

Physical and Biological Release of Poly- and Perfluoroalkyl Substances (PFASs) from Municipal Solid Waste in Anaerobic Model Landfill Reactors

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1 **Physical and Biological Release of Poly- and Perfluoroalkyl Substances (PFASs) from Municipal**

2 **Solid Waste in Anaerobic Model Landfill Reactors**

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32 **Abstract:**

33 A wide variety of consumer products that are treated with poly- and perfluoroalkyl substances
34 (PFASs) and related formulations are disposed in landfills. Landfill leachate has significant concentrations
35 of PFASs and acts as secondary point sources to surface water. Here, we model how PFASs enter
36 leachate using four lab-scale anaerobic bioreactors filled with municipal solid waste (MSW) and
37 operated over 273 days. Duplicate reactors were monitored under live and abiotic conditions to
38 evaluate influences attributable to biological activity. The biologically-active reactors simulated the
39 methanogenic conditions that develop in all landfills, producing ~140 mL CH₄/dry g refuse. The average
40 total PFAS leaching measured in live reactors (16.7 nmol/kg dry-refuse) was greater than the average for
41 abiotic reactors (2.83 nmol/kg dry-refuse), indicating biological processes were primarily responsible for
42 leaching. The low level leaching in the abiotic reactors was primarily due to PFCAs ≤C8 (2.48 nmol/kg
43 dry-refuse). Concentrations of known biodegradation intermediates, including methylperfluorobutane
44 sulfonamide acetic acid and the n:2 and n:3 fluorotelomer carboxylates, increased steadily in
45 concentration after the onset of methanogenesis, with the 5:3 fluorotelomer carboxylate becoming the
46 single most concentrated PFAS observed in live reactors (9.53 nmol/kg dry-refuse).

47

48 **INTRODUCTION**

49 Municipal solid-waste (MSW) management within the U.S. over the last century has largely
50 involved the collection and disposal of waste in landfills.^{1,2} Of the 251 million tons of MSW generated in
51 2012, 34.5 % by mass was recovered for recycling and composting, 11.7% was combusted with energy
52 recovery and 53.8% was discarded in landfills.³ Leachate is the water that percolates through the waste
53 discarded into landfills and contains a collection of toxic and persistent chemicals including
54 pharmaceuticals and other environmental pollutants.^{1,2,4,5} Within the consortium of environmental
55 pollutants contained in landfill leachate are poly- and perfluoroalkyl substances (PFASs) that are applied
56 to a variety of commercial products that are commonly discarded.⁶ Most modern landfills include liners⁷
57 and collect leachate for treatment at wastewater treatment plants (WWTPs). However, WWTPs are
58 reportedly not equipped to remediate many of the contaminants of concern in landfill leachate.⁸⁻¹⁰

59 PFASs are of environmental and toxicological concern because of their ubiquity, persistence and
60 long-chain PFAS bioaccumulation.¹¹⁻¹³ Landfill leachate contains greater concentrations of PFASs than
61 most other environmental media with the exception of firefighting training and manufacturing impacted
62 sites.¹³⁻¹⁸ Perfluorooctane sulfonic acid (PFOS) production and use was restricted by the Stockholm
63 Convention for Persistent Organic Pollutants in 2009,¹⁹ and industry has begun to discontinue the
64 production of long-chain PFASs (seven or more perfluorinated carbons) that are generally considered to
65 be more toxic and bioaccumulative.²⁰ Despite any potential phase-out of select PFASs, landfills will
66 continue to act as a long-term point repository, highlighting the need for further investigation.²

67 While the impact of leachate treatment technologies on PFAS concentrations have been
68 studied,^{16,21,22} and PFASs have been identified as a source of groundwater contamination,²³ no research
69 has connected leachate PFAS composition and MSW under the time dependent conditions relevant to
70 landfills. Benskin et al. (2012) reported that concentrations of three perfluoroalkyl carboxylic acids
71 (PFCAs) were significantly correlated with pH, electrical conductivity, and 24 hour precipitation in

72 leachate collected over five months from a landfill operated over 30 years.¹⁴ On a smaller scale, Zhang et
73 al. (2013) reported fluorotelomer alcohol (FTOH) degradation in anaerobic digester sludge under
74 methanogenic conditions preferentially yielded fluorotelomer carboxylic acids (FTCAs) to PFCAs.²⁴
75 However, these experiments were focused on a select subset of PFASs, were at concentrations
76 substantially greater than those observed in landfills, and were performed in aqueous systems that are
77 simpler than the landfill ecosystem.

78 Here we constructed lab-scale reactors and filled them with shredded residential MSW and an
79 anaerobic microbial inoculum. Four reactors (two biologically active and two killed controls) were
80 operated to determine the roles of abiotic leaching and biological activity on the temporal trends and
81 concentrations of 70 PFASs (12 compound classes) in leachate associated with MSW. A list of PFAS
82 compound class names, acronyms, and structures investigated for this study can be found in the SI
83 (Table S1). We hypothesized that the temporal trends of PFAS concentrations would differ between
84 Abiotic and Biotic reactors for some compound classes, such as those associated with biodegradation
85 pathways (e.g. FTCAs), and not for those with no known degradation pathways (e.g. perfluorosulfonic
86 acids, PFSAs).

87

88 **EXPERIMENTAL METHODS**

89 **MSW collection and pre-treatment.** Fresh MSW was sampled from a transfer station after
90 collection from residential neighborhoods. Prior to shredding in a slow-speed, high-torque shredder
91 (ShredPax. Corp., AZ-7H, Wood Dale, Illinois), the shredder was rinsed with methanol and the MSW was
92 sorted to remove metals with a diameter of >1.5 cm. Approximately 120 L of the initially-shredded
93 material was discarded to minimize contamination from previously-shredded materials. Once shredded
94 to approximately 2 cm x 5 cm, the MSW was collected in 200 L high density polyethylene bins
95 (previously rinsed with methanol) and stored overnight at 4°C. MSW from two bins was mixed in an

96 effort to homogenize the sample. The MSW was then used to fill four 8 L HDPE reactors (1-2 kg per
97 reactor). Subsamples of refuse were collected for moisture, cellulose, and hemicellulose content
98 analysis to characterize the starting material and to document the loss of degradable organic matter in
99 the Biotic reactors.

100 **Reactor operation, characterization, and sampling.** Reactor materials were tested for
101 background PFAS leaching using model leachate phases. No PFAS analytes were measured on day 30
102 above the limit of quantification with the exception of low levels of perfluorooctane sulfonate (PFOS)
103 that were subtracted from reactor leachate concentrations. Reactor materials were therefore
104 determined to largely be an insignificant source of PFASs to reactor leachate (see supporting
105 information (SI) for more detail).

