P-159

Development and application of USEPA method 1633 and total oxidizable precursor assay for the determination of PFASs in waste-related samples

Rosamond Tshumah-Mutingwende[1]*, Tomoya Nojima[1], Tomohiro Seki[1], Akihiko Tsujimura[1], Yoshinori Yabuki[2] and Hidenori Matsukami[3]

[1]Eurofins Nihon Kankyo K.K., [2] Research Institute of Environment, Agriculture and Fisheries, Osaka Prefecture, [3]National Institute for Environmental Studies, Japan

* RosamondTshumah-Mutingwende@eurofins.com

INTRODUCTION

1. Background

- There is growing concern about the environmental emissions and potential human exposure to per-and polyfluoroalkyl substances (PFASs).
- Information about the presence of PFASs in waste-related samples such as landfill leachate, firefighting foam, water repellents and solid waste is crucial for controlling PFASs emissions and reducing environmental and human health risks posed by PFASs.
- However, owing to the limited information regarding the presence of perfluoroalkyl acids (PFAAs) precursors and their potential oxidative conversion products in landfill leachate[1)], firefighting foam[3)] and durable water repellents (DWR)[2)]; the risk of underestimating the total PFASs discharged to the environment is high.
- Furthermore, consideration of suitable PFASs emission control measures is a challenge.

2. Objectives

- To determine the presence of PFASs including PFAAs precursors and their oxidation products in landfill leachate, firefighting foam and DWR samples
- To optimize the USEPA 3rd Draft Method 1633
- To optimize the original TOP assay method by Houtz and Sedlak, 2012 [4)]

3. USEPA 3rd Draft Method 1633 overview [5)]

- This is the first PFASs method issued by the US EPA for non-drinking water matrices
- It measures 40 PFASs in aqueous (wastewater, surface water, ground water and landfill leachate), solid (soil, biosolids, sediment) and tissue samples using LC-MS/MS
- Compared to drinking water methods USEPA Method 1633 offers longer sample holding times of up to 90 days for all sample matrices stored at ≤ -20°C and protected from light
- Though it is a single laboratory validated method, the USEPA 3rd Draft Method 1633 includes the wastewater results of the multi-laboratory validation study.
- All sample matrices must undergo carbon clean-up for the adsorption of interferent organics
- Loose carbon or carbon cartridges can be used for the removal of interferent organics in wastewater samples as long as all method QC criteria applicable to wastewater analyses are met.
- Compared to USEPA drinking water methods, USEPA draft method 1633 tests for many precursors such as; 3:3 FTCA, 5:3 FTCA, 7:3 FTCA, 4:2FTS, 6:2FTS, 8:2FTS, PFOSA, NMeFOSA, NEtFOSA, NMeFOSAA, NEtFOSAA, NMeFOSE and NEtFOSE
- This, therefore, makes it a suitable option for pre-TOP assay analysis of samples
- Isotope dilution is used to quantify analytes present in each sample

4. Total Oxidizable precursor (TOP) Assay

- The Total Oxidizable Precursor (TOP) assay is an in-lab method which oxidatively converts polyfluoroalkyl substances into measurable PFAAs [4)]
- In this study, the original Houtz and Sedlak method which consists of adding 60 mM $K_2S_2O_8$ and 150 mM NaOH to 125 mL of an aqueous sample and digesting it at 85°C for 6 h; was optimized by adding 20 mL of 400 mM NaOH and 150 mM $K_2S_2O_8$ mixed solution to 20 mL of aqueous sample before digesting it at 85°C for 12 h on a DigiPrep digestion block (SCP Science, Canada)

5. Sample description

- Three landfill leachate samples (LE-1, LE-2, and LE-3) were collected from solid waste landfills in Japan.
- Three firefighting foam samples (aqueous film forming foam (AFFF), protein foam (PF), synthetic surfactant foam (SSF)) and two DWR samples (DWR-2011-2 and DWR-2011-5) were obtained for examining the use of TOP assay.
- All samples first underwent a rapid screen, after which the sample volumes for pre-and post-TOP assay analysis were determined based on the screening results
- For each sample, two aliquots were used. One aliquot followed the USEPA 3rd Draft Method 1633, however, slightly modified by concentrating the final extract to 1 mL (pre-TOP assay sample).
- The second aliquot (post-TOP assay sample) was subjected to our in-house TOP assay method, after which the same SPE, concentrating and analysis method as pre-TOP assay samples was followed.

