

Article

Untargeted Screening of Per- and Polyfluoroalkyl Substances (PFASs) in Airborne Particulate of Three Italian E-Waste Recycling Facilities

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Abstract: Poly- and perfluorinated alkyl substances (PFASs) are widely used in the electrical and electronic appliance industry to the point that waste of electrical and electronic equipment (WEEE), also known as e-waste, creates significant potential for PFAS exposure (by inhalation, ingestion, or dermal exposure) for people handling and recycling e-waste. The aim of this work was the development of an untargeted analytical approach in order to detect the presence of possible unknown PFASs in particulate matter collected in three Italian e-waste facilities through liquid chromatography coupled to high-resolution tandem mass spectrometry (LC-HR-MS/MS) in negative ionization mode. By means of three acquisition experiments, nine compounds were detected as candidate PFASs, and three were definitively confirmed by comparison with their authentic standards. Among these, bistriflimide (bis (trifluoromethylsulfonyl) imide), an ionic liquid with several promising technological applications, was the most abundant compound detected in all three recycling plants. This is the first study associating the presence of fluorinated ionic liquids with e-waste, and as these chemicals are not only toxic and persistent but also highly mobile, our results indicate the need to include them in future PFAS research. Only further data on their actual environmental diffusion will determine whether they are emerging pollutants or not.

Keywords: per- and polyfluoroalkylated substances (PFASs); waste of electrical and electronic equipment (WEEE); LC-HRMS/MS; untargeted analysis; bistriflimide

1. Introduction

Waste electrical and electronic equipment (WEEE) or e-waste is one of the fastest growing pollution problems, and since the late 2010s, the issues regarding its impact are becoming of global concern [1–7]. The increasing use of electrical and electronic devices such as freezers, refrigerators, fans, personal computers, and cell phones and their short lifespans result in the generation of a huge volume of e-waste. While recycling of WEEE is a significant source of secondary raw materials with important environmental benefits, grinding and mechanical crushing operations at WEEE treatment plants cause the spread

of airborne particles which contain toxic compounds. These chemicals originate from electrical circuits, electronic components, and polymers commonly used for electrical and electronic equipment housings.

Exposure to e-waste is associated with high levels of numerous organic chemicals such as phthalates, brominated flame retardants, polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs), chlorofluorocarbons, and per- and polyfluoroalkyl substances (PFASs). In addition, airborne particulates contain several toxic elements (lead, cadmium, chromium, lithium, copper, manganese, nickel, arsenic, aluminum, etc.) widely used in the manufacturing of a variety of electronic products [8,9]. Therefore, it is difficult to exactly ascertain the effect of exposure to a specific e-waste-related compound or element in isolation, since inhibitory, synergistic, or additive effects of multiple exposures are all factors that can influence health outcomes. Systematic reviews of epidemiological studies published from 1965 to early 2020 demonstrated that elevated concentrations of toxic chemicals negatively impact neonatal growth indices and hormonal alterations in e-waste-exposed people. Moreover, possible connections between chronic exposure to e-waste and DNA lesions, telomere attrition, inhibited vaccine responsiveness, alteration of immune function, and high oxidative stress have been observed [10,11].

Among the organic contaminants associated with e-waste, PFASs are particularly insidious because they constitute a constantly growing group of thousands of chemicals. The enormous number of PFASs (currently about 5000) is due to the continuous synthesis of new compounds and the formation of by-products during production processes as well as the formation of new molecules resulting from the degradation of PFASs released into the environment. The structures of many of these compounds are also frequently unknown because manufacturers tend to provide little information to protect industrial patents. This, together with the toxicity and great persistence of PFASs, means that they are currently one of the groups of contaminants of greatest global concern [12,13].

PFASs are widely used as additives within the electronic, metal finishing, and packaging or surface treatment industries for their outstanding thermo-chemical resistance and stability, providing unique properties to goods and materials [14]. In particular, PFASs are used in electronic devices as heat transfer fluids/cooling agents, in cleaning solutions, and for etching piezoelectric ceramic fillers. Thanks to their dielectric properties, fluoropolymers are applied for the manufacturing of carbon fiber-reinforced composites and structural components; the production of photovoltaic cells, seals, and gaskets; and in smaller and powerful electronic devices. Moreover, in many electrical and electronic applications, fluoropolymers such as polytetrafluoroethylene (PTFE) are used to insulate and sheath components of cables [15,16]. However, since PFASs are not covalently bound to materials, when they interact with particulate matter, they are constantly released and spread throughout the atmosphere. Their widespread distribution, in combination with their long-range aerial transportation, makes PFASs potential threats not only to the health of e-waste recycling workers but also for residents living close to e-waste dismantling sites. Peng et al., analyzing the serum and urine of workers from five Chinese WEEE facilities, found that workers directly exposed to PFASs (drivers, sorters, and loaders) had higher levels of these chemicals than those not directly exposed such as managers and other workers [17]. In addition, investigations also conducted in China reported significantly higher concentrations of PFASs in the biological fluids of people living near e-waste dismantling areas than in those of individuals residing in reference areas [18–20].

The production and use of long-chain perfluoroalkyl carboxylates (PFCAs) and perfluoroalkyl sulfonates (PFASs) such as perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate (PFOS) have stopped in the United States, Europe, and Japan. Therefore, production of PFOS and PFOA has declined since 2003. In 2009 and 2019, PFOS and PFOA were included under the list of Persistent Organic Pollutants (POPs) of the Stockholm Convention, respectively [21,22]. This removal left a significant void in the global market, leading to the subsequent increase in short-chain PFAS production, considered less bioaccumulative, as well as the synthesis of various substitutes such as Gen-X (ammonium perfluoro (2-methyl-

3-oxahexanoate)), ADONA (sodium dodecafluoro-3H-4,8-dioxanonanoate), and F53B, a mixture of 9-chlorohexadecafluoro-3-oxanonane-1-sulfonate and 11-chlororeicosafuoro-3-oxaundecane-1-sulfonic acid.

