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

Supporting Information

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Testing for background contamination in reactor materials. Reactors were tested for background poly- and perfluorinated alkyl substances (PFASs) by exposing fully constructed reactors (but no MSW) to deionized water and synthetic leachate matrices that modeled leachate compositions typical of the acid and methane phases of landfill degradation. The acid-phase matrix contained acetic, propionic and butyric acid at 11.8, 1.3, and 11.28 g/L, respectively. The methane-phase matrix contained 4.01 g/L of humic acids in addition to acetic, propionic, and butyric acid at 0.37, 0.185, and 0.185 g/L, respectively. The three reactors containing deionized water, synthetic acid phase or methane phase leachate, were operated for 90 days. Leachate samples were taken periodically over 90 days and initially analyzed for perfluorinated carboxylic (PFCAs) and sulfonic acids (PFSAs). Leachate from each of the three reactors taken on day 30 was also analyzed for the other 11 PFAS classes measured in refuse-filled reactors besides PFCAs and PFSAs. Observed PFAS concentrations were limited to C6-8 PFCAs that fell below the limit of quantification whenever detected with the intermittent exception of PFOS at low concentrations. The cumulative PFOS concentration potentially contaminating reactor leachate was subtracted from future reactor leachate concentration measurements. The reactor housing materials were determined therefore to largely not contribute significantly to PFAS concentrations in reactor leachate.

The laser print paper replaced laboratory filter paper for anaerobic microbial culture growth when some PFASs were detected using a methanol solid-liquid extraction adapted from Begley et al. (2005).[1] The anaerobic microbial culture used to inoculate refuse-filled reactors was subsequently extracted, using the micro liquid-liquid extraction[2] applied to all aqueous samples, and tested for PFASs. The C6-8 PFCAs and n-methyl perfluorooctane sulfonamido acetic acid were detected, but were below their respective limits of quantification. Relative to actual reactor leachate concentrations the microbial culture is not considered a significant source of PFASs to reactor leachate.

Antimicrobial selection. Several known anti-microbial compounds were tested to find the optimal compounds that inhibited microbial activity in the laboratory scale reactors while resulting in little to no interference with PFAS measurements by LC/MS/MS. Tested compounds were selected based on prior documentation of microbial inhibition, including silver nitrate, sodium chloride (NaCl), sodium 2-bromoethanesulfonate **(**BES), penicillin, streptomycin, and DBNPA. To test the ability of each compound to inhibit biological activity, two sets of refuse reactors were constructed and operated. For the first set of reactors, a mixture of all the compounds listed above, except for DBNPA, was added to one reactor with a refuse only control. For the second set of reactors, 40 g/L of NaCl was added to one reactor with a refuse only control. These laboratory scale reactors were operated for >3 months at 37°C to assess the long term effectiveness of these biological inhibitors on methanogenic degradation of refuse. The absence of significant methane production in reactors treated with the inhibition mixture indicates successful suppression of anaerobic biological activity. While initially the biological refuse plus NaCl reactor seemed to be suppressed relative to the control, methane production started to increase after 50 day, indicating that anaerobic microbes became acclimatized to the high salt conditions.

DBNPA was not included in the original compound assessment and was only tested for microbial inhibition in serum bottles not reactors due to time limitations. DBNPA was successful at inhibiting methane production in serum bottles. When DBNPA was added to the synthetic leachate at room temperature, the compound was visibly undissolved in the bottom of the flask. The first set of refuse reactors was started using the undissolved DBNPA in the abiotic reactors, but the compound was not sufficient in inhibiting methane production and all the reactors for this set were taken down and restarted. Research on DBNPA revealed low dissolution at room temperature, but near complete dissolution at 50°C. Synthetic leachate for all subsequent abiotic reactors was heated to 50°C prior to DBNPA addition and methane production was suppressed.

With the exception of streptomycin, signal suppression on the LC/MS/MS system was so high that the mixture of inhibitors and NaCl could not be used (Figure S1). Streptomycin and DBNPA had the least negative impact on analytical method performance, consequently streptomycin and DBNPA were selected to be added to abiotic control reactors.

Micro-Liquid-Liquid Extraction (Micro-LLE) and Liquid Chromatography Tandem Mass spectrometry (LC-MS/MS). Leachate samples were thawed and centrifuged at 1650 g for 10 min prior to moving 3 mL to a new 15 mL centrifuge vial. Mass-labeled internal standards (0.72 ng each) were added and samples were titrated to pH 7–8. The 3 mL sample was then extracted in triplicate by adding 10 % trifluoroethanol (TFE) ethyl acetate (EtOAc), shaking for 30 sec and then centrifuging at 10,000 g (4 °C) for 10 min using a Sorval Evolution RC ultracentrifuge from Thermo Scientific (Waltham, MA). The stronger centrifugal forces were needed to break the emulsions formed when shaken. Subsequently 333 µl of the organic extract in the top layer were collected in a 2 mL polypropylene autosampler vial. The extraction was repeated with two additional aliquots of 10% TFE in EtOAc such that a total extract volume of 1 mL is collected and 200 µl of methanol was added prior to LC-MS/MS analysis. A total 900 µl of extract was injected onto two zirconium modified diol guard cartridges under high aqueous conditions. A concave methanol and ammonium acetate gradient moved the extracted PFASs off of the diols and onto a reverse-phase C18 column where they were separated and subsequently detected by MS/MS using specific parent and daughter ions for each PFAS.