106 Reactor construction and operation have been described previously.^{25,26} Following refuse
107 addition to the reactor body, two solutions containing an anaerobic consortium (1 L) and a model
108 leachate matrix (1 L) were added. The anaerobic consortium used to inoculate reactors was acclimated
109 to the conversion of solid refuse to methane and was grown and maintained on laser print paper, with
110 30% recycled content (Office Depot, FL) that was largely PFAS-free (see SI for details). Humic matter
111 (1.203 g/L), acetate (0.37 g/L), and butyrate (0.185 g/L) were obtained from Sigma-Aldrich Inc. (St. Louis,
112 MO) and used to produce a synthetic leachate^{4,27} with propionate (0.185 g/L) purchased from Thermo
113 Fisher Scientific (New Jersey, U.S.). Deionized water (0.45 –2 L) was added in sufficient quantity to
114 saturate the refuse and provide 1L of leachate in the collection bag. As a result, the shredded refuse was
115 partially submerged and leachate was recirculated through the top of the reactor (1/wk), to enhance the
116 rate of decomposition and to provide a saturated system for leachate sampling.

117 Once the four reactors were constructed, two were kept biologically active (Biotic 1 and Biotic 2)
118 while two received anti-microbial compounds and served as abiotic controls (Abiotic 1 and Abiotic 2).
119 The two abiotic control reactors received 0.17 g/L streptomycin and 2 g/L 2,2-dibromo-3-

120 nitrilopropionamide (DBNPA) purchased from the Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan). See
121 the SI for more information on the selection of anti-microbial compounds. All reactors were operated in
122 a room maintained at 37 °C for 273 days, which is past the completion of significant methane production
123 in Biotic reactors.

124 The methods employed to measure gas volume, composition, pH, and chemical oxygen demand
125 (COD) were presented previously.²⁶ Measurements were made two to three times a week until the
126 leachate pH was neutral, after which reactors were characterized weekly for the next month of
127 operation and monthly thereafter. During the first two weeks of operation, Biotic 1 and 2 were
128 neutralized with the addition of sodium hydroxide to accelerate the initiation of methane production.
129 Abiotic reactors were not sampled/analyzed for pH and methane production given that the pH was
130 stable and they did not produce methane.

131 Each reactor was sampled for PFAS analysis approximately every seven days for the first 48 d,
132 after which leachate was collected approximately every 14 d by collecting 42 mL, which was then split
133 into three 15 mL and one 50 mL centrifuge tube (VWR International, Radnor, PA). Small volumes (5-15
134 mL) of 2 M NaOH were added periodically to the reactor and dilution was taken into account when
135 reporting leachate PFAS concentrations (see the SI). All samples were immediately frozen and stored at
136 -4 °C. Two of the 15 mL centrifuge samples were shipped overnight on ice to Oregon State University
137 where they were stored at -20 °C prior to PFAS analysis. The remaining 15 mL and 50 mL sample tubes
138 were used for reactor characterization. To assess refuse biodegradation, the cellulose, hemicellulose
139 and lignin concentrations were measured²⁶ in both the fresh MSW and the refuse remaining at the end
140 of reactor operation. At the end of reactor operation, the leachate was drained into HDPE containers
141 and immediately frozen. The solids were then dried to constant weight in methanol-rinsed fiber glass
142 pans. It was beyond the scope of the project to measure volatile PFASs in reactor gas.

143 **Micro-Liquid-Liquid Extraction (Micro-LLE) and Liquid Chromatography Tandem Mass**
144 **spectrometry (LC-MS/MS).** PFAS extraction and analysis in leachate was described previously.¹⁵ Briefly,
145 leachate samples were centrifuged, titrated to pH 7-8, and extracted with trifluoroethanol and ethyl
146 acetate (see SI for details). Then 900 μL of the extract was injected, using orthogonal column chemistries
147 to separate and tandem mass spectrometry for detection (see SI for details). Briefly, the accuracy of the
148 method (internal standard relative to standard addition measured values) ranged from 81–120% and
149 whole-method precision (combined intra- and interday relative standard deviation, RSD) ranged from
150 5.5–33 %.¹⁵ Method detection limits were low to sub-ng/L.¹⁵

151 Single samples were analyzed for each reactor at each sampling time point. To compute the
152 uncertainty about the measured PFAS concentrations in reactor leachate, the follow steps were
153 taken. First, as part of each batch of sample analyzed, a single leachate sample was analyzed in
154 triplicate. In addition, of the duplicate reactor samples collected, 27% were analyzed over the
155 project. Except for six PFASs, the RSDs from the triplicate analyses of a single leachate and duplicate
156 reactor samples were found to be at or below the previously-determined analytical variability of the
157 whole method (5.8 – 33%).²⁸ For this reason, for most analytes, the error bars plotted in the Figures
158 represent the previously-reported analytical (whole method) variability.²⁸ In the case of six PFASs,
159 where the RSD of the duplicate analyses exceeded that of the previously-reported variability,²⁸ plotted
160 error bars represent the RSD of the duplicates, which never exceeded 20%.

161 **Data Analysis.** Concentrations for PFASs were first normalized to the initial reactor leachate
162 volume by accounting for any volume changes over the course of reactor operation (see SI for more
163 detail on accounting for dilution). PFAS concentrations were then normalized to the initial mass of MSW
164 in each reactor (pmol/kg refuse dry weight), which enabled comparisons between reactors.

165 Individual compounds and reactor parameters were tested for statistically significant
166 correlations using Kendall rank correlation coefficient (τ_b).²⁹ PFAS concentrations and reactor

167 parameters, with less than 30% censored data, were determined to have a significant correlation when
168 the absolute τ_b value exceeded the critical value (p-value < 0.05) for the degrees of freedom (df). A
169 majority of reactor parameter and PFAS concentrations were significantly correlated and select cases
170 with strong correlations will be discussed below.

171 The concentrations and behaviors (i.e. temporal trends) of PFASs over the course of reactor
172 operation will be discussed by compound class. The total mass of PFASs per kg of refuse is not reported
173 because the reactors were operated at an atypically high liquid to solids (L/S) ratio, which stimulated the
174 rate of biological processes and the rate of contaminant transport relative to even a very wet landfill.
175 Therefore, the water flux in the reactors is orders of magnitude greater than what would be experienced
176 at a typical landfill. In addition, the behavior and total mass of PFASs released from the municipal waste
177 tested here may differ significantly from that of PFASs from commercial waste (e.g., offices and
178 institutions) and industrial wastes (e.g., contaminated soil, auto shredder residue, biosolids, off-
179 specification products).

180 Classes including perfluoroalkyl sulfonates, fluorotelomer sulfonates, and perfluoroalkyl
181 carboxylates are discussed first because the behaviors of short-chain homologues within these classes
182 were governed predominantly by simple abiotic leaching. The discussion of di-alkyl phosphates,
183 perfluoroalkyl sulfonamides, and fluorotelomer carboxylates follow, because their behaviors were more
184 complex and governed by multiple processes. Concentrations for PFASs that were <LOQ in > 90% of the
185 reactor samples could not be treated quantitatively and are therefore not displayed graphically (data
186 not shown).

