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Invited Commentary

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 act as PFAS reservoirs at many contaminated sites, with significant amounts of PFAS accumulating over several decades. Because PFAS accumulated in soils may migrate downward to contaminate groundwater resources, understanding the fate and transport of PFAS in soils 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, Per- and polyfluoroalkyl substances, Fluid–fluid interfaces, Fate and transport, Soil, Groundwater, Adsorption

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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 (53). Large-scale manufacturing and applications (such as non-stick and stain-resistant coating, waterproofing treatment, and firefighting foams) (53) 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 (14), 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 versus 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 (37) and 45% of the United States drinking water was estimated to contain PFAS (96). 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 (28, 101). Note that these numbers may reflect only 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 (74). For example, the maximum contaminant levels for PFOS and PFOA have been set to 4 parts per trillion (ppt) in the United States (102). Even more restrictive regulations are used in some European countries such as Denmark (34) (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 (14), understanding and quantifying PFAS fate and transport in the vadose zone are central for characterizing, managing, and mitigating long-term groundwater contamination risks. These characteristics pose significant challenges in addressing the problem of PFAS contamination.

Furthermore, most PFAS are surfactants that tend to accumulate at fluid–fluid and solid–fluid interfaces (60). 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 (60), 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 (45, 110). Any effective characterization and remediation of contaminated vadose zones will require conceptualizations that incorporate these critical interfacial processes. In this commentary, we discuss 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

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 more than 90% of air–water interfaces (19, 20, 30, 55, 58, 76). 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 (10, 18, 22, 70, 71, 99), field observations (16, 89), and mathematical modeling (43, 45, 46, 94, 105, 109, 110, 111).

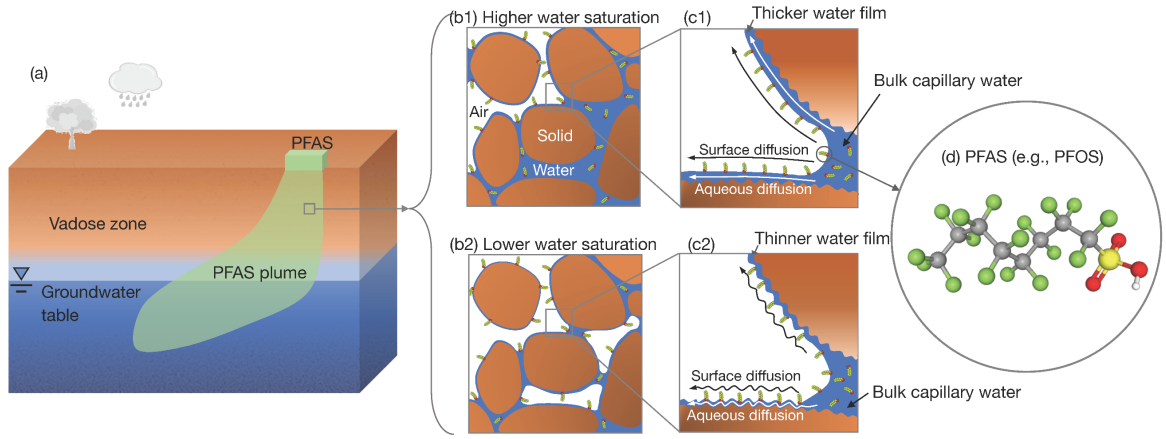


Figure 1: Interfacial retention processes for per- and polyfluoroalkyl substances (PFAS) in the vadose zone. **(a)** Schematic for PFAS contamination in the vadose zone and groundwater, **(b)** adsorption of PFAS at air–water interfaces arising from bulk capillary water and thin water films in soils 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., perfluorooctane sulfonic acid (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 (25) and used here with permission of the authors and Wiley.*

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 (9). The processes at fluid–fluid interfaces include adsorption and desorption of interfacially-active solutes (38, 56, 59, 86, 98), attachment and detachment of colloids (41, 63, 100, 106), and mass transfer between fluid phases (72, 81). 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 (48, 49, 50). 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 (48, 49, 50, 82). 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) (5, 15, 32, 33, 90, 107, 108). 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 via the mass of a tracer at fluid–fluid interfaces (6, 21, 25, 38, 59, 86, 88). 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 soil water characteristic curves using a thermodynamic approach based on energy balance (65, 73).

