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Assessing the potential contributions of additional retention processes to PFAS retardation in the subsurface

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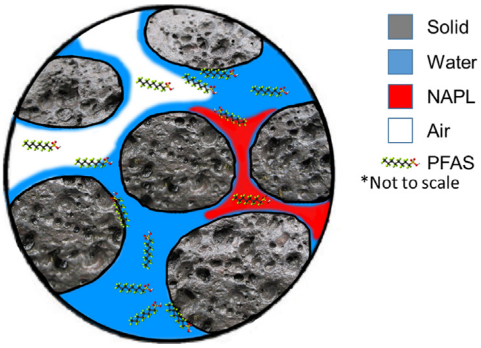
HIGHLIGHTS

- A comprehensive model for PFAS retention in porous media is proposed.
- Adsorption at the air-water interface contributes greatly to PFOA/PFOS retention.
- Adsorption at the NAPL-water interface and NAPL partitioning are also significant.

GRAPHICAL ABSTRACT



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ABSTRACT

A comprehensive understanding of the transport and fate of per- and poly-fluoroalkyl substances (PFAS) in the subsurface is critical for accurate risk assessments and design of effective remedial actions. A multi-process retention model is proposed to account for potential additional sources of retardation for PFAS transport in source zones. These include partitioning to the soil atmosphere, adsorption at air-water interfaces, partitioning to trapped organic liquids (NAPL), and adsorption at NAPL-water interfaces. An initial assessment of the relative magnitudes and significance of these retention processes was conducted for two PFAS of primary concern, perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), and an example precursor (fluorotelomer alcohol, FTOH). The illustrative evaluation was conducted using measured porous-medium properties representative of a sandy vadose-zone soil. Data collected from the literature were used to determine measured or estimated values for the relevant distribution coefficients, which were in turn used to calculate retardation factors for the model system. The results showed that adsorption at the air-water interface was a primary source of retention for both PFOA and PFOS, contributing approximately 50% of total retention for the conditions employed. Adsorption to NAPL-water interfaces and partitioning to bulk NAPL were also shown to be significant sources of retention. NAPL partitioning was the predominant source of retention for FTOH, contributing ~98% of total retention. These results indicate that these additional processes may be, in some cases, significant sources of retention for subsurface transport of PFAS. The specific magnitudes and significance of the individual retention processes will depend upon the properties and conditions of the specific system of interest (e.g., PFAS constituent and concentration, porous medium, aqueous chemistry, fluid saturations, co-contaminants). In cases wherein these additional retention processes are significant, retardation of PFAS in source areas would likely be greater than what is typically estimated based on the standard assumption of solid-phase adsorption as the sole retention mechanism. This has significant ramifications for accurate determination

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of the migration potential and magnitude of mass flux to groundwater, as well as for calculations of contaminant mass residing in source zones. Both of which have critical implications for human-health risk assessments.

1. Introduction

The use of per- and poly-fluoroalkyl substances (PFAS) in numerous industrial, commercial, and military applications has resulted in their widespread distribution in the environment (cf., EPA, 2009a; Rayne and Forest, 2009; Ahrens, 2011; Krafft and Riess, 2015a; Cousins et al., 2016). For example, it has been demonstrated that PFAS contamination of soil and groundwater exists at many Department of Defense firefighting training sites and other areas (Moody and Field, 2000; Moody et al., 2003; Ahrens, 2011; Backe et al., 2013; Anderson et al., 2016). While many of the PFAS-contaminated sites are associated with military facilities, groundwater contamination is also observed for non-military sites such as manufacturing plants and airports (EPA, 2009a; Rayne and Forest, 2009; Cousins et al., 2016). Perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) are two primary PFAS of concern. A recent tabulation of their occurrences in groundwater shows measured concentrations ranging up to >2000 and 300 μg/L for PFOS and PFOA, respectively (Cousins et al., 2016).

There is increased scrutiny and concern regarding the bioaccumulation and toxicity potential of PFAS, particularly for PFOS and PFOA (EPA, 2009a; EPA, 2014). In 2009, the US EPA established provisional health advisory values of 0.4 μg/L for PFOA and 0.2 μg/L for PFOS (EPA, 2009b). In 2016, a lifetime health advisory of 0.07 μg/L was issued for the combined total of PFOA and PFOA for long-term exposure through drinking water (EPA, 2016). The observed concentrations of PFOS/PFOA in groundwater noted above are orders of magnitude greater than US EPA's drinking water health advisory value. Hence, the occurrence of PFAS in groundwater and the resultant potential ramifications for human exposure are of significant interest. For example, a recent survey was conducted to determine the occurrence of select PFAS in drinking water for all 4064 public water supplies that serve >10,000 individuals in the US. The results showed that drinking water supplies for 6 million U.S. residents exceed US EPA's lifetime health advisory for PFOS/PFOA (Hu et al., 2016). The preceding information indicates that there is potential significant risk posed to water resources and human health by PFAS-contaminated sites.

