

**Assessing the Potential Contributions of Additional Retention Processes to PFAS
Retardation in the Subsurface**

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1 **Abstract**

2 A comprehensive understanding of the transport and fate of per- and poly-fluoroalkyl
3 substances (PFAS) in the subsurface is critical for accurate risk assessments and design of
4 effective remedial actions. A multi-process retention model is proposed to account for potential
5 additional retardation processes for PFAS transport in source zones. These include partitioning to
6 the soil atmosphere, adsorption at air-water interfaces, partitioning to trapped organic liquids
7 (NAPL), and adsorption at NAPL-water interfaces. An initial assessment of the relative
8 magnitudes and significance of these retention processes was conducted for two PFAS of
9 primary concern, perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), and
10 an example precursor (fluorotelomer alcohol, FTOH). The illustrative evaluation was conducted
11 using measured porous-medium properties representative of a sandy vadose-zone soil. Data
12 collected from the literature were used to determine measured or estimated values for the
13 relevant distribution coefficients, which were in turn used to calculate retardation factors for the
14 model system. The results showed that adsorption at the air-water interface was a primary source
15 of retention for both PFOA and PFOS, contributing approximately 50% of total retention for the
16 conditions employed. Adsorption to NAPL-water interfaces and partitioning to bulk NAPL were
17 also shown to be significant sources of retention. NAPL partitioning was the predominant source
18 of retention for FTOH, contributing ~98% of total retardation. These results indicate that these
19 additional processes may be, in some cases, significant sources of retention for subsurface
20 transport of PFAS. The specific magnitudes and significance of the individual retention
21 processes will depend upon the properties and conditions of the specific system of interest (e.g.,
22 PFAS constituent and concentration, porous medium, aqueous chemistry, fluid saturations, co-
23 contaminants). In cases wherein these additional retention processes are significant, retardation

24 of PFAS in source areas would likely be greater than what is typically estimated based on the
25 standard assumption of solid-phase adsorption as the sole retention mechanism. This has
26 significant ramifications for accurate determination of the migration potential and magnitude of
27 mass flux to groundwater, as well as for calculations of contaminant mass residing in source
28 zones. Both of which have critical implications for human-health risk assessments.

29

30 **Keywords:** Perfluoroalkyl; PFOS; PFOA; retardation; partitioning; air-water interface; NAPL-
31 water interface

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35 **1. Introduction**

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

49 There is increased scrutiny and concern regarding the bioaccumulation and toxicity
50 potential of PFAS, particularly for PFOS and PFOA (EPA, 2009, 2014). In 2009, the US EPA
51 established provisional health advisory values of 0.4 µg/L for PFOA and 0.2 µg/L for PFOS
52 (EPA, 2009). In 2016, a lifetime health advisory of 0.07 µg/L was issued for the combined total
53 of PFOA and PFOA for long-term exposure through drinking water (EPA, 2016). The observed
54 concentrations of PFOS/PFOA in groundwater noted above are orders of magnitude greater than
55 US EPA's drinking water health advisory value. Hence, the occurrence of PFAS in groundwater
56 and the resultant potential ramifications for human exposure are of significant interest. For
57 example, a recent survey was conducted to determine the occurrence of select PFAS in drinking

58 water for all 4064 public water supplies that serve >10000 individuals in the US. The results
59 showed that drinking water supplies for 6 million U.S. residents exceed US EPA's lifetime
60 health advisory for PFOS/PFOA (Hu et al., 2016). The preceding information indicates that there
61 is potential significant risk posed to water resources and human health by PFAS-contaminated
62 sites.

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

73 The high potential health risks associated with PFAS-contaminated sites, and the
74 difficulty and costliness of their remediation, makes it imperative that risk assessments are as
75 accurate as possible to support effective decision-making. Accurate risk assessments require a
76 comprehensive and definitive understanding of the subsurface transport and fate behavior of
77 PFAS, including accurate determination of migration potential from sources to groundwater.
78 Rates of migration are governed in part by the retention and attenuation capacities of the system,
79 which are a function of site conditions and inherent physicochemical properties of the

80 compounds. Primary retention-attenuation processes in general include diffusive flux into lower-
81 permeability units, phase partitioning (e.g., sorption), and transformation reactions.