In this context, the application of non-targeted approaches is fundamental to discover new molecules, as only a few dozen of the several thousand existing per- and polyfluoroalkyl chemicals can be monitored by traditional targeted analysis. Accordingly, by applying liquid chromatography coupled with high-resolution mass spectrometry (LC-HRMS/MS), recent studies of biotic and environmental samples have revealed several PFASs not previously described [23–35].

Indoor air sampling activities at WEEE facilities are complex and require authorization, time, and appropriate equipment (fractionating impactors). Therefore, although air is a well-known pathway for human exposure, there are no studies to date on PFAS contents in airborne particles collected within e-waste recycling plants. Recently, we performed a first exploratory study in which the concentrations of various organic and inorganic contaminants were measured in three Italian e-waste facilities. Among the other organic pollutants, five perfluoroalkylated substances were found [8,9]. PFOS, PFOA, perfluorobutansulfonate (PFBS), perfluorooctanesulfonamide (PFOSA), and Gen-X were identified by applying a targeted method able to measure 26 different PFASs. In order to complete this study, the application of an untargeted approach is here realized, analyzing the same airborne particles.

2. Materials and Methods

2.1. Chemicals and Reagents

Methanol of LC-MS grade was purchased from Honeywell (Charlotte, NC, USA). Water of LC-MS grade was purchased from VWR International (Radnor, PA, USA). Ammonium acetate and *n*-nonane were obtained from Merck (Darmstadt, Germany).

2.2. Sample Collection

Sampling operations have been described in detail by Pomata et al. [9]. In WEEE plants P1 and P2, two sampling campaigns were performed (C1 and C2 in P1, C3 and C4 in P2), whereas in WEEE plant P3, only one campaign (C5) was carried out. At each of the two zones of the three plants, three samplings per campaign (one per day) were performed. Two independent air samplers (DLPI+, Dekati, Kangasala, Finland) operating at a flow rate of 10 L/min were simultaneously utilized during each sampling, with 2-h sample runs with an average total collected volume of 1.2 m³ per sampler. Two sizes of particulate matter (PM) were collected: particles with an aerodynamic diameter lower than 1 µm (fine) and particles with an aerodynamic diameter ranging from 1 to 10 µm (coarse). Samples collected during one of the three samplings were extracted for untargeted PFAS searching. Along with the sample filters, blank and field samples were provided to check background contamination. Table S1 summarizes the sampling detailing plants, zones, and campaigns as well as specific activities performed at each plant according to Pomata et al. [9].

2.3. Sample Extraction

Samples were extracted as reported by Pomata et al. [9] with slight modifications. Briefly, an accelerated solvent extraction (ASE, Dionex, ThermoFisher Scientific, Waltham, MA, USA) was carried out with 6 mL *n*-hexane followed by 6 mL ethyl acetate, collected together in the same vial, and with 6 mL of 2-propanol/methanol (90:10). Labeled PFASs were not added since they could interfere with data processing for untargeted analysis. Florisil for clean-up was directly added in the ASE cell. The two fractions were then reunited and evaporated under a nitrogen stream at 40 °C in presence of 50 µL of *n*-nonane. The residue was dissolved in 200 µL of methanol/4 mM ammonium acetate (80/20, *v/v*) and injected.

2.4. Chromatographic and MS Conditions

Chromatographic separation was performed on a Thermo Ultimate 3000 High Performance Liquid Chromatography system (Thermo Fisher Scientific, San Jose, CA, USA) using a Kinetex XB C18 column (100 × 3.0 mm; 2.6 μm, Phenomenex, Torrance, CA, USA) connected with a C18 guard column (Phenomenex, Torrance, CA, USA). Between the pump and injector, two mini-LC columns (Oasis WAX 20 × 2.1 mm and Oasis HLB 20 × 2.1 mm, Waters, Milford, MA, USA) were installed in order to avoid interference due to the mobile phases. The mobile phases were water (A) and methanol (B), both containing 5 mM of ammonium acetate. The gradient was initiated with 100% eluent A at 0.05 mL/min. In 1 min, the flow increased to 0.3 mL/min and eluent B increased to 30%. The gradient continued with a curve increase to 60% B in 9 min followed by a linear increase in mobile phase B up to 70% in 5 min. Another linear increase was performed to obtain 100% mobile phase B in 6 min. After 5 min, the system returned to 100% A and a flow rate of 0.05 mL/min in 2 min. The re-equilibration was 2 min for a total run time of 30 min. The column temperature was 40 °C, and the sample temperature was kept at 16 °C. The injection volume was 20 μL. The mass analyzer Q-Orbitrap (Q-Exactive Plus, Thermo Scientific, San Jose, CA, USA) was equipped with a heated electrospray ionization source (HESI-II) operating in negative mode. The optimized HESI-II temperature was set at 320 °C, the capillary temperature was 300 °C, and the electrospray voltage was 3.5 kV. The S-lens value was adjusted at 50 V. Sheath and auxiliary gas were 40 and 15 arbitrary units, respectively.

2.5. Data Acquisition

Three acquisition experiments were performed during three separate runs: Full MS/dd-MS² (data-dependent acquisition, TopN), Full MS/DIA (data-independent acquisition), and Full MS/AIF (all ion fragmentation)/NL dd-MS² (TopN). The settings of each acquisition experiment are detailed in Tables S2–S4. Full MS/dd-MS² (TopN) combines full mass acquisition followed by MS² experiments in which the N most intense ions (TopN) detected during full scan acquisition are selected and fragmented, except ions eventually included into the exclusion list.

Full MS/DIA combines a full scan experiment followed by a series of MS² experiments where subsequent windows of m/z 60 are fragmented along all the scan range (m/z 110–1650). Since PFASs are characterized by common neutral losses (NLs) (e.g., perfluoroalkyl carboxylates show a characteristic NL corresponding to CO₂ + C_nF_{2n} moiety), the Full MS/AIF/NL dd-MS² (TopN) experiment was useful to detect this group of compounds. After full scan acquisition, all ion fragmentation (AIF) was performed, and if specific NL was observed, MS² fragmentation was triggered. The monitored NLs are listed in Table S5. During Full MS/dd-MS² (TopN) and Full MS/AIF/NL dd-MS² (TopN) experiments, an exclusion list was used in order to avoid undesired fragmentations. This list contained the most 50 intense ions detected every 30 s in a procedural blank sample run.