The LC-MS/MS was calibrated daily ($R^2 > 0.97$) with a standard solution run with each calibration to ensure between-day calibration consistency. Replicate calibration standards were analyzed every 8-10 samples. One sample was analyzed in triplicate per day to verify that precision fell within the prescribed limit measured during analytical method validation.[2] Solvent and method blanks were

analyzed daily. Samples would be reanalyzed for specific PFASs if solvent and method blanks concentrations constituted more than 1% of sample concentrations.

Dilution Factor: In order to compare reactors with varying refuse masses and leachate volumes a dilution factor was calculated to adjust each time course concentration to represent as if it were in the initial leachate volume according to the following equation.

$$DF = \prod_{n=1}^{n} DF_n = \prod_{n=1}^{\infty} \frac{V_0 + \sum_{n=0}^{n} VA_n - \sum_{n=0}^{n-1} VR_n}{V_0 + \sum_{n=0}^{n-1} VA_n - \sum_{n=0}^{n-1} VR_n}$$

$DF =$ dilution factor to normalize concentrations back to original reactor leachate volumes

$n =$ day sampled

$DF_n =$ dilution factor between successive days

$V_0 =$ original reactor leachate volume

$VA_n =$ volume added to reactor

$VR_n =$ volume removed from reactor

In principle, the concentration of PFASs was multiplied by the leachate volume to find the mass analyte, which was then divided by the previous reactor leachate volume. Together the leachate volume divided by the previous volume is the dilution factor (DF_n). Because liquid volumes were taken and added over the course of reactor operation the dilution factor (DF) to convert a given sample's concentration into a version normalized to the initial reactor volume was the product of all dilution factors of each successive volume adjustment ($\prod_{n=1}^{\infty} DF_n$).

135 **Table S1:** Acronyms and structures of PFAS compound classes.

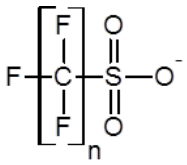
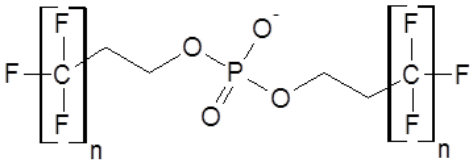
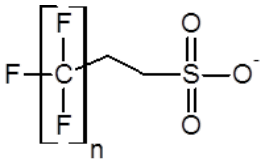
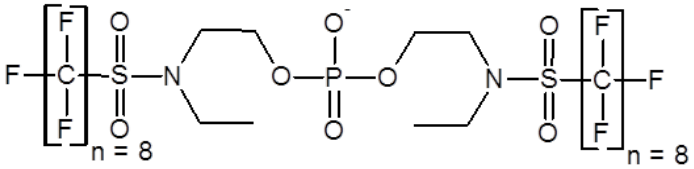
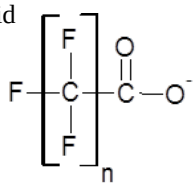
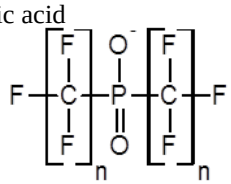
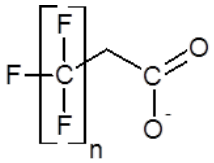
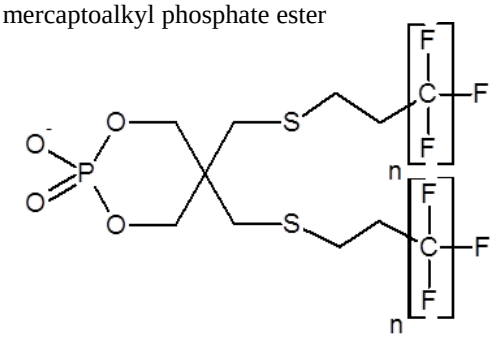
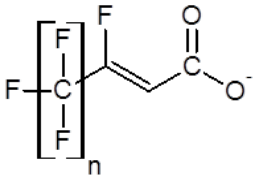
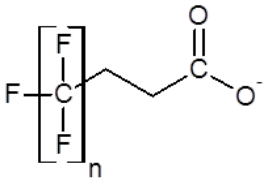
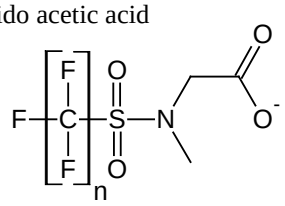
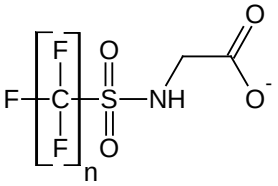
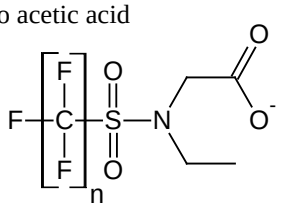
Perfluoroalkyl sulfonic acid PFSA n = 4-10 	Di-substitued polyfluorinated phosphate ester DiPAP n = 4, 6, 8, 10 
Fluorotelomer sulfonic acid n:2 FTSA n = 4, 6, 8 	Bis(N-ethyl perfluoroalkylsulfonamidoethane) phosphate DiSAmPAP n = 8 
Perfluoroalkyl carboxylic acid PFCAs n = 3-17 	Disubstitued perfluoroalkyl phosphinic acid PFPIA n = 4, 6, 8 
Fluorotelomer carboxylic acid n:2 FTCA n = 4, 6, 8, 10 	Fluorotelomer mercaptoalkyl phosphate ester FTMAP n = 4, 6, 8, 10 
Fluorotelomer unsaturated carboxylic acid n:2 FTUCAs n = 4, 6, 8, 10 	
Fluorotelomer propanoic acid n:3 FTCA n = 3, 5, 7, 9 	N-methyl fluoroalkyl sulfonamido acetic acid MeFASAA n = 4-8 
Fluoroalkyl sulfonamido acetic acid FASAA n = 4-8 	N-ethyl fluoroalkyl sulfonamido acetic acid EtFASAA n = 4-8 

