorotelomer sulfonamidopropyl betaines were the key components of samples from the second supercluster corresponding to recent sewage sludge and composted urban wastes (2009−2018), being detected in all samples (Figure 4b). On average, the summed X:2 FTSA-PrB in these samples represented 55% of the summed PFAS. This may reflect their prevalence in current-use formulations available in the European market[66] and possibly in other types of applications.[14] The predominant homologue within this class was the 6:2 FTSA-PrB, with concentrations often surpassing 100 μg/kg (maximum: 1230 μg/kg). Though not dominant in pre-2000 OWP, we noted frequent detections of 6:2 FTSA-PrB among historical sewage sludge and composted urban wastes (60% of samples with hits, the concentration range of 0.2−16 μg/kg), with the oldest detection for a 1985 municipal WWTP sludge (Couhins/Ambarès).

Specific ESI(−) fluorotelomers were also in the opposing quadrant to PFOS (Figure 4a). The HCA identified a subgroup of recent-year composts of green wastes and sewage sludge (C-GWS) from QualiAgro and PROspective (but not Réunion) characterized by higher contributions of long-chain X:3 acids (Figure 4b). These compounds are not known to be produced/used in industrial processes but have been reported among the major degradation intermediates of fluorotelomers.[67]

Vectors of bisperfluoroalkyl phosphinic acids (X:Y PhiA), 6:2 polyfluoroalkyl phosphate diester (diPAP), and perfluorobutanesulfonate (PFBS, C4) were orthogonal (i.e., dissimilar) to the previous two groups of variables (i.e., PFSA/ECF precursors and fluorotelomer precursors), which may indicate more limited temporal variations and distinct sources. For instance, PhiA and diPAPs are not known to be AFFF components but could be rather related to industrial coating applications.[68] PFBS and related C4 precursors are short-chain alternatives to PFOS used in fabric protection sprays[69] and in metal plating (defoamer).[70] Interestingly, PFOA was also unrelated to the previous two groups of variables. While direct PFOA emissions are reported to be on the decline, the lack of clear temporal trends may reflect continued secondary emission from the degradation of long-chain fluorotelomers.

4. SIGNIFICANCE

Organic waste products for land application in France were subject to prospective PFAS screening. Regardless of the geographical unit considered, PFAS levels were much higher in sewage sludge and composted urban wastes than in livestock effluents. Perfluoroalkyl acids were the most frequently detected, with profiles resembling equivalent products analyzed in the U.S.[20,28] Target and homologue-based nontarget screening resulted in the detection of 160 PFAS (42 classes) in waste samples. A large share of these correspond to previously discovered classes[3,4] but are evidenced for the first time in land-applied organic waste products. Though only 10% of the homologues were zwitterions and cations, the concentrations of ESI(+) PFAS were sometimes orders of magnitude greater than commonly targeted anions. This agrees with reports that zwitterionic and cationic PFAS may represent a considerable portion of the PFAS burden,[6,7] evidenced for the first time for biosolids and composted urban wastes.

PFAS profiling of urban OWP spanning 40 years indicated drastic differences between historical and recent samples. Old samples (1978−1998) were dominated by PFOS and other ECF compounds including ESI(−) (Me/EtFOSAA) and ESI(+) precursors (TAmPr-FOSA). In recent samples (2009−2017), fluorotelomer ESI(+) precursors represented 55% of the summed PFAS, with X:2 FTSA-PrB (FTAB) as the dominant class. This shift is likely a result of the gradual elimination of ECF products based on C8 chemistry and replacement with shorter-chain alternatives, such as 6:2 fluorotelomers.[71]

PFAS contamination in organic waste products could stem from a variety of sources, depending on product origin and site characteristics. Short-chain PFAAs were the predominant PFAS in landfarm manure waste products. Short-chain PFAAs are known to occur in surface water and groundwater and may persist through the treatment train due to their high mobility.[72,73] Short-chain PFAAs exhibit distinct pharmacokinetics compared to long-chain homologues;[2] cattle exposure may thus translate in extensive excretion compared to the more biopersistent long-chain PFAAs.

