State University System of Florida
Hinkley Center for Solid and Hazardous Waste Management

PROGRESS REPORT 4

January 16, 2024

TITLE: PFAS in e-waste: Occurrence, types, and estimated quantities of PFAS in e-waste and appropriate management strategies for PFAS containing e-waste components

COMPLETION DATE: March 31, 2024 (new completion date)

Project was extended.

PRINCIPAL INVESTIGATORS:

- Berrin Tansel, Ph.D., P.E., Professor, Civil and Environmental Engineering Department, Florida International University
- Yelena Katsenovich, Senior Research Scientist, Applied Research Center (ARC), Florida International University
- Natalia Soares Quinete, Assistant Professor, Environmental and Bioanalytical Chemistry, Florida International University

During the first quarter of this project, the following activities have been performed:

During this initial period, the following activities have been performed:

1. Preparation of e-waste samples
    - Shredding of parts appropriate for analyses
    - Leaching experiments

Selected e-waste components will be separated from the following units (examples):

Keyboards
CPU monitors
CPUs
Display units
Printed wiring boards
Data storage systems

2. Refined test methods

Preprocessing needs:

Disassembly → separating → sorting → shredding → grinding → sieving

Test plans and methods for leaching experiments, PFAS analyses (expanded for 40 PFAS compounds), and biosolids characterization for (TS, organic content, and protein) have been finalized. Test standards have been received. Test steps have been optimized.

3. PFAS leaching experiments (Dr. Katsenovich)
   One undergraduate student, Zariah Nasir, continued working with Dr. Katsenovich.

   - Developing leaching procedures for e-waste experiments to evaluate the release of PFAS from e-waste under site-specific conditions.

4. Sample preparation

   Suitability of 8530 ShatterBox® ring and puck mill is being tested for grinding different e-waste components (after shredding and crushing).

Fig. 1. 8530 ShatterBox® ring and puck mill

2. E-waste leachate PFAS analyses (Dr. Quinete)

One undergraduate student, Maria Mendoza Manzano, and one graduate student, Joshua Ocheje, in the Ph.D. program in the Chemistry and Biochemistry department are working with Dr. Quinete.

- Assessment of PFAS content and component profile in e-waste leachate.

Procedures for e-waste leachate sample preparation are the same as for biosolids leachate.

Sample preparation/extraction steps: To avoid cross-contamination, all containers, bottles and tubing used during extraction and sample preparation are rinsed twice with solvents of different polarities: methylene chloride, hexane, acetone, methanol. All the solvents used in this analysis are HPLC grade and previously evaluated for potential PFAS contamination. Leachate samples were processed through solid phase extraction (SPE) using Strata-XL AW (500 mg/3 mL) cartridges on a semi-automated SPE equipment for extraction and preconcentration of PFAS (Figure 2) . In short, cartridges were successively pre-conditioned with 12 mL of 0.3% ammonia (NH_4) in methanol, 12 mL of methanol and equilibrated with 5 mL of water, before loading of 45 mL biosolid leachate sample spiked with 50 µL of the labeled extraction standard (MPFAC-HIF-ES) mixture (2.5 ng mL^{-1}). Samples are loaded (Figure 2A) into the cartridges under vacuum and after all has passed, cartridges are left to dry for about 1-2 hours. In the second stage (Figure 2B), cartridges are eluted with 10 mL of 0.3% NH_4 in methanol, which is further evaporated to dryness under a gentle nitrogen flow in a heated water bath at 40 °C (Figure 3), then reconstituted to a 450 µL volume with 95:5% (vol/vol) 2mM ammonium formate/methanol. Reconstituted samples are transferred into LC polypropylene vials and 50 µL of 2.5 ng mL^{-1} labeled internal standard mixture (MPFAC-HIF-IS) are added before injection. Samples are kept refrigerated until LC-MS/MS analysis.
For quality control purposes, blanks, spiked blanks, and duplicate analysis are processed for each experiment through the same procedure as the samples. Blank samples consist of 45 mL LC-MS grade water spiked with the labeled extraction standard (MPFAC-HIF-ES) mixture (2.5 ng mL^{-1}), while spiked blanks are prepared with 45 mL LC-MS grade water spiked with 250 µL of 2.5 ng mL^{-1} of native standard mixture (containing 40 PFAS from PFAC-MXF, PFAC-MXG, PFAC-MXH, PFAC-MXI and PFAC-MXJ) and 50 µL the labeled extraction standard (MPFAC-HIF-ES) mixture (2.5 ng mL^{-1}). List of PFAS being analyzed is shown in Table 1.