2.6. Data Processing

COMPOUND Discoverer[®] 3.2 (Thermo Scientific, San Jose, CA, USA) is a software for data elaboration focused on untargeted, semi-untargeted, and suspect screening analysis. It is based on a series of clustered nodes: input/output, spectrum processing, trace creation, expected compounds, compound detection, peak area refinement, compound identification, pathway mapping, compound scoring, and post-processing elaboration. This software was applied to elaborate our data. After the alignment of retention times and the detection of compounds, ten nodes were used: *mzCloud* search (*Search mzCloud*), *mzVault* search (*Search mzVault*), database search (*Search ChemSpider*), predicted composition (*Predict Compositions*), custom mass list (*Search Mass Lists*), custom fragments list (*Compound Class Scoring*), neutral loss list (*Search Neutral Losses*), and mass defect calculator (*Calculate Mass Defect*). The optimized workflow created to achieve the aim of this study is shown in Figure S1.

The “Predicted Compositions” node was applied to determine n (in our case, $n = 100$) theoretical formulas of compounds on the basis of the m/z value and relevant isotopic

pattern. To restrict the number of possible candidates for the formula generation, C, H, O, P, S, Cl, F, and N ($C_{35}H_{20}Br_2C_{12}F_{80}N_3O_{20}P_2S_2$) were set as preferred atoms. The m/z detected values were submitted for searching in different online databases (ChemSpider, FDA, EPA, DSSTox, and Toxcast). Moreover, m/z and MS^2 spectra for each feature were submitted to mzCloud and mzVault, which are, respectively, online and offline databases containing MS^n spectra as well m/z values of precursors. In these two nodes (“Search mzCloud” and “Search mzVault”), the experimental spectrum is compared to spectra stored in databases, and candidate compounds with scores higher than 50% are shown. “Search Mass List” uses a custom offline database where a high number (>6600) of formulas related to PFASs are included. This node compares both the predicted formulas and mass values to the values reported in the PFASs mass list. In the case of positive matching, the name reported in the mass list is shown. The “Search Neutral Losses” node uses a custom list where the most common NLs of PFASs are included (Table S5). The software output highlights the presence of these NLs. “Compound Class Scoring” is a custom list with characteristic PFAS fragments searched in the experimental MS^2 spectra. Based on the number of fragments detected in the experimental spectrum compared to the number of total fragment ions reported in “Class Scoring List”, a match scoring expressed as a percentage is assigned. Fragment ions are listed in Table S6. Both the NL and fragment lists were built on the basis of experimental and literature data. Perfluorinated and polyfluorinated alkyl molecules generally have a negative mass defect value, and therefore, this characteristic is also exploited to search for possible PFASs. Two different mass defect calculations were set in the workflow: standard mass defect and Kendrick mass defect. Standard mass defect is calculated by subtracting the nominal mass from the exact mass. Using this approach, homologous series are identified based on similarity of mass defects. The Kendrick mass defect approach is similar, but repetitive units are normalized in order to obtain a constant mass defect for homologous series of compounds. Filtering results setting standard mass defect between 0.85 and 1.1, the number of possible candidates was reduced from about 21,000 to about 1600. Combining the mass defect filter with the presence of fluorine atoms in the predicted formula, the number of possible candidates was about 700. The remaining compounds were then evaluated manually. Details on the set parameters are reported in Table S7.

3. Results

Based on the experimentally measured m/z values, predicted compositions, MS^2 spectra, and online search, nine suspected compounds other than common PFASs were tentatively identified. Their putative names, molecular formulas, and retention times (RTs) are listed in Table 1, and the hypothesized structures are shown in Figure 1. We used the criteria established by Schymanski et al. [36] to assign the confidence levels to structural annotations in Table 1. The identities of three out of nine compounds were confirmed (confidence level 1) by comparison with the pure standards: bistriflimide (2), heptafluoro-1-propanesulfonic acid (3), and 1,1,2,2-tetrafluoro-2-(perfluoroethoxy) ethanesulfonic acid (5). Compound 4 was identified at a confidence level of 2b, meaning that analytical data supported the single structure proposed in Figure 1, but no standard or literature information was available for definitive confirmation. The remaining five PFASs were identified with a confidence level of 3, meaning that the analytical data support the proposed structure, but two or more isomers are possible. Accordingly, the structures drawn in Figure 1 are indicative. Figures S2–S10 show the extracted-ion chromatograms (EICs) and full MS and MS^2 spectra of the nine compounds. It is worth pointing out that in MS^2 spectra, the Compound Discoverer package displays in green the fragment ions included in the in-house library (Table S6).

Table 1. Suspected PFASs detected at the three WEEE sites (P1, P2, and P3).

Compound	Presumptive/Definitive Identification	Neutral Formula	[M-H] ⁻ <i>m/z</i>	RT (min)	Error (ppm)	Confidence Level
1	Mono-H-substituted perfluoro-1-butansulfonic acid	C ₄ H ₂ F ₈ SO ₃	280.9524	5.9	1.3	3
2	Bis(trifluoromethylsulfonyl) imide (bistriflimide) ¹	C ₂ HF ₆ NO ₄ S ₂	279.9178	6.0	2.1	1
3	Heptafluoro-1-propansulfonic acid (L-PFPtS) ¹	C ₃ HF ₇ SO ₃	248.9462	6.0	2.6	1
4	1,1,2,2,3,3-hexafluoro-3-(trifluoromethoxy)propane-1-sulfonic acid (1:3 PFESA)	C ₄ HF ₉ SO ₄	314.9379	8.2	1.2	2b
5	1,1,2,2-tetrafluoro-2-(perfluoroethoxy)ethanesulfonic acid (2:2 PFESA) ¹	C ₄ HF ₉ SO ₄	314.9379	8.5	0.7	1
6	Di-unsaturated 5:4 perfluoroether carboxylic acid (5:4 PFCEA)	C ₉ HF ₁₃ O ₃	402.9645	10.0	1.6	3
7	Mono-H-substituted perfluorodecanoic acid	C ₁₀ H ₂ F ₁₈ O ₂	494.9695	14.5	2.7	3
8	Mono-H-substituted perfluorooctenoic acid	C ₈ H ₂ F ₁₂ O ₂	356.9790	15.4	2.9	3
9	Di-H-substituted perfluoroundecylenic acid	C ₁₁ H ₃ F ₁₇ O ₂	488.9789	19.3	1.3	3

¹ Compounds definitively confirmed by means of the commercially available authentic standard.