187

188 **RESULTS AND DISCUSSION**

189 **Reactor Characterization and Anaerobic Degradation.** MSW decomposition in the Biotic
190 reactors progressed through the acid phase and the methane production phase, as is typical of U.S.

191 landfills (Figure 1),^{4,27} but on an accelerated time-scale (273 days instead of years). Initially, the reactor
192 pH was acidic, but it reached a neutral pH in Biotic reactors, as acidic decomposition intermediates were
193 converted to methane, while remaining acidic in the Abiotic reactors. Significant methane production
194 (>10% total) began at different times for Biotic 1 (26–34 days) and Biotic 2 (70–82 days) with leachate
195 pH rising above 7.5 concurrently (Figure 1) and correlating significantly, $r_b = 0.68$ ($p = 2 * 10^{-10}$, $df = 43$).
196 While efforts were made to homogenize the MSW sample prior to reactor loading, the particle size and
197 heterogeneous nature of MSW made it impossible to achieve a completely mixed sample, which likely
198 explains the different periods prior to the onset of methane production. Variations in methane
199 production are not uncommon for laboratory-scale landfill reactors.³⁰

200 The COD also peaked concurrent with the onset of methanogenesis in Biotic reactors, but
201 remained relatively steady in Abiotic reactors after day 27 (Figure S2). The rise and fall of COD
202 concentrations in Biotic reactors represents the production of volatile fatty acids and their subsequent
203 consumption in the methane phase. Both the methane production data (Figure 1) and the solids
204 analyses confirm that streptomycin and DBNPA successfully inhibited decomposition in the Abiotic
205 reactors. The cellulose and hemicellulose concentrations of the dry, fresh refuse were 39% and 9%,
206 respectively. The amount of cellulose and hemicellulose converted was calculated from their
207 concentrations in the reactors at the completion of the decomposition cycle. Cellulose and
208 hemicellulose decomposition were an average of 79 and 78% in Biotic reactors, and 3 and 21% in the
209 Abiotic reactors, respectively. The decrease in cellulose and hemicellulose in the Biotic reactors
210 represents the readily biodegradable MSW fraction, and is typically composed of paper products and
211 food and yard waste.³¹ For purposes of brevity, and given the similarities in the performance of the
212 replicate reactors, only Biotic 1 and Abiotic 1 will be discussed in detail unless otherwise noted.

213 **Perfluoroalkyl sulfonates (PFSA)s.** Of the PFSA compound class, PFBS (C4) and PFHxS (C6) were
214 present at time zero in leachate from all reactors (Figures 2a, S3a, and S4a), consistent with their use in

215 surfactant products³² and formulations applied to fabrics, papers, metal plating and photolithography.³³
216 Although PFBS and PFHxS may also result from the degradation of C4- and C6- based fluoroalkane
217 sulfonamide derivatives,¹² there were no statistically-significant differences between concentration
218 trends in Biotic and Abiotic reactors. Thus, PFBS and PFHxS leachate concentrations likely result from
219 abiotic leaching and not from precursor biodegradation. The C5, 7, 9, and 10 PFSA homologues were not
220 detected above the LOQ and were below detection limits (LODs) in > 90% of reactor samples (data not
221 shown).

222 The temporal trends of PFOS differed from those of PFBS and PFHxS with a significant decline in
223 PFOS concentrations occurring immediately after the first day of reactor operation (Figures 2b and S4b).
224 The reason for the initial decrease in PFOS concentrations in both Biotic and Abiotic reactors is unclear.
225 It is likely however, that the PFOS was concentrated in a small quantity of refuse and showed up as a
226 spike in the leachate until the leachate was recirculated which allowed some PFOS to equilibrate with
227 the solid phase.

228 The temporal trends in PFOS concentrations in both Biotic reactors differ significantly from
229 those of the Abiotic reactors (Figure 2b and S4b). The increase in PFOS concentrations in the Biotic
230 reactors, relative to the Abiotic reactors, was concurrent with the start of methane production and the
231 rise in pH (Figure 1). For example PFOS concentrations increased between days 14–27 in Biotic 1,
232 whereas Biotic 2 concentrations increased between days 62–90. Such increases may result from the
233 transformation of precursors.¹² Alternatively, PFOS may be released at the onset of methanogenesis
234 (signaled by methane gas production) as substrates, such as paper products, begin to degrade
235 anaerobically. Lastly, a rise in pH in Biotic reactors may result in organic matter deprotonation and
236 electrostatic repulsion³⁴ of any associated PFOS, resulting in elevated aqueous PFOS concentrations. The
237 apparent changes in PFOS concentrations in Biotic 1 and 2 that occurred late in reactor operations (>

238 day 260) may or may not be meaningful, given that several data points were close to the limit of
239 quantification.

240 **Fluorotelomer sulfonates (FTSAs).** The 6:2 and 8:2 FTSA homologues were present in leachate
241 from all four reactors at time zero, indicating the association of FTSAs and MSW as surfactants and
242 alternatives to PFOS in other applications.^{35,36} The 4:2 FTSA homologue was not observed above the LOD
243 in all samples and the 8:2 FTSA was <LOQ in >90% of samples. Temporal trends of 6:2 FTSA
244 concentrations for Biotic and Abiotic reactors did not deviate significantly from each other (Figure S3b)
245 such that abiotic leaching from MSW likely accounts for most of the observed 6:2 FTSA concentrations.
246 So, while FTSA formation due to precursor degradation has been suggested to be an important source of
247 FTSAs to the environment,^{10,38} it did not contribute significantly to 6:2 FTSA leachate concentrations in
248 this study. Likewise, FTSA persistence in leachate from both Biotic reactors is consistent with the
249 observed persistence of FTSAs in oxygen-depleted groundwater contaminated by aqueous film forming
250 foams.³⁷

251 **Perfluoroalkyl carboxylates (PFCAs).** The C4-12 PFCA homologues were detected at time zero in
252 leachate from all reactors, which is consistent with their association with commercial products via
253 surfactants and fluoropolymer production.³² Temporal trends of short-chain PFCA (C4–C7)
254 concentrations were similar in Biotic and Abiotic reactors (Figures 3, S3c-d, and S5) indicating their
255 presence in leachate results primarily from abiotic leaching.

256 In contrast, PFOA concentrations increased in Biotic reactors but not in Abiotic reactors (Figures
257 4, S3e-f, and S6), occurring after day 27 in Biotic 1, which coincides with the onset of methanogenesis
258 and the increase in pH (day 26–34, Figure 1). The C9 and longer PFCA homologues demonstrate similar
259 concentration increases in Biotic reactors, but at lower concentrations (Figure 4). Such increases in
260 concentration may result from substrate degradation, pH effects, and precursor transformation.³⁸ All
261 such long-chain PFCA increases in concentration occur simultaneously, but PFAS precursors typically

262 have slower transformation rates with increasing chain-lengths.^{12,38} Zhang et al. (2013) observed that
263 under methanogenic conditions, the 8:2 FTOH (PFOA precursor) half-life was approximately three times
264 longer than the 6:2 FTOH half-life.²⁴ And if transformation rates continue to decrease with increasing
265 chain-length, then precursor transformation is not likely to have contributed significantly to the
266 observed concurrent concentration increases.

