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Perspective

Environmental Source Tracking of Per- and Polyfluoroalkyl Substances within a Forensic Context: Current and Future Techniques

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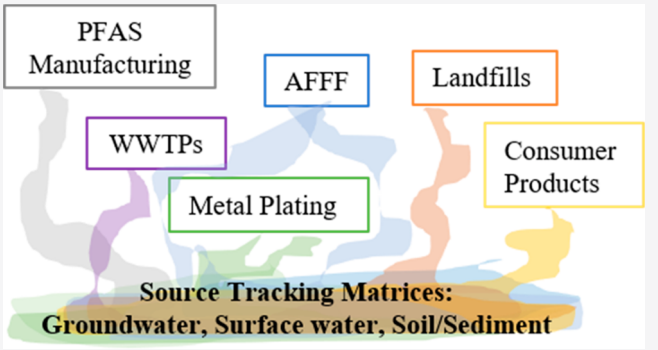
ABSTRACT: The source tracking of per- and polyfluoroalkyl substances (PFASs) is a new and increasingly necessary subfield within environmental forensics. We define PFAS source tracking as the accurate characterization and differentiation of multiple sources contributing to PFAS contamination in the environment. PFAS source tracking should employ analytical measurements, multivariate analyses, and an understanding of PFAS fate and transport within the framework of a conceptual site model. Converging lines of evidence used to differentiate PFAS sources include: identification of PFASs strongly associated with unique sources; the ratios of PFAS homologues, classes, and isomers at a contaminated site; and a site's hydrogeochemical conditions. As the field of PFAS source tracking progresses, the development of new PFAS analytical standards and the wider availability of high-resolution mass spectral data will enhance currently available analytical capabilities. In addition, multivariate computational tools, including unsupervised (i.e., exploratory) and supervised (i.e., predictive) machine learning techniques, may lead to novel insights that define a targeted list of PFASs that will be useful for environmental PFAS source tracking. In this Perspective, we identify the current tools available and principal developments necessary to enable greater confidence in environmental source tracking to identify and apportion PFAS sources.



KEYWORDS: *per- and polyfluoroalkyl substances, environmental forensics, conceptual site models, multivariate statistics, source tracking, high-resolution mass spectrometry*

INTRODUCTION

Contamination from per- and polyfluoroalkyl substances (PFASs) is a pressing environmental problem due to the widespread use and disposal of PFASs and the bioaccumulative, persistent, mobile, and toxic characteristics of many members of this class of compounds.[1−3] Stakeholders, including academics, industry, government, and public interest groups, are increasingly interested in robust methods for characterizing and differentiating one or more PFAS sources at a PFAS-contaminated site, a process we refer to herein as PFAS source tracking. PFAS source tracking falls within the broader context of PFAS forensics.[4−8] To date, source tracking has focused on characterizing specific PFAS sources or single contamination events with less emphasis on contamination from commingled sources.[9−11] The tools used for PFAS source tracking must accurately discern separate PFAS sources and/or releases and be accessible to academics and practitioners evaluating chemical and geospatial data.

Environmental forensics conventionally encompasses the *historical* application and source of contaminants using analytical tools and site-specific understanding of contaminant fate, transport, and environmental distribution.[12] Determining the timing and type of a PFAS release based solely on its chemical signature is likely to be challenging for reasons including: the use of PFAS materials over long time periods, shifts in manufacturing, common manufacturing feedstocks, and an incomplete understanding of PFASs present. Further, conventional environmental forensic fingerprinting techniques include carbon dating, stable isotope analysis, characterization of additives or impurities, temporal changes due to environ-

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mental transformation, and analysis of chemical ratios.[12] However, the unique physicochemical properties of PFASs limit the efficacy of some conventional forensic techniques. For example, stable isotope analysis is unsuitable because PFASs are highly stable in the environment, there is a single stable fluorine isotope, and the environmental concentrations of PFASs are often below stable isotope detection limits. Consequently, PFAS source tracking should focus on determining the contributing sources, fate, and transport of PFASs using PFAS fingerprints and a conceptual site model (CSM) composed of the hydrogeochemical characteristics of a given site. In this Perspective, we define a site as a geographical area of interest wherein one or more environmental matrices (e.g., groundwater, soil, surface water, sediment) are contaminated by PFASs.

