Challenges and opportunities for porous media research to address PFAS groundwater contamination

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Abstract

Per- and polyfluoroalkyl substances (PFAS) have become one of the most important contaminants due to their ubiquitous presence in the environment and potentially profound impacts on human health and the environment even at parts per trillion (ppt) concentration levels. A growing number of field investigations have revealed that soils serve as PFAS reservoirs at many contaminated sites after accumulating significant amounts of PFAS mass over many decades. Because PFAS accumulated in soils may migrate downward to contaminate groundwater resources, understanding the fate and transport of PFAS in soil is of paramount importance for characterizing, managing, and mitigating long-term groundwater contamination risks.

Many PFAS are surfactants that adsorb at air–water and solid–water interfaces, which leads to complex transport behaviors of PFAS in soils. Concomitantly, PFAS present in porewater can modify surface tension and other interfacial properties, which in turn may impact variably saturated flow and PFAS transport. Furthermore, some PFAS are volatile (i.e., can migrate in the gas phase) and/or can transform under environmental conditions into persistent PFAS. These nonlinear and coupled processes are further complicated by complexities of the soil environment such as thin water films, spatial heterogeneity, and complex geochemical conditions.

In this commentary, we present an overview of the current challenges in understanding the fate and transport of PFAS in the environment. Building upon that, we identify a few potential areas where porous media research may play an important role in addressing the problem of PFAS contamination in groundwater.

Keywords: Porous media, PFAS, fluid–fluid interfaces, fate and transport, soil, groundwater, adsorption

1. The PFAS contamination problem

PFAS is an acronym that stands for per- and polyfluoroalkyl substances, which are a family of thousands of synthetic chemicals widely used since the 1950s[1]. Large-scale manufacturing and applications (such as non-stick and stain-resistant coating, waterproofing treatment, and firefighting foams)[1] have led to their ubiquitous presence in the environment, contaminating surface water, soils, sediments, and groundwater. A growing body of field data demonstrates that vadose zones (below land surface and above groundwater table) at PFAS-contaminated sites have become significant PFAS reservoirs after accumulating mass over decades[2], posing a long-term threat to groundwater resources underneath.

The problem of PFAS contamination is distinctive compared to most of the previous contaminants due to a combination of the following aspects. *First*, PFAS have been widely used for many industrial applications and consumer products over many decades. Long-term releases from various pathways and sources at different concentration levels (e.g., local concentrated sources of aqueous film forming (AFFF)-impacted sites vs. wider and much-less concentrated sources of agricultural lands receiving PFAS-containing biosolids) have resulted in their widespread presence in the environment. For example, at least 6,189 sites are known to be contaminated by PFAS in the United States[3] and 45% of the United States drinking water was estimated to contain PFAS[4]. Similarly, 22,934 contaminated sites have been reported across 32 European countries with several countries (Belgium, Netherlands, Italy, Denmark, Germany, United Kingdom, and France) having more than 1,000 sites[5,6]. Note that these numbers may only reflect a fraction of the problem due to incomplete sampling and investigation. *Second*, unprecedentedly restrictive concentration levels have been established or are being discussed by regulatory agencies internationally. These concentration levels are several orders of magnitude lower than regulatory levels established for most prior contaminants[7]. For example, the maximum contaminant levels for PFOS and PFOA have been set to 4 parts per trillion (ppt) in the United States[8]. Even more restrictive regulations are used in some European countries such as Denmark[9] (i.e., 2 ppt for the sum of four PFAS). *Third*, PFAS consist of thousands of species with significantly different physicochemical properties (e.g., anionic vs. cationic vs. zwitterionic vs. neutral species, different functional groups, and carbon chain lengths) and transport behaviors.

Fourth, because vadose zones at many contaminated sites are PFAS reservoirs[2], understanding and quantifying PFAS fate and transport in the vadose zone are central for characterizing, managing, and mitigating long-term groundwater contamination risks. The above-discussed characteristics lead to significant challenges to address the PFAS contamination problem.

