

# Evaluation of Fluorochemical Leaching from Lithium-Ion Batteries Under Simulated Solid Waste Landfill Conditions

Marzieh Shojaei, Jennifer L. Guelfo, Morton A. Barlaz, Grisel Cogollo-Carcamo, Nelson A. Rivera, Jr., Heileen Hsu-Kim, and P. Lee Ferguson\*



Cite This: <https://doi.org/10.1021/acs.est.5c10116>



Read Online

ACCESS |

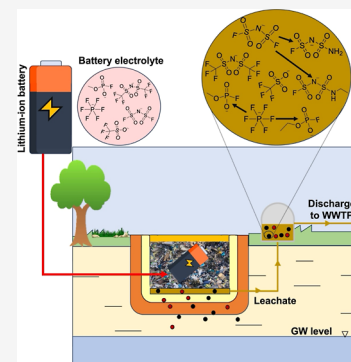
Metrics & More

Article Recommendations

Supporting Information

**ABSTRACT:** Lithium-ion batteries (LiBs) are widely used in electronic devices and renewable energy systems. Fluorochemicals are essential components of LiBs, as a component of electrolytes, electrodes, and coatings. However, there are concerns about the environmental release of fluorochemicals, especially within landfills after disposal, due to the fact that landfill leachate is typically treated in facilities not designed to attenuate fluorochemicals. We have evaluated the occurrence of fluorochemical compounds in commercial LiBs and fluoropolymer binders and the release of LiB-derived fluorochemicals in simulated municipal solid waste (MSW) leaching experiments. Our survey of 19 LiBs found per- and polyfluoroalkyl substances (PFAS) including bis(perfluoroalkyl)sulfonimide (bis-FASI, up to 36 mg) and inorganic fluorochemicals such as hexafluorophosphate ( $\text{PF}_6^-$ , up to 1.4 g) and bis(fluorosulfonyl)imide (bis-FSI, up to 250 mg). PFAS were also measured in fluoropolymer binders in the range of 2–2000 ng/g. Nontargeted analysis resulted in detection of diverse fluorinated sulfonimides and organic phosphofluoridates in batteries as well as 6 novel PFAS in fluoropolymer binders. Analysis of MSW landfill leachates indicated the presence of LiB-derived fluorochemicals up to 76  $\mu\text{g/L}$ . Simulated MSW leaching experiments showed that LiBs released PFAS (up to 100 mg/L) and inorganic fluorochemicals (up to 1.4 g/L) into the landfill leachate over a period of 220 days. Furthermore,  $\text{PF}_6^-$  and bis-FSI transformed in landfill leachate to form organic phosphofluoridates and novel amino sulfonyl fluorosulfanomides. This is the first report of PFAS and fluorochemical release from LiBs and transformation under landfill leaching conditions.

**KEYWORDS:** per- and polyfluoroalkyl substances, phosphofluoridates, nontargeted analysis, landfill leachate



## INTRODUCTION

Rechargeable lithium-ion batteries (LiB) are widely used in various electronic devices and applications due to their high energy density, long cycle life, and relatively low self-discharge rate.<sup>1</sup> The growing demand for LiBs has led to a corresponding increase in end-of-life battery waste.<sup>2,3</sup> Globally, only 5–7% of LiBs are collected for recycling where the goal is to recover transition metals (Ni and Co),<sup>4–6</sup> with the majority of LiBs disposed of in landfills.<sup>7,8</sup> Depending on the process and the type of battery, the recycling process itself can result in emission of contaminants in the environment.<sup>2,3</sup> The growth of LiB waste has increased concern about the fate of associated contaminants.

Organic and inorganic fluorochemicals have been used in various components of LiBs, including electrolytes, binders, and separators to enhance their performance, thermal stability, and longevity.<sup>6,8</sup> Per- and polyfluoroalkyl substances (PFAS, as defined by OECD<sup>9</sup>) are often employed in LiB components such as electrode binders and electrolytes due to their chemical stability, heat resistance, and ability to enhance performance under high-stress conditions.<sup>3,6–8,10</sup> Bis-perfluoroalkyl sulfonimides (bis-FASIs) (e.g., the  $\text{Li}^+$  salt of bis-(trifluoromethylsulfonyl)imide or bis-FMeSI) are used as a

LiB electrolytes and as antistatic agents in polyvinylidene fluoride (PVDF) electrode binders and separators.<sup>11,12</sup> We have previously shown that bis-FASIs are released to the environment through manufacturing and disposal and that bis-FMeSI concentrations as low as at 10 ng/L can influence the behavior and energy metabolic processes of aquatic organisms.<sup>11</sup> Long-chain bis-FASIs have been discovered as bioaccumulative PFAS in mice exposed to aqueous film forming foams (AFFF).<sup>13</sup> In addition, certain perfluoroalkyl acids (PFAAs) especially perfluoromethanesulfonate (PFMeS) have been disclosed as electrolyte and additive salts in LiBs.<sup>6</sup> Recently, C1–C8 perfluoroalkyl sulfonates (PFSAs) and C4–C13 perfluoroalkyl carboxylic acids (PFCAs) were detected in soils collected from a LiB recycling facility in China,<sup>3</sup> suggesting LiB recycling can also be a source of PFAS contamination.

Received: July 24, 2025

Revised: November 25, 2025

Accepted: November 26, 2025

In addition to PFAS, inorganic fluorochemicals are used in LiBs as electrolytes and additive salts.<sup>6</sup> Lithium hexafluorophosphate ( $\text{LiPF}_6$ ) is used as the primary salt in some battery electrolytes, while lithium tetrafluoroborate ( $\text{LiBF}_4$ ) and lithium bis(fluorosulfonyl)imide (LiFSI) are less commonly used as electrolytes.<sup>6,14,15</sup> These fluorinated salts are crucial for LiB functionality, contributing to the electrolyte's ionic conductivity and stability.<sup>15</sup> However, during battery degradation, unintentional destruction, or leakage events during use, such fluorochemicals can be released to the environment.<sup>6,8,16</sup> In particular, when LiBs reach the end of their life, they are sent to recycling facilities or disposed in landfills.<sup>17</sup> When landfilled, they may degrade due to mechanical stress, corrosion, and exposure to moisture in landfills, releasing these fluorinated compounds to leachate.<sup>7</sup> Little is currently known about the toxic effects of these inorganic fluorochemicals in the environment, but exposure to  $\text{LiPF}_6$  has been shown to cause development abnormalities in aquatic organisms and impacts their swimming behavior.<sup>18</sup> Hexafluorophosphate ( $\text{PF}_6^-$ ) and tetrafluoroborate ( $\text{BF}_4^-$ ) have been detected in surface water in Germany<sup>19,20</sup> and drinking water in China and Sweden,<sup>21,22</sup> suggesting possible release of fluorinated LiB electrolyte salts through various mechanisms.

Disposing LiB waste in municipal landfills can lead to various environmental problems such as the release of toxic contaminants and fire hazards.<sup>4,6</sup> Recalcitrant compounds, such as Bis-FASIs and other fluorochemicals, may be released into landfill leachates after the disposal and burial of used lithium batteries. These compounds could potentially accumulate in landfill leachate.<sup>11,23,24</sup> Leachates are collected in engineered landfills and typically sent to wastewater treatment plants (WWTPs) for treatment, which makes them an important potential route of PFAS to such WWTPs.<sup>25,26</sup> Similar to PFAS, advanced water and wastewater treatment methods (e.g., ion exchange and electrochemical approaches) are needed for removal of inorganic fluorochemicals such as  $\text{PF}_6^-$ .<sup>27–30</sup> Although leachate undergoes treatment before being discharged,<sup>31,32</sup> conventional wastewater treatment processes do not effectively destroy LiB-derived fluorochemicals, resulting in their release in both treated effluent and biosolids.<sup>20,25,30,33</sup>

Release of heavy metals from LiBs under landfill leaching conditions has been studied.<sup>34</sup> However, despite the growing volume of LiB waste associated with increased use in consumer products and electric vehicles, to the best of our knowledge, release of fluorochemicals from LiBs into landfill leachates and potential transformation afterward have never been explicitly evaluated. This knowledge gap is particularly concerning given the potential toxicity of inorganic fluorochemicals, the environmental persistence of PFAS, and the fact that some of them are bioaccumulative.<sup>35–37</sup> In this study we utilized a combination of targeted and nontargeted analysis to assess the occurrence of PFAS and inorganic fluorochemicals in commercial LiBs as well as fluoropolymer binders, which are used to formulate LiBs and might contribute to leachable PFAS in batteries under landfill conditions. By simulating the leaching conditions of LiBs with environmentally sourced landfill leachates, we aimed to evaluate the leaching and subsequent transformation of fluorochemicals from LiBs. These findings provide insights into the fate of LiB-derived fluorochemicals during disposal, contributing to a better understanding of the environmental impacts of LiBs discarded

in landfills and informing future waste management strategies for battery recycling and disposal.

## MATERIALS AND METHODS

**Materials.** Authentic standards of all measured PFAS and their isotopically labeled standards for use as internal standards (IS, Table S1 and the Supporting Information, SI) were purchased from Wellington and Cambridge Laboratories except for bis-FASI standards. Lithium salts of bis-FASIs and inorganic fluorochemicals were acquired from Sigma-Aldrich and Fisher Scientific, respectively. All other solvents and chemicals were purchased from Fisher Scientific and VWR at the highest available purity. Batteries, from new and discarded consumer electronics (labeled “A” to “S”), and binders used in this study are listed in Table S2. Leachate samples (labeled 1 to 11) were collected from active and closed municipal landfills in central and southern North Carolina and kept at 4 °C before analysis and use in batch leaching experiments.

**Battery Extraction.** To measure the initial fluorochemical content, batteries and 1.0 g of each fluoropolymer binder were extracted using a Soxhlet extraction technique for 24 h using methanol.<sup>11</sup> Batteries were discharged and disassembled prior to extraction. 200 mL of extracts was then concentrated to 10 mL and analyzed for organic and inorganic fluorochemicals. More details regarding battery and fluoropolymer extraction are provided in SI Section S1.

**Batch Experiments. LiBs Leaching.** Batch leaching experiments were adapted from a previously published leaching experiment.<sup>24,38</sup> The experiments were conducted in 1 L high density polyethylene (HDPE) bottles containing 900 mL of landfill leachate 1 and LiB B or S (Table S2). This leachate was chosen for the leaching experiment because it was collected from a landfill which closed during the 1990s and thus it contained none of the LiB-derived fluorochemical analytes above detection limits. Chemical characteristics of Leachate 1 are provided in Table S3. Battery B and S were used because of their high bis-FMeSI and bis-FSI masses, respectively. Three initial battery conditions were tested in this study: disassembled, opened (cap removed), and intact LiB. These three treatments were intended to simulate the range of initial battery conditions that could be present in a landfill after disposal. Reactors were closed with a rubber stopper to ensure a gastight environment. Stoppers were modified using an airlock to allow gas venting with a 21G hypodermic needle and a luer-lock stopcock coupled with 1/16” ID PEEK tubing for periodic sampling of leachates from reactors. All reactors were shaken and purged with  $\text{N}_2$  for 30 min to initiate anaerobic conditions. Reactors were then incubated at 37 °C and 140 rpm shaking for up to 220 days. Control experiments were conducted to evaluate fluorochemical background concentrations in reactors (leachate control) and the effect of leachate matrix on leaching of fluorochemicals (DI water control). Leachate controls were prepared without addition of batteries, while DI water controls were prepared using 900 mL of DI water and intact batteries. Reactor sampling was conducted using 3 mL polypropylene (PP) syringes without opening reactors. Samples of 0.5 mL reactor aqueous phase were collected through the stopcock using a PP syringe and transferred into PP microcentrifuge tubes at each time point. Samples were stored at 4 °C for 3–14 days prior to analysis. Following completion of batch experiments, batteries were Soxhlet extracted and analyzed for any residual fluorochemicals that were not released during exposure to MSW leachates.