Stakeholders, including impacted populations, may have a vested interest in determining the source of PFASs found in biotic matrices, particularly human serum. However, factors such as toxicokinetics, differing exposure pathways, and the mobility of fauna complicate PFAS source tracking in biological matrices.[13] Therefore, such efforts are outside of the scope of this Perspective.

The types of PFASs present in specific products are often proprietary information, but a PFAS fingerprint, defined as the types and percentages of PFASs observed in a sample, may contain markers of the manufacturing process or product. The different production processes used to manufacture PFASs are associated with unique fingerprints: compounds produced by electrochemical fluorination (ECF) differ in isomer (i.e., branched and linear) composition, distribution of perfluoroalkyl chain length (i.e., even or odd number of consecutive perfluorinated carbons), and terminal functional groups from those produced by fluorotelomerization (FT).[14,15] The PFAS fingerprint may vary between lot and formulation for a given manufacturer, reflecting commercial and regulatory drivers. PFAS source tracking efforts should account for differences in the chemistry of similar products based on variations in formulation, particularly where repeated environmental contamination events have occurred. For example, many manufacturers changed the formulations of their commercial products following the implementation of the U.S. Environmental Protection Agency (EPA) Perfluorooctanoic Acid (PFOA) Stewardship Program,[16] the Chinese Ministry of Environmental Protection announcement No.[2014]21,[17] and the listing of PFOS to the Stockholm Convention.[18]

Because PFASs have variable physical chemical properties, accounting for differential transport and transformation on the distribution of PFASs in environmental samples is an integral part of PFAS source tracking. Apparent differences in the PFAS fingerprint may be the result of the media sampled, the distance from the release, the transport pathway(s), and other aspects of the CSM such as the redox conditions that influence microbial transformation, rather than separate sources. Effective source tracking efforts will integrate and reconcile the different components of the CSM and the chemical fingerprint data in an iterative way to find converging lines of evidence on sources (Figure 1).

Commercially available analytical techniques may not facilitate the differentiation of separate inputs to a mixed-source PFAS impacted area. The more commonly quantified PFASs may be of limited utility for distinguishing sources because of their use in multiple applications.[5,6,19] For example, releases from separate applications may be dominated by

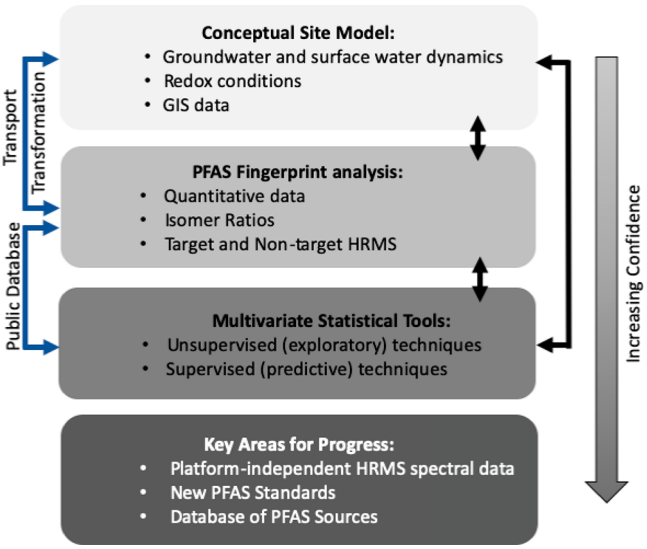

Figure 1. PFAS source tracking tools and opportunities. Black arrows depict the integration of individual tools into a forensics approach, and blue arrows represent two-way information exchange between categories.

similar constituents (e.g., one or more perfluoroalkyl carboxylates (PFCAs) and perfluoroalkyl sulfonates (PFSAs)). However, a more detailed characterization of environmental samples with target or nontarget analysis can identify different sources of the same predominant compounds at contaminated sites (e.g., detection of 8:2 fluorotelomer alcohol in one section of a PFOA-dominant plume).

