P-7 Analysis of per- and polyfluoroalkyl substances in soil – Application of the Total Oxidizable Precursor (TOP) assay

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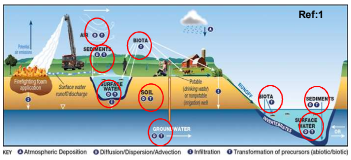
INTRODUCTION

1. Background

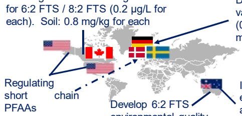


- The replacement of legacy PFOS Aqueous Film-Forming Foams (AFFFs) with high purity C6 fluorotelomer foams has not yielded the desired results (Ref:2)
- Once discharged in the environment through various activities such as firefighting drills, these modern fluorotelomer AFFF are known to degrade to intermediate transformation products such as 6:2 FTS, 8:2 FTS and 5:3 FTCA, a potential bio persistent
- 6:2 FTS, 8:2 FTS and 5:3 FTCA are Perfluoroalkyl acid (PFAA) precursors and they have the potential to undergo biotic and abiotic transformation resulting in short chain PFAAs e.g. PFBA, PFHxA which are easily soluble and highly mobile compared to their long chain counterparts.
- In addition, it is estimated that 90% of the PFAS pool in the environment are potential PFAA precursors (Ref:3)
- Therefore, in order to estimate the future risk from the transformation of PFAA precursors there is need for a lab-scale method that can mimic the environmental transformation of PFAA precursors

2. Total Oxidizable precursor (TOP) Assay

- Total Oxidizable Precursor (TOP) assay is an in-lab method which oxidatively converts polyfluoroalkyl substances into measurable perfluorinated alkyl acids (PFAAs) (Ref:4).
- TOP assay helps us to determine the concentration of innumerable PFAS that cannot be covered by conventional analytical methods.
- PFASs are known endocrine-disrupting chemicals (EDCs) which result in, for example, increased risk of birth defects, poor liver, kidney and thyroid function (Ref:5). Thus, TOP assay data can be useful in the protection of human health and the environment since it can be used to: ① estimate the future risk from PFAA precursor transformation ② decision making: (i) to establish regulatory values for human health and environmental protection and (ii) deciding the best remediation and /or wastewater treatment technologies.

What has been done in some countries?



3. Objectives

1. To compare the extraction efficiency of automated extraction (using EDGE unit (CEM Corporation, USA) vs our in-house soil extraction method
2. To identify and quantify PFAAs post oxidation (based on the Houtz and Sedlak (2012) method)
3. To investigate the effect of oxidant concentration (Houtz and Sedlak (2012) vs Eurofins' method)
4. To investigate the effect of carbon clean-up

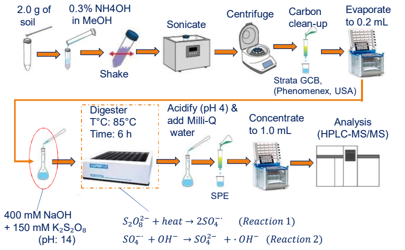
Best Practice sample preparation steps required for total oxidation were established based on the findings of objectives 3 and 4.

METHODOLOGY

1. Preparation of 6:2 FTS/ 8:2 FTS-artificially-contaminated soil

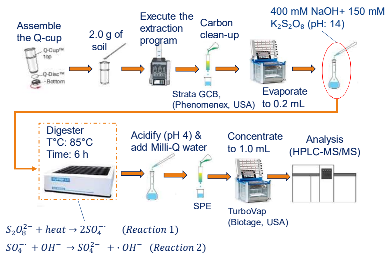
Weigh 100 g of Akadama / Organic soil into a 500 mL HDPE container
↓
Add 100 mL of 10 μg/L 6:2 FTS / 8:2 FTS standard solution
↓
Mix on a pot mill rotating stand at 15 rpm for 24 h
↓
Centrifuge
↓
Air dry for at least 6 h
↓
Using a mortar and pestle, crush the contaminated soil to uniform particles

2. In-house Soil extraction method +TOPA



- Sample preparation procedure: In-house method based on USEPA Draft Method 1633 (Ref:6)
- Sample analysis procedure: Method 537 modified (537 M)
- The concentration of PFAAs was determined by comparing the PFAAs concentrations before and after oxidation.

3. Automated Extraction (using EDGE unit) + TOPA

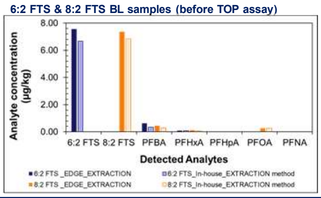


- Sample preparation procedure: EDGE extraction program based on USEPA Draft Method 1633
- Sample analysis procedure: Method 537 modified (537 M)
- The concentration of PFAAs was determined by comparing the PFAAs concentrations before and after oxidation.