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

92 The processes discussed in the preceding paragraph are the standard factors typically
93 considered in conceptual and mathematical models of subsurface contaminant transport and fate.
94 Indeed, these factors are predominant for solute transport within groundwater contaminant
95 plumes. However, there are additional retention/attenuation processes that may influence the
96 transport and fate of PFAS in source zones. These include (i) adsorption to air-water interfaces in
97 the vadose zone, (ii) partitioning to the soil atmosphere in the vadose zone, (iii) partitioning
98 (absorption) to nonaqueous-phase liquids (NAPL) trapped in source zones (both vadose and
99 saturated zones), and (iv) adsorption to NAPL-water interfaces in NAPL-contaminated source
100 zones. Recent in-depth assessments of PFAS occurrence and fate at field sites have demonstrated
101 that vadose-zone sources are a primary subsurface reservoir of PFAS, serving as long-term
102 (decades) contaminant sources to groundwater (Shin et al., 2011; Xiao et al., 2015; Weber et al.,

103 2017). In addition, it is likely that PFAS co-occur with NAPLs at certain types of sites, as has
104 been observed for fire training areas (e.g., Moody et al., 2003; McGuire et al., 2014). Hence, it is
105 critical to examine the potential contribution of these additional retention processes to PFAS
106 transport and fate. This is relevant for example for accurate characterization and modeling of
107 PFAS migration potential from sources to groundwater in support of robust risk assessments, and
108 selection and design of cost-effective remediation systems.

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

120

121 **2. Evaluation of Retention Processes**

122 **2a. Solid-phase Sorption**

123 Research investigating PFAS adsorption by solids has become a focus over the past
124 decade, with investigations examining water treatment applications (as reviewed in Du et al.,
125 2014 and Merino et al., 2016) and subsurface porous media--- soils and sediments (Liu and Lee,

126 2005, 2007; Higgins and Luthy, 2006, 2007; Johnson et al., 2007; Carmosini and Lee, 2008;
127 Chen et al., 2009; Pan et al., 2009; Ferrey et al., 2012; Guelfo and Higgins, 2013; Zhao et al.,
128 2014; Milinovic et al., 2015; Zhang et al., 2015; Hellsing et al., 2016). Adsorption of PFAS by
129 solids is complex due to the nature of the molecular structure of PFAS. For example, the sorption
130 of PFAS such as the telomers can be relatively large, due primarily to organic-carbon
131 partitioning associated with hydrophobic interactions (e.g., Liu and Lee, 2005; Goss et al., 2006).
132 Conversely, PFOS and PFOA in their anionic forms have relatively high aqueous solubilities and
133 generally have lower sorption potential. However, the sorption of ionizable PFAS can be
134 influenced by electrostatic interactions, based on the properties of the functional group(s) of the
135 PFAS (Higgins and Luthy, 2007; Johnson et al., 2007; Ferrey et al., 2012; Du et al., 2014; Zhao
136 et al., 2014; Hellsing et al., 2016; Merino et al., 2016). In such cases, zwitterionic and especially
137 cationic species would likely have increased retention.

138 Sorption of constituents by subsurface porous media is typically more complex than
139 adsorption by water-treatment solids because the media used for water treatment are generally
140 comprised of homogeneous materials designed to behave ideally. Conversely, subsurface media
141 are typically physically and geochemically heterogeneous. As would be anticipated, research has
142 shown that PFAS sorption by subsurface media is greatly affected by the geochemical properties
143 of the solid, particularly with respect to specific components present. Critical factors investigated
144 for PFAS include the magnitude and nature of organic carbon, magnitude and type of metal
145 oxides, and clay mineralogy (Higgins and Luthy, 2006; Liu and Lee, 2007; Ferrey et al., 2012;
146 Milinovic et al., 2015; Zhang et al., 2015). In addition, it is well known that the adsorption of
147 surfactants is sensitive to water chemistry. This has been demonstrated for PFAS, wherein
148 research has shown that factors such as ionic strength, salt composition, pH, and presence of co-

149 contaminants affect solid-phase adsorption (Higgins and Luthy, 2006; Chen et al., 2009; Pan et
150 al., 2009; Guelfo and Higgins, 2013; Zhao et al., 2014).