**Bis-FSI Transformation.** A benchtop experiment was conducted to further examine the putative abiotic transformation of bis-FSI observed during the LiB leaching experiments. This experiment was carried out in 60 mL HDPE bottles under the same environmental conditions used for the leaching experiment. We tested bis-FSI transformation under three different conditions. Reactors were prepared with 60 mL of DI water containing 21 mg/L bis-FSI, and then, separate duplicate reactors were amended with 250 mM ammonium hydroxide, ethylamine, or ethanolamine, respectively. Experiments to assess the reaction of bis-FSI with ammonium hydroxide, ethylamine, or ethanolamine were conducted based on hypothesized mechanisms that could explain the appearance of the observed bis-FSI transformation products in battery leaching experiments. One additional reactor was prepared using Leachate 1. For the leachate reactor, 60 mL of leachate 1 was used instead of DI water, and 21 mg/L bis-FSI was added to the bottle. Control reactors were prepared by transferring 60 mL of DI water amended with 21 mg/L bis-FSI (DI water control) and 60 mL of leachate 1 (leachate control) into the HDPE bottle. Reactors and control bottles were then purged with N<sub>2</sub> for 30 min to create an anaerobic environment and incubated at 37 °C and 140 rpm shaking for 28 days. Reactors were sampled every 3–7 days using PP syringes and analyzed for bis-FSI and its degradation products.

#### Instrumental Data Acquisition and Processing.

**Fluorochemical Analysis.** Field-collected MSW landfill leachates from multiple sites around North Carolina, USA, and battery extracts and reactor leachates were analyzed for fluorochemicals. All samples were prepared in autosampler vials to a final composition of 70% water and 30% methanol containing 50 ng/L IS and analyzed for PFAS by direct-injection liquid chromatography tandem mass spectrometry (LC–MS/MS) as described in the SI. To minimize matrix effects, leachate samples were diluted 10× in 70% DI water and 30% methanol before PFAS analysis. For inorganic fluorochemicals and ultrashort PFAS (Table S1), samples were diluted 10–200,000× in 86% acetonitrile and 14% water and monitored using HILIC LC–MS/MS as described in the SI.

Targeted and nontargeted analysis were performed using high-performance liquid chromatography (HPLC, Vanquish, Thermo Fisher, CA, USA), triple quadrupole mass spectrometry (TSQ Altis, Thermo Fisher, CA, USA), and HPLC–Orbitrap mass spectrometry (Orbitrap Fusion Lumos, Thermo Fisher, CA, USA), respectively. For targeted analysis, samples were acquired in multiple reaction monitoring (MRM) acquisition mode. TraceFinder (version 5.1, ThermoFisher Scientific, San Jose, CA) was used for both data acquisition and processing in target analysis. Targeted analytes were quantified over a calibration range of 1–1000 ng/L ( $R^2 > 0.99$ ) using isotope dilution. Full-scan MS data and data-dependent MS<sup>2</sup> data were acquired for nontargeted and suspect screening analysis. Compound Discover (version 3.3, ThermoFisher Scientific, San Jose, CA) coupled with a custom-written (R programming language) processing node was used for data processing during nontargeted analysis. Additional information regarding chromatographic and mass spectrometer conditions is available in Section S1.

**Fluorochemical Recovery and Mass Balance.** Fluorochemical aqueous phase recovery and mass balance in all reactors at the conclusion of batch experiment were calculated as follows:

$$\text{Recovery in aqueous phase (\%)} = \frac{m_L}{m_{PB}} \quad (1)$$

$$\text{Total mass balance (\%)} = \frac{m_L + m_B}{m_{PB}} \quad (2)$$

where  $m_L$  is the mass measured in reactor leachate,  $m_B$  is the mass of fluorochemical measured in battery after leaching, and  $m_{PB}$  is the mass of each fluorochemical in the intact battery before leaching.

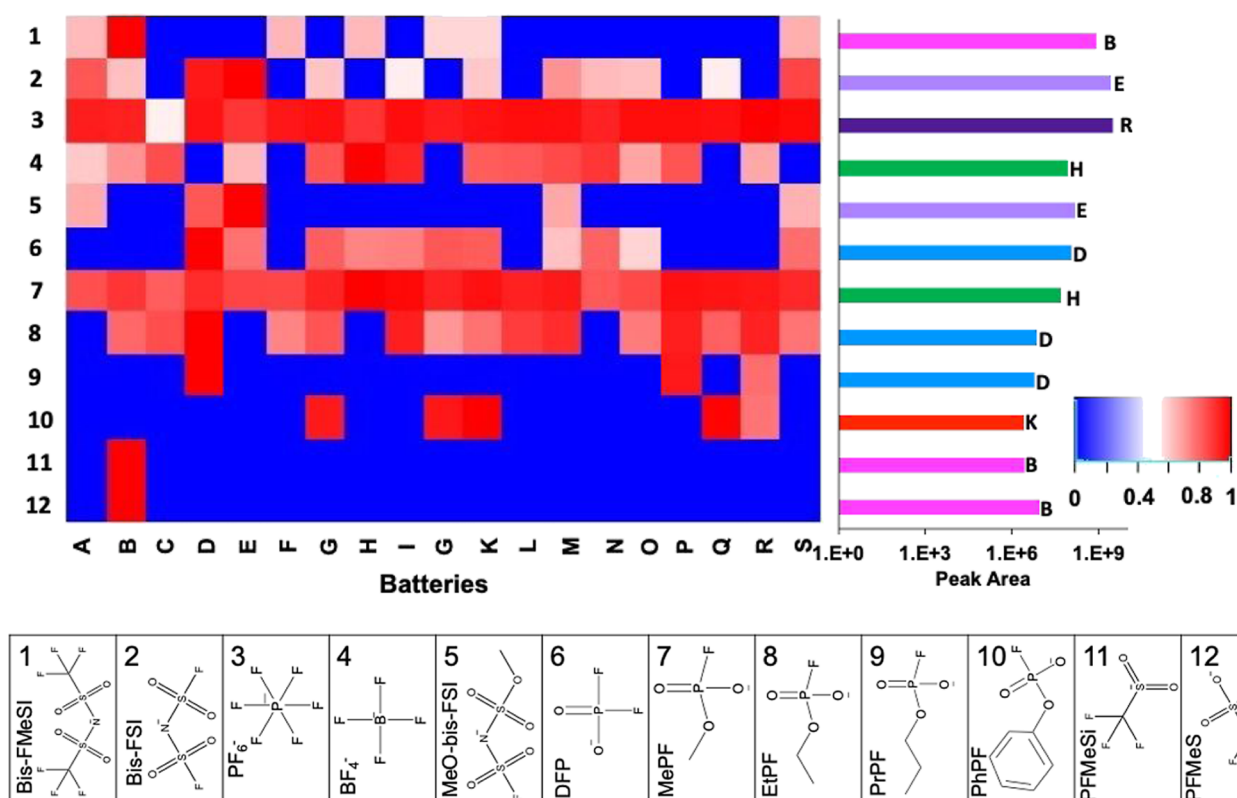
**Metal Analysis.** At the conclusion of the leaching experiments, dissolved concentrations of trace metals in batch reactor aqueous phases were analyzed by inductively coupled plasma–mass spectrometry (ICP–MS, Agilent 7900). Samples were diluted into an acid matrix, amended with 20 μg/L internal standards, and analyzed for a panel of 38 elements (including Li) by ICP–MS under helium (collision) mode or hydrogen (reaction) mode. Additional details regarding metal analysis are provided in Section S1.

**Chemically Bonded Fluorine Analysis.** Reactor aqueous phases in leaching experiments were sampled at the last day of monitoring, diluted 4–100-fold in 10% [v/v] methanol/water and analyzed for CBF by combustion ion chromatography (CIC) using a Profiler<sup>F</sup> Wastewater Analyzer (Metrohm). This system directly measures both free fluoride and total fluorine in aqueous samples. CBF concentrations were calculated by subtracting the concentration of free fluoride from the total fluorine concentration. More details regarding CBF analysis are available in Section S1.

## RESULTS AND DISCUSSION

### Fluorochemicals in Batteries and Fluoropolymer Electrode Binder Agents. Targeted Analysis.

A total of 13 PFAS were detected in battery extracts (Table S4). Three classes of PFAS, PFCAs (C<sub>4</sub>–C<sub>10</sub>), bis-FASIs (C<sub>2</sub>–C<sub>8</sub>), PFSA (C<sub>1</sub> and C<sub>4</sub>), and perfluoromethane sulfonamide (FMeSA) were detected in batteries. PFCA masses were 0.5 (perfluoroheptanoic acid, PFHpA)- 907 ng (perfluorooctanoic acid, PFOA) and PFSA masses were 0.6 (perfluorobutanesulfonate, PFBS)-290,600 ng (perfluoromethanesulfonate, PFMeS) per battery. FMeSA was detected in Battery B in a mass of 49,400 ng. LiB, and fluoropolymer bis-FASI results were published in our previous work.<sup>11</sup> Masses of bis-FASIs in battery extracts ranged from 0.6 ng (bis-perfluorobutane sulfonamide, bis-FBSI) to 35 mg (bis-FMeSI, Table S4). The varying levels of bis-FMeSI detected across the analyzed batteries indicate that this compound may have various uses in LiB, including as an electrolyte salt and as an additive. We detected bis-FMeSI in commercial LiB fluoropolymer electrode binder powders at levels ranging from 2.16 (PTFE) to 385 ng/g (PVDF),<sup>11</sup> indicating that some of the bis-FMeSI found in batteries may have been residual from use as an antistatic agent in the electrode binder polymers.<sup>12</sup> Bis-FETSI and bis-FBSI were detected in some batteries (Table S4) but at lower quantities relative to bis-FMeSI, suggesting that they may have been impurities in electrolyte formulations or may have been added as low level additives to improve battery properties.<sup>6,39–41</sup> C<sub>4</sub>–C<sub>14</sub> PFCAs were the most abundant targeted PFAS detected in PTFE battery binder (1140–2021 ng/g). PFAS have been used as surfactants in emulsion polymerization of fluoropolymer binders.<sup>42</sup> PFCAs and per- and polyfluoroalkylether carboxylates (PFECAs) were previously reported in fluoropolymers including PVDF and PTFE.<sup>8,43–45</sup> High concentrations



**Figure 1.** Summary of results from HRMS nontargeted analysis of fluorochemicals in LiBs. The color of heat map cells was based on  $\frac{\log_{10} \text{Peak Area}}{\log_{10} \text{Max Peak Area}}$  where the max peak area is the maximum peak area detected for each compound across the set of batteries. The acronyms in red highlight are compounds annotated from nontargeted analysis. The bar plot on the right side shows the maximum observed peak area for compounds 1–12 listed in the table, color coded to the batteries in which the maximum peak area was observed.

of PFCAs measured in PTFE binder suggest that they were likely either used intentionally as polymerization aids or formed unintentionally during polymer production/processing. PFOA has been measured in fluoropolymers and their products with concentrations up to 1100  $\mu\text{g/g}$ ,<sup>43,44,46</sup> and this suggests detection of this compound in LiBs such as battery F (Table S4) could be associated with fluoropolymer binders used in their manufacturing. Low concentrations of C<sub>4</sub>–C<sub>10</sub> PFCAs were also measured in Solvne 200/P400 and PVDF fluoropolymer binders (Table S5), while, of the targeted PFAS analyzed in this study, Nafion byproducts were the major components of Solvne 200/P400 and Solvne 250/P400 (864–14,900 ng/g, Table S5). Emerging PFAS such as per- and PFECAs and per- and polyfluoroalkylether sulfonate (PFESA) have been used as alternatives to PFCAs in fluoropolymer manufacturing.<sup>42,43</sup> PFECAs were detected in PTFE binders with lower concentrations (6–95 ng/g, Table S5) in comparison with PFCAs. This suggests PFECAs might be impurities added to PTFE binders during fluoropolymer manufacturing.