Preliminary source tracking efforts have focused on the differentiation of select PFAS sources. For example, Kibbey et al. used machine learning to differentiate PFASs derived from aqueous film-forming foam (AFFF) and non-AFFF sources in environmental water samples;[20] however, the relatively focused training set applied to this algorithm also prevented its broader application to many sources of PFAS contamination. Supervised learning algorithms must be trained on comprehensive data sets to recognize patterns of PFAS contamination from many possible sources. Washington et al. determined which of two candidate manufacturing facilities was likely responsible for atmospheric deposition of chloroperfluoropolyether carboxylates by mapping the abundance of certain congeners and associated PFCAs.[21] Studies have thus far either sought to differentiate simple contamination scenarios (e.g., typically one or two environmental matrices impacted by one probable, predominant source) or included a limited analyte list, which may not be best suited to broader environmental source tracking.[4−8,20,21] In this Perspective, we identify the current tools available and principal developments necessary in detection, quantification, and multivariate analysis to differentiate multiple commingled PFAS sources in the environment. These developments may be particularly useful where distinct PFAS inputs mix due to natural (e.g., convergent hydrology) or engineered (e.g., waste aggregation and discharge) processes.

■ ANALYTICAL METHODS

The analytical instrument and methods employed dictate the ability to confidently perform PFAS source tracking. Inherent limitations exist in any analytical method (e.g., extraction conditions, resolving power, ionization, polarity, and analyte

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list) and analytical instrumentation used (e.g., liquid chromatography (LC)- or gas chromatography (GC)-mass spectrometry (MS, MS/MS, or high-resolution MS)). The limitations of each technique should be evaluated, and complementary tools should be used in tandem to more completely characterize the PFAS fingerprint of a given sample or matrix.

Total Organofluorine Methods. Tools and techniques that measure multiple PFASs as a simplified parameter such as total organofluorine (e.g., adsorbable organofluorine (AOF) or particle induced gamma-ray emission (PIGE) spectroscopy) do not capture the complexity of source fingerprints.[22,23] The total oxidizable precursor (TOP) assay simplifies the complexity of a PFAS mixture by forming several common perfluoroalkyl acid (PFAA) products from multiple polyfluorinated compounds. The TOP assay is capable of some differentiation between FT and ECF-based precursors via analysis of the ratio of oxidation products and the inspection of branched and linear isomers.[24−26] However, given their limitations, data generated by these total organofluorine methods cannot serve as a crucial line of evidence in PFAS source tracking.

Target Analytical Methods. Commercially available analytical methods, such as U.S. EPA drinking water methods 533 and 537.1, enable the quantification of PFASs predominantly associated with different manufacturing processes and product categories.[27,28] For example, methyl- and ethyl-perfluorooctane sulfonamido acetic acid (MeFOSAA and EtFOSAA) are associated with ECF-derived surface coatings for textiles,[29] and fluorotelomer sulfonates (FTSs) are exclusively associated with FT manufacturing. An analyte list that contains FT compounds (e.g., FTSs), sulfonamide compounds (e.g., EtFOSAA), short and long chain PFCAs and PFSAs (e.g., perfluorobutanoic acid (PFBA) and perfluorodecanesulfonate (PFDS)), and perfluoroalkyl ether compounds (e.g., 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy) propanoate (GenX)) will generate a simple PFAS fingerprint reflecting the nuance of different contributing sources. Quantitative evaluation of the PFAS fingerprint in environmental samples collected at a site, including the ratios of different analytes, can be used to trace the origin and pathways of commingled PFAS sources. For example, commercially available analyses of dozens of PFASs from multiple locations can be used to identify where PFAS plumes intersect or how mixtures change with distance from their release, thereby providing insight into PFAS geographical origins.[7,30] PFAS mixture analyses, which can be visually rendered (e.g., via radar diagrams or pie charts) or input into supervised or unsupervised machine learning techniques, can be used to rapidly assess differences among samples using readily obtainable LC-MS/MS PFAS data.

A disadvantage of currently available commercial methods is that analyte reporting lists may omit potentially useful compounds for PFAS source tracking (e.g., 5:3 fluorotelomer carboxylic acid, primarily associated with landfills;[31,32] perfluorohexane sulfonamide, observed in AFFF-impacted surface water;[25] mono- and disubstituted polyfluoroalkyl phosphates associated with food packaging).[33] In some cases, analytical standards are unavailable for PFASs of interest. Additionally, commercially available PFAS analytical methods are typically limited to anionic, nonvolatile compounds; methods that measure volatile PFASs are not easily merged with methods that measure primarily anionic PFASs.

