

Total Fluorine, Extractable Organofluorine, Per/Polyfluoroalkyl Substances and Total Oxidizable Precursor Assay on Contaminated Soil

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Background/Objectives. Contamination of per/polyfluoroalkyl substances (PFAS) in water and soil are of great concern. To date, only PFOS or limited suite of PFASs (e.g., C4-C8 perfluoroalkyl carboxylates (PFCAs) and C4-C10 perfluoroalkane sulfonates (PFASs)) and precursors such as sulfonamides are measured in environmental programme. Since more and more precursor compounds of PFASs and PFCAs have been discovered, many precursor compounds are also included in some studies. Due to the unavailability of analytical standards, measurements of novel precursor compounds are limited. It is necessary to evaluate the levels of these precursors in the samples in research and risk assessment, as they have the potential to form persistent PFCAs/PFASs. Analyses of total fluorine (TF) and extractable organofluorine (EOF) give the levels of TF and EOF in a sample, which in turn allow a mass balance analysis of fluorine in the sample to assess how much unidentified OF present in the sample. A method known as total oxidizable precursor (TOP) assay help reveal any precursor compounds that may give rise to persistent PFCAs/PFASs. The purpose of this investigation was to construct fluorine budgets in ten contaminated soil samples by measuring quantifiable PFAS and EOF, and quantifiable PFAS in the same samples after subjected to TOP assay; all samples were also analyzed for TF and inorganic water extractable fluoride (IF).

Approach/Activities. Soils were sampled from five different locations within one investigated site in Sweden where aqueous film forming foams are and have been historically used. Each sample was collected from three test pits within a 10x10 m grid; topsoil (0-0.5 m) was collected in HDPE-bottles and were denoted as Soil 1-10. Soils were first dried at 35°C, sieved <2 mm and milled. Extraction and analyses of PFAS (alkaline digestion followed by methanol extraction and Solid phase extraction cleanup), EOF and TF followed published methods. Levels of EOF and TF were measured using combustion ion chromatography in the SPE extracts and whole soil, respectively. Thirty PFAS initially present and after TOP assay were determined by UPLC-MS-MS. Branched and linear isomers of PFASs were separated and quantified. Levels of IF was extracted at L/S 5:1 in water; IF in the extract was analyzed using IC.

Results/Lessons Learned. For the 10 soil analyzed, the sum of thirty PFAS ranged from 50 ng/g to 23000 ng/g dry weight. Anionic PFAS comprised >98% of the total PFAS except in soil 3 (93%). The most commonly detected PFAS was PFOS, which dominant in soils 3 and 4. In contrast, soil 2 had the highest concentrations of 6:2 and 8:2 FTSA. The composition and concentrations of PFAS both before and after TOP varied among the samples. After TOP assay, the sum of PFAS of soil 2 became the second highest. Measurable precursors such as 6:2, 8:2 FTSA and FOSA were reduced by 85% or further. Initial measurable PFAS could explain 1-80% and after TOP assay 7-78% of total EOF. As expected TOP assay raised the fraction explained for most soils, but could not fully account for the EOF determined. Applications of the methods in environmental assessments will be discussed.