X-ray computed tomography (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 (5, 15). The actual thin-film fluid–fluid interfacial area is typically much greater, as XMT tends to underestimate the thin-film fluid–fluid interfacial area in sand and soil media. This underestimation occurs because XMT does not capture the additional thin-film interfacial area resulting from microscale grain surface roughness (15, 20). For example, by combining XMT and liquid-phase tracer methods, Brusseau et al. (20) reported that thin-film fluid–fluid interfacial areas in a sandy soil accounted for more than 90% of the total fluid–fluid

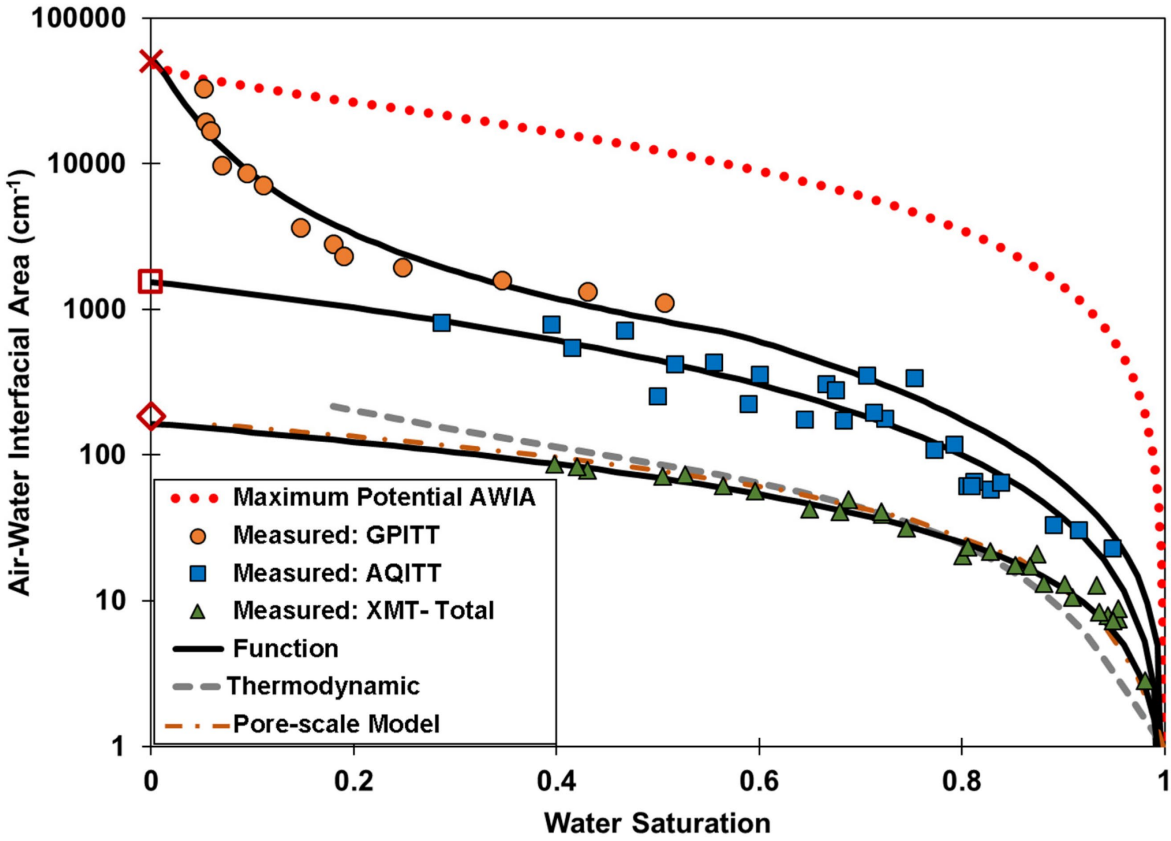


Figure 2: Air–water interfacial area as a function of water saturation for a sand determined by different measurement methods and models. "GPITT" denotes gas-phase interfacial tracer test, "AQITT" denotes aqueous interfacial tracer test. "XMT-total" is the total air–water interfacial area (bulk capillary 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 (65, 73). "Pore-scale Model" refers to the air–water interfacial area computed by the model from Jiang et al. (55). Figure originally reported in Brusseau (13) and used here with permission of the author and Elsevier.

interfacial area at water saturations less than 0.5. Furthermore, the fluid–fluid interfacial area measured by gas-phase tracer methods is greater than that by liquid-phase tracers, especially under drier conditions (20, 30, 77). The significant difference between fluid–fluid interfacial areas measured by liquid- and gas-phase tracers is not yet fully understood, although it has been hypothesized that gas-phase tracers may access additional air–water interfacial domains (13, 30). **Figure 2** provides an example of the differences in air–water interfacial areas determined by various methods (13).