Mono-hydrogen-substituted perfluoro-1-butansulfonic acid, H-PFBS (compound 1, C₄H₂F₈SO₃), corresponds to the legacy PFAS and PFBS (perfluoro-1-butansulfonic acid), with the replacement of one fluorine with a hydrogen atom. Its retention time was consistent with that expected, eluting before PFBS (5.9 min vs. 7.6 min). To the best of our knowledge, H-PFBS was described for the first time by Newton et al. [32] when analyzing river water downstream from a manufacturing facility in Alabama (USA), probably as a by-product of PFBS manufacturing. Examining the MS² spectrum, H-PFBS corresponded with compound 1, showing the same characteristic fragment ions at *m/z* 130.9922 (C₃F₅⁻), *m/z* 180.9890 (C₄F₇⁻), and *m/z* 260.9455 (C₄F₇SO₃⁻, NL of HF) along with SO₃⁻ (*m/z* 79.9580) and SO₃F⁻ (*m/z* 98.9556) (Figure S11A,C). Gebbink et al. [31] found mono-H-substituted perfluoro-1-butansulfonic acid in river water near a fluorochemical production plant in the Netherlands. In this case, the recorded spectrum did not show the ions C₃F₅⁻, C₄F₇⁻, and C₄F₇SO₃⁻, but this evidence could be explained by different experimental conditions such as the different applied collision energies, CEs (Figure S11B). These authors excluded the possibility that this chemical could derive from the fluorochemical plant since it was detected both upstream and downstream the manufacturing facility. On analyzing aqueous film-forming foams (AFFFs), Barzen-Hanson and coworkers tentatively identified 40 PFAS classes, including H-PFSAs [33]. AFFFs are synthetic foams designed for flammable liquid fires in which PFASs serve as surfactants that spread the foam to cool and suppress fire. Recently, Joerss et al. [28] described a homologous series of H-PFSAs in German and Chinese rivers near fluorochemical plants, as did Yao et al. [30] in a Chinese oilfield environment (Figure S11D). None of these researchers could determine the exact position of hydrogen; however, based on the detected ions and coherent NLs, Newton et al. [32] hypothesized that it was unlikely that H was bound to the carbon in α-position. In addition, with the H-PFBS isomer 1,1,2,2,3,3,4,4-octafluorobutanesulfonate (CAS 70259-86-8) being reported as an impurity in the production of PFBS, they proposed the structure with H on the terminal carbon as the most likely candidate.

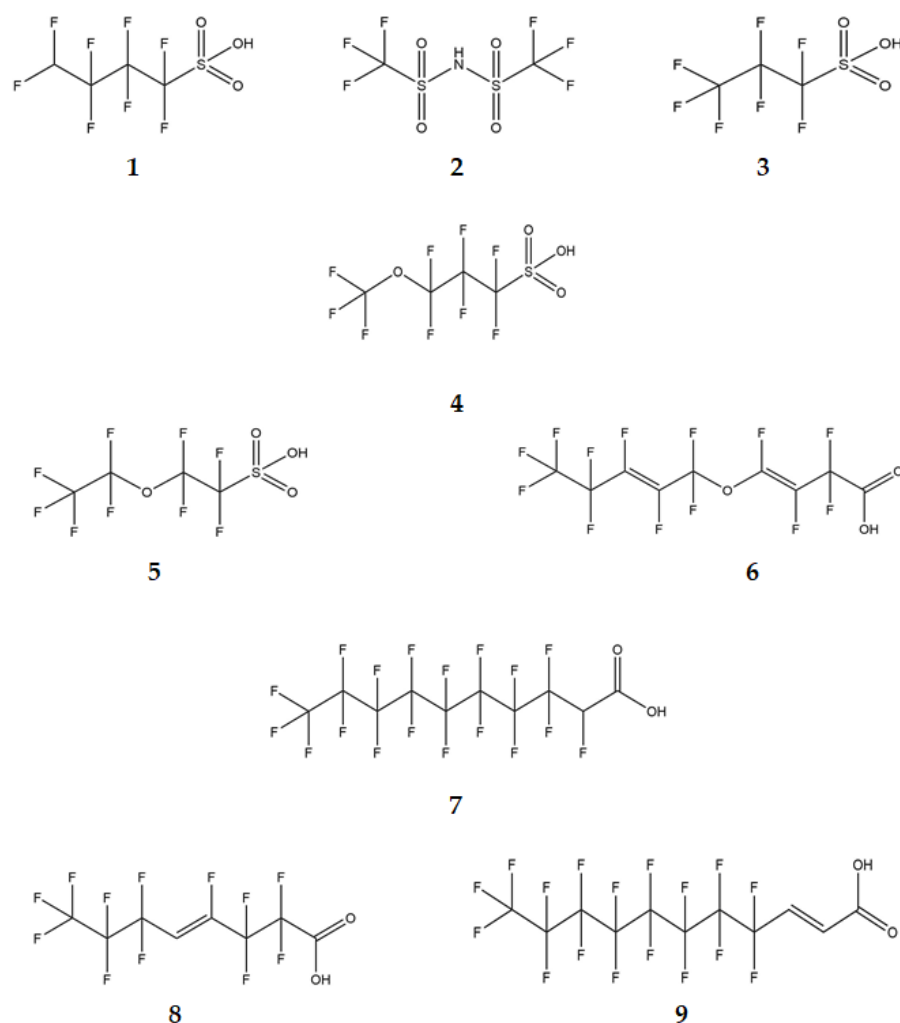


Figure 1. Putative structures of the nine detected PFASs. Structures **2**, **3**, and **5** have been definitively confirmed.