Sample analysis: After SPE, 100 µL of samples were injected and analyzed by an Agilent 1290 Infinity II LC interfaced to an Agilent 6470 triple quadrupole LC-MS/MS system equipped with Agilent Jet Stream electrospray ionization (ESI) source in negative mode. The LC system was modified with PFAS free tubing and a delay column (Hypersil GOLD aQ C18, 20 × 2.1 mm, 12 µm) was placed

between the mobile phase mixer and the sample injector. A Hypersil GOLD pentafluorophenyl (PFP) column (150 mm × 2.1 mm, 3 µm) with a PFP guard column (Hypersil Gold PFP 5 µm drop-in guards) was used as analytical column for PFAS separation and maintained at a temperature of 50 °C using 95:5 2mM ammonium acetate:methanol and methanol as mobile phases in a flow rate of 0.4 mL/min. Sample acquisition are performed using a multiple-reaction monitoring (MRM) method in negative mode for the simultaneous quantification of multiple PFAS, which included when available two transitions per compound for quantitative and identification (qualitative) purposes.

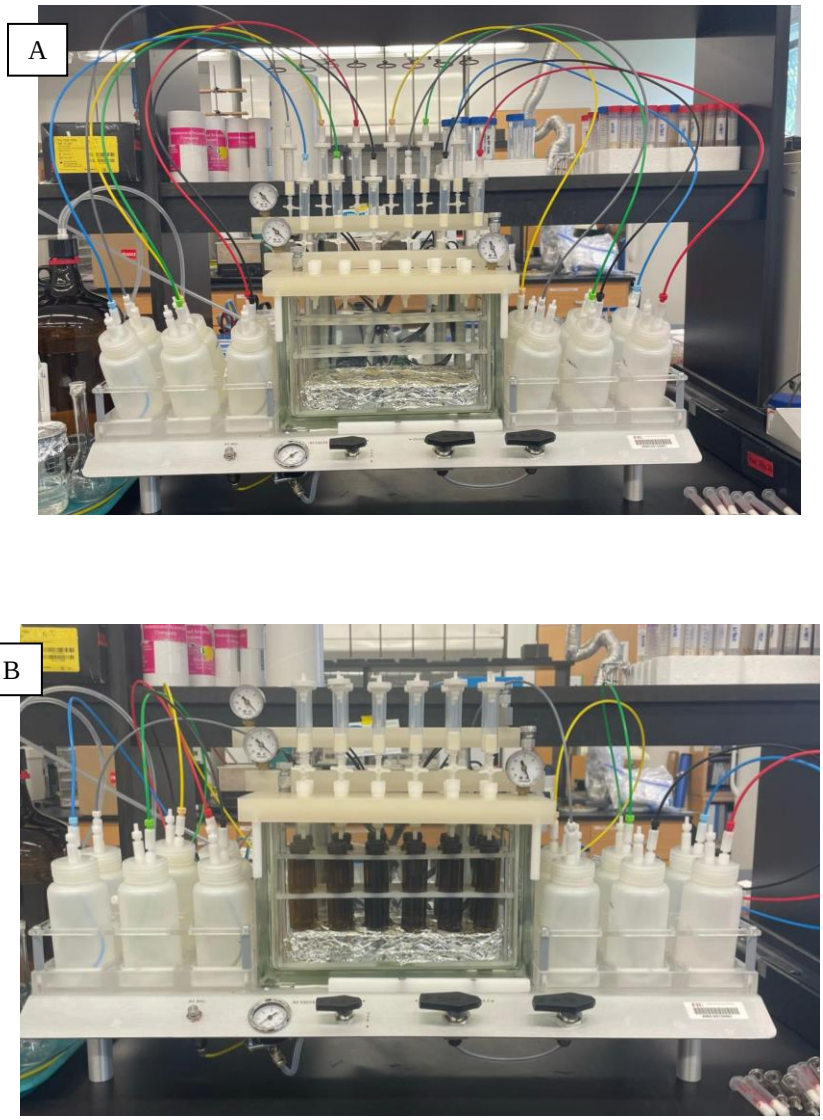

