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Poly- and perfluoroalkyl substances experts Symposium 2: Key advances in poly- and perfluoroalkyl characterization, fate, and transport

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Abstract

The Poly- and perflouroalkyl substances (PFAS) experts Symposium 2, held virtually from June 29 to July 1, 2021, brought together experts from a wide range of disciplines to discuss recent advances and current thinking regarding PFAS in the environment. Within the general areas of characterization and fate and transport, three topics were identified that are of relevance for site assessment and remediation, and for which our understanding has greatly expanded or evolved since the first PFAS Experts Symposium in 2019: the significance of background PFAS sources to the environment, the relevance and use of nonselective analytes in site characterization, and PFAS retention in soil and the vadose zone. PFAS have been identified in shallow soil nearly worldwide, including far from known or suspected PFAS sources, and PFAS detected in soil and groundwater at sites under environmental investigation may not reflect on-site sources. New advances in nonselective preparation and analytical methods offer promise for more rapid site screening and for assessing the presence and relative concentration of nontargeted PFAS. We also now recognize that a wide range of soil characteristics and processes may affect PFAS sorption and desorption from soil, and ultimately influence PFAS mobility and concentration in groundwater and surface water.

KEYWORDS
hazardous site characterization, remediation

1 | INTRODUCTION

This paper was developed as an outcome from presentations by the Characterization, Fate, and Transport group given as part of the poly- and perfluoroalkyl (PFAS) Experts Symposium 2 (Symposium), a virtual, invitation-only conference held from June 29 to July 1, 2021. The Symposium was a follow-up to a previous PFAS Experts Symposium held in May 2019 (Simon et al., 2019). The primary objective of the Symposium was to share current and emerging information and thinking regarding per- and polyfluoroalkyl substances (PFAS) among experts representing a wide range of different scientific and technical fields, and to serve as an update to

ideas and concepts first developed in the 2019 Symposium. Each of the listed authors participated in the Symposium and contributed to the discussions and presentations.

Our understanding of the sources, fate, and transport of PFAS in the environment is rapidly evolving and is of critical interest for risk assessment, remediation, regulation, and liability. Within the general areas of characterization, fate, and transport, the Symposium organizers and participants identified three topics of particular interest for which our understanding has greatly expanded or evolved significantly since the 2019 Symposium. These include significance and magnitude of off-site (or background) PFAS sources, the relevance and use of nonselective preparation and analytical methods in PFAS site characterization and fate and transport assessment, and retention of PFAS in source areas. The purpose of this paper is to summarize the relevance of each issue, evaluate critical uncertainties, and offer recommendations for practitioners and for future research.

2 | RURAL, SUBURBAN AND URBAN BACKGROUND, AND NONSITE RELATED SOURCES

PFAS have been manufactured since the 1950s and, after decades of use in a vast number of industrial, commercial, and household products, PFAS are widely distributed in the environment today. Commonly recognized primary sources to the environment include facilities where PFAS have been synthesized; manufacturing facilities were PFAS have been used for production of personal, commercial, and/or industrial products (e.g., cosmetics, fabric coatings, and mist suppressants for chromium electroplating); and fire training or accident response areas where aqueous film forming foam (AFFF) was utilized for fire suppression. Potential secondary sources of PFAS to the environment include waste management units such as landfills and wastewater treatment plants that have historically received PFAS-bearing wastes; land application of biosolids, landfill leachate, and wastewater treatment plant effluent; stormwater runoff (Page et al., 2019); and deposition from upwind atmospheric releases from industrial facilities that use or manufacture PFAS (Schroeder et al., 2021). Less obvious sources include rainwater contaminated by atmospheric releases; aerial spraying of pesticides impacted by PFAS associated with chemical storage containers; and residential septic discharges of PFAS associated with consumer products. Due to the long history and wide variety of use, disposal practices, and transport mechanisms, PFAS detected in environmental media at a particular site may not be related to on-site activities. Determining if PFAS are site-related or not is a key issue because site owners and responsible parties may not be liable for PFAS from background or off-site sources. This is particularly relevant for management of sites at which PFAS use or release are not suspected, there are other known or suspected local or regional PFAS sources that are not site-related, and/or the site is located in an area with a recognized regional surface water and/or groundwater PFAS background.