METHODOLOGY

In-house TOP assay coupled with modified Method 1633 (USEPA 3rd Draft Method 1633)

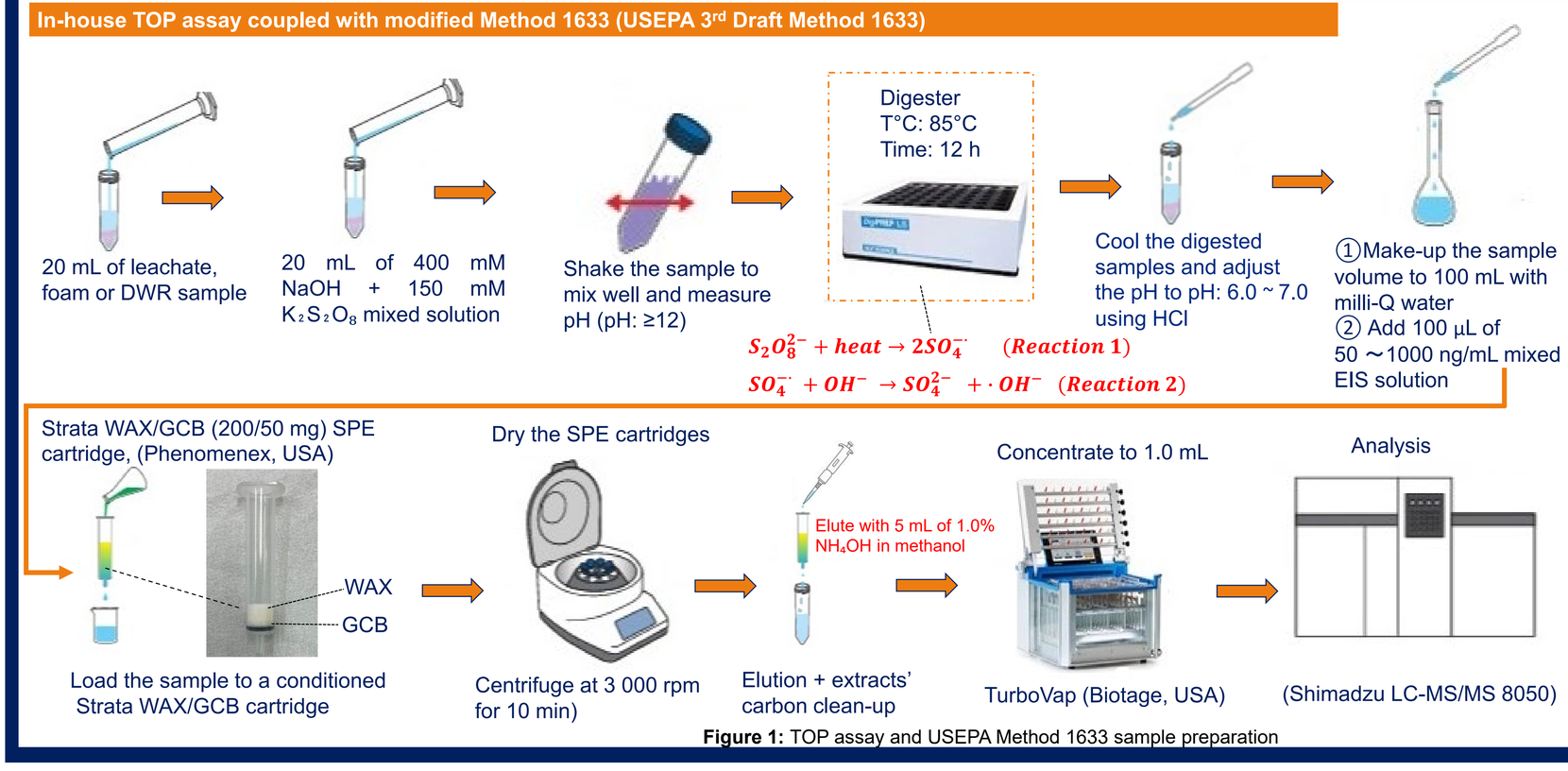

Figure 1: TOP assay and USEPA Method 1633 sample preparation

Shimadzu LC-MS Analytical conditions

Table 1: Shimadzu LC-MS 8050 analytical conditions

Item	Condition	
Analytical instrument	LCMS 8050	
Analytical column	Kinetex® 1.7 µm EVO C18 100A°; 50×2.1 mm	
Guard column	Security Guard™ ULTRA cartridges for EVO C18. UHPLC, sub-2 µm and core-shell columns with 2.1 mm internal diameters	
Delay Column	Phenomenex Gemini® 3µm C18 100A°; 50×2 mm	
Column temperature	40 ℃	
Gradient conditions	A: 2 mM Ammonium acetate in 95:5 water / acetonitrile (%)	B: Acetonitrile (%)
0 min	98	2
0.20 min	98	2
4.00 min	70	30
7.00 min	45	55
9.00 min	25	75
10.00 min	5	95
11.00 min	5	95
11.40 min	98	2
12.00 min	98	2
Flowrate	0.4 mL/min	