Figure 2: Semi-automated SPE equipment showing (A) stage 1- leachate samples being loaded in the cartridges and (B) stage 2- samples being eluted into 60 mL glass amber vials.

Figure 3: Nitrogen evaporation of the leachate samples after elution

Table 1. List of analyzed PFAS.

Abbreviation	Compound Name	Molecular Formula	Molecular Weight
Perfluoroalkyl carboxylic acids			
PFBA	Perfluorobutanoic acid	$C_4HF_7O_2$	214.04
PFPeA	Perfluoropentanoic acid	$C_5HF_9O_2$	264.05
PFHxA	Perfluorohexanoic acid	$C_6HF_{11}O_2$	314.05
PFHpA	Perfluoroheptanoic acid	$C_7HF_{13}O_2$	364.06
PFOA	Perfluorooctanoic acid	$C_8HF_{15}O_2$	414.07
PFNA	Perfluorononanoic acid	$C_9HF_{17}O_2$	464.08
PFDA	Perfluorodecanoic acid	$C_{10}HF_{19}O_2$	514.08
PFUdA	Perfluoroundecanoic acid	$C_{11}HF_{21}O_2$	564.09
PFDoA	Perfluorododecanoic acid	$C_{12}HF_{23}O_2$	614.10
PFTrDA	Perfluorotridecanoic acid	$C_{13}HF_{25}O_2$	664.11
PFTeDA	Perfluorotetradecanoic acid	$C_{14}HF_{27}O_2$	714.11
Perfluoroalkyl sulfonic acids			
PFBS	Perfluorobutanesulfonate	$C_4HF_9O_3S$	300.10