2.1 | What is background for PFAS?

PFAS are commonly regulated at concentrations in the range of tens of nanograms per liter (or parts per trillion) in drinking water and in groundwater. In some cases, regulatory agencies have proposed goals and standards that are far lower (e.g., California Environmental Protection Agency Pesticide and Environmental Toxicology Branch Office of Environmental Health Hazard Assessment, 2021). Due to these low-regulatory thresholds and associated analytical quantitation levels and their widespread distribution in the environment, detection of PFAS in environmental media such as soil and groundwater is relatively common even far from known or potential sources. Complete "nondetects" are possible but are often atypical.

Brusseau et al. (2020) compiled soil PFAS data from published surveys from approximately 2500 sites around the world, including urban and rural sites representing background, primary source sites, and secondary source sites. PFAS concentrations at sites considered to represent background were generally orders of magnitude lower than at primary and secondary source sites; however, PFAS were detected in soil at almost every site tested, even in remote regions far from potential PFAS sources. Detected concentrations of PFAS in soil do not necessarily result in detectable concentrations in groundwater at all sites; corresponding concentrations in groundwater are generally far lower than in soil, with considerable variability correlated to soil characteristics (Anderson et al., 2019). However, stormwater, surface water, and groundwater in urban and some rural areas far from known sources have yielded detectable PFAS concentrations (e.g., Bai & Son, 2021; Goodrow et al., 2020; Vedagiri et al., 2018). As a result of the many possible but commonly unknown sources of PFAS in the environment, there is often an "urban background" concentration of PFAS present in soil and shallow groundwater that may exceed regulatory thresholds but is not related to an on-site source.

2.2 | Site setting considerations

A challenge in PFAS site investigation is to differentiate site-related PFAS from off-site (or background) sources of PFAS. That is, were PFAS released at the site of interest, and if so, what is the relative contribution of impacts from the site relative to background and off-site sources? This differentiation starts by developing a conceptual site model (CSM) for PFAS that incorporates evaluation of potential background and off-site sources, followed by data collection, evaluation, and synthesis with a refined CSM to verify the nature and extent of PFAS due to on-site activities. If PFAS detected at a site are determined to be site-related, then the sampling results should be sufficient to support risk assessment and evaluation of remedial alternatives. More specific considerations are described below.

Site setting is an important consideration for sampling design at scales ranging from the site, adjacent properties, and region. On-site PFAS source assessment may be straightforward for primary source areas such as AFFF discharge locations and manufacturing plants

where PFAS have been used, secondary source areas such as landfills, areas where biosolids have been applied, and where irrigation has occurred using known impacted surface water or groundwater (Brusseau et al., 2020; Eggen et al., 2010; Lindstrom et al., 2011). Source assessment is more difficult at sites where PFAS were not known to be utilized in operations, or where PFAS sources may include short- and long-range transport of PFAS from off-site sources via atmospheric deposition or stormwater runoff (Galloway et al., 2020; Xiao et al., 2012). For example, an urban area may have nearby industrial sources; a suburban area may have nearby landfills; and a rural area could have used biosolids or have active or abandoned septic systems, all of which may contribute to PFAS background at a specific site of interest. Thus, evaluation of PFAS sources should extend well beyond the fence line and include characterization of regional groundwater and surface water flow patterns and prevailing wind direction. Identification of known PFAS sources upwind and/or upgradient of a site (potentially available through state agency databases), review of local newspapers (which may discuss other sources in the vicinity of a project site), consideration of prevailing wind directions, and an understanding of area and region-specific hydrogeology and hydrology should factor into the evaluation (Shimizu et al., 2021). PFAS concentrations at nearby sites should be considered based on proximity and orientation relative to air and water flow directions (e.g., upgradient, local, and downgradient), when those data are available. PFAS are known to leach from soil to surface water and groundwater, thus a multi-media analysis may be appropriate.