Compound **2** was unambiguously identified as bistriflimide (bis (trifluoromethylsulfonyl) imide), an ionic liquid with several technological applications (Figure 1). Bistriflimide was the most frequently found contaminant among the nine detected substances being present in all the three e-waste facilities. In Figure 2, the comparison between the chromatograms and MS² spectra recorded for bistriflimide (authentic standard) and for the suspect compound **2** in the sample P1-Z1-C1 is shown.

The ultra-short chain L-PFPrS (**3**) is not an unknown perfluorinated substance since it belongs to the series of PFASs, but generally, the analytes included in targeted methods start from C4 homologue (PFBS). In Figure S12, the comparison between L-PFPrS and its pure standard is shown. The two isomers **4** and **5** belonged to perfluoroether sulfonic acids (PFESAs), whereas the hypothesized compound **6** belonged to perfluoroether carboxylic acids (PFECAs). By means of its authentic standard, compound **5** was definitively identified as 1,1,2,2-tetrafluoro-2-(perfluoroethoxy) ethanesulfonic acid (CAS 113507-82-7) as shown in Figure S13. This PFESA has been recently found by Joerss and coworkers in wastewater and sediments from Chinese and German fluoropolymer manufacturing facilities [28].

The confirmation of PFESA **5** increased the confidence in the identification of its isomer, namely compound **4**. In its MS² spectrum, the fragment ions at m/z 79.9555, m/z 84.9888, and m/z 98.9540, attributable to SO₃⁻, CF₃O⁻, and FSO₃⁻ species, respectively, were found. The base peak at m/z 84.9888 is characteristic of a terminal perfluoromethoxy group, which was not present in the MS² spectrum of 1,1,2,2-tetrafluoro-2-(perfluoroethoxy)

ethanesulfonic acid (5). Instead, in the spectrum of the latter, the base peak was the ion at m/z 134.9858 ($C_2F_5O^-$), characteristic of a terminal perfluoroethoxy group.

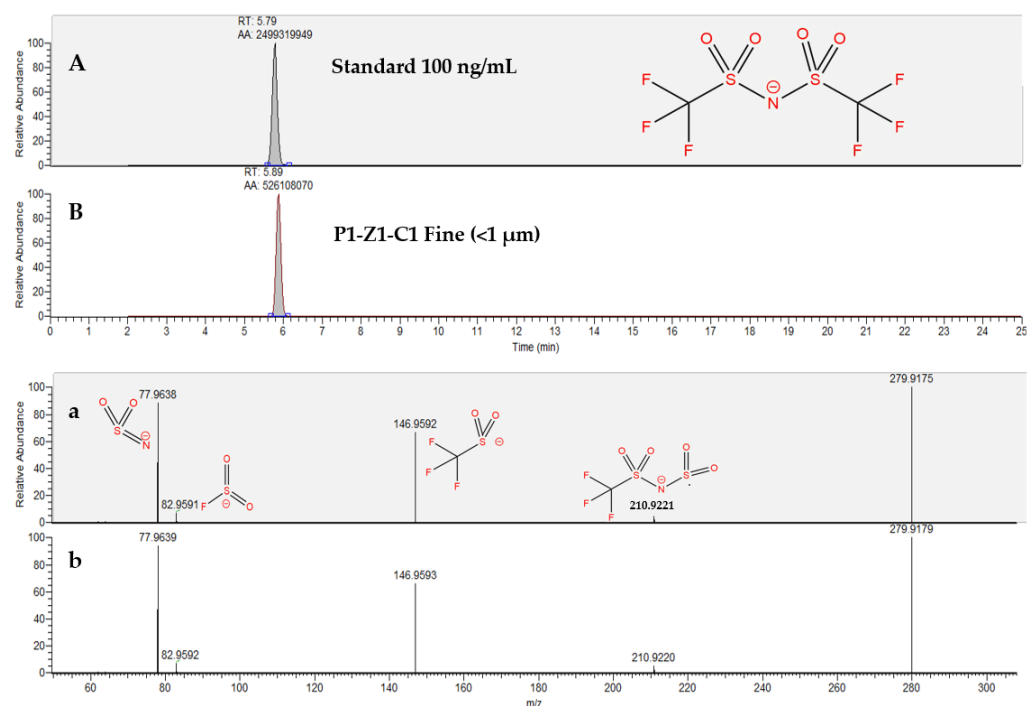


Figure 2. Comparison between chromatograms and MS² spectra of bistriflimide authentic standard (A,a) and airborne particles sampled at P1, Zone 1, Campaign 1 (B,b).

A H-substituted perfluorodecanoic acid (compound 7, H-PFDA) was detected in all three WEEE facilities, as shown in Figure 3. Its retention time was consistent with that expected, eluting before PFDA (14.5 min vs. 18.8 min). A substance with the same molecular formula ($C_{10}H_2F_{18}O_2$) was detected in wastewater of a fluoropolymer plant in the U.S. [37], and series of H-PFCA homologues have been reported in wastewater and sediments from Chinese and German fluoropolymer manufacturing facilities [23,25,28]. None of these researchers could ascertain the location of the H substitution, but according to Liu et al. [23] and Wang et al. [25], the presence of $C_nF_{2n+1}^-$ ions, namely $C_2F_5^-$ (m/z 118.9926) and $C_3F_7^-$ (m/z 168.9894), would rule out the hydrogen atom being near the terminal perfluoromethyl group. However, Awchi et al. [38] showed that for 11H-PFUnDA (11H-perfluoroundecylic acid), $C_2F_5^-$ and $C_3F_7^-$ ions were formed, although H was placed on the terminal methyl. All these researchers observed that H-PFCA homologues are characterized by the neutral loss of m/z 64 ($HF + CO_2$), which for compound 7 should involve the formation of a fragment at m/z 430.9729 ($C_9F_{17}^-$). This ion was not detectable in our spectrum, whereas it was in both MS² spectra published by Liu et al. (2015) and Wang et al. (2018) (Figure S14). Additionally, for compound 7, the $C_2HF_4^-$ fragment (m/z 101.0005) was well detectable, and conversely, the $C_2F_5^-$ ion (m/z 118.9931) did not appear in its spectrum, but there was $C_3F_7^-$ (m/z 168.9894). Clearly, compound 7 was not the same isomer described by Liu et al., Wang et al., and Joerss et al. [23,25,28]. A possible hypothesis could be a ramified structure in which one of the fragmentation patterns gives the formation of the cyclic neutral loss, $C_8F_{14}O_2$, and the ion $C_2HF_4^-$ (m/z 100). Another pattern could be the neutral loss of C_2HF_4 and the ion $C_8F_{14}O_2^-$ (m/z 412.9). After the CO_2 loss, this latter ion gives $C_7F_{15}^-$, justifying the presence of the fragment at m/z 268.