LiBs and fluoropolymer binder extracts were screened for the inorganic fluorochemicals bis-FSI, PF<sub>6</sub><sup>−</sup>, and BF<sub>4</sub><sup>−</sup>. LiPF<sub>6</sub> has been used as a principal electrolyte salt in LiBs due to its high ion conductivity.<sup>6</sup> However, due to its low thermal stability and high moisture sensitivity, it is often used in combination with other lithium salts like LiFSI and LiBF<sub>4</sub>.<sup>47</sup> PF<sub>6</sub><sup>−</sup> was detected in all batteries at quantities of 17,000–1,400,000  $\mu\text{g/battery}$ , the highest levels of any measured analyte monitored in this study (Table S4). LiFSI and LiBF<sub>4</sub>

are less common electrolyte salts and have mainly been used as electrolyte additives.<sup>6,48</sup> Bis-FSI was detected in some batteries in the range of 5–250,000  $\mu\text{g/battery}$ , with the highest mass detected in Battery E, where it was measured in higher quantity than PF<sub>6</sub><sup>−</sup> suggesting its use as the primary electrolyte in this case. Detection of low masses of BF<sub>4</sub><sup>−</sup> (13–13,100  $\mu\text{g}$ , Table S4) in some batteries suggested its employment as an electrolyte additive where PF<sub>6</sub><sup>−</sup> was the primary electrolyte. No inorganic fluorochemicals were detected in fluoropolymer binder formulations, suggesting that they are used in LiBs exclusively as electrolytes and electrolyte additives.

**Nontargeted Fluorochemical Analysis.** Twelve fluorinated compounds were detected and structurally annotated in battery extracts after high-resolution mass spectrometry (HRMS) analysis, including five of the targeted fluorochemicals mentioned above, included here for relative abundance reference (Figure 1 and Table S6). Of the 12 suspect fluorinated compounds annotated, PFMeS and perfluoromethane sulfinate (PFMeSi) were identified only in Battery B albeit at lower relative abundance compared to the structurally related bis-FMeSI. Detection of PFMeS in Battery B was confirmed by authentic standards, and its MS/MS spectrum is shown in Figure S2. Fragment 68.9955 (CF<sub>3</sub><sup>−</sup>) was observed in the MS/MS spectrum of PFMeSi (CF<sub>3</sub>SO<sub>2</sub><sup>−</sup>,  $m/z$  = 132.9571) after neutral loss of its polar headgroups. Structure annotation of PFMeSi was supported by the fragment at  $m/z$  82.9606 (SO<sub>2</sub>F<sup>−</sup>) (Figure S3). PFMeS has been disclosed as an electrolyte in LiBs since 1970,<sup>6</sup> but Battery B showed LiPF<sub>6</sub> and Li bis-FMeSI present as the

primary electrolyte salts. So, our detection and quantitation of PFMeS in Battery B suggest this compound may have been used as an electrolyte additive, or it is possible that its presence results from bis-FMeSI degradation or impurities in the bis-FMeSI salt. PFMeSi was detected at approximately the same relative abundance as PFMeS in this battery (Figure 1). To the best of our knowledge, PFMeSi has not been reported as a known LiB fluorinated component,<sup>6,8,15</sup> suggesting that this compound could be an impurity or transformation product of either bis-FMeSI or PFMeS used in battery formulation.

Thermal decomposition of alkylcarbonate-based solvents in LiB electrolytes during use and/or disposal has been shown to form RO radical species, which subsequently react with  $\text{PF}_6^-$  to form phosphofluoridates.<sup>49–51</sup> As described in the reaction scheme shown in Figure S4, thermal decomposition of  $\text{LiPF}_6$  in the LiB cell generates  $\text{PF}_5$  and  $\text{LiF}$ .<sup>52</sup> Reaction of  $\text{PF}_5$  with trace water or alcohol impurities in electrolytes generates difluorophosphoric acid (DFP,  $\text{PF}_2\text{O}_2^-$ ) which can then react with dimethyl carbonate or RO to form methylphosphofluoridate ( $\text{MePF}$ ,  $\text{CH}_3\text{FPO}_3^-$ ). Subsequent esterification of methylphosphofluoridate may form ethylphosphofluoridate ( $\text{EtPF}$ ,  $\text{C}_2\text{H}_5\text{FPO}_3^-$ ) and propylphosphofluoridate ( $\text{PrPF}$ ,  $\text{C}_3\text{H}_7\text{FPO}_3^-$ ).<sup>49,51,53,54</sup> This pathway (Figure S4) is supported by putative identification of difluorophosphoric acid and 3 homologues of phosphofluoridates, ranging from C1–C3, in the nontargeted analysis of methanolic battery extracts (Figure 1, compounds 6–9). To determine if alkylphosphofluoridates may have been formed from MeOH during the solvent extraction process, a second Soxhlet extraction of Battery D was repeated by using water as the solvent. We observed ethylphosphofluoridate ( $\text{C}_2\text{H}_5\text{FPO}_3^-$ ) and propylphosphofluoridate ( $\text{C}_3\text{H}_7\text{FPO}_3^-$ ) in the water extract, confirming that these compounds were not generated during methanol extraction but were likely formed as products of  $\text{LiPF}_6$  electrolyte salt reaction with electrolyte solvents in the batteries. Masses 78.9587 ( $\text{PO}_3^-$ ) and 98.9650 ( $\text{HPO}_3\text{F}^-$ ) are characteristic fragments of phosphofluoridates (Figures S5–S7). We extracted a mixture of used and newly purchased LiBs. Methyl- and ethylphosphofluoridate, thermal aging products of  $\text{LiPF}_6$ , were detected in most batteries, including newly purchased ones, that we extracted (Figure 1), suggesting that these compounds are common in LiBs. As a part of the production process, the electrolyte is added to the battery cell and then a charge and discharge cycle is applied to the cell. We hypothesize that phosphofluoridates were generated in new batteries during this stage of LiB production.<sup>55–57</sup> Kubot et al. (2022) reported generation of alkylphosphofluoridates during electrochemical aging of dialkylcarbonate-based electrolyte containing  $\text{LiPF}_6$ .<sup>51</sup> Their electrochemical aging test included 10 charge and discharge cycling in cut off voltage <4.8 V close to the voltage used in formation cycling.

Phenyl phosphorofluoridate ( $\text{PhPF}$ ,  $\text{C}_6\text{H}_5\text{PO}_3\text{F}^-$ ,  $m/z$  174.9958) was tentatively annotated in some of the tested LiBs. Fragments consistent with the structure of this compound were observed at  $m/z = 78.9587$  ( $\text{PO}_3^-$ ), 93.0340 ( $\text{C}_6\text{H}_5\text{O}^-$ ), and 98.9650 ( $\text{HPO}_3\text{F}^-$ , Figure S8). Methyl phenyl carbonate (MPC) and diphenyl carbonate (DPC) are used as electrolyte additives in LiBs to enhance cell storage properties.<sup>58,59</sup> MPC and DPC can be reduced on the graphite surface, and they generate benzene, phenyl, and carbon dioxide.<sup>58</sup> It is possible that phenyl phosphorofluoridate was generated in the battery as a result of the

difluorophosphoric acid reaction with MPC/DPC or their reduction products.

Methoxy-substituted bis(fluorosulfon)imide (MeO-bis-FSI,  $\text{CH}_3\text{S}_2\text{O}_5\text{NF}^-$ ,  $m/z$  191.9437) was tentatively annotated in some batteries. This compound is structurally related to bis-FSI, and it may be an additive or impurity in LiBs. It has been disclosed as a secondary nonaqueous electrolyte or additive to LiBs to improve low temperature characteristics and high temperature durability.<sup>60,61</sup> Structure annotation of this compound is supported by fragments at  $m/z$  77.9651 ( $\text{SO}_2\text{N}^-$ ), 96.9634 ( $\text{SO}_2\text{NF}^-$ ), and 176.9203 ( $\text{S}_2\text{O}_5\text{NF}^-$ , Figure S9). An elimination of  $\text{CH}_3$  followed by loss of an oxygen yield to formation of a fragment at  $m/z$  160.9254 ( $\text{S}_2\text{O}_2\text{NF}^-$ ), which is a part of the structure this compound has in common with bis-FSI.

Suspect screening and nontargeted analysis of PTFE fluoropolymer binders resulted in tentative annotation of 3 PFAS in extracts:  $\text{C}_{16}$ ,  $\text{C}_{17}$ , and  $\text{C}_{18}$  PFCAs (Table S7) with a confidence level of 2a based on the scale published by Charbonnet et al. (2022).<sup>62</sup> The presence of these long-chain PFCAs in the PTFE binder was consistent with elevated levels of targeted PFCAs for this material as reported above. These results are supported by previous reports of PFCA occurrence in PTFE formulations, which may be due to their use as fluorosurfactants in formulation or as byproducts of polymer heating or processing. Bis-FMeSI was the only fluorinated compound detected in PVDF, as discussed above. The nontargeted analysis result of Solvne 200/P400 and Solvne 250/P400 fluoropolymer binders (Figures S10–S18, Table S6) revealed 8 related oligomeric fluorinated compounds. Several PFAS were tentatively annotated for the first time in Solvne 200/P400 extracts, including perfluoropolyethers with  $\text{CF}_2\text{O}$  (perfluoromethoxy) repeat units, with branching evident from  $\text{CF}_3$  fragments (Figures S10–S13). Four chloroperfluoropolyether carboxylates (CIPFPECAs, Figure S14) were tentatively annotated in Solvne 250/P400 (Figures S15–S18). These compounds have been previously reported as Solvay products.<sup>63–67</sup> The general structure of CIPFPECA is shown in Figure S14, where  $n$  and  $m$  are the number of perfluoroalkyl and perfluoropropyl groups, respectively. These compounds were detected with precursor mass  $-\text{CF}_2\text{CO}_2$ , consistent with earlier findings.<sup>64</sup> CIPFPECAs were detected in soils collected close to the Solvay facility and in a water sample downstream of the facility in Italy.<sup>64</sup> Solvne 200/400 and 250/400 tested in this study were both Solvay products, and perfluoropolyethers alongside Nafion by product 1 and 4 might be used as aids in their emulsion polymerization.