2.3 | Considerations and recommendations for collection of background samples

The following considerations and recommendations are offered to evaluate the presence and quantify the potential contribution of background PFAS at a site.

- Analyze as many individual PFAS as possible, rather than restrict the targeted compounds only to those that are regulated at the time of the investigation. Commercial laboratories can currently quantify about 75 PFAS in a variety of environmental matrices, however in some cases, samples are only analyzed for a short list of specifically regulated compounds. The diversity of PFAS and the presence of different structural isomers (i.e., linear and branched isomers) provide opportunities to potentially differentiate off-site and on-site sources. Additional analytes may also become critical in the future as the number of regulated PFAS constituents evolves over time.
- Consider the need to identify or quantify precursors, including nontargeted analytes. Many nontargeted PFAS may partially transform in the environment, resulting in relative PFAS compositions that evolve during transport to a downgradient receptor.
- Consider future property access availability and resampling costs. Access in some instances may be a one-time event, thus it is

important to determine all the data needed before negotiating access. This can be particularly important in a litigation context, in which obtaining all the relevant data in a timely manner is crucial and having data from multiple environmental media (e.g., soil, surface water, and groundwater) may be important.

- Consider a tiered approach to data analysis. A first step may be to evaluate the relative concentrations of specific PFAS among different samples, for example, using graphical approaches and/or multivariate statistical methods such as principal components analysis.
- Consider that data needs for evaluation of potential background sources may differ from data needs commonly utilized for risk assessment. Brusseau et al. (2020) demonstrated that PFAS concentrations often exhibit exponential decreases with sample depth below the surface and exhibit differential sorption of long-chain versus short-chain PFAS, due to a variety of factors including PFAS source properties (e.g., PFAS type, source input conditions, and co-contaminants), soil properties, and meteorological conditions. Evaluation of potential background sources such as atmospheric deposition should focus on shallow surface soils (e.g., from 0 to 3 inches or 0 to 6 inches below grade), rather than a common convention of 0 to 2 feet (or similar) often utilized in risk assessment. This may result in replicate samples over a depth profile to meet data quality objectives, for example, very shallow samples to evaluate potential background sources and deeper samples (or longer composite depth intervals) to meet standard risk assessment needs.

Our understanding of the wide distribution of PFAS in the environment and potential background sources is rapidly evolving. What may be considered "background" has evolved from focusing only on PFOA and PFOS to a wider range of compounds, including transformative precursors (e.g., fluorotelomers). Analytical methods are also evolving to include agency-accepted methods for media other than drinking water. Laboratory analyte lists continue to expand rapidly as standards become available for more PFAS, and new preparation and analytical methods are developed for various purposes (e.g., Total Organic Fluorine, Total Oxidizable Precursor Assay, and nontargeted analysis). Analytical laboratory detection limits are decreasing, and data validation methods are being developed. The regulatory environment is also changing. PFAS standards in sediment, surface water, and new standards for more PFAS are all on the horizon. New regulatory limits and limits in additional media will present new delineation and remedial challenges.

3 | RELEVANCE AND USE OF "NONSELECTIVE" ANALYTES IN SITE CHARACTERIZATION AND FATE AND TRANSPORT EVALUATIONS

According to the 2020 USEPA Master List of substances, there are over 9000 compounds that fit the generally accepted definition of PFAS, and over 6300 have Chemical Abstract Service Numbers (U.S.

