

DoD Environmental Data Quality Workgroup Memorandum

Subject: Issues with Applying the Incremental Sampling Methodology (ISM) to PFAS Investigations

January 31, 2025



INTRODUCTION: Incremental sampling methodology (ISM) is a protocol consisting of field composite sampling followed by laboratory processing and subsampling of the field sample. The ISM protocol is designed so a single sample result represents the mean concentration of contaminant(s) in a defined area designated as a decision unit (DU). To implement ISM, a number of increments of equal depth and mass (no less than 30) are collected in the field and combined into a large (typically 1 kilogram (kg)) sample that is submitted to the laboratory. The entire field sample is processed and then incrementally subsampled by the laboratory prior to extraction and analysis. Depending upon the composition of the sample and the nature of the contaminant, processing may include sieving, drying, and grinding/milling of the sample prior to subsampling. Processing and subsampling of the entire field sample is necessary to attain the degree of homogenization necessary for the analytical result to be representative of the entire sample collected and the DU. However, due to issues associated with the potential for positive and negative bias and questions about the applicability of the approach to perfluoroalkyl and polyfluoroalkyl substances (PFAS), the DoD EDQW recommends avoiding the use of ISM for PFAS sampling and analysis for the following reasons:

- The requirement to add extracted internal standard (EIS) compounds to a 1kg or larger sample or creating a large volume/mass laboratory control sample (LCS) spiked with all targeted PFAS is impractical.
- An ISM protocol/method has not been validated for evaluation of PFAS;
- There is an increased risk of cross contamination from additional sample processing that is exacerbated by extremely low screening levels for some PFAS;
- There is also a risk of analyte loss during the drying and grinding/milling procedures for certain PFAS;
- ISM only provides an average concentration result for the entire area sampled and, in most cases, it will not be appropriate to meet all project goals. Using ISM could result in the collection of insufficient information on the spatial concentration behavior (nature and extent) across the site that is required as a part of CERCLA investigations.

BACKGROUND: Incremental Sampling Methodology (ISM) was first introduced as an appendix in *EPA SW-846 Method 8330B* ⁽¹⁾ *Nitroaromatics, Nitramines, and Nitrate Esters by High Performance Liquid Chromatography (HPLC), Appendix A, Collecting and Processing of Representative Samples for Energetic Residues in Solid Matrices From Military Training Ranges*. The processes described therein were designed to minimize the spatial and particle-associated heterogeneity associated with constituents that are distributed as particles across a closed firing range, at or near the surface. Since publication of this method, the ISM processes described in EPA Method 8330B have been applied to the determination of a wide range of other contaminants and in media types other than solids. However, the EPA has not validated the use of ISM for any contaminants or media types beyond those included in EPA Method 8330B. In recent years, the Interstate Technology Regulatory Council published a guidance document (ITRC 2020⁽²⁾) to provide general guidance for use of ISM beyond munitions constituents. This document states that ISM procedures may require modification or may not be appropriate for

For Open Publication

Jan 31, 2025

Department of Defense

OFFICE OF PUBLICATION AND SECURITY REVIEW

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some specific contaminants and some media types, acknowledging that the processes included in ISM may impact the ability to provide a true mean concentration of other contaminants and in other media types. Despite the lack of appropriate validation, the demand for applying ISM to other applications has been partially driven by different state regulatory entities requesting/requiring its use. The DoD EDQW does not recommend the use of ISM for PFAS investigations.

Concerns Regarding Project Objectives and Establishing an Appropriate ISM DU

Most DoD PFAS releases are the result of historic fire-training exercises or firefighting with PFAS-containing aqueous film-forming foam (AFFF). For many releases under investigation, only estimated locations of the release are known and discrete samples are necessary to identify and delineate the actual release areas. Fire training was conducted using AFFF in designated fire-training areas for years until DoD policy prohibited training with AFFF on land in 2016. Studies (Brusseau et. al. 2020⁽³⁾) have shown that the depth at which the highest concentration PFAS is found in soil is dependent on the individual PFAS, mode of AFFF application, soil properties, meteorological conditions, age of the release, and other factors. In general, longer chain ($C \geq 7$) PFAS concentrations are greatest in surface soils (up to 1 meter depth), whereas shorter chain PFAS concentrations are greatest in subsurface soils (up to 2 meter depth). Over decadal timeframes however, due to the geochemical properties of the soil and the physicochemical properties of PFAS, there is significant retention of PFAS in the vadose zone. If ISM were to be used to sample only the surface, or near surface depth (2.5 to 5.0 cm), the highest concentrations of some individual PFAS, especially shorter chain PFAS, could be missed. Both surface or near surface, and subsurface samples at varying depths must be collected. The ITRC 2020 guidance document states alternate sample collection strategies (e.g., discrete samples) may need to be considered for evaluation of subsurface samples due to the higher sampling costs incurred from the amount of time required to sample and equipment costs (e.g., drilling rigs). The granularity provided by discrete samples may still be necessary to understand movement/retention of PFAS and design remediation strategies that not only address direct contact with soils, but also migration to groundwater.