Furthermore, most PFAS are surfactants that tend to accumulate at fluid–fluid and solid–fluid interfaces[10]. These interfacially-active properties lead to their relatively unique transport behaviors in the environment, particularly in the vadose zone due to abundant air–water and solid–water interfaces in soils. Concomitantly, PFAS accumulating at fluid–fluid and solid–fluid interfaces can also modify the properties of the interfaces[10], including surface tension and wettability. The changes in interfacial properties may in turn impact variably saturated water flow and the transport of PFAS in the vadose zone[11,12]. Any effective characterization and remediation of contaminated vadose zones will require conceptualizations that incorporate these critical interfacial processes. In this commentary, we focus on discussing these complexities of PFAS fate and transport in the vadose zone and identify the challenges and opportunities where porous media research may be relevant.

2. Complexity of the PFAS problem from a fate and transport perspective.

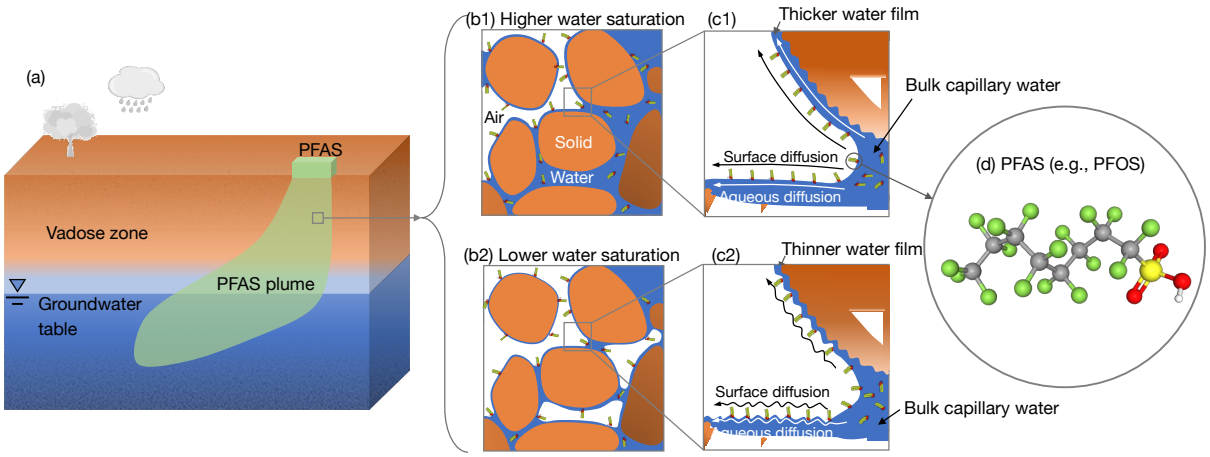

Figure 1. *Interfacial retention processes for PFAS in the vadose zone. (a) Schematic for PFAS contamination in the vadose zone and groundwater, (b) adsorption of PFAS at air–water interfaces arising from bulk capillary water and thin water films in soils under different wetting conditions, (c) mass transfer of PFAS between bulk capillary water and thin water films, and (d) an example PFAS molecule (e.g., PFOS), where the colors denote different atoms: gray–carbon, green–fluorine, red–oxygen, yellow–sulfur, and white–hydrogen. In panel (d), the molecule consists of a hydrophobic and oleophobic tail (the fluorocarbon chain on the left) and a hydrophilic head (the sulfonic acid functional group on the right). Figure originally reported in Chen & Guo (2023)[65] and used here with permission of the authors and Wiley.*

Air–water interfaces in the vadose zone may arise from the bulk water (e.g., pendular rings) between soil grains (i.e., bulk capillary air–water interfaces) and the thin water films on grain surfaces (Fig. 1). Under most field-relevant conditions, the latter accounts for >90% of air–water interfaces[13–18]. Air–water interfacial adsorption has been demonstrated to be a major mechanism controlling the fate and transport of PFAS in the vadose zone by laboratory column transport experiments[19–24], field observations[25,26], and mathematical modeling[11,12,27–32]. These studies highlight the importance of understanding and quantifying partitioning of PFAS at air–water interfaces in soils and how it controls PFAS transport in the vadose zone.