267 The temporal trends of C10-12 PFCA concentrations deviate from those of PFOA and PFNA by
268 decreasing below the limit of quantification by day 202 in Biotic 1 (Figure 4). We hypothesize that after
269 the release of C10-C12 PFCAs from the biodegraded MSW substrate, they sorb to other MSW or reactor
270 components as leachate was recirculated during sampling. The C13, 14, and 16 PFCAs fell below their
271 respective LOQs in >90% of samples and C15, 17, and 18 PFCAs were not detected in reactor leachate.
272 The occurrence of >C12 PFCAs in the reactor leachates is consistent with reports of >C12 PFCAs in
273 leachates from full-scale landfills.^{15,21} Because >C12 PFCAs are not often observed in natural waters,¹³
274 their presence may be due to enhanced solubility through association with the hydrophobic moieties of
275 dissolved organic matter that abound in leachate.⁴ Consequently, detecting up to C16 in reactor
276 leachate speaks to the ability of the reactor system to model landfill leachate. Concentrations of long-
277 chain PFCAs likely represent conservative estimates if sorption onto particulate matter occurs during
278 sample centrifugation. However, any losses onto particulate matter would occur continuously and,
279 therefore, would not be expected to impact trends in PFAS concentrations with time.

280 **Di-alkyl Phosphates (DiPAPs, DiSAMPAP, PFPIAs, and FTMAPs).** Di-substituted fluorotelomer
281 phosphate esters (6:2 – 10:2 DiPAPs) and n-ethyl perfluorooctane sulfonamido ethanol-based
282 polyfluoroalkyl phosphate diester (DiSAMPAP) were measured at time zero in both Biotic and Abiotic
283 reactors (Figures 5, S7, and S8a-b). The presence of these classes in reactor leachate during the first
284 sampling event is attributable to their application to and release from commercial products including

285 paper and food packaging materials,³⁹ which was estimated to constitute 14.8 % by mass of discarded
286 U.S. MSW in 2012.³

287 Over the 273 days that the reactors were in operation, DiPAP concentrations varied significantly,
288 presumably due to the concurrent impacts from multiple sources. Initial DiPAP concentration decreases
289 (6:2, 6/8:2, and 8:2) in both Biotic and Abiotic reactors (Figure 5, S7, and S8a) may reflect the effects of
290 uneven initial DiPAP distribution and recirculation described above for PFOS. DiPAPs in Biotic reactors
291 then follow temporal trends similar to those of long-chain PFCAs (C10-12) by increasing in concentration
292 with the onset of methanogenesis and a pH increase (days 26–34 in Biotic 1) and decreasing shortly
293 thereafter (Figure 5a). As there are no known DiPAP precursors, the increases in Biotic reactor
294 concentrations are likely a result of MSW substrate degradation with the concurrent pH increase driving
295 DiPAPs into the aqueous phase. DiPAPs with increasing chain-lengths remained in solution longer in
296 Biotic reactors which suggests that hydrophobic sorption was not wholly responsible for their decreasing
297 concentrations over time. Indeed, the prolonged presences of high molecular-weight DiPAPs was more
298 consistent with observations of decreasing monoPAP degradation rates with increasing chain-length.⁴⁰

299 DiSAmPAP concentrations follow similar trends to those described for DiPAPs, except that they
300 start close to the limit of quantification and do not exhibit a dramatic initial decrease. Benskin et al.
301 reported little to no DiSAmPAP degradation on marine sediments (120 d half-life), but poor
302 degradability was attributed to strong DiSAmPAP sorption to particulate matter and low microbial
303 activities in sediment.⁴¹ Therefore anaerobic biodegradation may still be instrumental to the decreasing
304 DiSAmPAP concentrations in Biotic 1 (Figure 5) and 2 (Figure S7) over time. Disubstituted perfluoroalkyl
305 phosphinic acids (PFPIAs) and fluorotelomer mercaptoalkyl phosphate esters (FTMAPs) were not
306 detected in any reactor leachate sample.

307 **Fluoroalkyl sulfonamide acetic acid derivatives.** The C4 (data not shown) and C8 (Figure S8c)
308 ethyl fluoroalkyl sulfonamide acetic acids (EtFASAAs) were detected at time zero. EtFASAAs are

309 associated with MSW for two possible reasons. First, EtFASAA is the ionic surfactant in 3M Fluorad
310 fluorosurfactant FC-129, which was recommended as a leveling agent in floor polishes.⁴² Second,
311 EtFASAA may result from the biodegradation products of *N*-ethyl perfluorooctane sulfonamide ethanol
312 (EtFOSE),⁴³ which are used as paper and package protectants^{43,44} and in the synthesis of DiSAmPAP.⁴¹

313 The C4 homologue of the methyl fluoroalkyl sulfonamide acetic acid class (MeFASAA) was
314 detected at time zero in Biotic and Abiotic reactors (Figure S8d). In addition, intermittent and low
315 concentrations of the C5 and 8 MeFASAA homologues were detected over the time course of the
316 experiment (data not shown). The MeFASAA class may be the biotransformation products of *N*-methyl
317 perfluorooctane sulfonamido ethanols, which are used to synthesize polymeric surface treatment
318 products for carpets and textiles,⁴⁵ in a manner analogous to the degradation of EtFOSE. The detection
319 of MeFASAA in time zero samples from Biotic and Abiotic reactors may result from aerobic precursor
320 biodegradation prior to reactor loading. Residential MSW is collected weekly and, under moist aerobic
321 conditions, could biodegrade for up to 7 days prior to the sampling and reactor loading.

322 Unsubstituted fluoroalkyl sulfonamide acetic acids (FASAA) are metabolites of both Me- and
323 EtFASAA,⁴⁴ but were not observed in any reactor and may indicate that precursors, such as Me- and
324 EtFASAA, degrade very slowly under anaerobic conditions. Rhoads et al. (2008) found that even under
325 aerobic conditions, EtFOSAA degradation was the rate limiting step in the conversion of EtFOSE to PFOS
326 and that EtFOSAA was ultimately the major degradation product.⁴³

327 In both Biotic and Abiotic reactors, EtFOSAA concentrations followed temporal trends similar to
328 those of PFOS by decreasing to below the limits of detection before increasing significantly with the
329 onset of methanogenesis in Biotic reactors (Figure S8c). EtFOSAA concentrations then stabilized and
330 remained relatively constant for the remainder of reactor operation. EtFOSAA concentrations were
331 significantly correlated with DiSAmPAP ($\tau_b = 0.61$, $p = 1 \times 10^{-5}$) in Biotic reactors (df =25), indicating that
332 these two forms may originate from a common source and are impacted by similar processes. The C4

333 EtFASAA fell below the LOQ in >90% of samples and the C5–7 EtFASAs were not detected in >90% of
334 reactor samples.

335 In contrast, MeFBSAA concentrations increased steadily after the onset of methanogenesis in
336 Biotic 1, but not in Biotic 2, while no significant production of MeFBSAA occurred in either Abiotic
337 reactor (Figure S8d). The steady increase in MeFBSAA concentrations in Biotic 1 likely result from the
338 continuous transformation of precursor compounds. The most plausible explanation for the
339 disagreement between Biotic 1 and 2 temporal trends is that Biotic 1 contained a source of MeFBSAA
340 not found in Biotic 2 and possibly Abiotic 1 and 2.