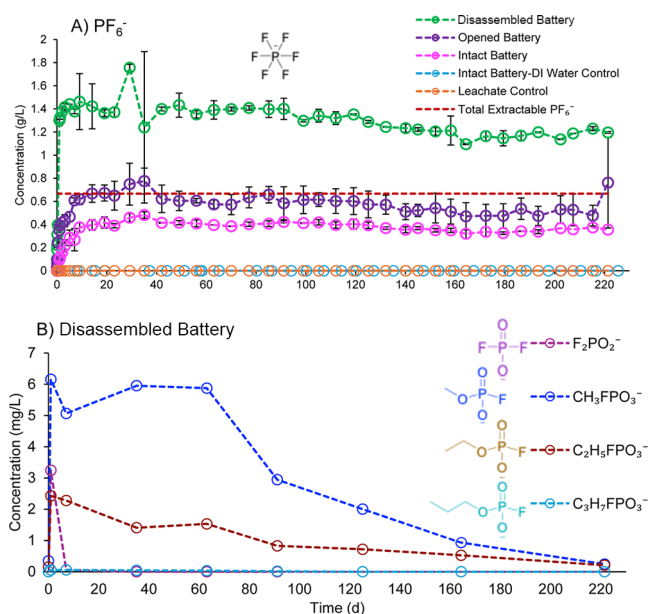
**Fluorochemicals in Landfill Leachates.** In total, 20 targeted PFAS including  $\text{C}_4$ – $\text{C}_{10}$  PFCAs,  $\text{C}_1$ ,  $\text{C}_4$ – $\text{C}_8$  PFSAs, and 8 PFAS precursors were detected in leachates, with total concentrations of 10,600 (leachate 2)–95,600 ng/L (leachate 8, Table S8, and Figure S23). Concentrations and composition of PFAS were consistent with previous studies of PFAS in U.S. landfill leachate.<sup>68,69</sup> PFMeS (4250–21,800 ng/L) and 5:3 FTCA (1570–35,900 ng/L) were the dominant PFAS, followed by PFHxA with concentrations of 1041–13,900 ng/L. PFAS can be released into MSW leachates as result of abiotic and biological activities in landfills.<sup>70</sup> The high measured concentration of 5:3 FTCA and  $\text{C}_4$ – $\text{C}_6$  PFCAs was likely due to biotransformation of 6:2 fluorotelomer-based precursors present in disposed waste.<sup>71,72</sup> Zhang et al. (2013) showed that 5:3 FTCA can be generated as a result of anaerobic biotransformation of 6:2 FTOH.<sup>73</sup> Lang et al.

(2016) showed that anaerobic biotransformation of carpet and clothing fabric in simulated landfills resulted in release of 5:3 FTCA and PFCAs.<sup>70</sup>

Bis-FMeSI was detected in leachates 2–11 at levels quantitatively similar to PFCAs, up to 2000 ng/L (Table S8). Notably, Bis-FMeSI, bis-FSI, and  $\text{PF}_6^-$  were not detected in leachate 1, although the total PFAS in this sample was similar to the other leachates measured. Also, MSW leachate 1 had the highest PFOS concentration of all measured leachates and was the only sample in which measurable quantities of N-EtFOSAA and N-MeFOSAA were detected. While MSW leachates 2–11 were collected from active or recently closed landfills, MSW leachate 1 was collected from a landfill that closed in the 1990s when PFOS-based coatings and products were still in widespread use ahead of phase-out in the early 2000s. LiBs containing Bis-FMeSI were commercially introduced after 1991,<sup>15</sup> and the widespread adoption of LiBs did not occur until the late 1990s or early 2000s.<sup>74</sup> The lack of bis-FMeSI, bis-FSI, and  $\text{PF}_6^-$  in MSW leachate 1 provides evidence that the occurrence of these compounds in the other MSW leachates analyzed was due to release from disposed LiBs in the respective MSW landfills. Of the abundant inorganic fluorochemicals detected in LiBs, Bis-FSI and  $\text{PF}_6^-$  were measured in leachates 2–11 (Table S8), where their concentrations were in the ranges 40–446 ng/L and 26–76  $\mu\text{g/L}$ , respectively. HRMS was applied to monitor MSW landfill leachates for other LiB-derived fluorochemicals identified above (including phosphofluoridates and other putative transformation products), but none of these were detected.

**Release of Fluorochemicals from Batteries under MSW Leaching Conditions.** Given the measurement of LiB-derived fluorochemicals in recent/current MSW landfill leachates from NC, we assessed the potential for release of these and other fluorochemicals from LiBs into landfill leachate under laboratory conditions. We used MSW leachate 1 (described above) in leaching experiments given the absence of a LiB-derived fluorochemical background in this material. Results of CBF measurements revealed higher release of fluorochemicals from disassembled batteries (407–520 mg/L of  $\text{F}^-$ ) relative to opened and intact batteries (161–316 mg/L), consistent with facile access of liquid to the inside of the disassembled batteries. However, it is not obvious that the fluorochemicals and other electrolyte components of a LiB should be “readily” available simply because of disassembly. The disassembled battery consists of a roll of electrode/separator sheets. The wetting steps in LiB manufacturing include injection of the electrolyte into the battery cell at temperature 30–50 °C.<sup>56</sup> This leads to the absorption of the electrolyte into the pores of the electrodes and the separator. Separator pores hold the electrolyte, allowing lithium ions to pass while preventing the electrodes from touching.<sup>75</sup> Disassembling the battery does not therefore lead to immediate release of all electrolyte from the roll but rather leaching of electrolyte associated with the electrode/separators. Additionally, more chemically bonded fluorine was measured in Battery S reactors vs Battery B reactors (Table S9), perhaps due to the higher  $\text{PF}_6^-$  mass in Battery S.

**$\text{PF}_6^-$  Release.** Reactor leachates were monitored for  $\text{PF}_6^-$  leaching from LiBs and were assessed for hydrolysis and other reactions that may have occurred for this precursor during the experiments.  $\text{PF}_6^-$  release was observed in all reactors, the fastest from the disassembled batteries (Figure 2A and S28).



**Figure 2.** Measured concentration of  $\text{PF}_6^-$  (A) and phosphofluoridates (B) in the battery S leaching batch experiment. Concentrations of phosphofluoridates were estimated using SQ approach with  $\text{PF}_6^-$  response factor. Measured concentration of  $\text{PF}_6^-$  is shown on the primary (left) y-axis and phosphofluoridate estimated concentrations are shown on the secondary (right) y-axis.

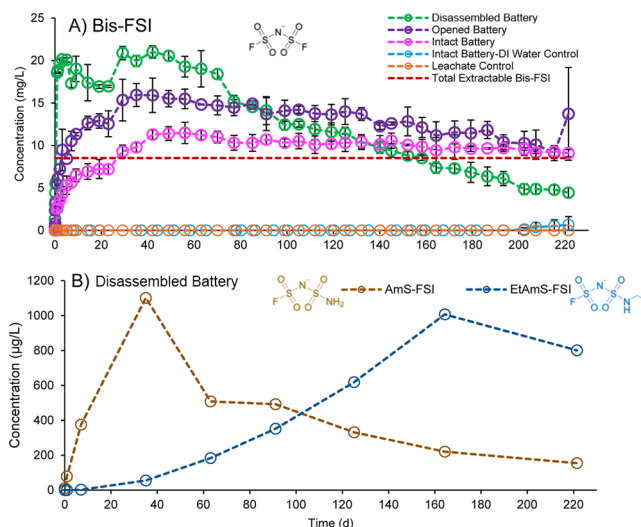
$\text{PF}_6^-$  was observed to be released from intact Battery S beginning at 23 h of the experiment; however, this compound was detected in the leachate of intact Battery B after day 19 as a result of battery case corrosion (Figure S24). Recovery of  $\text{PF}_6^-$  in the aqueous phase of Battery B and S reactors was in the range of 115–225% and 53–179%, respectively. High recovery of  $\text{PF}_6^-$  measured in reactors may have been due to the low extraction efficiency from batteries in the initial experiments (Section S1). Additionally, the predicted fluorine concentration using  $\text{PF}_6^-$  results were 60–120% higher than the leachate CBF concentrations (Section S2, Table S14) which could be because of incomplete combustion of inorganic fluorochemicals in CIC.  $\text{PF}_6^-$  was not detected in leachate controls (without batteries), and measured concentrations in DI water control were less than the method limit of quantification (10  $\mu\text{g/L}$ ).  $\text{LiPF}_6$  was the predominant electrolyte salt utilized in both Battery B and Battery S, resulting in it being the major fluorochemical measured in leachates as a consequence of leaching from LiBs.

Although generally stable in purely aqueous solution due to dipole-induced solvation effects,<sup>76</sup>  $\text{PF}_6^-$  appears to undergo hydrolysis with water or hydroxyl ion in landfill leachates to form  $\text{PF}_3\text{O}$  and  $\text{PF}_2\text{O}_2^-$ . Further reaction of these two inorganic fluorophosphidates with organic compounds in leachates can generate organic fluorophosphidates, such as methylphosphofluoridate, as discussed above. Reactor leachates were monitored for phosphofluoridates which could have either been released from LiBs or formed via reaction of  $\text{PF}_6^-$  with landfill leachate constituents. Results demonstrated release, generation, and decay of various phosphofluoridates in reactor leachates, consistent with observations in the nontargeted analyses of battery extracts described above. Difluorophosphoric acid ( $\text{PO}_2\text{F}_2\text{H}$ ), methylphosphofluoridate ( $\text{CH}_3\text{FPO}_3^-$ ), and ethylphosphofluoridate ( $\text{C}_2\text{H}_5\text{FPO}_3^-$ ) were detected in preleaching batteries and battery leachates,

indicating that these compounds were released from LiBs (Figures 2A, S29). However, the maximum intensity of ethylphosphofluoridate measured in Battery S reactors at day 7 was 12 times higher than the total extractable intensity of this compound in this LiB, suggesting that this compound may also have been generated through reaction with leachate. Additionally, propylphosphofluoridate ( $C_3H_8FPO_3$ ) was not detected in LiB S extracts (Figure 1) but was detected in battery leachates, indicating that it was likely generated in leachates (Figure 2B) as a result of  $PF_6^-$  hydrolysis and esterification or by methylation of other phosphofluoridates.

Results of fluorine analysis showed that the free fluoride concentration in leachates increased by up to 50 $\times$  in Battery B and 25 $\times$  in Battery S leaching experiments (Table S9).  $PF_6^-$  was the major fluorochemical detected in both batteries (Table S4) and was presumably the only major compound that could have degraded significantly during hydrolysis in the Battery B leaching experiments. This suggests that  $PF_6^-$  hydrolysis or degradation of its product  $PF_3O$  and  $PF_2O_2^-$  generated HF as free fluoride in leachate. The concentration of  $PF_6^-$  decreased by 280 mg/L in the disassembled Battery B reactors. Depending on the extent of hydrolysis and esterification, as indicated in Figure S4, this could result in the generation of 36–148 mg/L fluoride, which is consistent with the increased fluoride levels measured in the leachates (Table S9). As shown in Figures 2B and S33, phosphofluoridate intensities decreased in reactor leachates over time, and in some cases such as difluorophosphoric acid, they dropped below detection limits in leachates after day 35. Phosphofluoridates can react with organic carbonates in LiBs to generate mixed organophosphates.<sup>49</sup> Previous studies have reported that phosphofluoridates such as Sarin (isopropyl methylphosphofluoridate,  $C_4H_{10}FPO_2$ ) may hydrolyze in water.<sup>77</sup> Sarin hydrolysis results in P–F bond breakage and the generation of isopropyl methylphosphonic acid. Sarin hydrolysis rate increases in alkaline pH.<sup>77</sup> This suggests that LiB-derived phosphofluoridates may react with nucleophiles such as organic carbonate solvents, hydroxide, or water in LiB leachate reactors. Fast degradation of LiB-derived phosphofluoridates might be because of reactor alkaline pHs. Phosphofluoridates are known to be highly toxic due to the extreme reactivity of the P–F bond in these compounds.<sup>78–80</sup> This P–F bond can react irreversibly with the catalytic active site of the acetylcholinesterase enzyme and results in permanent stimulation of the neuromuscular junctions leading to paralysis or death.<sup>51,81</sup> This is the mechanism by which many chemical nerve agents (e.g., Sarin) and organophosphate pesticides (e.g., chlorpyrifos) act.