Fluid–fluid interfaces have been long recognized as an important factor controlling flow, transport, and reactions in porous media[33]. The processes at fluid–fluid interfaces include adsorption and desorption of interfacially-active solutes[34–38], attachment and detachment of colloids[39–42], and mass transfer between fluid phases[43,44]. One of the earlier drivers to quantify air–water interfacial area was to test a functional relationship among capillary pressure, saturation, and fluid–fluid interfacial area in a porous medium derived from thermodynamic principles[45–47]. A corollary of this functional relationship suggests that accounting for air–water interfacial area may eliminate hysteretic behaviors observed in capillary pressure and saturation relationships during cyclic drainage and imbibition processes[45–48]. Driven by this fundamental investigation and other more applied problems (e.g., dissolution of non-aqueous phase liquids [NAPL] in groundwater), multiple experimental methods have been developed to measure fluid–fluid interfacial areas in porous media since the late 1990s. One group of methods uses pore-scale imaging to explicitly count interfacial areas, such as X-ray computed tomography (XMT)[49–55]. Another group uses interfacially-active tracers to indirectly measure and compute fluid–fluid interfaces, either by retardation in the breakthrough curves during transport experiments or the mass of a tracer at fluid–fluid interfaces[34,35,37,56–59]. These interfacially-active tracers can be in the gas or liquid phase. Usually, the gas-phase tracer is an alkane (i.e., not charged) and the liquid-phase tracer an anionic hydrocarbon surfactant (i.e., negatively charged). Additionally, air–water interfacial area can also be estimated from measured soi water characteristic curves using a thermodynamic approach based on energy balance[60,61].

XMT (and other imaging-based methods) can separate thin-film fluid–fluid interfaces from bulk capillary interfaces. For a water saturation smaller than 0.5, the former measured by XMT is generally much greater than the latter in natural porous media[54,55]. The actual thin-film fluid–fluid interfacial area is usually even much greater because XMT underestimates the thin-film fluid–fluid interfacial area for sand and soil media. The cause is XMT not measuring the additional thin-film interfacial area due to the microscale grain surface roughness[13,55]. For example, by combining XMT and liquid-phase tracer methods, Brusseau et al. (2007)[13] reported that thin-film fluid–fluid interfacial areas in a sandy soil accounted for >90% of the total fluid–fluid interfacial area at water saturations smaller than 0.5. Further, the fluid–fluid interfacial area measured by gas-phase tracer methods is greater than that by liquid-phase tracers, especially under drier conditions[13,18,62]. The significant difference between the fluid–fluid interfacial area measured by liquid- versus gas-phase tracers remains not fully understood, though it was hypothesized that gas-phase tracers may access additional air–water interfacial domains[18,63]. An example of the differences between the air–water interfacial areas determined by the different methods is presented in Fig. 2[63].