RESULTS & DISCUSSIONS

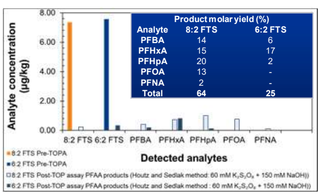
1. EDGE VS Soil standard method – Extraction Efficiency

6:2 FTS & 8:2 FTS BL samples (before TOP assay)



- EDGE unit-extracted soil samples had higher concentrations for all analytes compared to our in-house method
- EDGE unit was operated at high pressure (0.22 MPa) and temperature (65°C), thus the extraction efficiency is higher compared to our in-house sonicator method, which is conducted at room temperature and pressure.
- Internal Standard recovery rate was ≥ 80% for all analytes for both extraction methods
- Background PFBA, PFHxA and PFOA concentrations were subtracted in the final concentrations calculations post TOP assay

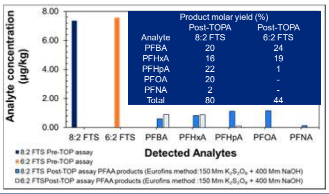
2. Detected PFAAs post Oxidation (Houtz and Sedlak, (2012) method)



Product molar yield (%)		
Analyte	8:2 FTS	6:2 FTS
PFBA	14	6
PFHxA	15	17
PFHpA	20	2
PFOA	13	-
PFNA	2	-
Total	64	25

- Based on the Houtz and Sedlak (2012), oxidant concentration, 6:2 FTS yielded PFBA, PFHxA and PFHpA (Total product molar yield: 25%).
- 8:2 FTS yielded PFBA, PFHxA, PFHpA, PFOA and PFNA (Total product molar yield: 64%).
- IS Recovery: 82-121% for all analytes
- 6:2 FTS and 8:2 FTS were detected post-oxidation, thus, 100% oxidation was not achieved.
- In order to optimize the oxidant concentration required for total oxidation, this investigation was repeated at a higher oxidant concentration
- Samples for both scenarios were extracted by EDGE unit

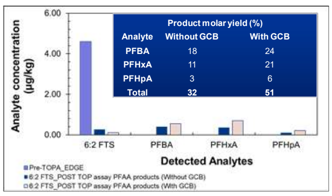
3. Effect of Oxidant concentration



Product molar yield (%)		
Analyte	Post-TOPA 8:2 FTS	Post-TOPA 6:2 FTS
PFBA	20	24
PFHxA	16	19
PFHpA	22	1
PFOA	20	-
PFNA	2	-
Total	80	44

- When the oxidant concentration was increased by more than 2.5 times of the Houtz and Sedlak, (2012) concentrations, total 6:2 FTS and 8:2 FTS oxidation was achieved
- Using our in-house method's oxidant dosages, the molar yield increased as follows: 6:2 FTS : from 25% to 44% and 8:2 FTS: from 64% to 80%
- Thus, the higher the oxidizer dosage, the greater the analyte molar yield.
- IS Recovery: 82-120% for both scenarios
- Samples for both scenarios were extracted by EDGE unit

4. Effect of Carbon clean-up before adding TOPA solution



Product molar yield (%)		
Analyte	Without GCB	With GCB
PFBA	18	24
PFHxA	11	21
PFHpA	3	6
Total	32	51

- By incorporating the Graphitized Carbon Black (GCB) clean-up step, we were able to optimize the extent 6:2 FTS oxidation.
- The product molar yield increased from 32% to 51%.
- GCB eliminates the interference of organics, thus, improving the efficiency of the oxidation process.
- Without the carbon clean-up step, the organics will "consume" the TOP assay solution thus reducing its concentration in the sample.
- IS Recovery: 86-108% for both scenarios
- Samples for both scenarios were extracted by EDGE unit

CONCLUSIONS

- EDGE extraction unit (CEM Corporation, USA) can be operated at high temperature and pressure, thus, the analyte recovery is greater than our in-house soil extraction method. Furthermore, spillages and human errors are eliminated due to the few human-related sample processing steps.
- The following degradation products were detected:
  ① 6:2 FTS: PFBA, PFHxA and PFHpA
  ② 8:2 FTS: PFBA, PFHxA, PFHpA, PFOA and PFNA
- However, our current analytical method does not include PFPeA, thus, it was not analyzed
- Carbon clean-up using Graphitized Carbon Black (GCB) SPE cartridge (Phenomenex, USA) removed interferent organics thus improving the efficiency of the oxidation process.
- A higher oxidant concentration resulted in total oxidation of the 6:2 FTS and 8:2 FTS precursors
- The IS recoveries for all analytes were within the acceptable range of 70-130%

Best Practice sample preparation steps
- Carbon clean-up for all samples (especially samples rich in organics)
- High oxidizer dosage / reduce the soil sample mass

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