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Figure S1: Impact of microbial inhibitors on select PFASs as indicated by whole method recovery.

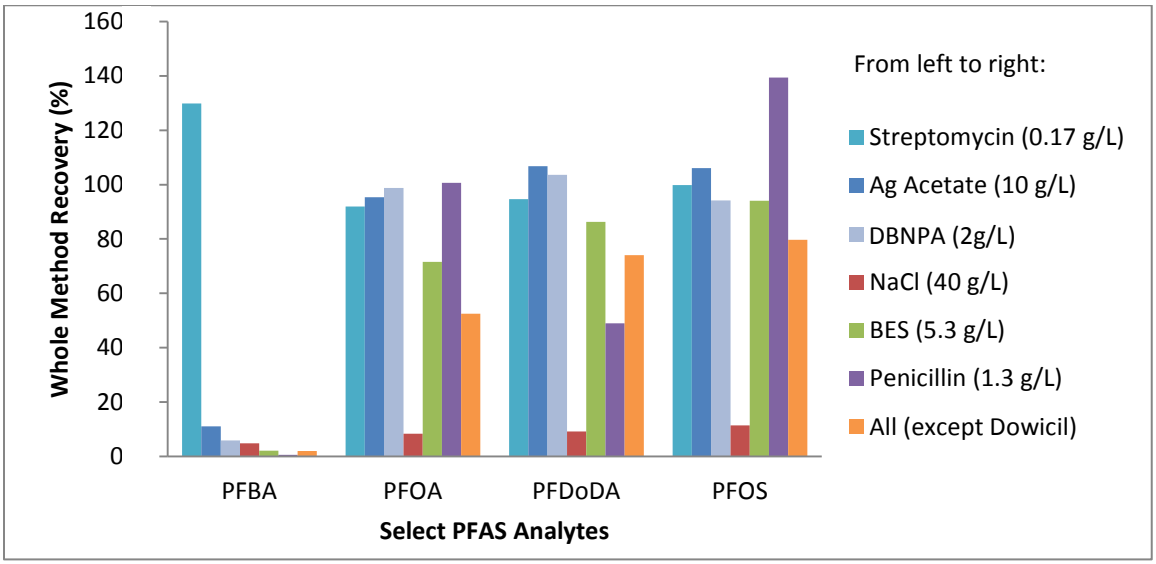


Figure S2: Chemical oxygen demand in Biotic and Abiotic reactors.