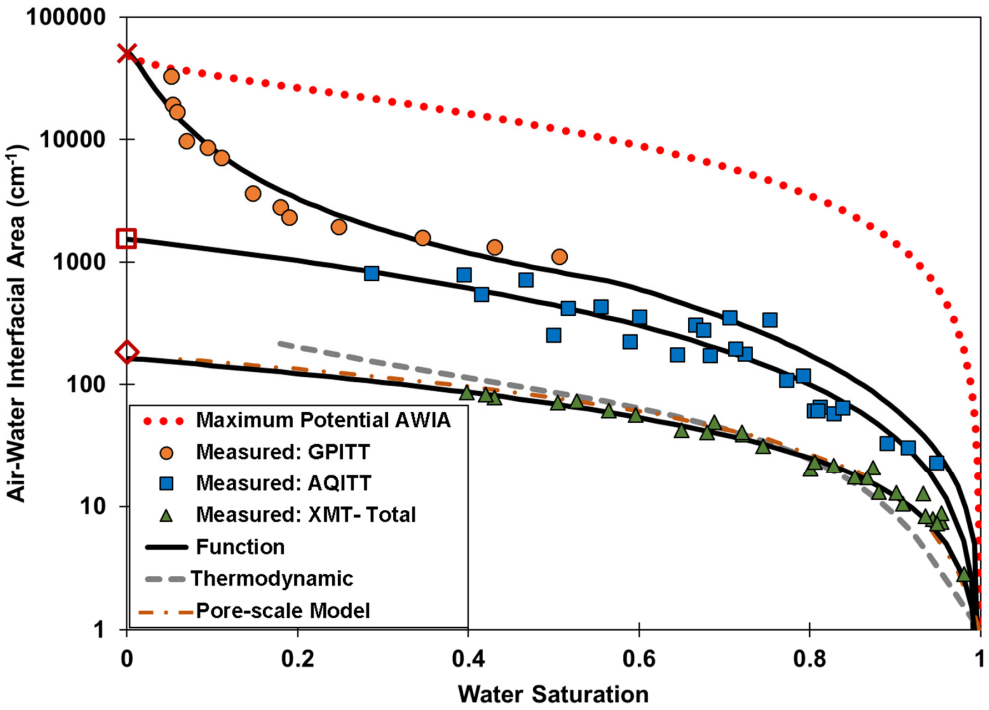

***Figure 2**. Air–water interfacial area as a function of water saturation for a sand determined by different measurement methods and models. "GPITT" denotes gas-phase interfacial tracer test, "AQITT" denotes aqueous interfacial tracer test. "XMT-total" is the total air–water interfacial area (bulk capillary and film-associated air–water interfacial area) measured by XMT. "Function" refers to an empirical fit. "Thermodynamic" denotes the results computed from the thermodynamic approach[60,61]. "Pore-scale Model" refers to the air–water interfacial area computed by the model from Jiang et al (2020)[17]. Figure originally reported in Brusseau (2023)[63] and used here with permission of the author and Elsevier.*

While the prior works quantifying the air–water interfacial area made the distinction between the bulk capillary and thin-water-film air–water interfaces, the two types of air–water interfaces are not differentiated in most transport model conceptualizations for the retention and transport of interfacially-active contaminants. These model concepts often build upon two premises that significantly underrepresent the role of thin water films: 1) adsorption at the bulk capillary and thin-film air–water interfaces can be treated the same; and 2) interfacially-active contaminants in the thin water films and the bulk capillary water are in chemical equilibrium. These assumptions may be challenged in the vadose zone, especially under drier conditions. Recent theoretical analysis[64] illustrated that the adsorption of PFAS at thin-film air–water interfaces can strongly deviate from that at a bulk capillary air–water interface due to complex surface forces from the solid surface (i.e., electrostatic and Van der Waals forces). Additionally, slow mass transfer in thin water films can greatly reduce the accessibility of thin-film air–water interfaces for PFAS, and thereby introduce nonequilibrium conditions between thin water films and bulk capillary water[65] (Fig. 1). Surface diffusion of the adsorbed PFAS along air–water interfaces, while rarely discussed in the hydrology and PFAS literature, was identified as a primary mechanism for transferring PFAS mass along the thin water films and between the thin water films and bulk water[65]. The potentially slow mass transfer along the thin water films may also provide a plausible explanation for some of the differences observed between the air–water interfacial areas measured by liquid- and gas-tracer methods. Because thin water films account for most air–water interfaces in the vadose zone, not representing the above thin-film-mediated fundamental processes may predict significantly different field-scale migration of PFAS.

It is important to point out that the impact of air–water interfaces has been studied previously for the transport of interfacially-active constituents before PFAS, such as the attachment and detachment of colloidal particles at air–water interfaces[66–69]. The impact of water films on colloidal transport was also examined, but the modeled mechanisms are simple—films trap and immobilize colloids with a diameter greater than their thickness[41,69]—without representing any of the complex surface forces. Additionally, non-PFAS surfactants in the subsurface were also studied for various applications including enhanced oil recovery[70,71], surfactant-enhanced aquifer remediation[72,73], and the impact of surfactant on unsaturated water flow[38,74–76]. Somewhat surprisingly, all the earlier surfactant-related work primarily focused on how surfactants affect fluid flow and dissolution with minimal discussion of air–water interfacial adsorption (see more detailed discussion in Guo et al. (2020)[11]). In contrast, the impact of air–water interfacial adsorption on transport has been a focal point of the recent PFAS work.