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 (112) 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 (26) (**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 (26). 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 (11, 62, 85, 95). 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 (11, 106)—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 (36, 80), surfactant-enhanced aquifer remediation (35, 78), and the impact of surfactant on unsaturated water flow (31, 51, 97, 98). 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. (45)). 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 (22, 23, 29, 42, 44, 61, 92, 112). The presence of co-PFAS and other interfacially-active solutes may also modify the strength of air–water interfacial partitioning (42, 44, 52, 93). Second, in addition to accumulating at air–water interfaces, it was also hypothesized that PFAS may form supramolecular structures (4) such as aggregated structures, micelles, and vesicles. Although micelles and vesicles are unlikely to form due to porewater concentrations at PFAS-contaminated sites being much lower than the critical micelle concentrations (16, 44), self-assemblies of different PFAS molecules may still occur 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 (110, 111).

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 (3, 8, 39, 68, 75, 84, 91). 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 (27, 67, 83). The fate and transport of these PFAA "precursors" in the vadose zone remain poorly understood. Additionally, some of the neutral PFAS have relatively high vapor pressure and may partition to the gas phase as PFAS vapor (2, 17). 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 (17).

3. CHALLENGES AND OPPORTUNITIES FOR POROUS MEDIA RESEARCH

While significant progress has been made in recent years to advance our understanding of PFAS fate and transport in the vadose zone, many critical areas are underexplored, and substantial challenges

remain. Here, we discuss some of the major challenges from both fundamental research and practical application perspectives.

3.1. 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. Since air–water interfaces play an important role in controlling the transport of interfacially-active substances like PFAS, it is critical to conduct comprehensive investigations of the air–water interfacial area across a wide range of soils and under different wetting conditions, as recently discussed (13). Detailed characterizations of the air–water interfacial area could enable the development of process-based models or robust empirical correlations based on more readily available parameters. These improved quantifications are expected to significantly enhance the modeling of PFAS fate and transport in the vadose zone.

3.2. Coupled nonlinear multi-physics processes

The transport of PFAS in soils 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 (45, 110), it could modify the transport behavior of PFAS at some of the highly contaminated AFFF-impacted sites (45, 103, 110), especially during the early period of PFAS release from fire training activities. Additionally, PFAS at contaminated sites are typically present as mixtures of numerous individual PFAS and other substances. Initial experimental studies have examined the effects of PFAS mixtures and hydrocarbon surfactants on interfacial tension (23, 47, 87, 93, 104) and transport (1, 52, 54, 66, 69). The Langmuir model extended for multiple components has been employed to describe potential competitive adsorption among different components (7, 42, 52, 54, 66). However, the multicomponent Langmuir model is thermodynamically inconsistent unless all components have equal maximum adsorption capacities (12, 40, 44, 57, 64). A more rigorous thermodynamically consistent model was recently developed for multicomponent adsorption of PFAS (44). 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. This is also the case for the transport of PFAS in the vapor phase and the transformation of PFAA precursors. In addition to the processes discussed above, PFAS transport in the vadose zone is driven by transient and nonlinear variably saturated flow, which has been considered one of the most computationally challenging processes in hydrology (24, 79). Understanding and quantifying how these processes and their coupling control PFAS transport in the vadose zone will require comprehensive experimental and field data, along with the development of new mathematical models and numerical methods.

3.3. Physical chemistry of PFAS interfacial partitioning and mass transfer in the thin water films

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 (26) 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 (26, 111). 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 (112). These detailed processes occurring in thin water films are potentially critical, but they are only begun to be explored.

3.4. Scale translation & 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 millimeters) 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 require 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 greater scales. Experimental data and more advanced models that represent a greater level of complexities may be used to aid the development of these practical models (26).

We note that the aspects discussed above are not an exhaustive list of important topics related to 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 greater scales. 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 focused on issues unique to PFAS compared to previous contaminants and how these processes manifest in the complex environment of porous media. It is evident that addressing PFAS contamination can greatly benefit from the expertise of the porous media community, both from fundamental and practical perspectives. This commentary highlights some of the opportunities where the porous media community could make substantial contributions.

STATEMENTS AND DECLARATIONS

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Author Contributions

Bo Guo: Conceptualization, Methodology, Formal analysis, Funding acquisition, Writing – original draft.
Mark L. Brusseau: Formal analysis, Funding acquisition, Writing – reviewing & editing.

Conflicts of Interest

There are no conflicts of interest to declare.

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Correction from March 24, 2025:

Please note that during the production process, citation errors affected eight references within the text. These have now been corrected to accurately reflect the intended sources.

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