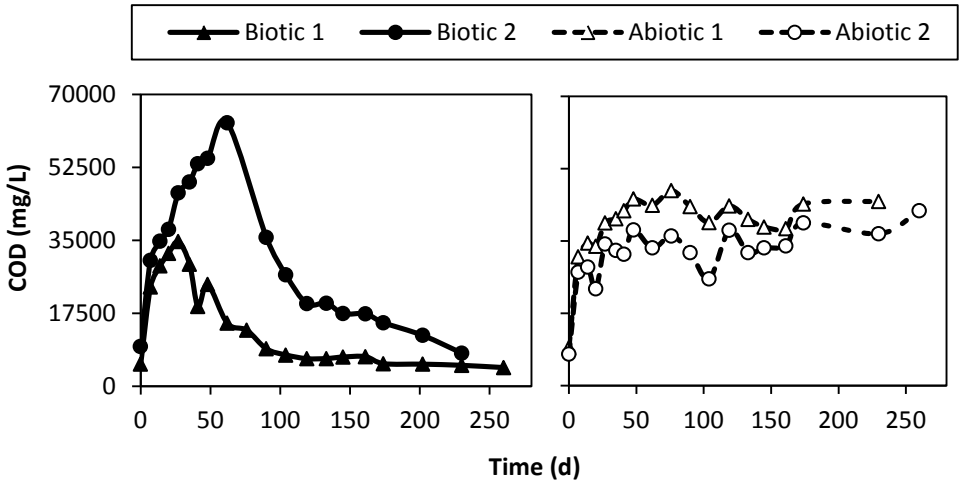


Figure S3: Select PFAS concentrations in Biotic and Abiotic reactors 1 and 2. Note Y axis scales for each panel differ significantly. Error bars represent the analytical variability (RSD) and variability between sample duplicates for each analyte.

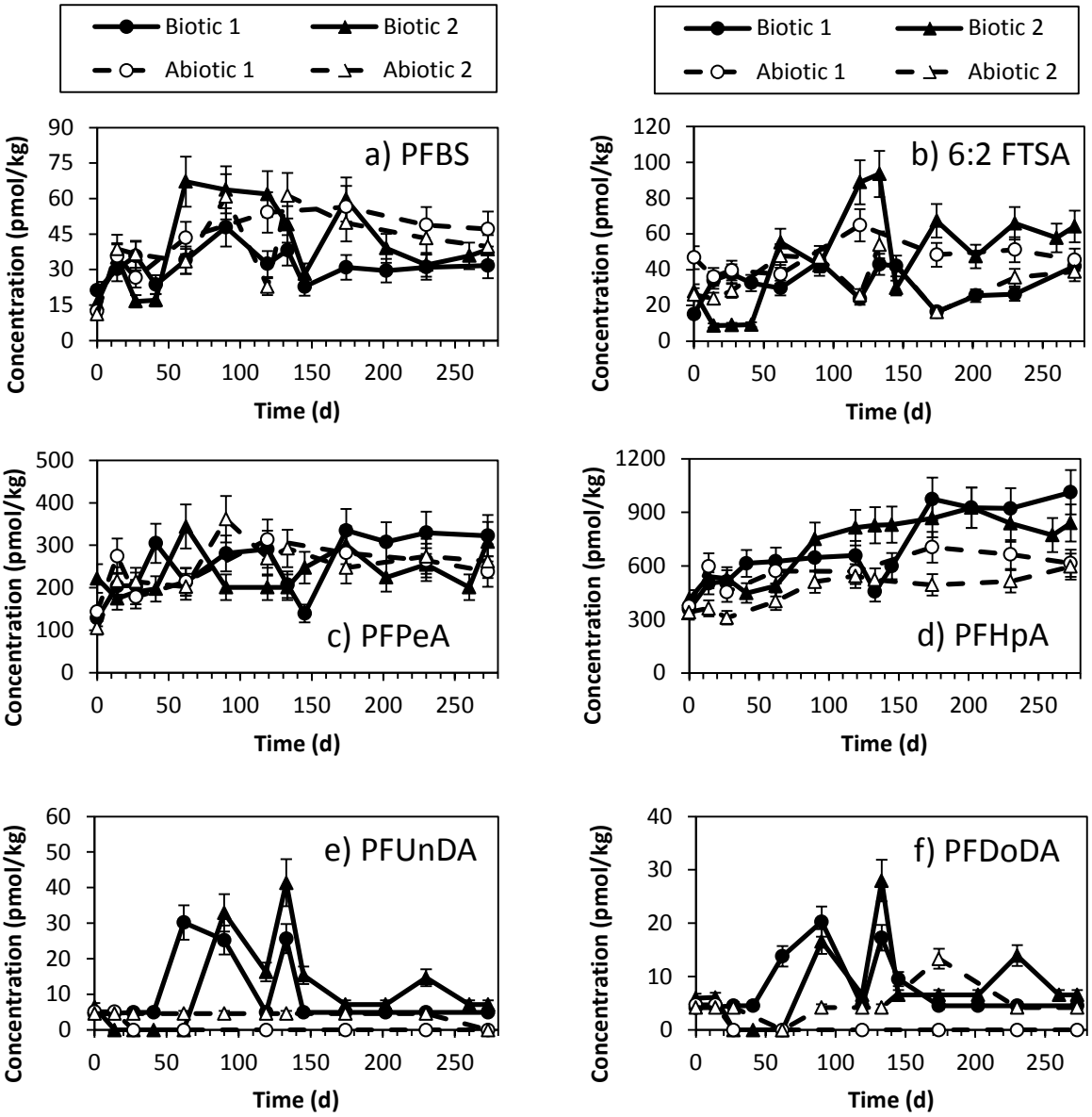


Figure S4: Time course trends of PFHxS (a) and PFOS (b) concentrations in Biotic and Abiotic 2 (complimentary to Figure 2 in the main text). Error bars represent the analytical variability (RSD) and variability between sample duplicates for each analyte.