151 The discussion above clearly shows that the sorption of PFAS is sensitive to
152 physicochemical properties of the compound, physical and geochemical properties of the porous
153 media, and water chemistry properties. Thus, an accurate evaluation of PFAS transport and
154 retention requires thorough investigation of the impact of these factors. Research conducted over
155 the past decade has significantly advanced our understanding of the sorption behavior of PFAS
156 in subsurface systems. While more remains to be done, research into the impact of solid-phase
157 sorption for PFAS is quite advanced compared to the status for the retention processes discussed
158 in the following subsections. Thus, the following processes are the focus of the present work.

159

160 **2b. Air-water Partitioning**

161 Partitioning to the soil atmosphere can serve as a source of retention during aqueous-
162 phase transport of volatile organic compounds in vadose-zone systems. For example, Kim et al.
163 (1998) demonstrated with a series of column experiments that such partitioning contributed
164 approximately 15-66% of total retardation for transport of several aromatic compounds. The
165 functioning of this retention process can differ in some circumstances from the standard
166 retardation behavior. First, the soil atmosphere may be subject to advective flux due to for
167 example soil-venting operations, landfill-gas generation, and barometric-pressure changes. In
168 such cases, vapor-phase advective transport of PFAS would need to be explicitly considered. In
169 addition, gas-phase diffusion coefficients are several orders of magnitude greater than aqueous
170 values. Hence, gas-phase diffusive flux may be a significant transport mechanism depending on
171 extant conditions. For situations wherein gas-phase advective flux is absent and gas-phase

172 diffusive flux is insignificant compared to aqueous advective flux, partitioning to the soil
173 atmosphere can be treated as a standard retention process.

174 Air-water partition coefficients (dimensionless Henry's constant, H) vary greatly among
175 the different PFAS. Measured and calculated H values for PFOA and PFOS are in the 10^{-3} range
176 (Ding and Peijnenburg, 2013). These values are typically determined for the protonated form,
177 and are thus influenced by dissociation. The reported pK_a values for PFOA are generally less
178 than 3 (Ding and Peijnenburg, 2013), and is likely close to 0 (Goss, 2008), which means that it
179 will occur in its dissociated form under most environmental conditions. Hence, the effective H
180 values for PFOA and PFOS are likely to be smaller than reported under environmentally relevant
181 pHs. Given their very small H values, partitioning to the soil atmosphere in the vadose zone is
182 unlikely to be a significant retention process for these two compounds. Conversely, H values for
183 other PFAS, such as fluorotelomer alcohols (FTOHs) and fluorotelomer olefins are quite large,
184 ranging approximately 0.05-4 and 100-10,000, respectively (Goss et al., 2006; Ding and
185 Peijnenburg, 2013). Thus, air-water partitioning is anticipated to be a significant process
186 influencing the transport behavior of these compounds. Indeed, atmospheric transport of the
187 fluorotelomers has been identified as the probable cause of their observed widespread
188 distributions in the environment (e.g., Ellis et al., 2003; Ahrens, 2011; Ding and Peijnenburg,
189 2013).

190 The retardation factor (R) for aqueous-phase transport of solute undergoing partitioning
191 to soil atmosphere is given by (e.g., Kim et al., 1998):

$$192 \quad R = 1 + H\theta_a/\theta_w \quad (1)$$

193 where H is the air-water partition (Henry's) coefficient (-), θ_a is volumetric air content (-), and θ_w
194 is volumetric water content (-).