341 **Fluorotelomer carboxylic acids.** The 6:2 fluorotelomer carboxylic acid (FTCA), unsaturated
342 fluorotelomer carboxylic acid (FTUCA) and 5:3 FTCA were present at time zero in Biotic and Abiotic
343 reactors (Figures 6, S8f, and S9). The fluorotelomer carboxylates are products of fluorotelomer-based
344 compound degradation,^{24,40,46} and their detection at time zero indicated that aerobic precursor
345 transformation may have occurred prior to MSW sampling and reactor loading as described previously.
346 Additionally, 6:2 FTCA may have found a place in commercial applications as an alternative to PFOA
347 based processing aids.⁴⁷ The 4:2, 8:2, and 10:2 FTCAs and FTUCAs, as well as 3:3 and 9:3 FTCAs, were
348 largely not detected in reactor leachate and never appeared above their respective LOQs.

349 The 5:3 FTCA concentrations remained constant initially and then increased with 6:2 FTCA after
350 the onset of methanogenesis in Biotic reactors (Figures 6 and S9). The 6:2 FTUCA (Figure S8f) was
351 detected less frequently in reactors and was highest in concentration at latter time points when 6:2 and
352 5:3 FTCA concentrations were greatest. As anaerobic degradation products of 6:2 FTOH, the greater
353 abundance of 6:2 and 5:3 FTCA relative to 6:2 FTUCA and PFHxA is consistent with the corresponding
354 molar yields reported by Zhang et al. (2013).²⁴ The 6:2 and 6/8:2 DiPAPs measured in reactor leachate
355 are potential FTCA precursors but could only account for less than 20% of FTCAs formed on a molar
356 basis, indicating the presence of other precursors unmeasured in reactor leachate. By day 273, 5:3 FTCA

357 became the single most concentrated PFAS in Biotic 1 and 2 (14,000 and 5400 pmol/kg, respectively)
358 and is indicative of significant, unidentified sources of 6:2 fluorotelomer precursors. The disparity
359 between final 5:3 concentrations in Biotic 1 and 2 is potentially a result of the delayed microbial activity
360 in Biotic 2 relative to Biotic 1 (Figures 1 and S2) which began and ended later than Biotic 1 by
361 approximately 40 and 100 days respectively (as indicated by methane production). Had Biotic 2 been
362 operated longer, 5:3 FTCA concentrations may have increased in Biotic 2 to a similar magnitude. Indeed,
363 production stalled temporarily in Biotic 1 from day 90 to 133 (Figure 6a) similarly to days 202 to 273 in
364 Biotic 2 (Figure S9).

365 Similar to 5:3 FTCA, 7:3 FTCA ($\tau_b = 0.80$, $p = 1 \times 10^{-8}$, $df = 25$) increased steadily in concentration in
366 Biotic 1 and 2 respectively, but remained below detection limits in Abiotic reactors (Figure S8e).
367 MeFBSAA (Figure S8d) also had a strong positive correlation with 5:3 FTCA, $\tau_b = 0.85$ ($p = 6 \times 10^{-5}$, $df = 11$),
368 but only in Biotic 1 (no significant correlation in Biotic 2) indicating that 7:3 FTCA and MeFBSAA
369 increases resulted from similar processes, namely methanogenic biotransformations.

370 **Reactor and landfill leachate composition comparison.** The summed PFAS class concentrations
371 were generally of low abundance in reactor leachate relative to landfill leachate, which was not
372 surprising as reactors contained a higher leachate volume relative to mass of MSW than some landfills.
373 Therefore the summed molar composition of PFAS classes (% of total) were used to better compare
374 Biotic reactor and landfill leachate from six U.S. landfills previously analyzed for the same compounds
375 (Table 1).¹⁵ In general, the median and ranges of PFAS class compositions in reactors were comparable to
376 those of U.S. landfill leachate samples, with only two exceptions; DiPAPs and DiSAmPAP had greater
377 relative abundances in Biotic reactors than landfill leachate, but by the end of reactor operation, both of
378 these classes had decreased substantially in concentration and more closely resembled the composition
379 of mature landfill leachate. Because both anaerobic biodegradation (Figure 1) and PFAS class

380 composition (Table 1) compare well with landfill conditions, the phenomena and factors impacting PFAS
381 concentrations in reactors represent an important insight into the processes occurring in landfills.

382 **Environmental Implications, Limitations, and Future Research.** The study of MSW
383 biodegradation in lab-scale reactors elucidated the combined effects of multiple factors that contribute
384 to PFAS concentrations in landfill leachate including abiotic leaching, pH, substrate (e.g., paper) as well
385 as precursor biodegradation, and sorption. PFCAs and PFSAAs demonstrated chain-length specific
386 behavior, where abiotic leaching accounted for the temporal trends of short chain-length
387 concentrations but long-chain homologues increased in concentration concurrent with the onset of
388 methanogenesis. DiPAPs and DiSAmPAP also increased in concentration in Biotic reactors and are
389 susceptible to biodegradation, which would explain their subsequent decrease in the Biotic reactor
390 concentrations and their relative absence from full-scale landfills. The anaerobic degradation of
391 fluorotelomer based compounds leads to the most dramatic differences between Biotic and Abiotic
392 reactors as evidenced by the increases measured in saturated and unsaturated FTCAAs. The 6:2 and 5:3
393 FTCAAs were the two most concentrated PFASs, measured at 4700 and 14000 pmol/kg, respectively
394 (Biotic 1). The abundance of FTCAAs is significant given reports that they are several orders of magnitude
395 more toxic to freshwater organisms than PFCAs.⁴⁸ To the extent that studies of MSW systems fail to
396 include FTCA analysis, the results may significantly underestimate the PFAS load and toxicity.
397 Additionally, as reactor gas was not analyzed for fluorinated compounds (e.g., fluorotelomer alcohols),
398 no inference can be made as to the degree to which volatile fluorotelomers are released from MSW and,
399 thus, remains a question for future research. Ultimately, landfills are likely to act as long-term sources of
400 PFASs to the environment and additional studies of PFAS behavior and biodegradation under anaerobic
401 conditions are needed.

402 On-going research includes estimating PFAS release from landfills using a mechanistic approach
403 that considers the manner in which landfills are operated. Specifically, data for PFASs in leachate from

404 45 landfill cells located in multiple climate zones in the U.S. are being analyzed as a function of waste
405 age and operational strategy. The PFAS concentrations in leachate will be combined with independent
406 estimates of leachate flow to estimate the mass of PFASs released from landfills in the U.S.