Diagnostic Use of Branched and Linear Isomers. Liquid chromatography can separate many branched PFAS isomers from their linear counterparts. The presence of branched isomers typically indicates ECF manufacturing, whereas FT-based products are predominantly linear.[34−36] The ratio of branched to linear isomers in the original ECF product is known or can be estimated (e.g., 22−35 branched/65−78 linear).[37] For compounds like PFOA and other PFCAs that have been manufactured by both ECF- and FT-based processes, their isomer ratios in environmental samples can help to identify the manufacturing source of the compound or to infer the release and subsequent transformation of ECF- or telomer-based precursors.[38−40] Like PFAAs more broadly, individual isomers are unlikely to transform in the environment, but isomers do exhibit differences in partitioning behavior that can change their distribution.[41,42] Because precursors transform primarily within the nonfluorinated part of the molecule,[43,44] the isomeric signature of the perfluoroalkyl group is mostly retained during precursor transformation.

Branched isomer standards are not readily available for all ECF-derived PFASs, but their availability would greatly improve source tracking analysis. Standards of several individual branched isomers are commercially available for PFOA and perfluorooctanesulfonate (PFOS),[45] and mixtures of branched isomers are commercially available for perfluorohexanesulfonate (PFHxS), EtFOSAA, and MeFOSAA.[46] At present, most laboratories quantify only the branched isomers of PFASs for which authentic branched and linear analytical standards are available. Exclusion of branched PFAS isomers from quantification results in a low concentration bias. Even in the absence of branched isomer-containing technical mixtures and standards, environmental analyses, especially for source tracking, should integrate and report the approximate relative abundance of total branched and linear isomers.

Isomeric distribution could also be one of several converging lines of evidence for comprehensive environmental source tracking. For example, Benotti et al. proposed isomer distribution as one "tier" of forensic analysis.[8] However, they acknowledged that source attribution beyond determining ECF vs FT synthesis is not currently feasible using only isomer distribution, since isomer patterns alone may not differ enough between products to confidently fingerprint a source.[8]

Nonstandardized Methods. Researchers and other stakeholders use widely available tools (e.g., LC-MS/MS, GC-MS) to detect and quantify target analytes beyond those included in methods employed by commercial laboratories. Frequently, the analytes measured vary from method to method, particularly between studies of different environmental matrices. For example, different analytes have been targeted in studies of landfill leachate,[47,48] AFFF-impacted groundwater,[49,50] and ambient air.[51,52] A comprehensive understanding of PFASs associated with particular sources and matrices would facilitate determination of an optimized analyte list for environmental source tracking.

Typically, the inclusion of analytes without any matched native or isotopically labeled internal standard requires semiquantification in which a high-confidence analytical standard is used to estimate the concentration of analytes lacking matched standards. Semiquantification is especially critical for source tracking because it enables the comparison of concentrations of compounds without analytical standards with the concentrations of confidently quantified compounds.

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Semiquantitative analytes, particularly those with matched native standards but without mass-labeled internal standards (e.g., perfluorobutane sulfonamide), can be incorporated into analytical methods[53,54] with sufficient confidence to benefit source tracking when used as part of multivariate statistical models.

Future research should seek to identify "sentinel" PFASs, defined as PFASs that are primarily observed in only one type of PFAS source. For example, certain fluorotelomer carboxylic acids are typically found in much greater abundance in landfill leachate than other candidate sources.[55] Ideal sentinel compounds may be context dependent: when verifying the connection of impacts some distance away from a potential release location, sentinel compounds must be environmentally mobile and have long transformation half-lives. Sentinel compounds should then be candidates for inclusion in the standard target analyte lists offered by commercial laboratories.