195 **2c. Adsorption at the Air-Water Interface**

196 One retention factor that may be of significance for vadose-zone systems is adsorption at
197 the air-water interface. Interfacial adsorption is distinguished from air-water partitioning wherein
198 the former represents accumulation of constituents at the fluid-fluid interface and whereas the
199 latter represents transfer of constituents into the bulk fluid. For aqueous-phase constituent
200 transport, air-water interfaces provide an additional domain for retention and retardation for
201 conditions wherein the interface is immobile or moves at a velocity lower than that of the bulk
202 aqueous phase. While this factor is often ignored for characterizing the transport and fate of
203 organic contaminants in water-unsaturated systems, it has been demonstrated to be important in
204 some cases. For example, Brusseau and colleagues demonstrated for a bench-scale system that
205 adsorption at the air-water interface contributed 29-73% of total trichloroethene (TCE)
206 retardation for gas-phase transport, depending on porous-medium type (Brusseau et al., 1997).
207 They later determined that air-water interface adsorption contributed ~24% of total TCE
208 retardation for an intermediate-scale field experiment (Costanza-Robinson et al., 2013). Kim et
209 al. (1998, 2001) demonstrated similarly that adsorption at the air-water interface contributed
210 significantly to total retardation of various organic compounds for both gas-phase and aqueous-
211 phase transport. Several studies have investigated the impact of air-water interfacial adsorption
212 on retention of surfactants during transport in unsaturated porous media, primarily in terms of the
213 use of surfactants as tracers for interfacial partitioning tracer tests (e.g., Karkare and Fort, 1996;
214 Kim et al., 1997; Anwar et al., 2000; Schaefer et al., 2000; Brusseau et al., 2007, 2015).

215 PFAS contamination is likely to be present in the vadose zone at many sites as a result of
216 waste disposal, spillage, and specified applications (e.g., fire training). PFOS, PFOA, and related
217 PFAS of concern are surfactants, and by their nature will accumulate at air-water interfaces.

218 Thus, it is anticipated that adsorption to air-water interfaces may be a significant retention and
219 attenuation mechanism for these PFAS in vadose-zone sources. However, this process has not
220 yet been investigated for the transport and fate of PFAS in the subsurface environment.

221 Fluorinated surfactants are typically more surface active than the analogous standard
222 hydrocarbon surfactants (e.g., Krafft and Riess, 2015). This is related to the unique nature of the
223 “tail” portion of the compound. The tail of fluorinated surfactants is hydrophobic due to its
224 nonpolar, fully saturated nature, just as are the tails of standard hydrocarbon surfactants.
225 However, unlike hydrocarbon surfactants, the tails of fluorinated surfactants are also lipophobic
226 due to the low polarizability of the C-F bond. This unique property results in significantly greater
227 reductions in surface tension caused by fluorinated surfactants. For example, PFOA reduces
228 surface tension to ~22 mN/m at the critical micelle concentration (CMC) of ~12,400 mg/L
229 (Downes et al., 1995; Lopez-Fontan et al., 2005; Vecitis et al., 2008), compared to 45 mN/m for
230 SDS (at CMC of ~2000 mg/L), a standard anionic hydrocarbon surfactant. The CMC values for
231 PFOA and PFOS (500 mg/L) are much larger than the concentrations that have been observed in
232 groundwater. Hence, it is anticipated that micelle formation in aqueous solution would not be a
233 significant factor for most subsurface conditions.

234 Research results from investigations related to chemical applications of perfluorinated
235 surfactants demonstrate that PFOS, PFOA, and related compounds are very strongly adsorbed at
236 the air-water interface. For example, Psillakis et al. (2009) measured enrichment factors for
237 perfluoro-n-alkyl carboxylate $F(CF_2)_nCO_2^-$ and sulfonate $F(CF_2)_nSO_3^-$ surfactant adsorption at the
238 air-water interface. The enrichment factors measured for PFOS and PFOA were 158 and 63,
239 respectively, demonstrating very large preferential adsorption at the interface. Others have
240 reported similar measurements of strong air-water interface adsorption, measured in terms of

241 surface excess, for PFOS and PFOA (Downes et al., 1995; Vecitis et al., 2008; Lunkenheimer et
242 al., 2015). Recently, it has been hypothesized that adsorption to the air-water interfaces of air
243 bubbles trapped on the surfaces of carbonaceous water-treatment sorbents is a primary source of
244 the retention they afford (Meng et al., 2014). These results indicate that adsorption at air-water
245 interfaces has the potential to be a significant retention mechanism for PFAS transport in vadose-
246 zone systems.