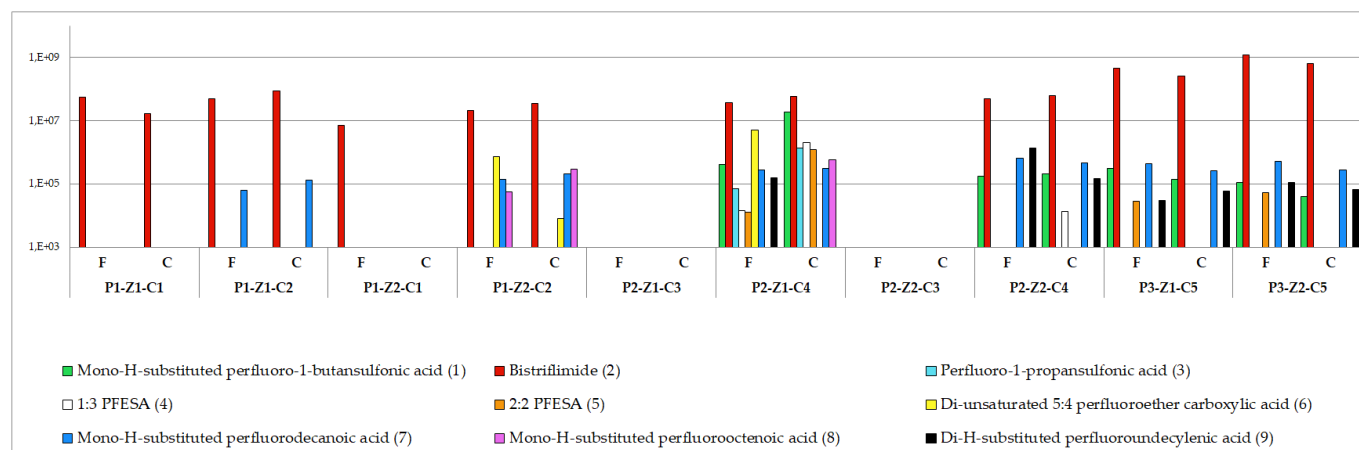


Figure 3. Signal intensities of the nine found PFASs in fine (F) and coarse (C) airborne particles collected in the two zones (Z1, Z2) of the three WEEE sites (P1, P2, P3) during the five sampling campaigns (C1, C2, C3, C4, C5). For details, see Table S1 of the Supplementary Material.

However, it is worth noting that in our EIC, there was another isomer eluting approximately half a minute later the compound 7 (Figure S15). This molecule was not fragmented by the mass analyzer, but its in-source spontaneous fragmentation gave an ion at m/z 430.9734 (neutral loss of HF + CO₂), indicating that this might be the structure detected in wastewater and sediments near the various fluoropolymer plants [23,25,28,37].

The structure of compound 8 (C₈H₂F₁₂O₂) is unclear. At first, a mono-H-substituted perfluorooctenoic acid was hypothesized, and accordingly, the commercially available possible isomer 2H-perfluoro-2-octenoic acid (CAS 70887-88-6) was purchased and analyzed, but it did not match with compound 8 (Figure S16). In addition, the structure of a mono-H-substituted perfluorooctenoic acid does not justify the presence of the fragment ion at m/z 186.9812 containing two oxygen atoms (C₅O₂F₅[−], exact m/z 186.9824). An explanation for this fragment could be found by hypothesizing a diketonic structure—more specifically, 4H,4H-perfluorooctane-3,5-dione—but no data were found to corroborate this speculation. Since diketonic polyfluorinated compounds (e.g., 1,1,1,5,5,6,6,7,7,8,8,8-dodecafluorooctane-2,4-dione) are used as ion-conductive polymeric compounds for electrochemical cells or trifluoroborate-substituted lithium pyrazoles and as conducting salts for lithium-based energy storage, it is plausible that compound 8 belongs to this class of substances.

Compound 9 is presumably a di-H-substituted perfluoroundecylenic acid (C₁₁H₃F₁₇O₂). The presence of the fragment ion at m/z 418.9730 (C₈F₁₇[−]) indicated that a double bond should be at position 2. The esters vinyl heptafluoronanoate (CAS 54640-64-1) and heptafluorooctyl acrylate, two structural isomers of 9, were excluded as possible candidates due to the very poor ionizability of these molecules. To the best of our knowledge, this PFAS was not previously reported.

The predicted isotopic patterns were experimentally confirmed except for 3 and 7, (Figures S2–S10), but this failure is due to their low abundance in real samples, as demonstrated by compound 3 (heptafluoro-1-propanesulfonic acid) which was definitively confirmed by its pure standard. Due to the wide diffusion of PFASs in several industrial products, it is important to underline that only compounds 2 and 9 were sporadically detected during laboratory and field blank sample analyses. However, their responses were at least 10 times higher than those for the blank samples injected in the same analytical sequence [23]. Suspect molecules without a clear distinction between real and blank samples are not included in Table 1. Finally, with regard to quantitative evaluation, as mentioned before, the limited amounts of sample extracts did not allow for sample re-injection after standard purchasing (some months later). Therefore, for definitively identified PFASs, only a posteriori semi-quantitative estimation was carried out (Table S8). Moreover, the injection of pure standards months apart from the analysis was the cause of the difference in reten-

tion times between the compounds to be confirmed and the standard. The instrumental signals of the nine PFASs showing their distribution in the three e-waste plants and zones are summarized in Figure 3.