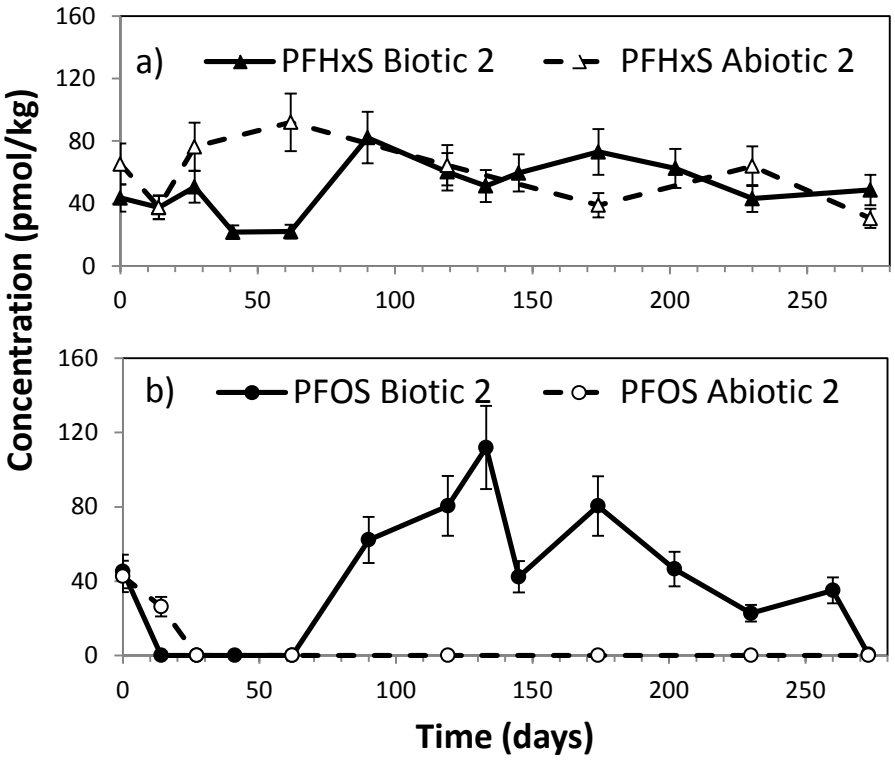


Figure S5: Time course trends for PFBA and PFHxA in Biotic 2 and Abiotic 2 (complimentary to Figure 3 in the main text). Error bars represent the analytical variability (RSD) for each analyte.