The risk posed by PFAS soil and groundwater contamination, as well as the effective remediation of such contamination, is mediated by the transport and fate behavior of PFAS in the subsurface. PFOA, PFOS, and related PFAS are typically highly recalcitrant owing to their strong C—F bonds. This, in addition to high aqueous solubilities and relatively low retardation for select compounds, can result in the generation of large, persistent groundwater contaminant plumes. Another complicating factor is that PFAS contamination generally consists of numerous compounds of varied physicochemical properties, some of which can transform to PFOA/PFOS (often noted as precursor compounds). Remediation of this complex system is highly challenging, and most available technologies have been shown to be ineffective, as noted in a recent review (Merino et al., 2016).

The high potential health risks associated with PFAS-contaminated sites, and the difficulty and costliness of their remediation, makes it imperative that risk assessments are as accurate as possible to support effective decision-making. Accurate risk assessments require a comprehensive and definitive understanding of the subsurface transport and fate behavior of PFAS, including accurate determination of migration potential from sources to groundwater. Rates of migration are governed in part by the retention and attenuation capacities of the system, which are a function of site conditions and inherent physicochemical properties of the compounds. Primary retention-attenuation processes in general include diffusive flux into lower-permeability units, phase partitioning (e.g., sorption), and transformation reactions.

PFOA, PFOS, and select other PFAS of concern are highly recalcitrant, as noted above. Therefore, transformation-related attenuation processes are likely to be of minimal impact under many natural conditions. However, transformation processes have been shown to be important for PFAS precursors (e.g., Houtz et al., 2013; Anderson et al., 2016). The impact of diffusive mass transfer on solute transport and plume attenuation/persistence in heterogeneous systems is well established. Sorption of PFAS by the solid phase of geologic media is one phase-partitioning retention process that may have significant impact on PFAS transport and attenuation. The sorption behavior of PFAS in geomedia has been investigated over the past decade, and is being considered in conceptual models of transport and fate, as will be further discussed in a following section.

The processes discussed in the preceding paragraph are the standard factors typically considered in conceptual and mathematical models of subsurface contaminant transport and fate. Indeed, these factors are predominant for solute transport within groundwater contaminant plumes. However, there are additional retention/attenuation processes that may influence the transport and fate of PFAS in source zones. These include (i) adsorption to air-water interfaces in the vadose zone, (ii) partitioning to the soil atmosphere in the vadose zone, (iii) partitioning (absorption) to nonaqueous-phase liquids (NAPL) trapped in source zones (both vadose and saturated zones), and (iv) adsorption to NAPL-water interfaces in NAPL-contaminated source zones. Recent in-depth assessments of PFAS occurrence and fate at field sites have demonstrated that vadose-zone sources are a primary subsurface reservoir of PFAS, serving as long-term (decades) contaminant sources to groundwater (Shin et al., 2011; Xiao et al., 2015; Weber et al., 2017). In addition, it is likely that PFAS co-occur with NAPLs at certain types of sites, as has been observed for fire training areas (e.g., Moody et al., 2003; McGuire et al., 2014). Hence, it is critical to examine the potential contribution of these additional retention processes to PFAS transport and fate. This is relevant for example for accurate characterization and modeling of PFAS migration potential from sources to groundwater in support of robust risk assessments, and selection and design of cost-effective remediation systems.

These additional processes have to date received minimal to no investigation for PFAS transport in the subsurface. The objective of this work is to provide an initial assessment of the potential impact of air-water interfacial adsorption, air-water partitioning, NAPL-water interfacial adsorption, and NAPL-water partitioning on PFAS retention and transport. Physicochemical properties of the two primary PFAS of concern, PFOA and PFOS, are reviewed to assess their distribution potential. A comprehensive conceptual model is presented for characterizing retention of PFAS in geomedia systems. Data reported in the literature are used to determine phase-distribution coefficients, which are then employed to calculate retardation factors. These results are used to characterize potential magnitudes of retention for the respective processes and to evaluate their relative significance to overall retardation for a model representative system.

2. Evaluation of retention processes

2.1. Solid-phase sorption

Research investigating PFAS adsorption by solids has become a focus over the past decade, with investigations examining water treatment