247 The R for aqueous-phase transport of solute undergoing adsorption at the air-water
248 interface is given as (e.g., Kim et al., 1998; Brusseau et al., 2007):

$$249 \quad R = 1 + K_{ai}A_{ai}/\theta_w \quad (2)$$

250 where K_{ai} is the air-water interface adsorption coefficient (cm^3/cm^2), A_{ai} is the specific air-water
251 interfacial area (cm^2/cm^3), and θ_w is volumetric water content (-). Inspection of equation 2 shows
252 that the magnitude of air-water interface adsorption depends upon the value of K_{ai} and the
253 amount of air-water interface present (A_{ai}).

254 The value of K_{ai} is determined by molecular properties of the compound, and is
255 influenced by water chemistry properties (e.g., ionic strength, pH, T) (Costanza and Brusseau,
256 2000). Prior research for PFAS has shown that surface activity (and air-water interface
257 adsorption potential) is influenced by compound chain length (Psillakis et al., 2009; Baba et al.,
258 2013; Lunkenheimer et al., 2015), water chemistry properties such as ionic composition
259 (Downes et al., 1995), and the presence of co-occurring PFAS compounds (Vecitis et al., 2008).

260 Regarding the amount of interface present, air-water interface is comprised of two
261 components, capillary interface associated with contact between bulk fluid phases (e.g., terminal
262 meniscii, pendular rings, wedges) and film interface associated with air in contact with water
263 films solvating the solid surfaces. The results of experimental, theoretical, and modeling

264 investigations have shown that the magnitude of air-water interface depends upon the amount of
265 water and air present. Specifically, total (capillary + film) air-water interfacial area increases
266 continuously as water content decreases, i.e., as air content increases (e.g., Cary, 1994; Kim et al.,
267 1997, 1999; Or and Tuller, 1999; Schaefer et al., 2000; Oostrom et al., 2001; Costanza and
268 Brusseau, 2002; Dalla et al., 2002; Peng and Brusseau, 2005; Brusseau et al., 2006, 2007). As
269 water content approaches very small values close to zero (equivalent to a few molecular layers of
270 adsorbed water) and the porous medium is almost fully saturated with air, the total interfacial
271 area asymptotically approaches the specific solid surface area of the porous medium. Research
272 has also demonstrated that fluid-fluid interfacial area is a function of soil properties such as grain
273 size, grain-size distribution, and surface roughness (Anwar et al., 2000; Cho and Annable, 2005;
274 Dobson et al., 2006; Brusseau et al., 2008, 2009, 2010; Peng and Brusseau, 2005).

275

276 **2d. NAPL-water Partitioning**

277 Another potential source of retardation of organic compounds is retention by organic
278 liquids in NAPL source zones. This is of potential significance for PFAS given that they often
279 occur in the presence of NAPL contamination at mixed-waste sites. For example, a primary
280 source of PFAS contamination is the prior use of aqueous film forming foams for fire
281 suppression. In some cases, sites that served as designated fire training areas were also used as
282 disposal sites for solvent and oil wastes.

283 Initial investigations of the impact of solute partitioning to NAPL (e.g., absorption or
284 “NAPL partitioning”) on aqueous-phase transport of organic solutes were reported by Bouchard
285 et al. (1990), Boyd and Sun (1990), and Brusseau (1990). Brusseau (1992) developed a model
286 that accounted explicitly for NAPL partitioning and solid-phase adsorption, and demonstrated

287 that the transport of organic contaminants can be greatly influenced by NAPL partitioning. For
288 example, simulations showed that the retardation factor for a TCE-like solute increased from 2
289 for the case of only solid-phase adsorption to 17 for a case including partitioning to NAPL, with
290 a NAPL saturation of 1%. The R increased to 152 when NAPL saturation was increased to 10%.
291 Studies conducted for the partitioning tracer test method of measuring NAPL saturations have
292 demonstrated the impact of NAPL partitioning on field-scale solute transport (Nelson and
293 Brusseau, 1996; Annable et al., 1998a; Cain et al., 2000; Brusseau et al., 2003).

294 The R for aqueous-phase transport of solute undergoing partitioning into an immobile
295 NAPL phase is given as (e.g., Brusseau 1990):

$$296 \quad R = 1 + K_{nw} \theta_n / \theta_w \quad (3)$$

297 where K_{nw} is the NAPL-water partition coefficient (-), θ_n is volumetric NAPL content (-), and θ_w
298 is volumetric water content (-). Treating NAPL as a retention phase for the transport of solute is
299 predicated on the condition that the NAPL is immobile. This is likely the case for most old sites,
300 with the exception of those with specific remedial operations that may promote significant
301 NAPL movement.