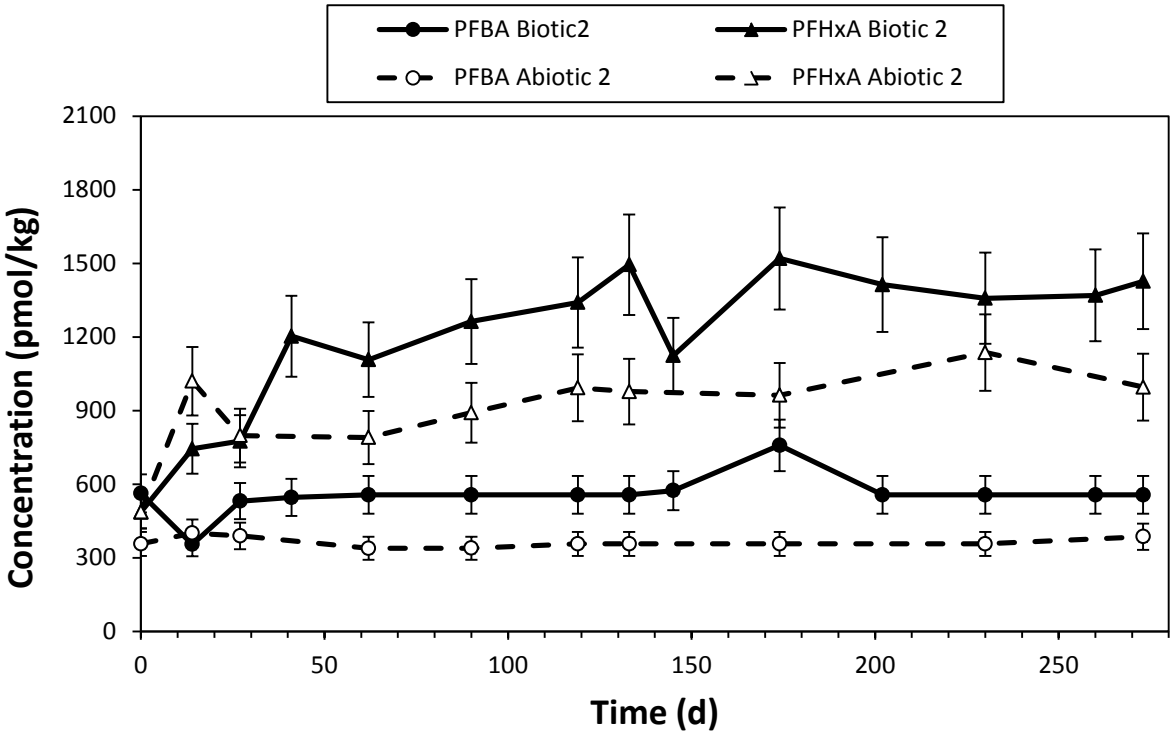


Figure S6: Log10(concentrations) of PFOA, PFNA, and PFDA in Biotic 2 and Abiotic 2. Complimentary to Figure 4 in the main text. Error bars represent the analytical variability (RSD) for each analyte.

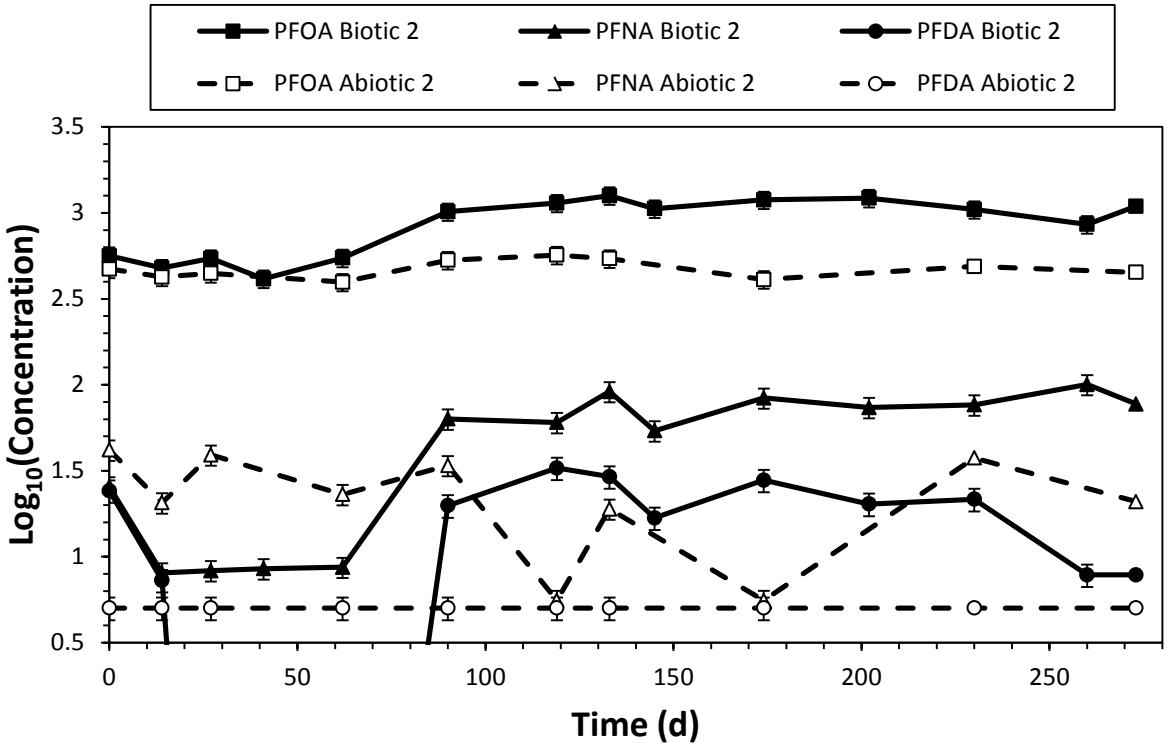


Figure S7: DiPAPs and DiSAmPAP concentrations in Biotic (a) and Abiotic 2 (b), complimentary to Figure 5 in the main text. Error bars represent the analytical variability (RSD) for each analyte.