PFPeS	Perfluoropentanesulfonate	$C_5HF_{11}O_3S$	350.11
PFHxS	Perfluorohexanesulfonate	$C_6HF_{13}O_3S$	400.11
PFHpS	Perfluoroheptanesulfonate	$C_7HF_{15}O_3S$	450.12
PFOS	Perfluorooctanesulfonate	$C_8HF_{17}O_3S$	500.13
PFNS	Perfluorononanesulfonate	$C_9HF_{19}O_3S$	550.14
PFDS	Perfluorodecanesulfonate	$C_{10}HF_{21}O_3S$	600.14
PFDoS	Perfluorododecanesulfonate	$C_{12}HF_5O_3S$	700.16
Fluorotelomer sulfonic acids			
4-2 FTS	1H,1H,2H,2H-perfluorohexanesulfonate	$C_6H_5F_9O_3S$	328.15
6-2FTS	1H,1H,2H,2H-perfluorooctanesulfonate	$C_8H_5F_{13}O_3S$	428.17
8-2 FTS	1H,1H,2H,2H-perfluorodecanesulfonate	$C_{10}H_5F_{17}O_3S$	528.18
Perfluorooctane sulfonamides			
FOSA	Perfluorooctanesulfonamide	$C_8H_2F_{17}NO_2S$	499.15
NMeFOSA	N-methyl perfluorooctanesulfonamide	$C_9H_4F_{17}NO_2S$	513.17
NEtFOSA	N-ethyl perfluorooctanesulfonamide	$C_{12}H_{10}F_{17}NO_3S$	571.25
Perfluorooctane sulfonamidoacetic acids			
N-MeFOSAA	N-methylperfluoro-1-octanesulfonamidoacetic acid	$C_{11}H_6F_{17}NO_4S$	571.21
N-EtFOSAA	N-ethylperfluoro-1-octanesulfonamidoacetic acid	$C_{12}H_8F_{17}NO_4S$	585.23
Perfluorooctane sulfonamide ethanols			
NMeFOSE	N-methyl perfluorooctanesulfonamidoethanol	$C_{11}H_4F_{21}NO_3S$	629.19
NEtFOSE	N-ethyl perfluorooctanesulfonamidoethanol	$C_{12}H_6F_{21}NO_3S$	643.21
Per- and Polyfluoroether carboxylic acids			
HFPO-DA	2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)-propanoic acid	$C_6HF_{11}O_3$	330.05
ADONA	4,8-Dioxa-3H-perfluorononanoic acid	$C_{10}H_{11}N_4NaO_5S$	322.27
PFMPA	Perfluoro-3-methoxypropanoic acid	$C_4HF_7O_3$	230.04
PFMBA	Perfluoro-4-methoxybutanoic acid	$C_5HF_9O_3$	280.04
NFDHA	Nonafluoro-3,6-dioxaheptanoic acid	$C_5HF_9O_4$	296.04
Ether sulfonic acids			
9Cl-PF3ONS	9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	$C_8HClF_{16}O_4S$	532.58
11Cl-PF3OUdS	11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	$C_{10}HClF_{20}O_4S$	632.60
PFEESA	Perfluoro(2-ethoxyethane)sulfonic acid	$C_4HF_9O_4S$	316.10

Fluorotelomer carboxylic acids			
FPrPA or 3:3FTCA	3-Perfluoropropyl propanoic acid	$C_6H_5F_7O_2$	242.09
FPePA or 5:3FTCA	3-Perfluoropentyl propanoic acid	$C_8H_5F_{11}O_2$	342.11
FHpPA or 7:3FTCA	3-Perfluoroheptyl propanoic acid	$C_{10}H_3F_{17}O_2$	478.10

3. The project activities are conducted in parallel with the PFAS in Biosolids project. The two undergraduate students who would be working on the biosolids project will also be working on this project activities.
4. All extractions and LC-MS/MS analysis have been conducted; data is currently being processed in the Agilent Masshunter software. Dilutions will be needed as some concentrations are showing to exceed the calibration curve.
5. Regular weekly progress meetings have been taking place with the co-PIs.
6. A project web page has been updated at the following address:

   ewaste.fiu.edu
7. Literature review on PFAS is on-going.
8. Manuscript preparation

   One manuscript is being prepared for journal submission. This manuscript focuses on:

   Characterization of PFAS in e-waste

9. Test plans for leaching experiments, PFAS analyses (expanded for 40 PFAS compounds), e-waste characterization, identification appropriate components, and sample preparation needs (e.g., crushing and pulverization) for PFAS testing is on-going.

Planned activities for the remainder of the project timeline:

- Finalize e-waste tests and analyses.
- Investigate PFAS related data and information as well as e-waste components and PFAS use in parts (for coating or otherwise) and potential runoff and partitioning data for e-waste related contaminants.
- Develop abstracts for submittal to solid waste and recycling conferences.
- Develop manuscript for publication.

Months	Planned Activities	Status
December	• Weekly project update meetings • Analysis of data from leaching tests •	• Continuing • Continuing
January	• Weekly project update meetings • Conduct PFAS analyses for solid and liquid samples • Manuscript preparation • Draft final report	• Continuing • Continuing • Continuing • Continuing • Continuing
February	• Weekly project update meeting • TAG Meeting (Feb 1, 2024) • Finalize partitioning and leaching analyses of different types of PFAS • Manuscript preparation • Draft final report	• Continuing • Scheduled • Continuing • Continuing • Continuing
March	• Weekly project update meeting • Manuscript preparation • Finalize project report	• Continuing • Continuing • Planned