High-resolution mass spectrometry (HRMS) is a means for identifying a wider range of PFASs, including possible sentinel compounds. Nontarget and suspect-screening methods on LC-HRMS and GC-HRMS are used to tentatively identify, or semiquantify, many PFASs that lack analytical standards.[9,50,56] Although HRMS analysis is primarily employed in academic research and niche commercial applications, it is highly effective for screening many PFASs in the environment and can be used to identify previously undocumented PFASs.[56−59] Compound identification is essential to environmental source tracking since recently identified PFASs (e.g., GenX) are frequently observed in the environment.[60,61] However, because quality assurance protocols for HRMS are not standardized, this technology has limitations. HRMS is prone to false positives and negatives, and novel PFASs identified by HRMS require further investigation for confident identification (e.g., a comparison to a standardized PFAS library, technical mixture, or commercially available standard). Nonetheless, HRMS is a valuable tool for qualitatively determining PFAS fingerprints because it can identify candidate structures from complex mixtures in environmental matrices at environmentally relevant concentrations. Sentinel compounds identified by suspect or nontarget MS techniques can be integrated into higher-confidence analytical techniques like LC-MS/MS using authentic standards over time.

HRMS data from forensic efforts can be archived for future analysis of as yet-undiscovered compounds without the need for reacquisition. Standardized data sets in an archive could help to rapidly refine source allocation algorithms after the discovery of a new compound without the need for additional sample collection and processing. Similar archives are already employed in other fields (e.g., Global Natural Products Social Molecular Networking).[62]

INTEGRATING PFAS SOURCE TRACKING INTO A CONCEPTUAL SITE MODEL

As a field, environmental forensics relies heavily on site-specific factors including the direction of groundwater flow and wind, variations in groundwater levels, surface water features and whether they gain or lose to groundwater, the composition of soil, the presence and depth of confining geologic layers, chemical redox conditions, engineered conditions, and the distribution of cocontaminants.[12] The elements of a conceptual site model (CSM) provide a baseline understanding of how chemical contaminants with different physicochemical properties migrate at a site. Publicly available geographic information system (GIS) data with regional hydrogeology, locations of point source discharges, relevant industrial operations, and chemical data can be used to identify and prioritize other PFAS releases near a site.[6,7,63] PFAS data, including ratios of PFASs, the presence of sentinel PFASs, and variations in isomer distributions, should be aligned with the CSM to draw conclusions about separate source releases and the potential convergence of migrating PFASs (Figure 1).[30,39]

The effects of the transformation of polyfluorinated substances on the PFAS fingerprint can be predicted within the context of the CSM. Redox conditions influence the rates and products of polyfluorinated compound transformation.[64,65] In laboratory experiments, transformation rates of polyfluorinated compounds increase under aerobic conditions and favor the production of terminal PFAAs.[7,43,64,66−68] Anaerobic transformation of polyfluorinated compounds has not been fully investigated and is an area requiring further research. Because different precursors often have common intermediate or terminal transformation products, natural processes may eliminate distinguishing sentinel compounds observed near sources.[38] For example, many PFASs with sulfonamido moieties (e.g., sulfonamido acetic acids and sulfonamido alcohols) are present in commercial products[69,70] and can transform into the more commonly observed perfluoroalkyl sulfonamides and PFSAs.[44,66] Similarly, remediation efforts may transform distinguishing precursor compounds into PFCAs or PFSAs.[39] The linear isomers of PFAAs may be enriched by preferential biotransformation.[40,71] In contrast, branched isomers are less retarded during subsurface transport and hence are often enriched with distance along the groundwater transport pathway.[38,41,42]

Transport phenomena also impact the PFAS fingerprint and may have convergent or divergent effects on PFAS concentrations and ratios relative to transformation processes. PFASs with higher partitioning coefficients (e.g., perfluorodecanoic acid, cationic precursors) are significantly enriched in unsaturated soils relative to underlying saturated soils and groundwater, which are conversely enriched with more mobile PFASs.[30,38,72,73] Soil composition and moisture content affect the partitioning behavior of PFASs in both the unsaturated and saturated zones.[74] The PFAS composition in plumes that move through sandy or fractured strata that allow for rapid advection may undergo minimal changes due to weaker partitioning effects. For lithologies such as organic-rich soils, where PFASs may be significantly retained, a greater proportion of the more mobile PFASs will be observed further from the source.[38,73−75]