407 **ACKNOWLEDGEMENTS**

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411 **SUPPORTING INFORMATION AVAILABLE**

412 Supporting Information contains additional information regarding reactor setup and operation
413 as well as reactor PFAS data not displayed here. This information is available free of charge via the
414 Internet at <http://pubs.acs.org>.

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540 **Table 1:** PFAS percent composition in biologically-active reactors (Biotic 1 and 2) and U.S. landfill
 541 leachate (n=6) by compound class. Landfill leachate PFAS data summarized from Allred et al. (2014).¹⁵

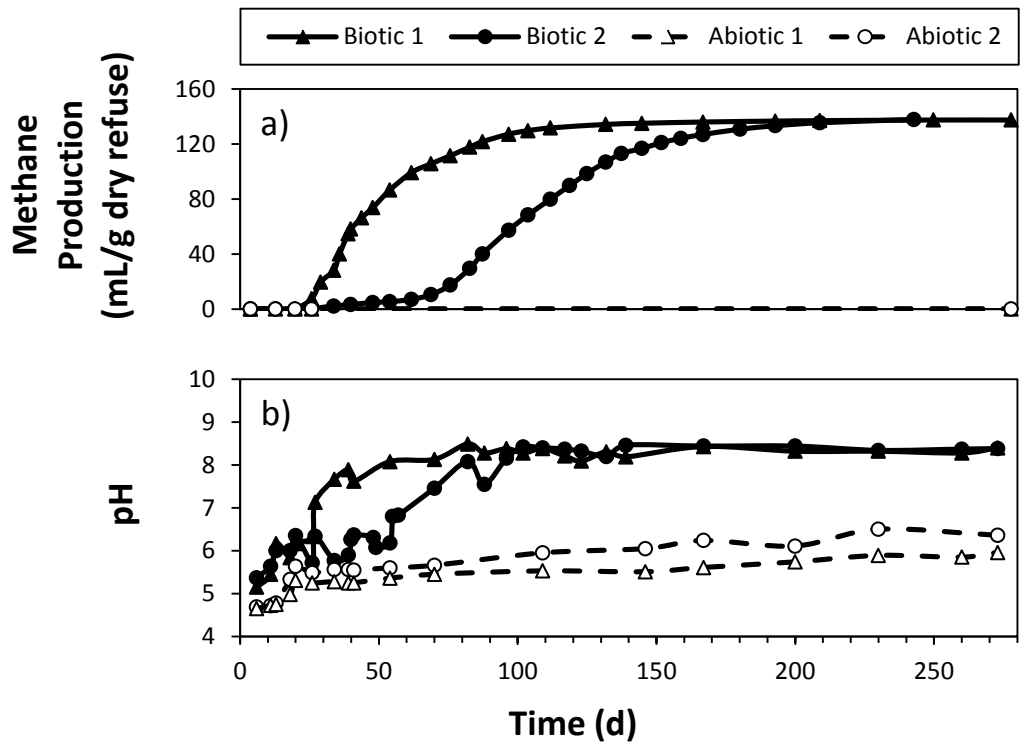
PFAS Class Molar Contributions (%)				
PFAS Class	Biotic Reactors		Landfill	
	Median	(Min-Max)	Median	(Min-Max)
PFSA	4.3	(1.3-16)	5.2	(2.5-8.5)
n:2 FTSA	0.6	(ND-1.8)	1.0	(0.3-1.6)
PFCA	50	(15-84)	45	(20-88)
PFPIA	ND	(ND-ND)	ND	(ND-<LOQ)
DiPAP	4.7	(0.3-17)	0.1	(ND-0.2)
FTMAP	ND	(ND-ND)	ND	(ND-<LOQ)
DiSAmPAP	0.2	(ND-0.8)	0.03	(ND-0.03)
FASAA	ND	(ND-ND)	0.1	(ND-0.4)
MeFASAA	1	(ND-4.3)	7.4	(3.0-8.8)
EtFASAA	0.3	(ND-1.3)	0.5	(0.1-1.5)
n:2 FTCA	6.6	(ND-25)	3.1	(0.1-43)
n:2 FTUCA	ND	(ND-8.8)	0.04	(ND-0.2)
n:3 FTCA	26	(4.0-60)	29	(2.3-44)

542 *Not detected (ND), less than the limit of quantification (<LOQ), Biotic Reactor median is the averaged
 543 median of Biotic 1 and 2.

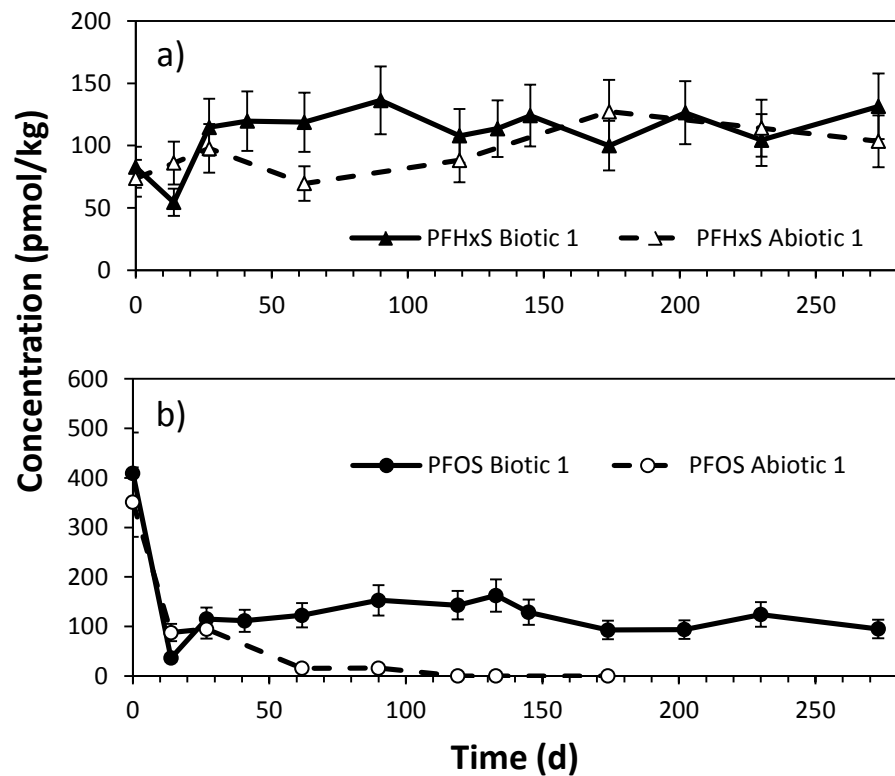
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545 **Figure 1:** Cumulative methane production (a) and pH (b) in Biotic and Abiotic reactors.