302 Minimal research has been conducted to examine this factor for PFAS retention or
303 transport in subsurface systems. Log K_{ow} values of 1.92 and 2.45 have been measured for PFOA
304 and PFOS, respectively, at circumneutral pH (Jing et al., 2009). Given these magnitudes, it is
305 anticipated that partitioning to NAPL may be a relevant retention process for PFAS. In one prior
306 study, the impact of oil added to soil on PFOS retention was examined with batch experiments
307 (Chen et al., 2009). The presence of the oil was observed to significantly increase sorption. Log
308 oil-water partition coefficients were estimated to be greater than 4. The impact of trichloroethene
309 NAPL on retention of a PFAS mixture was investigated using batch methods (Guelfo and

310 Higgins, 2013). The results showed complex impacts, wherein sorption was reduced, not
311 changed, or enhanced in the presence of TCE, depending upon the specific PFAS, its
312 concentration, and the specific soil. In both of these studies, the samples were prepared by
313 thoroughly mixing the NAPL with the soil. This approach most likely produces NAPL
314 distributions that are not representative of typical subsurface conditions (e.g., generation of
315 NAPL films coating a significant fraction of the grain surfaces). This distribution could cause
316 interference with solid-phase adsorption via site blockage (as hypothesized in Guelfo and
317 Higgins, 2013), and would produce maximal NAPL-water interface wherein some of the
318 enhanced sorption may be due to adsorption at such interfaces. Conversely, residual
319 trichloroethene NAPL saturation was emplaced using standard methods in the column study
320 reported by McKenzie et al. (2016), wherein the NAPL would be distributed as discrete blobs
321 and ganglia distributed nonuniformly throughout the soil pack. With such distribution, the
322 fraction of soil-grain surface contacted by NAPL would be relatively small, and thus there would
323 likely be minimal direct impact on solid-phase adsorption via surface blockage. This does not
324 discount the potential for indirect effects due to the presence of high aqueous concentrations of
325 trichloroethene. For this latter study, the presence of the residual NAPL was observed to
326 measurably increase overall retardation for most of the PFAS. In these studies, the retention was
327 attributed primarily to NAPL partitioning, while the potential for adsorption to the NAPL-water
328 interface was also noted. However, the specific, discrete impacts of partitioning versus interfacial
329 adsorption were not quantitatively differentiated. Log K_{nw} values ranging from approximately 0
330 to 0.5 were reported for PFOA and PFOS for the two trichloroethene NAPL studies. These are
331 much smaller than the reported log K_{ow} values and the PFOS log K_{nw} values reported for
332 retention by crude oil (Chen et al., 2009). This may perhaps be due in part to the impact of co-

333 solute effects for the trichloroethene studies, which employed a suite of PFAS. The magnitudes
334 of reported K_{ow} values, along with the results of the few initial studies, indicate that NAPL
335 partitioning may be a significant retention process for select PFAS.

336

337 **2e. Adsorption at the NAPL-Water Interface**

338 The adsorption of constituents at the NAPL-water interface is similar to adsorption at the
339 air-water interface, and is governed by the same factors as discussed above for the latter process.
340 Adsorption of surfactants to NAPL-water interfaces has been measured for a variety of porous
341 media (Saripalli et al., 1998; Cho and Annable, 2005; Dobson et al., 2006; Brusseau et al., 2008,
342 2009, 2010; Narter and Brusseau, 2010; McDonald et al., 2016; Zhong et al., 2016). These data
343 have been used to determine the impact of soil properties such as grain size on interfacial
344 adsorption (Cho and Annable, 2005; Dobson et al., 2006; Brusseau et al., 2009, 2010).