Injection volume	1 µL	
Ionization method	ESI-negative	

RESULTS & DISCUSSIONS

1. Method 1633 review

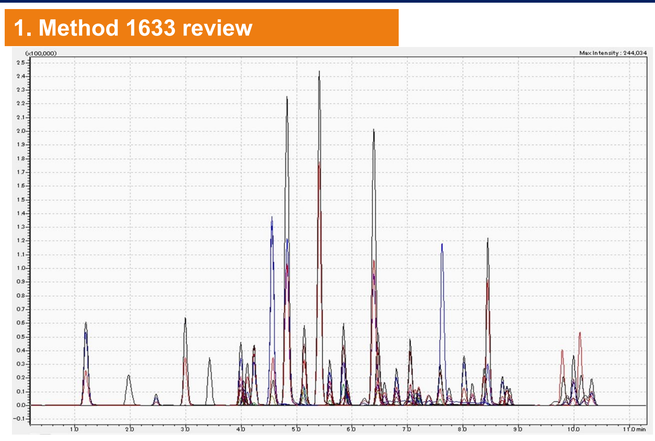

Figure 2: Calibration verification standard Total Ion Chromatogram

- So far, USEPA 3rd Draft Method 1633 is the only EPA method that offers the highest number of PFASs analytes measured (40 analytes) in non-drinking water matrices (Figure 2)
- Thus, USEPA 3rd Draft method 1633 coupled with TOP assay will be effective in the assessment of environmental samples
- However, it would be more beneficial to include ultra-short PFASs (C2-C3) since these are possible post-TOP assay products for many precursors
- A broader perspective of environmental contamination may be obtained if more precursors such as 6:2 diPAP and 8:2 diPAP are added to the suite of analytes measured by USEPA 3rd draft method 1633