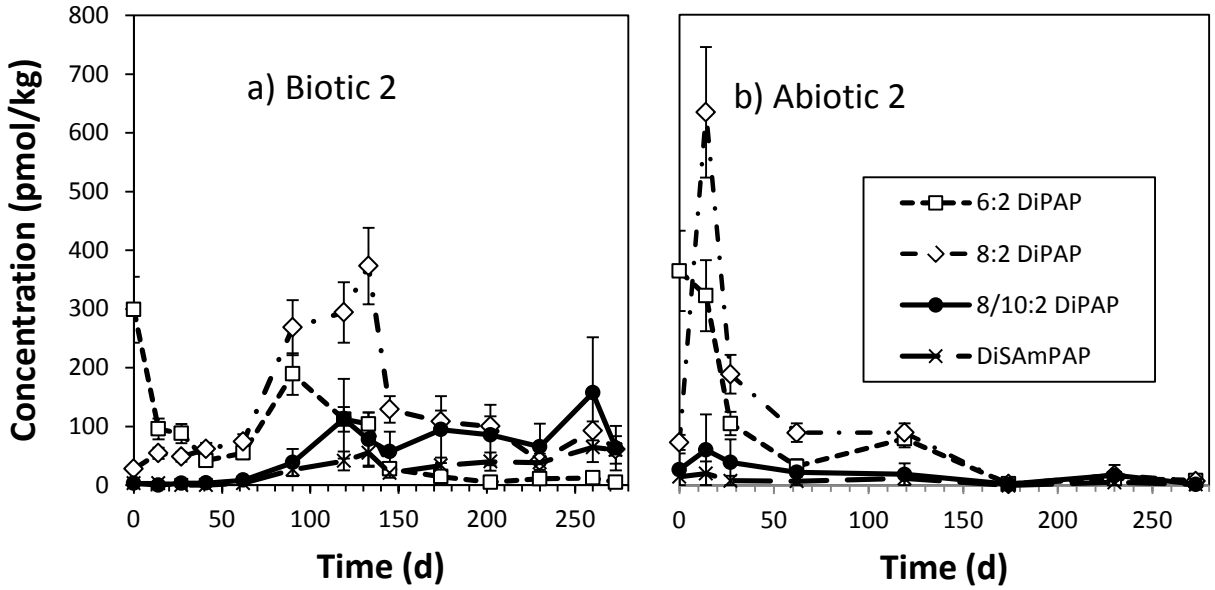


Figure S8: Select PFAS concentrations in Biotic and Abiotic reactors 1 and 2. Note Y axis scales for each panel differ significantly. Error bars represent the analytical variability (RSD) and variability between sample duplicates for each analyte.