Laboratory Component

ISM has not been validated for use in the analysis of PFAS. The laboratory processing steps included in EPA Method 8330B (sieving, drying, and grinding/milling) are extensive compared to the sample processing steps outlined in EPA PFAS methods (e.g., EPA Method 1633A⁽⁴⁾). Like the field component, laboratory supplies and equipment have been shown to either contain PFAS or have the potential to adsorb PFAS from the sample. Therefore, with the inclusion of additional sample processing steps, there is an increased risk of cross-contamination of the sample resulting in high bias or introducing a low bias through adsorption effects. Homogenizing samples without the inclusion of drying and grinding/milling steps may not produce the level of homogeneity that is necessary to help ensure laboratory results provide an accurate representation of the mean concentration of the DU.

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Sieving, drying, and grinding/milling steps all introduce a high potential for cross-contamination. The sieving and grinding/milling process is particularly problematic in this respect given the decontamination protocols required to ensure cross-contamination of soils does not occur. Another issue is the increased likelihood of volatilization of ultra-short and short chain PFAS during sieving and grinding/milling, resulting in another point at which low bias can be introduced. Some PFAS may also be physically destroyed or transformed to other PFAS of interest during grinding/milling to a currently uncertain degree, leading to potential low bias, given that ball-milling has been demonstrated as a destruction technology for PFAS in soils. Commercial laboratories that have attempted to implement ISM for PFAS have not only encountered these issues but have also identified the need to isolate these processes from all other laboratory processes, including the need for a designated air handling unit to avoid contamination of the entire laboratory. These issues, plus the increase in sample processing time and increased volume of solvents and PFAS-free water needed for decontamination, have resulted in laboratories not being able to or willing to offer an ISM PFAS method. Failure to perform these preparation steps may result in loss of representativeness depending upon the compositional heterogeneity of the sample.

Another element to the sample processing step is the need for inclusion of the quality control (QC) elements that are standard to EPA methods and DoD requirements (DoD QSM⁵) to provide a measurement of accuracy. These QC elements consist of the addition of EIS compounds to the entire sample that is processed (1 kg or more) as well as the processing of a laboratory control sample that is prepared using the same mass (1 kg) of reference media (typically Ottawa or PFAS-free sand) that has been spiked with all PFAS of interest. PFAS analytical standards are not commercially available at the high concentrations and volumes needed for this application. These laboratory issues reflect the need for validation of a PFAS-specific ISM laboratory process and availability of appropriate, commercially-available analytical standards.

Many of the sample collection and laboratory processing concerns documented above would also apply to other solid or tissue matrices. Consequently, at this time due to the sample collection and laboratory process issues noted above, the DoD EDQW does not recommend the use of ISM for PFAS investigations. Validation and publication of PFAS-specific ISM sample collection and laboratory processing methods by the EPA is required to help ensure data generated are of the quality required to make definitive decisions.

REFERENCES

- (1) USEPA SW-846 Method 8330B Nitroaromatics, Nitramines, and Nitrate Esters by High Performance Liquid Chromatography (HPLC), Revision 2, October 2006.
- (2) ITRC. 2020. Incremental Sampling Methodology (ISM) Update.

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- ⁽³⁾ Brusseau ML, Anderson RH, Guo B. PFAS concentrations in soils: Background levels versus contaminated sites. *Sci Total Environ.* 2020 Oct 20; 740:140017. doi: 10.1016/j.scitotenv.2020.140017. Epub 2020 Jun 6. PMID: 32927568; PMCID: PMC7654437.
- ⁽⁴⁾ USEPA. 2024. Method 1633A. Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS. EPA 820-R-24-007 Washington, DC: USEPA Office of Water (4303T).
- ⁽⁵⁾ DOD/DOE. 2023. DOD DOE Quality Systems Manual (QSM) for Environmental Laboratories, Version 6.0.