**Bis-FSI Release.** Bis-FSI leaching was observed in Battery S reactors starting from the first day of the experiment (Figure 3A). This compound was released from both opened and intact batteries and reached a maximum concentration of 16 and 11 mg/L, respectively, after 42 days. Fluorochemical release from intact Battery S into leachate was observed after 23 h, while bis-FSI showed slower release from the intact battery into DI water (observed at day 200). A comparison of Bis-FSI release from the intact battery into leachate and DI water suggests that microbial and/or chemical reactions within the leachate accelerated the corrosion of the battery case, thereby enhancing release of the battery electrolyte. Over the course of the experiment, the initial release of bis-FSI was observed followed by a decrease in concentration within reactors containing disassembled batteries. The observed decrease in bis-FSI concentration may be due to hydrolysis



**Figure 3.** Measured aqueous concentration of bis-FSI (A, mg/L), AmS-FSI and EtAmS-FSI (B,  $\mu$ g/L) in Battery S leaching experiments. Concentrations of AmS-FSI and EtAmS-FSI were estimated using a semiquantitative (SQ) approach and the bis-FSI response factor. The measured concentration of bis-FSI is shown on the primary (left) y-axis, and AmS-FSI and EtAmS-FSI estimated concentrations are shown on the secondary (right) y-axis.

in the leachate. Observation of increased dissolved fluoride concentrations in reactors containing batteries vs leachate controls (Table S9) supports the hypothesis that fluorochemicals may have degraded during the experiment to release fluoride as a transformation product. Bis-FSI and  $PF_6^-$  were both major electrolyte components of battery S (Figure 1, Table S4), and their degradation may have generated HF, contributing to increased total fluoride.<sup>51</sup> Observed  $PF_6^-$  and bis-FSI concentration decreases in Battery S reactors could have resulted in 29–111 mg/L increase in dissolved fluoride in leachates, depending on how many fluoride ions were produced by transformation of  $PF_6^-$  (1–4, Figure S4) and bis-FSI (1 or 2). The measured dissolved fluoride concentration in the reactors fell within this specified range (Table S9).

**Bis-FSI Transformation.** Bis-FSI is structurally related to the class of sulfonyl halides, which are highly reactive to nucleophilic residues. A widely known example is the use of phenyl-methylsulfonyl fluoride (PMSF) as a protease inhibitor, acting via covalent reaction with serine residues in protease active sites.<sup>1,2</sup> PMSF ( $F-SO_2CH_2C_6H_5$ ) like bis-FSI contains fluorinated sulfonyl groups ( $F-SO_2$ ). PMSF reacts with the nucleophilic amino acid serine in enzymes (Enzyme(active)-Ser-O-H), breaking the S–F bond to generate the Enzyme-Ser-O-SO<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> complex.<sup>82</sup> The mechanism is consistent with our proposed reaction of bis-FSI with nucleophiles such as ammonia ( $NH_3$ ) and ethylamine in landfill leachate. Zhou et al. (2023) investigated bis-FSI hydrolysis under the influence of temperature, acidity, basicity and water content conditions.<sup>83</sup> They reported that hydrolysis of this compound occurred under neutral and acidic conditions at the S–N to form  $FSO_2NH_2$  and  $FSO_3^-$ ; however, under alkaline condition, hydrolysis occurred at the S–F bond to produce  $FSO_2NSO_3^{2-}$  and  $SO_3NHSO_3^{2-}$ .

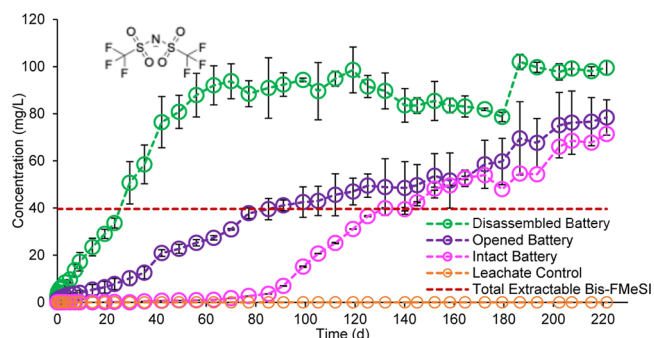
Nontargeted analysis was employed to identify the probable product of bis-FSI degradation in Battery S reactors. The pH of Battery S reactors was above 8.5 (Table S13); therefore,

Battery S reactor HRMS results were examined first for  $\text{FSO}_2\text{NSO}_3^{2-}$  and  $\text{SO}_3\text{NHSO}_3^{2-}$ , which were not detected. Examination of spectra from reactor leachates revealed two candidate precursors:  $m/z$  204.9758 and 176.9445, both of which had MS/MS spectra characteristic of bis-FSI based on fragments. MS/MS spectra and proposed structures of masses 204.9758 ( $\text{C}_2\text{H}_6\text{FS}_2\text{O}_4\text{N}_2^-$ ) and 176.9445 ( $\text{H}_2\text{FS}_2\text{O}_4\text{N}_2^-$ ) are shown in Figures S19 and S20, respectively. The amino sulfonyl fluorosulfonamides ( $m/z$  176.94450 and 204.9758) have been disclosed as electrolyte components, synthetic intermediates, polymer modifiers, and antistatic agents in batteries.<sup>84</sup> These molecules could also be generated during the synthesis of bis-FSI.<sup>85</sup> However, both  $m/z$  values of 204.9758 and 176.9445 were not detected in Battery S extracts prior to the leaching experiment. Detection of two amino sulfonyl fluorosulfonamides in leachates of Battery S could be explained by the reaction of bis-FSI with residual nucleophiles such as ammonia and ethylamine in the landfill leachate at alkaline pHs. Ammonia is a nucleophilic amine, and we measured 890 mg/L ammonia ( $\text{NH}_3$ ) in leachate 1 used in the LiB leaching experiment (Table S3). Ethylamine can be formed during the natural, microbial breakdown of organic materials in a landfill, for example, biodegradation of rotten fish and poultry waste in landfill can produce ethylamine.<sup>86</sup> Figure 3B shows the measured aqueous concentration of putatively identified amino sulfonyl fluorosulfonamide (AmS-FSI, 176.9445,  $\text{H}_2\text{FS}_2\text{O}_4\text{N}_2^-$ ) and ethyl amino sulfonyl fluorosulfonamide (EtAmS-FSI, 204.9758,  $\text{C}_2\text{H}_6\text{FS}_2\text{O}_4\text{N}_2^-$ ) in leachates of Battery S. AmS-FSI exhibited rapid generation and then slow decay, while EtAmS-FSI intensity slowly increased over time. The decrease in the AmS-FSI concentration indicates that it may be a metastable intermediate in the bis-FSI transformation pathway.

Given the observed decay of bis-FSI in disassembled Battery S reactors and appearance of potential transformation products, we evaluated the potential abiotic transformation of bis-FSI in reactors containing ammonium hydroxide ( $\text{NH}_4\text{OH}$ ), leachate 1, and the model nucleophiles ethylamine and ethanolamine. Results showed a decrease (11–61%) in bis-FSI concentration in all reactors, while the concentration remained unchanged in the DI water control. HRMS analysis of the samples revealed the formation of AmS-FSI in reactors containing  $\text{NH}_4\text{OH}$  (Figure S30) and leachate 1 (Figure S31). These findings were consistent with observations in Battery S reactors (Figure 3B) and demonstrated bis-FSI undergoes nucleophilic attack by ammonium ion under alkaline pH at the S–F bond to generate AmS-FSI. Bis-FSI reacted with ethylamine under basic conditions to produce EtAmS-FSI, consistent with observations in battery leachates (suggesting reaction with residual ethylamine in those reactors). Further reaction of EtAmS-FSI generated bis-ethyl amino sulfonamide (bis-EtAmSI,  $m/z$  230.0273,  $\text{C}_4\text{H}_{12}\text{N}_3\text{S}_2\text{O}_4^-$ , Figure S21). The concentration of bis-FSI in the ethylamine reactors decreased by 61% (Figure S32). EtAmS-FSI and bis-EtAmSI were the most abundant compounds after bis-FSI in ethylamine reactors based on MS peak area; therefore, they were considered to be the major products of bis-FSI degradation under the conditions applied. However, the sum of their estimated concentrations accounted for only 30% of the decrease in bis-FSI concentration, suggesting either formation of uncharacterized products or inaccuracy in the semiquantitative approaches used. Reaction of bis-FSI in reactors containing ethanolamine produced aminoethyl sulfonate fluorosulfona-

mides (AmEtS-FSI,  $\text{C}_2\text{H}_6\text{FS}_2\text{O}_5\text{N}_2$ ). Figure S22 presents the MS/MS spectra and structural annotation of AmEtS-FSI, and Figure S33 shows the changes in bis-FSI and AmEtS-FSI concentrations in those reactors. The formation of AmEtS-FSI in reaction of bis-FSI with ethanolamine raises concerns that bis-FSI, like PMSF, might be reactive with nucleophilic residues in biomolecules, suggesting a potential mode of toxicity.

**PFAS Release.** Bis-FMeSI release was observed in the Battery B reactors. Bis-FMeSI was released from disassembled and opened batteries on the first day and stabilized to a steady state concentration after 77–90 days. In contrast, this compound was detected in the aqueous phase of the intact battery reactor only after day 19 and reached a maximum dissolved concentration at day 164 (Figure 4). Corrosion of



**Figure 4.** Measured aqueous concentration of bis-FMeSI (mg/L) in battery B leaching batch experiments.

the battery cases in the leachate matrix (Figure S24) evidently caused cracks that exacerbated the fluorochemical release to leachate. Over the 220 day experiment, 180% to 251% of the total extractable bis-FMeSI mass measured in LiBs was released into the reactor leachate from Battery B, indicating that chemical extraction may not have been exhaustive (Table S10, Section S2). At the conclusion of the experiment, 0.85–1.90 mg of bis-FMeSI (Table S11) was recovered from the leached batteries via additional extraction. The total mass balance of bis-FMeSI in the reactors thus ranged from 184% to 256% relative to the extractable mass from the Battery B. These results suggest that occurrence of LiBs in MSW landfills can lead to the release of bis-FMeSI into leachate, where it may persist due to its demonstrated recalcitrance to biotic/abiotic degradation.<sup>11</sup>

PFMeS and FMeSA were released to the aqueous phase of Battery B leaching reactors with the same trend as bis-FMeSI (Figures S25 and S26) with recovery of 374–457% and 332–633% in leachate, respectively. Leachate controls contained  $-0.02$  mg/L PFMeS, similar to levels measured in leachate 1 prior to the experiment (Table S8). FMeSA and PFMeS were found in soil, water, and recycled LiB powder at a Chinese recycling facility, indicating LiBs may be a source of short-chain PFAS.<sup>3</sup> Bis-FMeSI was not detected, possibly due to electrolyte removal before crushing or its absence in the batteries. Though Qi et al. (2024) suggested biotransformation to FMeSA, prior studies show bis-FMeSI resists oxidation and hydrolysis,<sup>11,87</sup> implying it is also likely resistant to biotransformation. Results of nontargeted analysis showed release of PFMeSi from Battery B in all reactors (Figure S27). These results showed that LiBs can be a source of ultrashort

chain PFAS in leachate and consequently wastewater and surface water.