Environmental Protection Agency, 2020). However, currently approved analytical methods are only able to quantify a relatively limited number of PFAS. Commercial laboratories are currently able to quantify up to about 75 PFAS using targeted methods. The inability to identify and quantify a large percentage of PFAS potentially present in various environmental media is a substantial impediment to accurate characterization of sites for potential PFAS impacts and to evaluate the fate and transport of PFAS. With mounting public, regulatory, and political pressure to investigate and address PFAS contamination concurrently with calls to expand the list of regulated PFAS, adopt a class-based approach for regulation of PFAS, and regulatory agencies considering cumulative PFAS criteria, it is logical that responsible parties and practitioners consider employing strategies to evaluate more than just the relatively small list of targeted PFAS reported by conventional analyzes at sites where it is unclear if or what types of PFAS or PFAS-bearing products were utilized or discharged. Use of nonselective preparation and analytical methods may be a component of those strategies. Nonselective methods quantify a parameter that reflects the total amount or some specific fraction of PFAS and other organofluorine compounds present in a sample rather than quantify the concentration of a specific (or targeted) PFAS. Use of nonselective methods can play an important role in site investigations until analytical methods can quantify a larger variety of targeted PFAS. These methods may also be useful for mass balance evaluations and may provide relatively inexpensive and rapid screening tools in PFAS investigations. However, it is also important to note that these nonselective methods may create new challenges in risk communication, especially when the site is in litigation and before screening levels or formal criteria incorporating nonselective analyzes are developed by regulatory agencies.

Examples of currently available nonselective preparation and analytical methods outlined further below include total oxidizable precursor (TOP) assay, total organic fluorine (TOF), and extractable organic fluorine (EOF), and total fluorine methods such as particle-induced gamma ray emission (PIGE). The following paragraphs describe these methods and summarize their advantages and limitations within the context of site characterization, risk assessment, and fate and transport evaluations. When using one or more of these methods, it is critical to understand what the resulting analytical data represent (and do not represent) and as such, an upfront understanding of the objectives for the additional analyzes is very important. It is also important to understand that none of the nonstandard methods have standardized, regulatory agency-approved methodologies; thus, each laboratory may perform the method somewhat differently, which may result in high inter-laboratory variability and quality assurance issues.

3.1 | TOP assay

The TOP assay is a sample preparation method developed to evaluate the presence and concentrations of unidentified precursor compounds of perfluoroalkyl carboxylic (PFCA) and sulfonic (PFSA) acids in water samples (Houtz & Sedlak, 2012; Zhang et al., 2019). In the TOP Assay a water sample is exposed to a strong oxidant (hydroxyl radicals) generated by thermolysis of potassium persulfate under high pH and elevated temperature conditions. Perfluoroalkyl acid (PFAA) precursors are transformed during the oxidative treatment to PFCAs of related perfluorinated chain length. Targeted PFAS are analyzed in the water sample both before and after the oxidation procedure, and the presence and relative concentration of total PFAA precursors are inferred by comparison of PFCA concentrations before and after oxidation. For example, a significantly higher PFCA concentration in the oxidized sample relative to the untreated sample indicates the presence of nontargeted precursor compounds in the sample, which may transform in the environment into PFCAs because of remediation or natural attenuation mechanisms.

The TOP Assay provides a surrogate for the total concentration of PFAS that are not quantified by current targeted analyzes. Unlike the alternative analytical methods discussed below, this approach is specific to measuring PFAS and PFAS precursor compounds before and after oxidation. Currently, the TOP Assay is considered the most selective of PFAS surrogate analytical methods (McDonough et al., 2019). Since this preparation method can provide insight into concentrations of PFAS present in the sample that are not included in the suite of targeted PFAS, the results can provide a better understanding of the potential impacts due to the presence of nontargeted PFAS and precursor compounds. The TOP Assay can also help to assess potential changes in PFCA concentrations because of oxidative remediation methods and natural attenuation that can partially transform PFAA precursors. The TOP Assay relies upon standard PFAS analytical methods for quantification of targeted compounds, and thus can achieve quantitation limits in the low part per trillion range consistent with current regulations.

There are important limitations regarding use and interpretation of TOP Assay results. The method is an intensive assay requiring aggressive chemical oxidation procedures and analysis of duplicate samples to quantify pre- and post-oxidation PFAS concentrations. As a result, the TOP Assay is labor intensive and typically has longer turnaround times and higher cost. The results do not necessarily provide a measure of "total" PFAS concentration because not all PFAS are reactive and will be oxidized to PFAAs. A final factor for consideration is that the strongly oxidative conditions utilized in the TOP Assay may greatly exceed the capacity of natural processes under typical environmental conditions to oxidize the precursor PFAAs; thus, the TOP Assay has the potential to result in higher PFAA concentrations than could be realized in the field.