2. Leachate sample pre-and post-TOP assay results

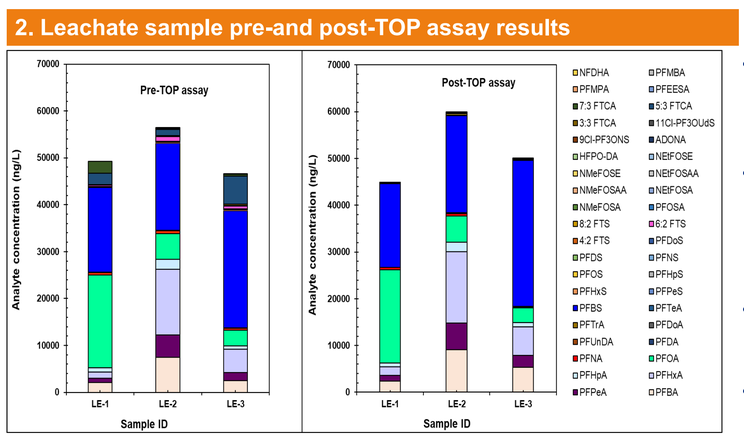

Figure 3: Pre-and post-TOP assay results of PFASs in leachate samples

- Pre-TOP assay, short chain Perfluoroalkyl carboxylic acids (PFCAs) (C4-C7 PFCAs) were the most dominant PFASs in leachate samples (Figure 3)
- This reflects industry's transition to the use of short-chain PFCAs as replacements of longer-chain homologues and/or the possible biotic/abiotic conversion of PFAAs precursors in landfills
- 5:3 FTCA and 6:2 FTS were the most dominant PFAAs precursors in all leachate samples.
- Overall oxidation rate is ≥ 90%, with most precursors achieving 100% oxidation rate.

3. Firefighting foam and DWR samples pre- and post-TOP assay results

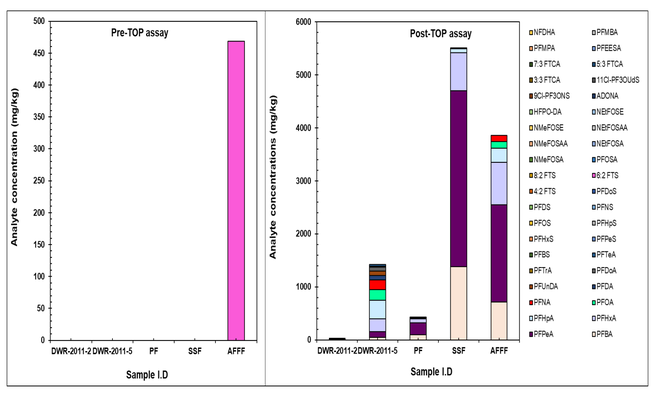

Figure 4: Pre-and post-TOP assay results of PFASs in firefighting foam and DWR samples

- Pre-TOP assay, most perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFSAs) were below our laboratory's lower detection limits for all analytes tested in the sample (Figure 4).
- For precursors, only 6:2 FTS was detected in the AFFF sample at nearly 470 mg/kg.
- Post-TOP assay, C4–C10 PFCAs were the most dominant PFAAs in all samples except for PFDA which was detected in the DWR-2011-5 sample only, at a concentration of 80 mg/kg
- It is unquestionable that unidentified precursors, e.g., precursor impurities from the manufacturing process; may have contributed to the observed increase in the C4-C10 PFCAs concentrations.

4. Leachate, firefighting foam and DWR sample EIS recovery vs EIS recovery stated in M1633

Table 2: Pre-and post-TOP assay EIS recoveries for leachate, firefighting foam and DWR samples