Because of transformation and transport phenomena, the environmental matrix from which samples were collected influences the PFASs and their relative concentrations observed. The analysis of colocated samples from multiple matrices can provide a more complete understanding of the compounds present at an impacted site and how the compounds are distributed at both large and local scales. Although the relative contribution of various sources will decrease with distance from the source input, it is possible to separate individual sources in commingled plumes by using converging lines of evidence (e.g., appearance of longer chain PFASs or new terminal analytes[76] with distance from a known source input).[10,38]

Aerial, surface, and subsurface release mechanisms influence the vertical and horizontal distribution of PFASs. Aerial discharges, such as those from a manufacturing facility with stack emissions, result in radial PFAS contributions to surficial

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soil that decline with distance from the release point and angle from the prevailing wind direction.[21,77,78] Surface releases, such as AFFF application, will also impact surrounding soil; however, the impact will be concentrated much closer to the point of release and biased toward overland flow pathways.[30] Subsurface releases, such as leaks in sewer lines, result in higher PFAS concentrations in the subsurface, providing a vertical concentration distribution that enables the differentiation of the route of PFAS release.[38,79,80] In comparison, aerial releases often leave the highest impact in surficial soil where the PFASs are deposited.[78,81] Concentration gradients that run at odds with the site-specific understanding of groundwater and surface water flows may indicate multiple releases, conveyance via stormwater or sewer infrastructure, or precursor transformation.[38,80]

MULTIVARIATE STATISTICAL ANALYSES

Analytical data from target or nontarget analysis coupled with site data from CSMs can yield data sets that are amenable to multivariate analyses for PFAS source tracking. Unsupervised multivariate analyses (e.g., clustering and ordination) are exploratory techniques that can be used to reveal obscured patterns within large environmental data sets. For example, several recent studies have used hierarchical clustering analysis (HCA) to explore PFAS composition profiles across spatially variable environmental samples.[7,82,83] The major clusters of PFASs identified in the resulting HCA dendrograms represent groups of PFASs with similar composition profiles and are typically inferred to be derived from the same source(s). Likewise, principal component analysis (PCA) is an ordination technique that has been widely used to summarize the variability that is present in complex multivariate data sets.[7,82] For example, PCA was previously used to discover relationships between spatially variable PFAS occurrence data and different types of PFAS sources to explain PFAS source contributions.[7] In Zhang et al.,[7] PCA loading plots were used to identify statistically distinct PFAS composition profiles across a group of environmental samples, and PCA score plots were used to reveal specific sample sites that were statistically associated with each PFAS composition profile. Complementary geospatial analyses enabled inferences on the putative sources of the groups of PFASs contained in each distinct PFAS composition profile.

Supervised multivariate analyses (e.g., classification and regression) are predictive techniques that can be used to infer functions from large environmental data sets that map input data to a particular response. For example, Kibbey et al. used several classification techniques to map PFAS concentration profiles to AFFF or non-AFFF sources; the classifiers were defined by patterns in PFCA and PFSA concentrations among samples, and the resulting models accurately classified new samples from a variety of sources.[20,84] Importantly, the classification performed well even for a subset of the AFFF test data that exhibited anomalously high fractions of PFCAs demonstrating the robustness of some classification techniques.[84] PCA has also been used in combination with multiple linear regression (MLR) to estimate the fractional contribution of different sources. In this PCA-MLR approach, the factor loadings obtained from PCA are used as independent variables in a MLR model to predict the measured contaminant concentrations; the coefficients of the parameterized MLR model can be used to estimate fractional contributions of each factor to the measured contaminant concentrations.[82,85]

Despite the adaption of a number of different types of multivariate analysis tools for the purposes of environmental source tracking, verification and validation of the resulting models have lagged behind and are a critical need for the future of environmental forensics. We recommend increased testing of learning algorithms and their individual classifiers using field collected data. We further note that the unsupervised techniques that are useful for revealing patterns in large environmental data sets are less likely to yield generalizable tools to explain source contributions from unknown samples. Rather, as has been demonstrated in other fields,[86−88] it is more likely that supervised techniques (alone or in combination with unsupervised techniques) will lead to more generalizable PFAS forensics tools that could be applied to unknown samples.