No other targeted PFAS and inorganic fluorochemical release was observed in battery leachates. Leachate 1 contained PFAS (Figure S23) prior to the battery leaching experiments, and those concentrations did not increase over the course of the leaching experiment (Figures S34 and S35). Concentrations of MeFOSAA and PFOS decreased over time in disassembled battery reactors (Figures S34J–K and S35J–K) possibly due to sorption of these compounds on electrode materials such as anode graphite. LiBs were retained after the leaching experiment, extracted, and analyzed for fluorochemicals. The results indicated an increase in the concentration of targeted PFAS  $\geq C_4$  (Table S11), suggesting the possibility of PFAS sorption from the leachate on LiB electrodes. PFAS  $\geq C_4$  was not detected in LiB B and S prior to the leaching experiment.

**Metal Release from Batteries.** Exposure of LiBs to MSW leachate resulted in release of soluble lithium (Li) at levels of 30 to 800  $\mu\text{g/L}$  and transition metals cobalt (Co), nickel (Ni), and copper (Cu) at levels ranging from 30 to 200,000  $\mu\text{g/L}$  (Table S12). Lithium is used in LiB electrolytes and cathodes, and transition metals are used in active materials of cathodes.<sup>6,88</sup> Similar to fluorochemicals, higher Li, Co, and Cu were released into leachate from disassembled batteries relative to leachate exposed to opened and intact batteries. However, the maximum Ni released (8500  $\mu\text{g/L}$ ) was observed in leachates of intact batteries. This result could be due to use of Ni-coated steel casings for 18,650-type cells,<sup>89</sup> such as Battery B and S. In the leachates of Battery B and Battery S, the molar concentration of Li correlated linearly with  $\text{PF}_6^-$  concentrations, as well as with levels of bis-FMeSI (Battery B) and with bis-FSI (Battery S) (Figures S36 and S37). Such correlations suggest that these compounds were used as electrolytes in LiBs and not released from fluoropolymer binders.

## ENVIRONMENTAL IMPLICATIONS

PFAS and inorganic fluorochemicals, including bis-FASIs and  $\text{PF}_6^-$ , were detected at significant levels in LiBs and their fluoropolymer binders. These substances are introduced primarily as constituents of electrolytes, binders, and separators either incidentally during manufacture or to enhance the performance and durability of batteries.  $\text{LiPF}_6$  was the predominant electrolyte salt; however, the quantification of bis-FMeSI and bis-FSI at milligram levels in several batteries indicates their use as additional electrolytes or additives. The detection of other fluorochemicals, such as phosphofluoridates derived from  $\text{PF}_6^-$  hydrolysis, suggests that fluorochemical transformation may occur during battery use, potentially leading to the release of toxic byproducts.

Our leaching experiments implemented under conditions relevant to solid waste disposal further indicate that LiBs may serve as a source of fluorochemicals to the environment via landfill leachate. Bis-FMeSI, PFMeS, and FMeSA were major PFAS released into leachates from LiBs, at concentrations above 0.2 mg/L. Additionally, leaching of  $\text{PF}_6^-$  and bis-FSI from LiBs and detection of their putative degradation products, fluorophosphates and amino sulfonyl fluorosulfanomides, in reactor leachates indicates that ongoing transformation processes may occur in the anaerobic environment of a landfill, generating potentially toxic byproducts. High water solubility and resistance to oxidative degradation increase

concern over LiB-derived fluorochemical occurrence in the environment. Identification of LiB fluorochemicals, particularly bis-FMeSI, in landfill leachates supports the hypothesis that LiBs and associated fluoropolymers can act as a fluorochemical contamination source and may contribute to human and environmental exposure to these chemicals after disposal, as these compounds are not attenuated during typical leachate treatment and are likely released to surface water.

The results provide evidence of environmental risks associated with the use and disposal of fluorochemicals in LiBs. Mitigating these impacts requires that LiBs be separated for recycling prior to disposal. While not studied here, the release of PFAS and inorganic fluorochemicals during LiB recycling requires scrutiny. Future efforts should focus on additional laboratory studies of LiB fluorochemical release during recycling operations and also under emergency/accident release scenarios.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.5c10116>.

LiB and fluoropolymer binder extraction, analytical and data processing methods, fluorochemical nontargeted results, LiB leaching experiment results, and bis-FSI transformation results (PDF).

Detailed tabulation of standards, LiB and fluoropolymer binders, fluorochemical target and nontarget results, LiB leaching experiment fluorine, metals, and pH results (XLS) (XLSX).

## AUTHOR INFORMATION

### Corresponding Author

P. Lee Ferguson – Department of Civil and Environmental Engineering, Duke University, Durham, North Carolina 27708, United States; Nicholas School of the Environment, Duke University, Durham, North Carolina 27708, United States; [orcid.org/0000-0002-8367-7521](https://orcid.org/0000-0002-8367-7521); Email: [lee.ferguson@duke.edu](mailto:lee.ferguson@duke.edu)

### Authors

Marzieh Shojaei – Department of Civil and Environmental Engineering, Duke University, Durham, North Carolina 27708, United States

Jennifer L. Guelfo – Department of Civil, Environmental, & Construction Engineering, Texas Tech University, Lubbock, Texas 79409, United States; [orcid.org/0000-0003-4461-228X](https://orcid.org/0000-0003-4461-228X)

Morton A. Barlaz – Department of Civil, Construction, and Environmental Engineering, North Carolina State University, Raleigh, North Carolina 27695, United States; [orcid.org/0000-0001-8028-3917](https://orcid.org/0000-0001-8028-3917)

Grisel Cogollo-Carcamo – Department of Civil, Environmental, & Construction Engineering, Texas Tech University, Lubbock, Texas 79409, United States

Nelson A. Rivera, Jr. – Department of Civil and Environmental Engineering, Duke University, Durham, North Carolina 27708, United States

Heileen Hsu-Kim – Department of Civil and Environmental Engineering, Duke University, Durham, North Carolina 27708, United States; [orcid.org/0000-0003-0675-4308](https://orcid.org/0000-0003-0675-4308)

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acs.est.5c10116>

## Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work was supported by funding from NIEHS (5P42ES010356) and by the North Carolina Collaboratory through an appropriation from the North Carolina General Assembly.

## REFERENCES

- (1) Mossali, E.; Picone, N.; Gentilini, L.; Rodríguez, O.; Pérez, J. M.; Colledani, M. Lithium-Ion Batteries towards Circular Economy: A Literature Review of Opportunities and Issues of Recycling Treatments. *J. Environ. Manage.* **2020**, *264*, 110500.
- (2) Baqar, M.; Zhao, M.; Saleem, R.; Cheng, Z.; Fang, B.; Dong, X.; Chen, H.; Yao, Y.; Sun, H. Identification of Emerging Per- and Polyfluoroalkyl Substances (PFAS) in E-Waste Recycling Practices and New Precursors for Trifluoroacetic Acid. *Environ. Sci. Technol.* **2024**, *58* (36), 16153–16163.
- (3) Qi, Z.; Cao, Y.; Li, D.; Wu, C.; Wu, K.; Song, Y.; Huang, Z.; Luan, H.; Meng, X.; Yang, Z.; Cai, Z. Nontarget Analysis of Legacy and Emerging PFAS in a Lithium-Ion Power Battery Recycling Park and Their Possible Toxicity Measured Using High-Throughput Phenotype Screening. *Environ. Sci. Technol.* **2024**, *58* (32), 14530–14540.
- (4) Pinegar, H.; Smith, Y. R. Recycling of End-of-Life Lithium Ion Batteries, Part I: Commercial Processes. *J. Sustain. Metall.* **2019**, *5* (3), 402–416.
- (5) Fan, X.; Song, C.; Lu, X.; Shi, Y.; Yang, S.; Zheng, F.; Huang, Y.; Liu, K.; Wang, H.; Li, Q. Separation and Recovery of Valuable Metals from Spent Lithium-Ion Batteries via Concentrated Sulfuric Acid Leaching and Regeneration of LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>. *J. Alloys Compd.* **2021**, *863*, 158775.
- (6) Rensmo, A.; Savvidou, E. K.; Cousins, I. T.; Hu, X.; Schellenberger, S.; Benskin, J. P. Lithium-Ion Battery Recycling: A Source of per- and Polyfluoroalkyl Substances (PFAS) to the Environment? *Environ. Sci. Process. Impacts* **2023**, *25* (6), 1015–1030.
- (7) Mrozik, W.; Rajaeifar, M. A.; Heidrich, O.; Christensen, P. Environmental Impacts, Pollution Sources and Pathways of Spent Lithium-Ion Batteries. *Energy Environ. Sci.* **2021**, *14* (12), 6099–6121.
- (8) Gao, W.; Yu, L.; Lin, H.; Meng, L.; Yu, S.; Li, J.; Lin, Y.; Zheng, Y. A Review on the Impacts of Fluorinated Organic Additives in Lithium Battery Industry—an Emerging Source of per- and Polyfluoroalkyl Substances. *Crit. Rev. Environ. Sci. Technol.* **2024**, *54* (17), 1285–1305.
- (9) List, O. G. P. Toward a New Comprehensive Global Database of Per- and Polyfluoroalkyl Substances (PFASs). **2018**.
- (10) Glüge, J.; Scheringer, M.; Cousins, I. T.; DeWitt, J. C.; Goldenman, G.; Herzke, D.; Lohmann, R.; Ng, C. A.; Trier, X.; Wang, Z. An Overview of the Uses of Per- and Polyfluoroalkyl Substances (PFAS). *Environ. Sci. Process. Impacts* **2020**, *22* (12), 2345–2373.
- (11) Guelfo, J. L.; Ferguson, P. L.; Beck, J.; Chernick, M.; Doria-Manzur, A.; Faught, P. W.; Flug, T.; Gray, E. P.; Jayasundara, N.; Knappe, D. R.; et al. Lithium-Ion Battery Components Are at the Nexus of Sustainable Energy and Environmental Release of per- and Polyfluoroalkyl Substances. *Nat. Commun.* **2024**, *15* (1), 5548.
- (12) Shamsuri, A. A.; Daik, R.; Md. Jamil, S. N. A. A Succinct Review on the PVDF/Imidazolium-Based Ionic Liquid Blends and Composites: Preparations, Properties, and Applications. *Processes* **2021**, *9* (5), 761.
- (13) McDonough, C. A.; Choyke, S.; Ferguson, P. L.; DeWitt, J. C.; Higgins, C. P. Bioaccumulation of Novel Per- and Polyfluoroalkyl Substances in Mice Dosed with an Aqueous Film-Forming Foam. *Environ. Sci. Technol.* **2020**, *54* (9), 5700–5709.
- (14) Duan, J.; Tang, X.; Dai, H.; Yang, Y.; Wu, W.; Wei, X.; Huang, Y. Building Safe Lithium-Ion Batteries for Electric Vehicles: A Review. *Electrochem. Energy Rev.* **2020**, *3* (1), 1–42.
- (15) Jow, T. R.; Xu, K.; Borodin, O.; Ue, M. *Electrolytes for Lithium and Lithium-Ion Batteries*; Springer, 2014; Vol. 58.
- (16) Garg, S.; Kumar, P.; Mishra, V.; Guijt, R.; Singh, P.; Dumée, L. F.; Sharma, R. S. A Review on the Sources, Occurrence and Health Risks of per-/Poly-Fluoroalkyl Substances (PFAS) Arising from the Manufacture and Disposal of Electric and Electronic Products. *J. Water Process Eng.* **2020**, *38*, 101683.
- (17) Baum, Z. J.; Bird, R. E.; Yu, X.; Ma, J. Lithium-Ion Battery Recycling—Overview of Techniques and Trends. *ACS Energy Lett.* **2022**, *7* (2), 712–719.
- (18) Yang, B.; Sun, L.; Peng, Z.; Zhang, Q.; Lin, M.; Peng, Z.; Zheng, L. Developmental Toxicity and Apoptosis in Zebrafish: The Impact of Lithium Hexafluorophosphate (LiPF<sub>6</sub>) from Lithium-Ion Battery Electrolytes. *Int. J. Mol. Sci.* **2024**, *25* (17), 9307.
- (19) Neuwald, I.; Muschket, M.; Zahn, D.; Berger, U.; Seiwert, B.; Meier, T.; Kuckelkorn, J.; Strobel, C.; Knepper, T. P.; Reemtsma, T. Filling the Knowledge Gap: A Suspect Screening Study for 1310 Potentially Persistent and Mobile Chemicals with SFC- and HILIC-HRMS in Two German River Systems. *Water Res.* **2021**, *204*, 117645.
- (20) Muschket, M.; Neuwald, I. J.; Zahn, D.; Seelig, A. H.; Kuckelkorn, J.; Knepper, T. P.; Reemtsma, T. Fate of Persistent and Mobile Chemicals in the Water Cycle: From Municipal Wastewater Discharges to River Bank Filtrate. *Water Res.* **2024**, *266*, 122436.
- (21) Jiao, E.; Larsson, P.; Wang, Q.; Zhu, Z.; Yin, D.; Kärrman, A.; Van Hees, P.; Karlsson, P.; Qiu, Y.; Yeung, L. W. Y. Further Insight into Extractable (Organo)Fluorine Mass Balance Analysis of Tap Water from Shanghai, China. *Environ. Sci. Technol.* **2023**, *57* (38), 14330–14339.
- (22) He, Z.; Plassmann, M.; Cousins, I. T.; Benskin, J. P. A Novel Fluorine Mass Balance Method for Improved Characterization and Quantification of Extractable (Organo)Fluorine in Drinking Water. *Environ. Sci. Technol. Lett.* **2025**, *12* (1), 73–78.
- (23) Huset, C. A.; Barlaz, M. A.; Barofsky, D. F.; Field, J. A. Quantitative Determination of Fluorochemicals in Municipal Landfill Leachates. *Chemosphere* **2011**, *82* (10), 1380–1386.
- (24) Allred, B. M.; Lang, J. R.; Barlaz, M. A.; Field, J. A. Orthogonal Zirconium Diol/C18 Liquid Chromatography–Tandem Mass Spectrometry Analysis of Poly and Perfluoroalkyl Substances in Landfill Leachate. *J. Chromatogr. A* **2014**, *1359*, 202–211.
- (25) Schaefer, C. E.; Hooper, J. L.; Strom, L. E.; Abusallout, I.; Dickenson, E. R. V.; Thompson, K. A.; Mohan, G. R.; Drennan, D.; Wu, K.; Guelfo, J. L. Occurrence of Quantifiable and Semi-Quantifiable Poly- and Perfluoroalkyl Substances in United States Wastewater Treatment Plants. *Water Res.* **2023**, *233*, 119724.
- (26) Collins, A.; Krause, M. J.; Bessler, S. M.; Brougham, A.; McKnight, T.; Strock, T.; Ateia, M. City-Scale Impacts of PFAS from Normal and Elevated Temperature Landfill Leachates on Wastewater Treatment Plant Influent. *J. Hazard. Mater.* **2024**, *480*, 136270.
- (27) Wu, L.-J.; Zhang, Z.-Y.; Zhang, C.-C.; Zhang, F.-S. An Innovative and Value-Added Approach to Recycle Hexafluorophosphate from Waste Lithium-Ion Batteries: New Perspective of Electrolyte Disposal and Recovery. *J. Environ. Chem. Eng.* **2024**, *12* (3), 112808.
- (28) Wu, L.-J.; Zhang, Z.-Y.; Zhang, F.-S. A Green and Innovative Approach to Separate Hexafluorophosphate from Wastewater. *J. Ind. Eng. Chem.* **2025**, *142*, 487–498.
- (29) Hu, X. C.; Andrews, D. Q.; Lindstrom, A. B.; Bruton, T. A.; Schaider, L. A.; Grandjean, P.; Lohmann, R.; Carignan, C. C.; Blum, A.; Balan, S. A.; Higgins, C. P.; Sunderland, E. M. Detection of Poly- and Perfluoroalkyl Substances (PFASs) in U.S. Drinking Water Linked to Industrial Sites, Military Fire Training Areas, and Wastewater Treatment Plants. *Environ. Sci. Technol. Lett.* **2016**, *3* (10), 344–350.
- (30) Houtz, E. F.; Sutton, R.; Park, J.-S.; Sedlak, M. Poly- and Perfluoroalkyl Substances in Wastewater: Significance of Unknown