3.2 | TOF and EOF

TOF and EOF analyzes measure the total concentration of different fractions of organically-bound fluorine (Miyake et al., 2007; Willach et al., 2016). TOF is commonly measured by isolating organofluorine compounds on activated carbon and then analyzing fluorine content by combustion ion chromatography (CIC). This analysis is also commonly referred to as adsorbable organic fluorine (AOF), and includes

all organofluorine compounds (including cationic, anionic, neutral, and zwitterionic compounds) that can be adsorbed to activated carbon (Willach et al., 2016). EOF is measured by solid phase extraction of organic fluorine species dissolved in water to an anionic exchange polymer, followed by elution and analysis of the extract by CIC to determine fluorine content. EOF comprises only neutral and anionic organofluorines (Willach et al., 2016) and thus is a fraction of TOF.

TOF and EOF methods utilize organic fluorine as a surrogate for PFAS. The advantage of TOF and EOF is that they generally provide a more rapid and lower cost screening tool to determine if a significant concentration of fluorine-bearing compounds is present in a sample. However, unlike the TOP Assay, the TOF and EOF methods are not specific to PFAS; other organofluorine compounds (such as chlorofluorocarbons and certain pharmaceuticals and pesticides) will also be quantified. It is also difficult to infer PFAS concentrations from TOF and EOF results because fluorine is a variable fraction of the formula weight of individual PFAS, depending upon chain length, alkyl group composition, and degree of polyfluorination. Detection limits are also generally much higher than TOP Assay and targeted methods; Willach et al. (2016) cite a detection limit of 0.77 μg of fluorine per liter, which is equivalent to a concentration of 13 μg per liter as PFOS (approximately four orders of magnitude higher than common detection limits for individual PFAS in a targeted analysis). Thus, TOF and EOF results are most effective as screening tools for relatively high concentration matrices such as at sites impacted by AFFF, rather than at concentrations approaching typical regulatory levels.

3.3 | Particle-induced gamma ray emission

PIGE is a nondestructive analytical method that measures emission of a gamma ray wavelength specific to fluorine when the sample is impacted with a proton ion beam (Ritter et al., 2017). The method can measure total fluorine content on the surfaces of a variety of materials, such as paper, textiles, food packaging, and soil. The technique can also be applied to water samples using solid phase extraction and then analyzing the anion exchange polymer. PIGE is not specific to PFAS and will quantify both organic and inorganic fluorine; and like TOF and EOF, it is also difficult to infer PFAS concentrations from PIGE results because fluorine is a variable fraction of the formula weight of individual PFAS. Fluorine content in solids measured by PIGE is commonly reported in units of nanomoles fluorine per square centimeter (nmol F/cm^2) of the material, and thus not directly comparable to units of measurement upon which regulatory and risk assessment criteria are typically based (weight per volume [e.g., ng/L] or weight per weight [ng/kg]). Reported detection limits range from 13 to 149 nmol F/cm^2 for a variety of materials (Ritter et al., 2017). PIGE analytical results for anion exchange polymers generated from solid phase extraction of water samples can be transformed to report the concentration in the extracted water sample on a weight per volume unit based upon the volume of water extracted. Typical detection limits for water samples are in the range of about 10 μg per

liter (similar to TOF and EOF analyzes), which are about four orders of magnitude higher than common detection limits for targeted PFAS analysis. This generally limits application of PIGE analyzes to screening at sites potentially impacted with relatively high concentration matrices such as at sites impacted by AFFF, rather than at concentrations approaching typical regulatory levels.

PIGE is different from the other nonselective analytes in that it can measure surface-bound fluorine rather than bulk sample concentrations, which may be relevant for certain types of assessments. Recent technological advancements and research may result in a field deployable PIGE system with detection limits potentially as low as approximately 10 to 50 ng per liter (https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Risk-Assessment/ER19-1142; retrieved November 24, 2021). This would allow application of PIGE to greatly reduce site investigation timeframes and costs.