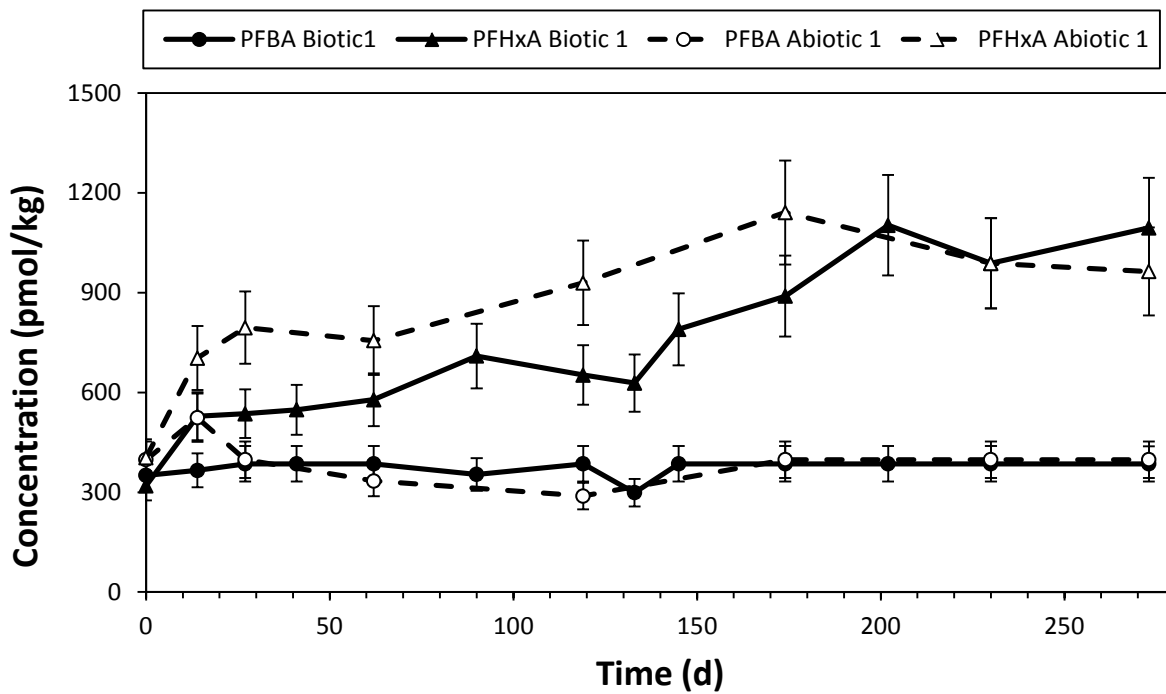
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547 **Figure 2:** Concentrations for PFHxS (a) and PFOS (b) in Biotic 1 and Abiotic 1 reactor leachate. Error bars
548 for some points are too small to be seen in plot 2b. Error bars plotted for PFOS and PFHxS represent the
549 RSD of duplicate reactor sample analysis; RSDs did not exceed 20%
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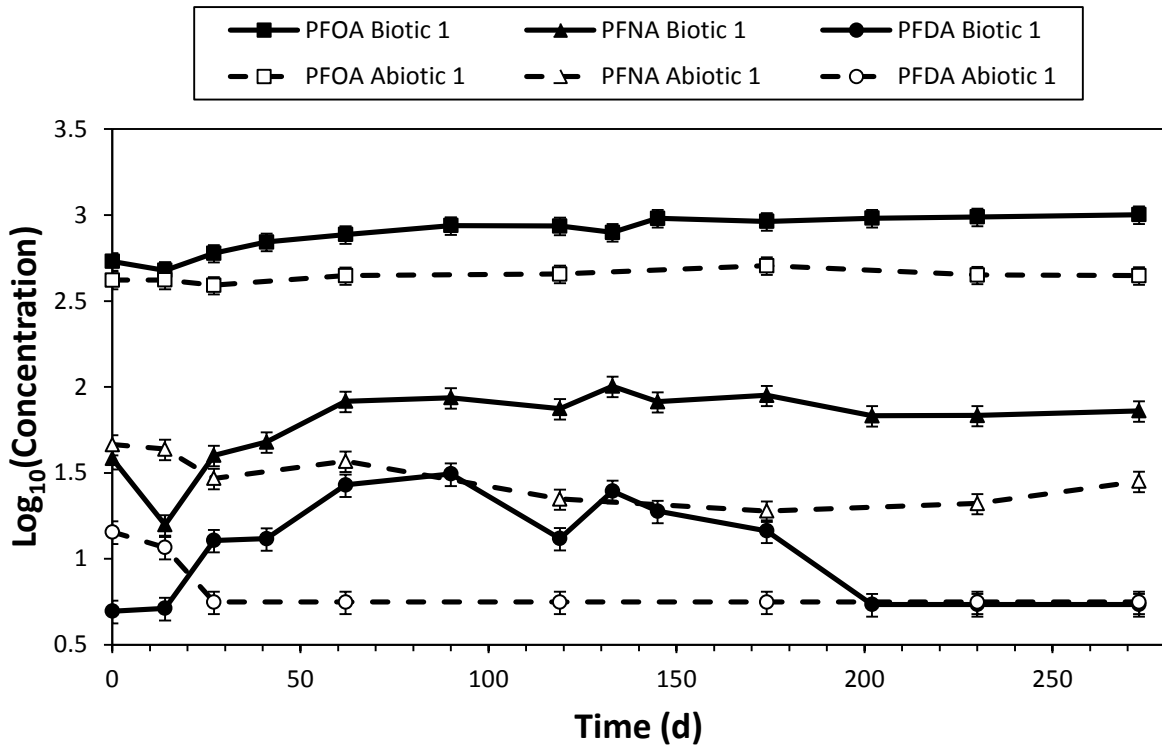
551 **Figure 3:** Concentrations of PFBA and PFHxA (short-chain PFCAs) in Biotic 1 and Abiotic 1 reactor
552 leachate. Concentrations less than or equal to the limit of quantification (\leq LOQ) are plotted graphically
553 as $\frac{1}{2}$ the calculated LOQ. Error bars represent the inter- and intraday analytical variability (RSD).¹⁵