Precursors, Manufacturing Shifts, and Likely AFFF Impacts. *Water Res.* **2016**, *95*, 142–149.

(31) Renou, S.; Givaudan, J. G.; Poulain, S.; Dirassouyan, F.; Moulin, P. Landfill Leachate Treatment: Review and Opportunity. *J. Hazard. Mater.* **2008**, *150* (3), 468–493.

(32) Bove, D.; Merello, S.; Frumento, D.; Arni, S. A.; Aliakbarian, B.; Converti, A. A Critical Review of Biological Processes and Technologies for Landfill Leachate Treatment. *Chem. Eng. Technol.* **2015**, *38* (12), 2115–2126.

(33) Tisler, S.; Zweigle, J.; Gotil, M. K.; Finckh, S.; Brack, W.; Braxmaier, E.-M.; Meyer, C.; Hollender, J.; Kosjek, T.; Schymanski, E. L.; Larsson, P.; Kärrman, A.; Selin, E.; Elabbadi, D.; Elliss, H.; Kasprzyk-Hordern, B.; Boogaerts, T.; Covaci, A.; Oberacher, H.; Flores Quintana, H.; Lai, F. Y.; Ahrens, L.; Assoumani, A.; Béen, F.; Christensen, J. H. Nontarget and Suspect Screening of Fluorinated Ionic Liquids and PFAS in European Wastewaters Using Supercritical Fluid Chromatography. *Environ. Sci. Technol.* **2025**, *59*, 21300–21311.

(34) Kayla Kilgo, M.; Anctil, A.; Kennedy, M. S.; Powell, B. A. Metal Leaching from Lithium-Ion and Nickel-Metal Hydride Batteries and Photovoltaic Modules in Simulated Landfill Leachates and Municipal Solid Waste Materials. *Chem. Eng. J.* **2022**, *431*, 133825.

(35) Ahrens, L.; Bundschuh, M. Fate and Effects of Poly- and Perfluoroalkyl Substances in the Aquatic Environment: A Review. *Environ. Toxicol. Chem.* **2014**, *33* (9), 1921–1929.

(36) Khan, B.; Burgess, R. M.; Cantwell, M. G. Occurrence and Bioaccumulation Patterns of Per- and Polyfluoroalkyl Substances (PFAS) in the Marine Environment. *ACS EST Water* **2023**, *3* (5), 1243–1259.

(37) Cho, C.-W.; Pham, T. P. T.; Zhao, Y.; Stolte, S.; Yun, Y.-S. Review of the Toxic Effects of Ionic Liquids. *Sci. Total Environ.* **2021**, *786*, 147309.

(38) Ye, Y.; Titaley, I. A.; Kim-Fu, M. L.; Moll, A. R.; Field, J. A.; Barlaz, M. A. Release of Volatile Per- and Polyfluoroalkyl Substances from Plant Fiber-Based Food Packaging and Municipal Solid Waste to Gas under Simulated Landfill Conditions. *Environ. Sci. Technol.* **2024**, *58* (48), 21295–21304.

(39) Takizawa, M.; Moriyoshi, H.; Ikeda, M. “Lithium Ion Secondary Batteries with Improved Electrolytes. JP 09106834, April 22, 1997.

(40) Terashima, H.; Fukushima, G. Nonaqueous Electrolyte Batteries. JP 2001236990.

(41) Oh, B.; Amine, K.; Hyung, Y.; Vissers, D. R.; Tsukamoto, H. Nonaqueous and Nonvolatile Liquid Type Polymer Electrolyte for Battery. U.S. Patent 20,030,180,625 A1, September 25, 2003.

(42) Puts, G. J.; Crouse, P.; Ameduri, B. M. Polytetrafluoroethylene: Synthesis and Characterization of the Original Extreme Polymer. *Chem. Rev.* **2019**, *119* (3), 1763–1805.

(43) Meng, L.; Song, B.; Lu, Y.; Lv, K.; Gao, W.; Wang, Y.; Jiang, G. The Occurrence of Per- and Polyfluoroalkyl Substances (PFASs) in Fluoropolymer Raw Materials and Products Made in China. *J. Environ. Sci.* **2021**, *107*, 77–86.

(44) Joudan, S.; Gauthier, J.; Mabury, S. A.; Young, C. J. Aqueous Leaching of Ultrashort-Chain PFAS from (Fluoro)Polymers: Targeted and Nontargeted Analysis. *Environ. Sci. Technol. Lett.* **2024**, *11* (3), 237–242.

(45) Meng, L.; Wan, R.; Hu, H.; Wu, D.; Yang, Z.; He, J.; Lu, G.; Yang, J.; Yang, Y.; Huang, Q. Leaching Behavior and Risk Assessment of Per- and Polyfluoroalkyl Substances in Typical Fluoropolymers. *ACS EST Water* **2024**, *4* (6), 2352–2360.

(46) Song, X.; Vestergren, R.; Shi, Y.; Huang, J.; Cai, Y. Emissions, Transport, and Fate of Emerging Per- and Polyfluoroalkyl Substances from One of the Major Fluoropolymer Manufacturing Facilities in China. *Environ. Sci. Technol.* **2018**, *52* (17), 9694–9703.

(47) Xu, G.; Shanguan, X.; Dong, S.; Zhou, X.; Cui, G. Formulation of Blended-Lithium-Salt Electrolytes for Lithium Batteries. *Angew. Chem., Int. Ed.* **2020**, *59* (9), 3400–3415.

(48) Ahmed, F.; Choi, I.; Ryu, T.; Yoon, S.; Rahman, M. M.; Zhang, W.; Jiang, H.; Kim, W. Highly Conductive Divalent Fluorosulfonyl

Imide Based Electrolytes Improving Li-Ion Battery Performance: Additive Potentiating Electrolytes Action. *J. Power Sources* **2020**, *455*, 227980.

(49) Vortmann, B.; Nowak, S.; Engelhard, C. Rapid Characterization of Lithium Ion Battery Electrolytes and Thermal Aging Products by Low-Temperature Plasma Ambient Ionization High-Resolution Mass Spectrometry. *Anal. Chem.* **2013**, *85* (6), 3433–3438.

(50) Guéguen, A.; Streich, D.; He, M.; Mendez, M.; Chesneau, F. F.; Novák, P.; Berg, E. J. Decomposition of LiPF<sub>6</sub> in High Energy Lithium-Ion Batteries Studied with Online Electrochemical Mass Spectrometry. *J. Electrochem. Soc.* **2016**, *163* (6), A1095–A1100.

(51) Kubot, M.; Von Holtum, B.; Winter, M.; Wiemers-Meyer, S.; Nowak, S. Organofluorophosphates as Oxidative Degradation Products in High-Voltage Lithium Ion Batteries with NMC or LNMO Cathodes. *J. Electrochem. Soc.* **2022**, *169* (11), 110534.

(52) Ravdel, B.; Abraham, K. M.; Gitzendanner, R.; DiCarlo, J.; Lucht, B.; Campion, C. Thermal Stability of Lithium-Ion Battery Electrolytes. *J. Power Sources* **2003**, *119–121*, 805–810.