Domestic solid wastes are likely contaminated with PFAS due to leaching from surface-coated materials (e.g., paper, cardboard, food packaging, and other consumer products).[68,74] Wastewater treatment plants receive household liquid effluents, which may be contaminated with PFAS from domestic use of cosmetics, detergents, washing of clothes and other textiles, and leaching from specific cookware.[75] Commercial/Professional laundry systems are also connected to some wastewater treatment plants. Washing of specific protection equipment, such as those used by firefighters and the military, could thus represent a significant PFAS source, either resulting from leaching of PFAS embedded into the fabric[76] or washing of clothes contaminated during AFFF deployments.[75] Another pathway for PFAS contamination of wastewaters is through surface runoff in roads, parking lots, airports, and other urban/residential areas during rain episodes; pluvial sewer waters may be treated separately or mixed with other influents once received at the WWTP, depending on site design. The high sorption propensity of ESI(+) PFAS and recalcitrance to degradation[10] may also explain their accumulation in sludge. Though high levels of X:2 FTSA-PrB were found in a composted sample of residual household waste, an AFFF source would be unlikely. Formulations based on FTSA-PrB may be used in other types of applications yet to be reported.

Recent monitoring activities in France pointed to the prevalence of 6:2 FTSA-PrB in industrial WWTP effluents from specific fluorochemical manufacture facilities.[14] 6:2 FTSA-PrB and longer-chain homologues were also widely detected in sediments from French Water Basins near airport sites.[41] The present study suggests that application of sewage sludge and composted urban wastes could also contribute to the introduction of 6:2 FTSA-PrB in the environment through agricultural recycling practices.

Zwitterionic/Cationic PFAS made up a large proportion in some OWP samples; however, their desorption potential from OWP has not been tested, and based on soil−water and soil−earthworm partitioning data, these compounds do not seem to be highly mobile[77] nor bioaccumulative.[78] The distribution of anionic PFAS was previously investigated in soil, groundwater, and vegetation of an AFFF-impacted area.[79] PFOS was predominant in soil and groundwater, while PFHxS, 6:2 FTSA and short-chain PFCAs predominated in foliage and stems/roots of most plant species.[79] Similar trends may be expected here, with higher accumulation of short-chain PFCAs and 6:2 FTSA in plants grown in soils amended with recent land-applied OWP, compared to historical samples. Future studies shall be conducted in Europe and elsewhere to address critical data gaps regarding the environmental pathways of emerging PFAS. These future data are essential to ensure the effectiveness and safety of agricultural organic waste recycling practices, and effectively contain the impact of PFAS on human and ecological health.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.1c03697.

> List of abbreviations and acronyms, Chemicals and materials, Sample preparation procedure for targeted PFAS analysis, Metadata and chemical properties of organic waste products, UHPLC-HRMS instrumental method, QA/QC, List of 160 PFAS detected in the present study, Detection frequency and concentration ranges, Chromatograms and elucidated MS/MS spectra, Principal component analysis (PDF)
>
> A supporting Excel table with detailed concentrations (μg/kg) of the 160 PFAS detected in organic waste products (n = 47) from the present study (XLSX)

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Notes

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■ ACKNOWLEDGMENTS

The field experiments are part of the INRAE SOERE-PRO (network of long-term experiments dedicated to the study of impacts of organic waste product recycling), certified and funded in 2013 by ALLENVI (Alliance Nationale de Recherche pour l'Environnement) and integrated as a service of the infrastructure "Investment for the future" AnaEE-France, overseen by the French National Research Agency (ANR 11-INBS-0001). We thank all those who participated in the field experiments and management of the SOERE-PRO sites, as well as the partners, notably the Mixed Syndicate Union for Agricultural Recycling Haut-Rhin (SMRA 68), the Association for Agronomic Recovery in Alsace and Grand-Est Chamber of Agriculture, Veolia Research and Innovation (VERI), Veolia Water, and the French Environment and Energy Management Agency (ADEME). The authors also thank the Natural Sciences and Engineering Research Council of Canada (STPGP 478774), the Fonds Québécois de la Recherche sur la Nature et les Technologies (2015-PR-183278), and the Canadian Foundation for Innovation (30044) for their financial support. We acknowledge funding by the Strategic Environmental Research and Development Program (SERDP ER19-1157). Min Liu is a recipient of the McGill Engineering Doctoral Awards.

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