4. Discussion

Among the nine uncommon or infrequently detected PFASs in airborne particles, the identification of bistriflimide (bis(trifluoromethylsulfonyl) imide) is the most interesting finding. Bistriflimide is a commercially available superacid, and its anion is important in the production of lithium-ion and lithium metal batteries. In addition, this compound is used in various fields, including analytics, extractions, catalysis, and lubrication technologies. Neuwald and collaborators first reported the detection of an ionic liquid, tris(pentafluoroethyl) trifluorophosphate ($[(C_2F_5)_3PF_3]^-$), in three German rivers, including the Rhine River. These researchers underlined the importance of monitoring these chemicals, considering them “of interest for the rapidly growing field of persistent, mobile, and toxic and very persistent and very mobile substances” [39]. Accordingly, the same research group later refined its analytical approach in order to detect a wider group of contaminants in two German river systems [40]. They found twenty compounds mainly used as ionic liquids. Among these, even seven were perfluorinated substances including bistriflimide. Due to their great persistence and mobility, fluorinated anions are more worrisome than non-fluorinated ones, and the ubiquitous detection of bistriflimide in all three WEEE plants supports the need for more thorough investigations into their occurrence, fate, and environmental impact. PFASs containing a fluorinated carbon chain interspaced with heteroatoms, such as per- and polyfluoroalkyl ether acids, are among the emerging families [41]. Our findings confirm their large introduction, and three out of the nine substances found were perfluoroethers, namely compounds 4, 5, and 6, although only 1,1,2,2-tetrafluoro-2-(perfluoroethoxy)ethanesulfonic acid could be definitively identified. Other emergent PFASs are short chain molecules such as compounds 1 and 3 (perfluoro-1-propanesulfonic acid, L-PFPrS). Traces of L-PFPrS have been mainly detected in groundwater near military bases, such as the New Zealand base of Ohakea [42] and several U.S. military bases [43]. Its presence was probably due to the use of AFFFs released to extinguish fuel-based fires. AFFFs contributed significantly to global PFAS pollution, and accordingly, many countries restricted or eliminated them, developing safer alternatives. Yeung et al. [44] found PFPrS in rain samples collected in Canada, estimating concentrations much lower than those reported in groundwater near military bases and thus demonstrating the transportation of this PFAS through the atmosphere. As shown in Figure 3, in our study, PFPrS was detected only at plant 2 (P2) during campaign C4 (P2-Z2-C4). Interestingly, in the period between C3 (May 2021) and C4 (February 2022), a fire occurred in the outdoor area of this WEEE facility, which could have been the cause of the PFPrS traces found a few months later as a consequence of AFFF usage. H-substituted PFASs such as mono-H-substituted perfluoro-1-butanesulfonic acid (1) and H-substituted PFCAs such as mono-H-substituted perfluorodecanoic acid (7) have frequently been discovered near fluoropolymer plants [23,31,32]. More recently, these compounds have also been reported in other contexts such as oil exploitation areas, probably also in this case as a result of the high usage of AFFFs and chemical oil additives [30]. For both H-PFASs and H-PFCAs, it has not been possible to ascertain the exact location of H on the basis of MS experiments alone, and contradictory data have been published [23,38].

Regarding the distribution of the nine PFASs detected among the three e-waste plants, the samples from P2 collected during campaign 3 (C3) were not contaminated at all (Figure 3). This observation is not easily explainable, but similarly, the results of targeted analyses carried out by Pomata et al. [9] showed the lowest PFAS concentrations (as a sum) in the same samples (P2-Z1-C3 and P2-Z2-C3), with values below 2 ng/m^3 . On the other hand, analysis of the other organic contaminants (PAHs, PCBs, brominated flame retardants, etc.) in the same samples did not show a similar decrease [9]. Finally, the estimated concentrations of bistriflimide were much higher in P3 ($11\text{--}61 \text{ ng m}^{-3}$) than in

P1 (0.3–3.1 ng m⁻³) and P2 (0.9–2.6 ng m⁻³). Compounds **3** and **5** were estimated in the order of a few picograms per cubic meter (Table S8).