(53) Campion, C. L.; Li, W.; Lucht, B. L. Thermal Decomposition of LiPF<sub>6</sub>-Based Electrolytes for Lithium-Ion Batteries. *J. Electrochem. Soc.* **2005**, *152* (12), A2327.

(54) Kraft, V.; Grütze, M.; Weber, W.; Winter, M.; Nowak, S. Ion Chromatography Electrospray Ionization Mass Spectrometry Method Development and Investigation of Lithium Hexafluorophosphate-Based Organic Electrolytes and Their Thermal Decomposition Products. *J. Chromatogr. A* **2014**, *1354*, 92–100.

(55) Lithium-ion Battery Production and Testing | Manufacturing & Inspection | Hioki. <https://www.hioki.com/us-en/industries-solutions/manufacturing/liion-production-testing.html> (accessed 2025 02 11).

(56) Schomburg, F.; Heidrich, B.; Wennemar, S.; Drees, R.; Roth, T.; Kurrat, M.; Heimes, H.; Jossen, A.; Winter, M.; Cheong, J. Y.; Röder, F. Lithium-Ion Battery Cell Formation: Status and Future Directions towards a Knowledge-Based Process Design. *Energy Environ. Sci.* **2024**, *17* (8), 2686–2733.

(57) Production of Lithium-Ion Batteries. <https://www.genre.com/us/knowledge/publications/2024/april/pmint24-2-en> (accessed 2025 02 14).

(58) Petibon, R.; Rotermund, L. M.; Dahn, J. R. Evaluation of Phenyl Carbonates as Electrolyte Additives in Lithium-Ion Batteries. *J. Power Sources* **2015**, *287*, 184–195.

(59) Qiu, W.; Xia, J.; Chen, L.; Dahn, J. R. A Study of Methyl Phenyl Carbonate and Diphenyl Carbonate as Electrolyte Additives for High Voltage LiNi 0.8 Mn 0.1 Co 0.1 O 2/Graphite Pouch Cells. *J. Power Sources* **2016**, *318*, 228–234.

(60) Morinaka, T.; Kawabata, W.; Kawahara, K.; Takahashi, M. Nonaqueous electrolyte and nonaqueous electrolyte secondary battery containing same. WO 2021006238, January 14, 2021.

(61) Takahashi, M.; Morinaka, T.; Shinmen, M.; Yamamoto, K.; Kawabata, W.; Kubo, M.; Fujimoto, M.; Matsuzaki, H.; Tsujioka, S. Ionic complexes having specific chemical structures, their preparation, nonaqueous electrolytic solutions containing them, and batteries using them. WO 2016002774, January 7, 2016.

(62) Charbonnet, J. A.; McDonough, C. A.; Xiao, F.; Schwichtenberg, T.; Cao, D.; Kaserzon, S.; Thomas, K. V.; Dewapriya, P.; Place, B. J.; Schymanski, E. L.; Field, J. A.; Helbling, D. E.; Higgins, C. P. Communicating Confidence of Per- and Polyfluoroalkyl Substance Identification via High-Resolution Mass Spectrometry. *Environ. Sci. Technol. Lett.* **2022**, *9* (6), 473–481.

(63) Wang, Z.; Cousins, I. T.; Scheringer, M.; Hungerbühler, K. Fluorinated Alternatives to Long-Chain Perfluoroalkyl Carboxylic Acids (PFCAs), Perfluoroalkane Sulfonic Acids (PFASs) and Their Potential Precursors. *Environ. Int.* **2013**, *60*, 242–248.

(64) Washington, J. W.; Rosal, C. G.; McCord, J. P.; Strynar, M. J.; Lindstrom, A. B.; Bergman, E. L.; Goodrow, S. M.; Tadesse, H. K.; Pilant, A. N.; Washington, B. J.; Davis, M. J.; Stuart, B. G.; Jenkins, T. M. Nontargeted Mass-Spectral Detection of Chloroperfluoropolyether Carboxylates in New Jersey Soils. *Science* **2020**, *368* (6495), 1103–1107.

- (65) Ellis, D. A.; Mabury, S. A.; Martin, J. W.; Muir, D. C. G. Thermolysis of Fluoropolymers as a Potential Source of Halogenated Organic Acids in the Environment. *Nature* **2001**, *412* (6844), 321–324.
- (66) Schlummer, M.; Sölch, C.; Meisel, T.; Still, M.; Gruber, L.; Wolz, G. Emission of Perfluoroalkyl Carboxylic Acids (PFCA) from Heated Surfaces Made of Polytetrafluoroethylene (PTFE) Applied in Food Contact Materials and Consumer Products. *Chemosphere* **2015**, *129*, 46–53.
- (67) Sajid, M.; Ilyas, M. PTFE-Coated Non-Stick Cookware and Toxicity Concerns: A Perspective. *Environ. Sci. Pollut. Res.* **2017**, *24* (30), 23436–23440.
- (68) Lang, J. R.; Allred, B. M.; Field, J. A.; Levis, J. W.; Barlaz, M. A. National Estimate of Per- and Polyfluoroalkyl Substance (PFAS) Release to U.S. Municipal Landfill Leachate. *Environ. Sci. Technol.* **2017**, *51* (4), 2197–2205.
- (69) Capozzi, S. L.; Leang, A. L.; Rodenburg, L. A.; Chandramouli, B.; Delistraty, D. A.; Carter, C. H. PFAS in Municipal Landfill Leachate: Occurrence, Transformation, and Sources. *Chemosphere* **2023**, *334*, 138924.
- (70) Lang, J. R.; Allred, B. M.; Peaslee, G. F.; Field, J. A.; Barlaz, M. A. Release of Per- and Polyfluoroalkyl Substances (PFASs) from Carpet and Clothing in Model Anaerobic Landfill Reactors. *Environ. Sci. Technol.* **2016**, *50* (10), 5024–5032.
- (71) Wang, Q.; Zhang, T.; Liu, X.; Liu, S.; Wang, X.; Wang, X. The Fate of 6:2 Fluorotelomer Alcohol in Anaerobic Landfill Leachate: Implication for Fugitive Emission from Waste Landfills. *Environ. Pollut.* **2025**, *376*, 126375.
- (72) Liu, J.; Wang, N.; Szostek, B.; Buck, R. C.; Panciroli, P. K.; Folsom, P. W.; Sulecki, L. M.; Bellin, C. A. 6–2 Fluorotelomer Alcohol Aerobic Biodegradation in Soil and Mixed Bacterial Culture. *Chemosphere* **2010**, *78* (4), 437–444.
- (73) Zhang, S.; Szostek, B.; McCausland, P. K.; Wolstenholme, B. W.; Lu, X.; Wang, N.; Buck, R. C. 6:2 and 8:2 Fluorotelomer Alcohol Anaerobic Biotransformation in Digester Sludge from a WWTP under Methanogenic Conditions. *Environ. Sci. Technol.* **2013**, *47* (9), 4227–4235.
- (74) Winter, M.; Barnett, B.; Xu, K. Before Li Ion Batteries. *Chem. Rev.* **2018**, *118* (23), 11433–11456.
- (75) Francis, C. F. J.; Kyrtatzis, I. L.; Best, A. S. Lithium-Ion Battery Separators for Ionic-Liquid Electrolytes: A Review. *Adv. Mater.* **2020**, *32* (18), 1904205.
- (76) Sheng, L.; Zhu, D.; Yang, K.; Wu, Y.; Wang, L.; Wang, J.; Xu, H.; He, X. Unraveling the Hydrolysis Mechanism of LiPF<sub>6</sub> in Electrolyte of Lithium Ion Batteries. *Nano Lett.* **2024**, *24* (2), 533–540.
- (77) Kingery, A. F.; Allen, H. E. The Environmental Fate of Organophosphorus Nerve Agents: A Review. *Toxicol. Environ. Chem.* **1995**, *47* (3–4), 155–184.
- (78) Tripathi, H. L.; Dewey, W. L. Comparison of the Effects of Diisopropylfluorophosphate, Sarin, Soman, and Tabun on Toxicity and Brain Acetylcholinesterase Activity in Mice. *J. Toxicol. Environ. Health* **1989**, *26* (4), 437–446.
- (79) Silver, S. D. The Toxicity of Dimethyl-, Diethyl-, and Diisopropyl Fluorophosphate Vapors. *J. Ind. Hyg. Toxicol.* **1948**, *30* (5), 307–311.
- (80) Raushel, F. M. Catalytic Detoxification. *Nature* **2011**, *469* (7330), 310–311.
- (81) Stenzel, Y.; Horsthemke, F.; Winter, M.; Nowak, S. Chromatographic Techniques in the Research Area of Lithium Ion Batteries: Current State-of-the-Art. *Separations* **2019**, *6* (2), 26.
- (82) Das, A. K.; Bellizzi, J. J.; Tandel, S.; Biehl, E.; Clardy, J.; Hofmann, S. L. Structural Basis for the Insensitivity of a Serine Enzyme (Palmitoyl-Protein Thioesterase) to Phenylmethylsulfonyl Fluoride. *J. Biol. Chem.* **2000**, *275* (31), 23847–23851.
- (83) Zhou, S.; Zhang, S.; Wang, S.; Zhang, W.; Liu, Y.; Lin, H.; Chen, J.; Yan, L.; Zhang, F.; Li, H.; Zheng, H. Direct Evidences for Bis(Fluorosulfonyl)Imide Anion Hydrolysis in Industrial Production: Pathways Based on Thermodynamics Analysis and Theoretical Simulation. *J. Power Sources* **2023**, *577*, 233249.
- (84) Okumura, Y.; Okajima, M.; Sato, S.; Obata, T.; Watabe, H.; Sato, Y.; Higuchi, Y. Preparation of (aminosulfonyl)(fluorosulfonyl)-imide salts. JP 2017122058, July 13, 2017.
- (85) Schmitt, E.; Le Guyader, F.; Roques, N. Composition Comprising an Alkali Metal Salt of Bis(Fluoro Sulfonyl)Imide with Improve Purity, Yield, and Cost Reduction Associated with Production. WO 202347804, December 28, 2023.
- (86) Fang, J.-J.; Yang, N.; Cen, D.-Y.; Shao, L.-M.; He, P.-J. Odor Compounds from Different Sources of Landfill: Characterization and Source Identification. *Waste Manag* **2012**, *32* (7), 1401–1410.
- (87) Steudte, S.; Neumann, J.; Bottin-Weber, U.; Diedenhofen, M.; Arning, J.; Stepnowski, P.; Stolte, S. Hydrolysis Study of Fluoroorganic and Cyano-Based Ionic Liquid Anions – Consequences for Operational Safety and Environmental Stability. *Green Chem.* **2012**, *14* (9), 2474.
- (88) Kalungi, P.; Yao, Z.; Huang, H. Aspects of Nickel, Cobalt and Lithium, the Three Key Elements for Li-Ion Batteries: An Overview on Resources, Demands, and Production. *Materials* **2024**, *17* (17), 4389.
- (89) Bree, G.; Horstman, D.; Low, C. T. J. Light-Weighting of Battery Casing for Lithium-Ion Device Energy Density Improvement. *J. Energy Storage* **2023**, *68*, 107852.



CAS BIOFINDER DISCOVERY PLATFORM™

**PRECISION DATA  
FOR FASTER  
DRUG  
DISCOVERY**

CAS BioFinder helps you identify  
targets, biomarkers, and pathways

**Unlock insights**

**CAS**  
A Division of the  
American Chemical Society