EIS Compound	Recovery Range (%)			EIS Compound	Recovery Range (%)		
	pre-TOP assay	post-TOP assay	USEPA M1633[5)]		pre-TOP assay	post-TOP assay	USEPA M1633[5)]
$^{13}C_4$-PFBA	101-111	15-78	10-130*	$^{13}C_8$-PFOS	82-115	76-95	45-140
$^{13}C_5$-PFPeA	102-115	66-94	35-150	$^{13}C_2$-4:2FTS	71-89	57-68	60-200*
$^{13}C_5$-PFHxA	98-111	80-88	55-150	$^{13}C_2$-6:2FTS	70-98	54-69	60-200*
$^{13}C_4$-PFHpA	101-110	79-92	55-150	$^{13}C_2$-8:2FTS	60-180	52-195	50-200*
$^{13}C_8$-PFOA	96-121	85-98	60-140	$^{13}C_8$-PFOSA	98-113	89-100	30-130
$^{13}C_9$-PFNA	89-120	78-101	55-140	D_3-NMeFOSA	70-111	47-90	15-130
$^{13}C_6$-PFDA	87-111	78-95	50-140	D_5-NEtFOSA	43-111	41-85	10-130
$^{13}C_7$-PFUnA	88-108	76-84	30-140	D_3-NMeFOSAA	70-91	70-81	45-200*
$^{13}C_2$-PFDoA	77-111	72-98	10-150	D_5-NEtFOSAA	83-89	69-81	10-200
$^{13}C_2$-PFTeDA	81-115	49-83	10-130*	D_7-NMeFOSE	93-165	91-119	10-150*
$^{13}C_3$-PFBS	95-110	80-89	55-150	D_9-NEtFOSE	86-165	93-118	10-150*
$^{13}C_3$-PFHxS	89-106	76-97	55-150	$^{13}C_3$-HFPO-DA	93-105	74-94	25-160

- The EIS recoveries for all analytes measured in all samples were within the QC acceptable limits for EIS recoveries in Wastewater sample (Table 2).
- This shows that the USEPA 3rd Draft Method 1633 was successfully optimized

CONCLUSIONS

- For leachate samples;
  ① Pre-TOP assay results showed that short chain PFCAs (C4-C7 PFCAs) are the most dominant PFASs in leachate samples.
  ② 5:3 FTCA and 6:2 FTS were the most dominant PFAAs precursors in all leachate samples.
  ③ TOP assay was efficient at converting PFAAs precursors into PFCAs, with a total oxidation rate of ≥ 90%.
  ④ C4-C7 PFCAs were the most abundant compounds in the post-TOP assay results.

- For firefighting foam and DWR samples;
  ① Pre-TOP assay results for firefighting foam and DWR samples revealed that most PFCAs and PFSAs were below our laboratory's lower detection limits for all analytes tested.
  ② Most precursors were not detected in all samples except for 6:2 FTS which was detected in the AFFF sample only
  ③ Post-oxidation, 6:2 FTS concentration was below our laboratory's lower detection limit; thus, it was assumed that 100% oxidation was achieved
  ④ Post-TOP assay, C4–C10 PFCAs were the most dominant PFAAs in all samples except for PFDA which was detected in the DWR-2011-5 sample only
  ⑤ It is without doubt that some unknown precursors could have contributed to the observed post-TOP assay PFAAs concentrations
- Results obtained in this study suggest that our in-house TOP assay method might be useful to elucidate the presence of PFAAs precursors in the waste-related samples and to consider PFASs including PFAAs precursors emissions comprehensively.
- Post-TOP assay oxidation products of each PFAAs precursor and molar yields of PFCAs will be determined in future studies.

REFERENCES

1. Hamid, H., Li, L., Grace, J., 2018. Review of the fate and transformation of per- and polyfluoroalkyl substances (PFASs) in landfills. Environ. Pollut., 235, 74-84.
2. van der Veen, I., Schellenberger, S., Hanning, A., Stare, A., de Boer, J., Weiss, J.M., Leonards, P.E.G., 2022. Fate of Per- and Polyfluoroalkyl Substances from Durable Water-Repellent Clothing during Use, Environ. Sci. Technol., 56 (9), 5886-5897
3. Amin, M.A., Luo, Y., Nolan, A., Robinson, F., Niu, J., Warner, S., Liu, Y., Dharmarajan, R., Mallavarapu, M., Naidu, R., Fang, C., 2021. Total oxidisable precursor assay towards selective detection of PFAS in AFFF. J. Clean. Prod. 328, 129568.
4. Houtz, E.F., Sedlak, D.L, 2012. Oxidative Conversion as a Means of Detecting Precursors to Perfluoroalkyl Acids in Urban Runoff. Environ. Sci. Technol., 46, 9342−9349.
5. United States Environmental Protection Agency (USEPA), 3rd Draft Method 1633, Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS, December 2022.