4 | SOIL RETENTION

Concentrations of PFAS found in vadose zone soil at contaminated sites are generally orders of magnitude higher than in underlying groundwater (Brusseau et al., 2020). This leads researchers to posit the question: what is the long-term migration potential to groundwater and surface water? Improved understanding of the processes and factors influencing PFAS retention in soil and the vadose zone is relevant to fate and transport of PFAS in groundwater and ultimately for risk assessment and remediation.

As surface active compounds, PFAS preferentially accumulate at phase interfaces (e.g., the air-water and nonaqueous phase liquid [NAPL]-water interfaces). The impact of air-water interfacial adsorption on retention and transport of PFOS, PFOA, and GenX in unsaturated porous media has been examined in miscible-displacement laboratory studies (Brusseau et al., 2021). Mathematical-model simulations of representative PFAS application scenarios have also illustrated the influence of air-water interfacial adsorption on PFAS retention and migration in the vadose zone (Guo et al., 2020; Silva et al., 2020). In aggregate, these studies demonstrate that air-water interfacial adsorption can be a significant source of retention. The magnitude and relative significance of such retention will depend upon the specific PFAS, solution conditions, and soil properties.

Brusseau (2019) examined the propensity of 42 fluorinated compounds (PFCAs, PFSAs, etc.) to adsorb at the air-water interface (as quantified by the interfacial adsorption coefficient, log K_i) and found a strong, positive correlation (r^2 of 0.94) between log K_i and molar volume (which is a measure of molecular size and is related to carbon chain length). This correlation demonstrates that the tendency of these compounds to accumulate at the air-water interface can be predicted by quantifiable physico-chemical parameters that represent their relative hydrophobicity. Recent surface-tension studies and transport-experiment investigations have examined the influence of solution ionic strength and composition (Brusseau & Van Glubt, 2019; Costanza et al., 2019; Silva et al., 2019), the presence of PFAS mixtures (Brusseau & Van Glubt, 2019; Huang et al., 2022; Silva et al., 2021),

and the presence of hydrocarbon surfactants (Ji et al., 2021) on air-water interfacial adsorption and retention of PFAS.

Sorption of PFAS by soil and sediment, that is, solid-phase sorption, is another generally significant retention process for both the saturated and unsaturated zones. It is generally agreed that soil organic matter (SOM) is the primary constituent that controls the capacity and kinetics of PFAS sorption onto soils and sediment in many cases, particularly for media with larger SOM contents (Higgins & Luthy, 2006; Y. Li et al., 2018; F. Li et al., 2019; Sima & Jaffé, 2021; Wei et al., 2017). However, it has been demonstrated that other soil constituents such as metal oxides and clay minerals can also contribute to PFAS sorption, particularly for shorter-chain PFAS and soils with lower SOM contents (Higgins & Luthy, 2006; Lyu et al., 2020; Pereira et al., 2018; Wang et al., 2021). PFAS sorption has in some cases been observed to be a function of pH, ionic strength, and the degree of ionization of the PFAS. Although these observations and correlations are generally universal, participants at PFAS Expert Symposium 2 noted that PFAS are a large and diverse group of compounds and that it is difficult to generalize about them as a group. Although, as cited above, some generalizations can be drawn between various PFAS and specific properties, attributing these generalizations to all PFAS could in some cases result in significant errors. All reference herein is specific to nonpolymeric PFAS.

The Symposium participants also noted that translation of laboratory measured sorption parameters to field applications can involve significant uncertainty. Sima and Jaffé (2021) noted that laboratory measured sorption isotherms in some cases may tend to overestimate the reversibility of sorption and the potential for PFAS migration resulting from desorption (Zareitalabad et al., 2013; Zhi & Liu, 2018). They go on to note that studies of PFAS sorption kinetics have found that hysteresis may increase with time for some systems, making it difficult to predict the mobility of PFAS that have been sorbed to soil for decades with short-term laboratory sorption experiments (Y. Li et al. 2018; F. Li et al., 2019; Miao et al., 2017; Pan et al., 2009; You et al., 2010; Zhi & Liu, 2018).