5. Conclusions

Our findings show that the application of untargeted approaches to airborne particles sampled in WEEE plants is able to furnish additional information on circulating PFASs, which is significant in view of the increasingly strategic importance of recovering valuable materials from e-waste. The main objective is certainly to protect the health of workers of recycling plants, but another aim is to obtain direct data on molecules arising from the disposal of electrical and electronic products. This information can then be used in other areas of interest such as environmental protection and food safety. The ubiquitous presence in airborne particles of bistriflimide, for example, highlights the need to include in future research perfluorinated ionic liquids, a group of pollutants that are not only toxic and persistent but also highly mobile. Only further data on their actual environmental diffusion will determine whether they are emerging pollutants or not.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/separations10110547/s1>, Table S1: Summary of the sampling campaigns: abbreviations of the sampling locations and description of the working operations; Table S2. Full MS/dd-MS² (TopN) settings; Table S3. Full MS/DIA settings; Table S4. Full MS/AIF/NL dd-MS² settings; Table S5. Neutral losses (NLs) included in the in-house library¹; Table S6. Fragment ions included in the in-house library¹; Table S7. Compound Discoverer parameters; Table S8. Estimated concentrations of confirmed PFASs; Figure S1. Compound Discoverer workflow for untargeted analysis of PFASs in airborne particles collected in WEEE sites; Figure S2. Mono-hydrogen-substituted perfluoro-1-butansulfonic acid (C₄H₂F₈SO₃, **1**): EIC (left side), full MS spectrum (center), and MS² spectrum (right side). Ions in green (*m/z* 196.98306 and *m/z* 98.9541) have been recognized by Compound Discoverer because they were inserted in the list of Table S6; Figure S3. Bistriflimide (C₂HF₆NO₄S₂) (**2**): EIC (left side), full MS spectrum (center), and MS² spectrum (right side). Green ions are those recognized by Compound Discoverer; Figure S4. Heptafluoro-1-propansulfonic acid (C₃HF₇SO₃, **3**): EIC (left side), full MS spectrum (center), and MS² spectrum (right side). Green ions are those recognized by Compound Discoverer; Figure S5. 1,1,2,2,3,3-hexafluoro-3-(trifluoromethoxy)propane-1-sulfonic acid (C₄HF₉SO₄, **4**): EIC (left side), full MS spectrum (center), and MS² spectrum (right side). Green ions are those recognized by Compound Discoverer; Figure S6. 1,1,2,2-tetrafluoro-2-(perfluoroethoxy)ethanesulfonic acid (C₄HF₉SO₄, **5**): EIC (left side), full MS (center), and MS² spectrum (right side). Green ions are those recognized by Compound Discoverer; Figure S7. Di-unsaturated 5:4 perfluoroether carboxylic acid (C₉HF₁₃O₃, **6**): EIC (left side), full MS (center), and MS² spectrum (right side). Green ions are those recognized by Compound Discoverer; Figure S8. Mono-hydrogen-substituted perfluorodecanoic acid (C₁₀H₂F₁₈O₂, **7**): EIC (left side), full MS (center), and MS² spectrum (right side). Green ions are those recognized by Compound Discoverer; Figure S9. Mono-hydrogen-substituted perfluorooctenoic acid (C₈H₂F₁₂O₂, **8**): EIC (left side), full MS (center), and MS² spectrum (right side). Green ions are those recognized by Compound Discoverer; Figure S10. Di-hydrogen-substituted perfluoroundecylenic acids (C₁₁H₃F₁₇O₂, **9**): EIC (left side), full MS (center), and MS² spectrum (right side). Green ions are those recognized by Compound Discoverer; Figure S11. MS² spectra of PFAS with formula C₄H₂F₈SO₃ found in various studies: (A) compound **1** (this study); (B) compound found by Gebbink et al., acquired by means of Q-Orbitrap (Thermo Fisher Scientific) applying CEs 20 eV and 80 eV [25]; (C) compound described by Newton et al., acquired by means of Q-TOF (Agilent, Santa Clara, CA, USA) using fragmentor voltages of 80 V, 125 V, and 190 V [26]; (D) compound reported by Yao et al. obtained by means of Fusion Tribrid (Thermo Fisher Scientific) using CEs 35 eV (±15%) [24]; Figure S12. Confirmation of compound **3** (heptafluoro-1-propansulfonic acid). Chromatogram and MS² spectrum of pure standard (A,a) and chromatogram and MS² spectrum of an airborne sample (B,b); Figure S13. Confirmation of compound **5** (1,1,2,2-tetrafluoro-2-(perfluoroethoxy)ethanesulfonic acid). Chromatogram and MS² spectrum of pure standard (A,a) and chromatogram and MS² spectrum of an airborne sample (B,b); Figure S14. (A) MS² spectrum of compound **7** (C₁₀H₂F₁₈O₂); (B) MS² spectrum of the isomer compound found by Liu et al. (adapted with permission. Copyright 2015 ACS) [17]; (C) MS² spectrum of the isomer compound found by Wang et al. (adapted with permission. Copyright 2018

ACS) [19]. In MS² spectra (B) and (C), the ions at m/z 118.99 (C₂F₅[−]) and m/z 430.97 (C₉F₁₇[−]) are recorded, but not ions at m/z 101.00 (C₂HF₄[−]) and m/z 368.98 (C₇F₁₅[−]) detected in MS² spectrum of compound 7 (A); Figure S15. EICs and MS² spectrum of compound 7, H-PFDA (A,a). In the chromatogram (B), the peak eluting at 15.05 min was an isomer of 7 which was not fragmented. Its spontaneous in-source fragmentation gave the ion at m/z 430.9734 (C₉F₁₇[−]) due to the neutral loss of CO₂ + HF; Figure S16. EICs and MS² spectra of 2H-perfluoro-2-octenoic acid (CAS 70877-88-6) (A,a) and unknown compound 8 (B,b).

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Abbreviations

ADONA	Sodium dodecafluoro-3H-4,8-dioxanonanoate
AFFF	Aqueous film-forming foam
AIF	All ion fragmentation
ASE	Accelerated solvent extraction
CE	Collision energy
EIC	Extracted-ion chromatogram
Gen-X	Ammonium perfluoro (2-methyl-3-oxahexanoate)
HESI	Heated electrospray ionization source
H-PFBS	Mono-hydrogen-substituted perfluoro-1-butansulfonic acid
H-PFDA	H-substituted perfluorodecanoic acid
L-PFPrS	Heptafluoro-1-propansulfonic acid
NL	Neutral loss
PFASs	Per- and polyfluoroalkylated substances
PFBS	Perfluorobutansulfonate
PFCA	Perfluoroalkyl carboxylate
PFECA	Perfluoroether carboxylic acid
PFESA	Perfluoroether sulfonic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctanesulfonate
PFOSA	Perfluorooctanesulfonamide
PFSA	Perfluoroalkyl sulfonate
PM	Particulate matter
PTFE	Polytetrafluoroethylene
RT	Retention time
WEEE	Waste electrical and electronic equipment
11H-PFUnDA	11H-perfluoroundecic acid
1:3 PFESA	1,1,2,2,3,3-hexafluoro-3-(trifluoromethoxy)propane-1-sulfonic acid
2:2 PFESA	1,1,2,2-tetrafluoro-2-(perfluoroethoxy)ethanesulfonic acid
5:4 PFECA	Di-unsaturated 5:4 perfluoroether carboxylic acid

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