In addition to the different interfacial area domains and thin water films, PFAS transport in the vadose zone involves several other complexities. *First*, PFAS interfacial partitioning is sensitive to geochemical conditions (e.g., water chemistry and interactions with other interfacially-active constituents). For example, the partitioning of PFAS at air–water interfaces can vary greatly under different ionic strengths and electrolyte compositions[20,64,77–82]. The presence of co-PFAS and other interfacially-active solutes may also modify the strength of air–water interfacial partitioning[80,81,83,84]. *Second*, in addition to accumulating at air–water interfaces, it was also hypothesized that PFAS may form supramolecular structures[85] such as aggregated structures, micelles, and vesicles. While micelles and vesicles are unlikely to be present due to porewater concentrations at PFAS-contaminated sites being much smaller than the critical micelle concentrations[26,81], self-assemblies of *different* PFAS molecules may still arise in complex PFAS mixtures. If present, the movement of these supramolecular structures can transport PFAS themselves as well as partitioning mass with the other phases (aqueous phase, air–water interfaces, and solid surfaces). *Third*, strong transient flow dynamics coupled with spatial heterogeneity may introduce transport behaviors unique to PFAS due to partitioning to air–water interfaces and mass redistribution among the different phases. An example is the amplified acceleration of PFAS transport along preferential flow pathways with reduced air–water interfacial retention due to greater water saturation collapsing air-water interfaces[12,31].

Finally, while most of the current PFAS fate and transport work focuses on anionic PFAS (i.e., perfluoroalkyl acids, [PFAAs]), other types of PFAS including cationic, zwitterionic, and neutral compounds have been shown to be present at contaminated sites[86–92]. Unlike the environmentally persistent PFAAs, some of these PFAS can react under environmental conditions—driven by either abiotic or biotic processes—and eventually transform into PFAAs[93–95]. The fate and transport of these PFAA "precursors" in the vadose zone remain poorly understood. Furthermore, some of the neutral PFAS have relatively high vapor pressure and may partition to the gas phase as PFAS vapor [96,97]. The migration of vapor-phase PFAS and their partitioning with the other phases represent another set of potentially important processes for PFAS transport in the vadose zone[96].

3. Challenges and opportunities for porous media research

While great progress has been made over the past few years that advances our understanding of the fate and transport of PFAS in the vadose zone, many important areas are under explored and significant challenges remain. Here we comment on some of the major challenges from the perspectives of both fundamental research and practical applications.

- *Quantification of air-water interfacial area*. Various methods including direct imaging-based and indirect tracer-based approaches were developed to measure or estimate air–water interfacial area at varying water saturations as discussed in Section 2. However, there are still internal inconsistencies among these different methods, e.g., different methods may measure different air–water interfacial areas under the same conditions for the same media. Furthermore, the characterization of air–water interfacial area has only been done on a very limited number of soils. Because air–water interfaces play a primary role in controlling the transport of interfacially-active substances such as PFAS, it is important to conduct comprehensive investigations of air–water interfacial area for a variety of soils and under different wetting conditions, as discussed recently[63]. These detailed characterizations may then allow for the development of process-based models or robust empirical correlations for the air–water interfacial area as functions of other more readily available parameters. These improved quantifications of air–water interfacial area are expected to significantly advance the modeling of PFAS fate and transport in the vadose zone.
- *Coupled nonlinear multi-physics processes*. The transport of PFAS is a multi-physics problem that involves various nonlinear processes in the vadose zone. For example, while surfactant-induced flow may not be significant for many lower concentration sites [11,12], they could modify the transport behavior of PFAS at some of the highly contaminated AFFF-impacted sites [11,12,98], especially in the early period of PFAS release from fire training activities. Additionally, PFAS are almost always present at contaminated sites as mixtures of a large variety of individual PFAS and other substances. A few initial experiment studies have examined the impact of PFAS mixtures and hydrocarbon surfactants on the interfacial tension[77,99–102] and transport[84,103–106]. The multicomponent Langmuir model was used to describe potential competitive adsorption among different components[80,84,105–107], but the multicomponent Langmuir model has been argued to be thermodynamically inconsistent unless all components have equal maximum adsorption capacity[81,108–111]. A more rigorous thermodynamically consistent model was recently developed for multicomponent adsorption of PFAS[81]. However, all the studies to date focus primarily on PFAS mixtures with no opposite charges. The potentially synergistic interactions among PFAS with opposite charges (e.g., between anionic and cationic PFAS) and how they affect the fate and transport of PFAS in the vadose zone remain minimally explored. The same goes to the transport of PFAS in the vapor phase and the transformation of PFAA precursors. On top of the processes discussed above, PFAS transport in the vadose zone is also driven by transient and nonlinear variably saturated flow, which has been considered as one of the most computationally challenging processes