Other factors in addition to solid-phase sorption and air-water interfacial adsorption may significantly control transport of PFAS in vadose zones and groundwater. It is well established that diffusive mass transfer between lower and higher permeability domains (i.e., back diffusion) can have a significant role in solute transport and plume attenuation/persistence in heterogeneous systems. Physical heterogeneity and preferential-flow phenomenon may be particularly relevant for air-water interfacial adsorption and migration of PFAS in the vadose zone. While abiotically and biologically mediated transformation of PFAS is not considered to be a significant factor in fate and transport of PFAAs, they can be of great importance for select PFAS precursors. Their presence and transformation to recalcitrant PFAS can complicate assessments of transport and fate.

A few essential characteristics shared by some (but not all) PFAS provide insight into their anticipated retention behavior, and into what we may still need to measure to understand the ultimate fate and transport of PFAS at contaminated sites. PFAS source (and site-specific chemical types), co-contaminants, background electrolyte concentration and composition, pH, soil organic carbon content and composition, metal-oxide content and composition, and clay mineralogy can influence PFAS sorption, making prediction complex. The complex chemistry of all PFAS includes compounds that may transform (e.g., oxidizable precursors), may be present under environmentally relevant conditions as zwitterions, cations, or anions, and may also be present as both branched and linear isomers for a given compound. Ultimately, possible electrostatic interactions with charged surfaces within the soil matrix, the affinity for interfacial accumulation, and the potential for nonlinear and hysteretic sorption can result in far more complex behavior than what we have come to expect for other organic contaminants. Moreover, saturated batch extraction methods routinely used in regulatory practice to estimate soil desorption potential are likely quite conservative primarily because any air-water interfacial area collapses under saturation of processed porous media. Site-specific distribution coefficients (e.g., McGuire et al., 2014) may be appropriate in some cases. However, given these complexities, the use of laboratory-derived solid-phase sorption parameters for field-scale modeling of PFAS migration through the vadose zone to groundwater should be done with caution and the acknowledgment that considerable uncertainty may exist for some applications.

The following recommendations were developed regarding retention of PFAS by soil:

- A critical analysis of published distribution coefficients suggests that due to the surfactant nature of some PFAS coupled with known dual hydrophobic/hydrophilic "ends," sorption coefficients (e.g., K_{oc} and/or K_d) for PFAS may be too oversimplified to broadly employ for modeling fate and transport, although there are some sites where sorption coefficients may be applicable with an appropriate evaluation of uncertainty, such as in the saturated zone within downgradient plumes.
- Focused studies are recommended for evaluating whether sorption coefficients are reliable tools or can be modified for broad conceptual assessments, meanwhile, mining of large (and growing) data sets for sites with detailed groundwater/soil concentration data should continue.

5 | CONCLUSIONS

The PFAS Experts Symposium 2, held virtually from June 29 to July 1, 2021, brought together experts from a wide range of disciplines to share their knowledge and current thought regarding PFAS in the environment. The characterization, fate, and transport group identified three key topics for which our understanding has evolved considerably since the first PFAS Experts Symposium in 2019: the significance of background PFAS sources to the environment, the relevance and use of nonselective analyzes in site characterization, and PFAS retention in soil and the vadose zone. PFAS have been identified in shallow soil nearly worldwide, including far from known or suspected PFAS sources, and PFAS detected in soil and groundwater at sites under

environmental investigation may not reflect on-site sources. New advances in nonselective analytical methods offer promise for more rapid site screening and to assess the presence and relative concentration of nontargeted PFAS. We also now recognize that a wide range of soil characteristics and processes may affect PFAS sorption and desorption from soil, and ultimately influence PFAS concentration in groundwater and surface water.

CONFLICT OF INTERESTS

The authors declare that there are no conflict of interests.

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