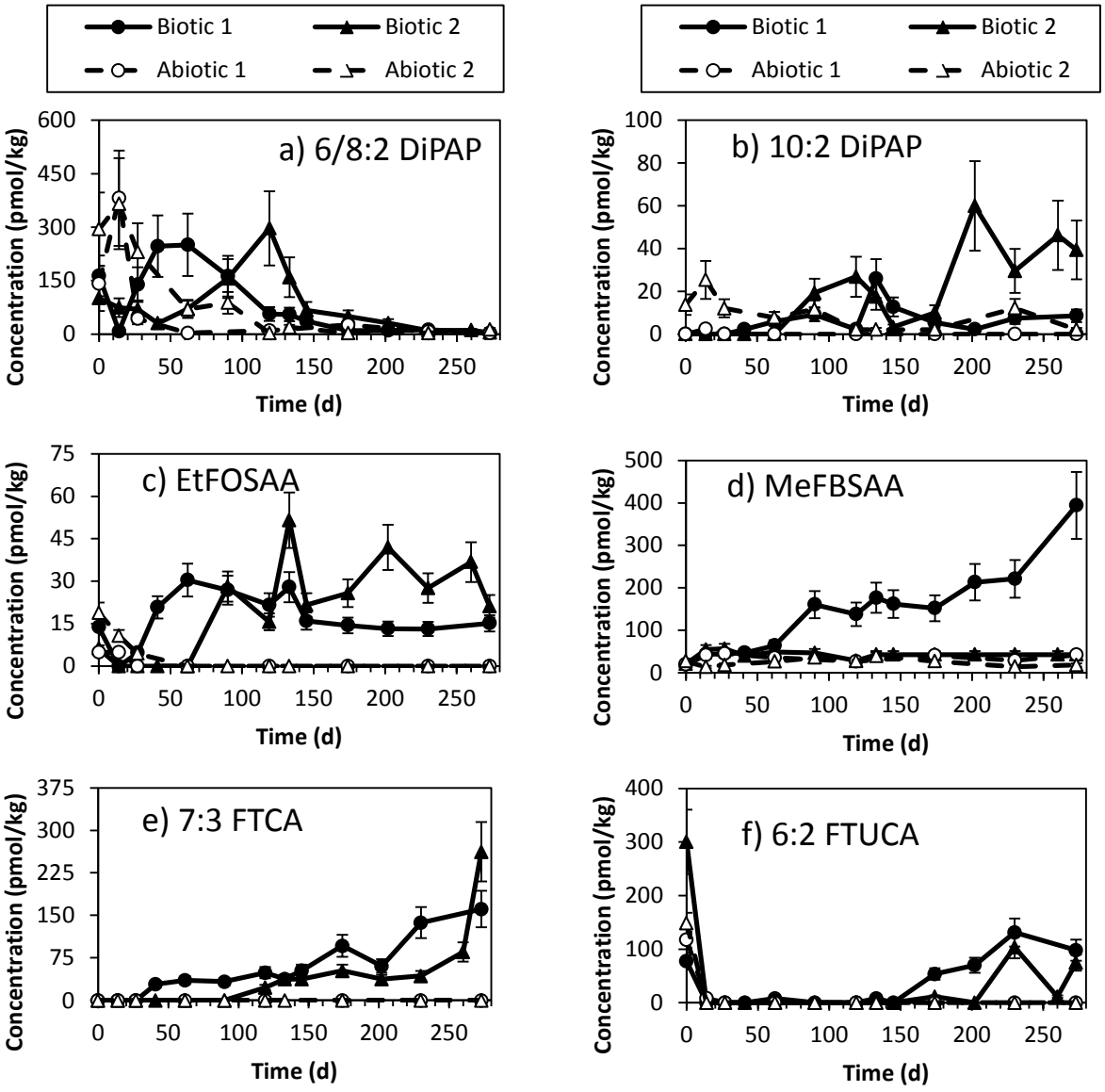
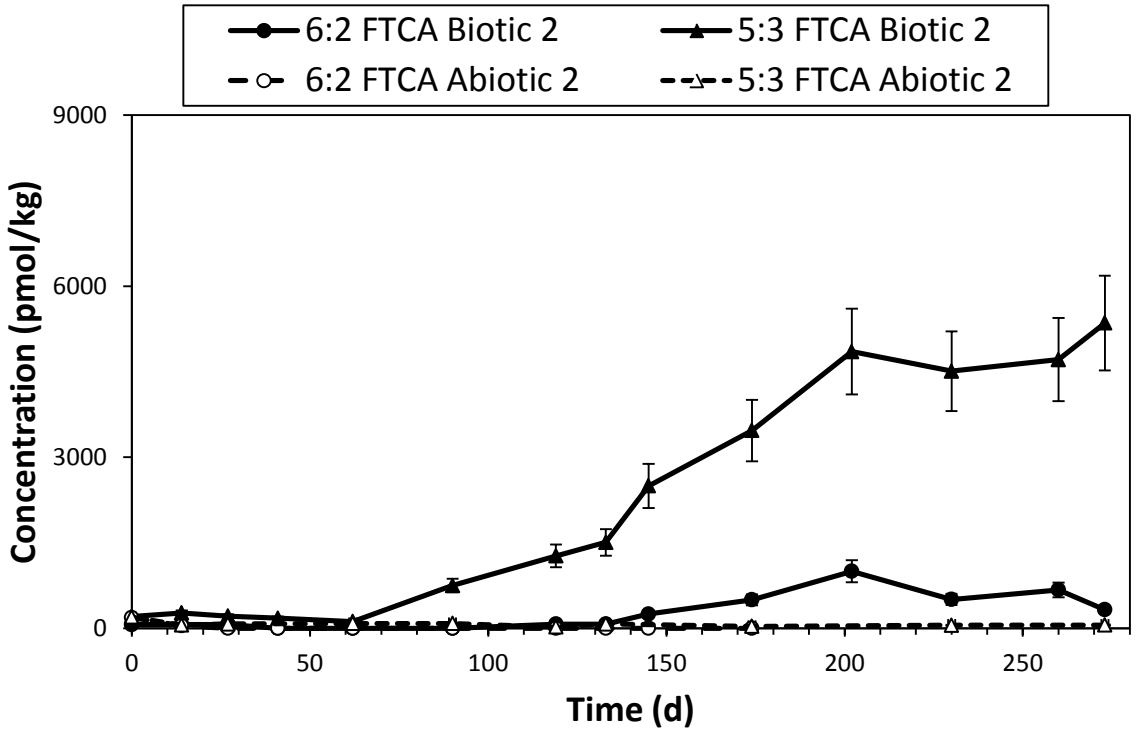


Figure S9: Abiotic 2 and Biotic 2 concentrations of 6:2 and 5:3 FTCA. Error bars represent the analytical variability (RSD) for each analyte.



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1. Begley, T. H.; White, K.; Honigfort, P.; Twaroski, M. L.; Neches, R.; Walker, R. A., Perfluorochemicals: Potential sources of and migration from food packaging. *Food Addit. Contam.* **2005,** *22*, (10), 1023-1031.
2. 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.