in hydrology[112,113]. Understanding and quantifying how all these processes and their coupling control PFAS transport in the vadose zone will require comprehensive experimental and field data, as well as development of new mathematical models and numerical methods.

- *Physical chemistry of PFAS interfacial partitioning and mass transfer in the thin water films, and how they manifest at greater spatial scales*. While the importance of thin water films has been recognized in porous media literature for fluid displacement, they are often considered insignificant for solute transport because they represent a tiny fraction of the total fluid volume and hence a negligible amount of the solute mass. This conceptualization needs to be revised for PFAS transport because the majority of the PFAS mass may be associated with the thin water films due to the significant amounts of air–water interfaces arising from the thin water films. Whether these thin water films can be accessed by PFAS, and under what conditions they occur, may directly affect PFAS transport in the vadose zone[31,65]. Furthermore, the physical chemistry of PFAS partitioning at the air–water interface in the vicinity of a complex solid surface may deviate from that at bulk air–water interfaces[64]. These detailed processes occurring in the thin water films are potentially critical but are only begun to be explored.
- *Scale translation and the development of practical modelling approaches*. An outstanding challenge prevalent in all subsurface-related problems is the significant disparity between the scales at which dominant physical and chemical processes occur (nanometers to milimeters) and that at which we make observations and engineering decisions (tens of centimeters to meters or larger). This is also the case for PFAS transport in the vadose zone. Ultimately, site characterization and remediation applications need models developed for the field scale that can be practically applied to real-world contaminated sites. These practical models must be computationally efficient and relatively simple to parameterize, which means that they likely cannot account for all the complexities discussed in Section 2. We will need to identify the sub-pore and pore-scale processes with a first-order impact and approximate them at macroscales. Experimental data and more advanced models that represent a greater level of complexities may be used to aid the development of these practical models[65].

We point out that the aspects discussed above are by no means an exhaustive list of important topics for PFAS transport in the vadose zone. Rather, they represent a sample of the topics that we think the porous media community may find interesting. Addressing each of these challenges will likely require an integrated investigation through experiments, field observations, and development of theory and computational models from sub-pore-scale, pore-scale, and macroscales. Just like the prior non-PFAS research efforts that helped to prepare us for tackling

the PFAS contamination problem, the fate and transport research of PFAS will likely generate new knowledge and tools that may find use in addressing emerging environmental problems in the future, with the interfacially-active micro- and nano-plastics being a potential example.

4. Conclusion

This commentary provides an overview of the complexities and challenges for understanding and quantifying the fate and transport of PFAS in the environment, with a particular focus on the vadose zone. We have centered on issues unique to PFAS relative to many of the previous contaminants, and how these processes manifest in the complex porous media environment. It has become clear that the PFAS contamination problem is one that can significantly benefit from the expertise of the porous media community both from fundamental and practical perspectives. This commentary is an attempt to highlight some of the opportunities to which the porous media community may make significant contributions.

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