Finally, we stress that multivariate analysis tools, including those mentioned in the preceding paragraphs, have been developed with explicit assumptions about the data structure; however, these assumptions are rarely discussed or evaluated. Inappropriate use of multivariate tools can lead to misleading or invalid conclusions. Ideally, practitioners relying on multivariate analyses should identify tools that are suitable for an anticipated data structure prior to sample collection to ensure computational integrity.

RECOMMENDATIONS FOR THE ADVANCEMENT OF PFAS SOURCE TRACKING

Approaches for PFAS source tracking are less established than for other contaminants, although existing analytical techniques are already being applied to support the characterization of PFAS sources and to determine source apportionment.[5,7,8] The existing PFAS source tracking approaches should be considered preliminary but in some cases may provide sufficiently clear forensic information when considered within a conceptual site model (CSM). The apportionment of PFAS contamination, a technical exercise involving the division of PFAS contamination into "shares" from sources,[12] is the ultimate goal of source tracking efforts. The apportionment, in turn, could lead to legal recourse for stakeholders impacted by PFAS contamination. Present source tracking techniques for PFASs have not yet been confirmed to meet this level of rigor but are developing rapidly.

PFAS fingerprints should be more fully characterized using existing targeted methods (e.g., LC-MS/MS, GC-MS) and semiquantitative or nontargeted methods (e.g., HRMS). The detection of legacy PFASs and the discovery of novel PFASs are becoming more routine, but more research is needed to identify sentinel compounds and distinguishing compound ratios (e.g., PFHxS/PFOS or branched/linear isomers) that may indicate a particular PFAS source. However, environmental PFAS fingerprints should be considered within the context of a CSM. Source tracking must incorporate chemical analysis and site-specific factors such as potential sources of release, PFAS partitioning to the matrix sampled, differential transport rates, and the transformation of polyfluorinated substances. These factors are necessary to interpret key chemical differences in PFASs originating from different sources.

Advances in HRMS and HRMS data processing, particularly for suspect screening, may make it a more commonplace technique for source fingerprinting in academia and industry. Platform-independent HRMS spectral data (e.g., mzXML format) from impacted sites should be made available to the

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research community for multivariate analyses. HRMS analyses should provide information for the development of target analyte lists and identify key compounds in need of analytical and technical standards.

Each individual PFAS source tracking effort can contribute to a publicly available collection of environmental PFAS fingerprints. This collection of data should include digitally accessible geospatial information, quantities of all measured target PFASs, and when available, platform-independent mass spectral data that could enable later analyses (e.g., for subsequently identified PFASs). Subsequent source tracking efforts could utilize a thoroughly characterized database of PFAS sources and contaminated site information. A comparison to publicly available data will lead to better identification of outliers in the CSM and PFAS fingerprints, which in turn will mitigate the report of false negatives and false positives. For instance, some lines of evidence may provide complementary or contradictory evidence relative to the public data, which could be resolved through critical analysis and additional iterations of data collection (e.g., more sample collection, improved hydrologic characterization). Tools that evaluate the statistical significance of differences in PFAS fingerprints along a transport pathway will add certainty to the attribution of PFAS mixtures to single or multiple sources. Pairing source fingerprints with spatial context using multivariate statistical analysis will facilitate the apportionment of PFAS contamination in the environment. We recommend further development of both supervised and unsupervised learning algorithms for PFAS source tracking and apportionment.

Each of the advances we propose will provide additional lines of evidence to a PFAS source tracking approach and more confidence to source apportionment (Figure 1). With more widespread detection of environmental PFASs and growing public concern about their health effects, the demand for PFAS source tracking will be high in the near future. The accurate determination of contributing sources will have important consequences for environmental interventions, public health, and liability concerns. The scientific community should be equipped with source tracking tools and forensic strategies to confidently and accurately identify sources of environmental PFASs.

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Notes

The authors declare no competing financial interest.

Biography

Dr. Houtz is a senior engineer at Arcadis. She has significant experience in developing analytical and experimental methods for the measurement of PFASs in environmental and human samples. She has also investigated and published on the fate and transport of PFASs in natural and engineered systems with a particular emphasis on the fate of PFASs found in aqueous film forming foams. At Arcadis, she is the PFAS analytical lead and a technical resource for PFAS site investigation and treatment technology evaluation.

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