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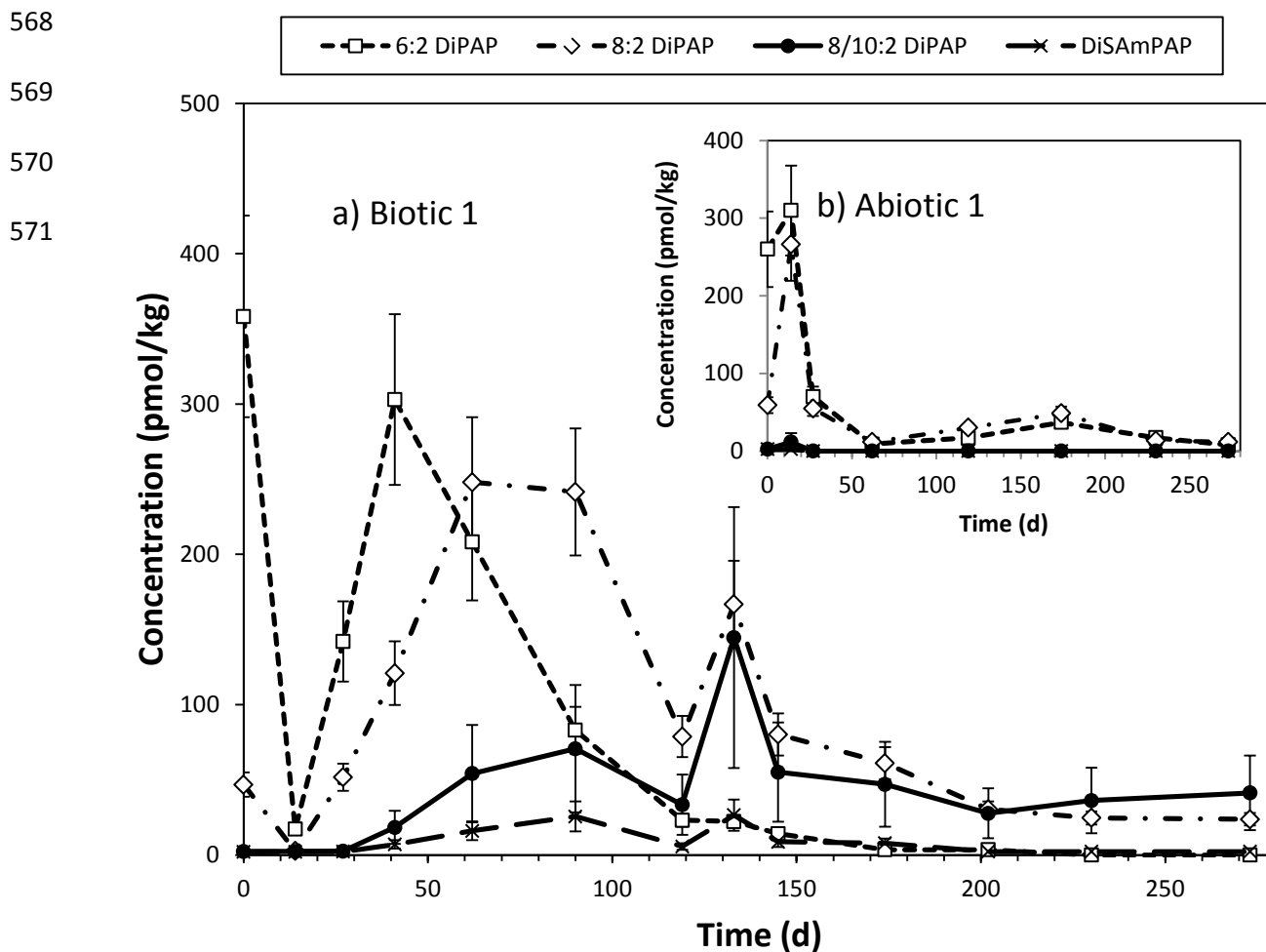
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556 **Figure 4:** Temporal trends for long-chain PFCAs including PFOA, PFNA, and PFDA in Biotic 1 and Abiotic 1
 557 reactor leachate. The \log_{10} of concentrations were used (e.g. $\log_{10}(540 \text{ pmol/kg}) = 2.73$) to include
 558 multiple PFCAs without obscuring analyte trends. Concentrations less than or equal to the limit of
 559 quantification ($\leq \text{LOQ}$) are plotted graphically as \log_{10} of $\frac{1}{2}$ the calculated LOQ. Error bars represent the
 560 inter- and intraday analytical variability (RSD).¹⁵

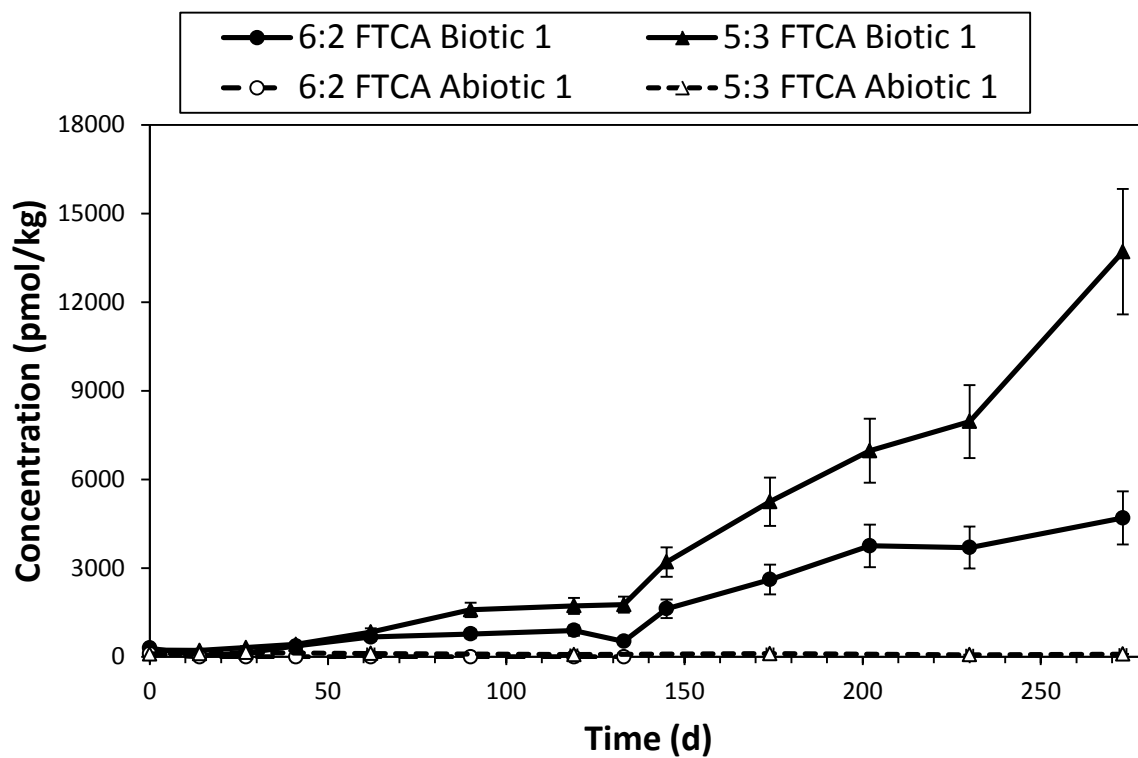


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565 **Figure 5:** Concentrations of 6:2, 8:2, 8/10:2 DiPAP (8:2 and 10:2 alkyl groups, Table S1) and DiSAmPAP in
566 Biotic 1 (a) and Abiotic 1 (b) reactor leachate. Error bars represent the inter- and intraday analytical
567 variability (RSD).¹⁵



572 **Figure 6:** Concentrations of 6:2 and 5:3 FTCA in Biotic 1 and Abiotic 1 reactor leachates. Error bars
573 represent the inter- and intraday analytical variability (RSD).¹⁵



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