345 The R for aqueous-phase transport of solute undergoing adsorption at the NAPL-water
346 interface is given as (e.g., Brusseau et al., 2008):

$$347 \quad R = 1 + K_{ni}A_{ni}/\theta_w \quad (4)$$

348 where K_{ni} is the NAPL-water interface adsorption coefficient (cm^3/cm^2), A_{ni} is the specific
349 NAPL-water interfacial area (cm^2/cm^3), and θ_w is volumetric water content (-). As discussed in
350 subsection 2c, it is expected that surfactant type PFAS will accumulate at fluid-fluid interfaces,
351 including NAPL-water interfaces. Thus, NAPL-water interface adsorption may be important for
352 transport of PFAS in the source zones of NAPL-contaminated sites. It should also be noted that
353 contaminants present in the vapor phase can adsorb at air-NAPL interfaces. Given the focus
354 herein on PFOA and PFOS, this process is not considered for the analysis. However, it may be
355 relevant for other PFAS.

356

357 **3. Comprehensive Retention Model**

358 Current published conceptual and mathematical models of PFAS transport and fate in the
359 subsurface focus on solid-phase adsorption as the sole source of retention. For example, all three
360 of the recent detailed assessments of field-scale PFAS transport and fate discussed above
361 employed this assumption (Shin et al., 2011; Xiao et al., 2015; Weber et al., 2017). In addition,
362 this assumption is present in the most recent comprehensive reports on PFAS management
363 (CONCAWE, 2016; CRCCARE, 2017) and in the PFAS section of the Environmental
364 Restoration Wiki (SERDP, 2017). However, the research discussed above examining the impact
365 of adsorption at air-water and NAPL-water interfaces, in conjunction with the strong surfactant
366 properties of some PFAS, indicates that we may anticipate significant retention of PFAS by these
367 processes. In addition, partitioning to NAPL and air phases may be relevant for select PFAS.
368 Thus, it is likely that retardation and transport of PFAS in source zones can be, under certain
369 conditions, influenced by multiple retention processes. In such cases, retardation of PFAS in
370 source areas may be significantly greater than what is typically estimated based on the standard
371 assumption of solid-phase adsorption as the sole retention mechanism. A comprehensive
372 conceptual model is proposed for PFAS retention and retardation to address this situation. It
373 includes the following retention processes: (i) solid-phase adsorption, (ii) adsorption at the air-
374 water interface, (iii) partitioning to the soil atmosphere, (iv) adsorption at the NAPL-water
375 interface, and (v) partitioning to NAPL. To our knowledge, this comprehensive, multi-process
376 retention approach has not been employed to date for PFAS.

377 The retardation factor for aqueous-phase transport of solute undergoing retention by all of
378 the aforementioned processes is given as:

379
$$R = 1 + K_d \rho_b / \theta_w + K_{ai} A_{ai} / \theta_w + H \theta_a / \theta_w + K_{ni} A_{ni} / \theta_w + K_{nw} \theta_n / \theta_w \quad (5)$$

380 where H is the air-water partition (Henry's) coefficient (-), K_d is the solid-phase adsorption
381 coefficient (cm^3/g), K_{nw} is the NAPL-water partition coefficient (-), K_{ai} is the air-water interface
382 adsorption coefficient (cm^3/cm^2), K_{ni} is the NAPL-water interface adsorption coefficient
383 (cm^3/cm^2), A_{ai} is the specific air-water interfacial area (cm^2/cm^3), A_{ni} is the specific NAPL-water
384 interfacial area (cm^2/cm^3), ρ_b is porous-medium bulk density (g/cm^3), θ_n is volumetric NAPL
385 content (-), θ_a is volumetric air content (-), and θ_w is volumetric water content (-). By phase
386 balance, $\theta_w + \theta_a + \theta_n = n$, where n is porosity, and $S_w + S_a + S_n = 1$, where S_w , S_a , and S_n are fluid
387 saturations of water, air, and NAPL, respectively (and $S_i = \theta_i/n$).

388 The conceptual approach employed has been validated for each of the individual
389 retention processes for a range of constituents in prior work (as noted in section 2), albeit not for
390 PFAS. Thus, while the approach has not been tested specifically for PFAS, there is general
391 confidence in its use to represent phase distributions in subsurface systems. The conceptual
392 model is focused solely on retention and retardation, not transport. Thus, factors such as rate-
393 limited mass transfer and spatial variability of system properties and conditions are not
394 considered. Application of the approach implicitly considers the system to be under pseudo-
395 equilibrium conditions. As discussed above, PFAS distribution coefficients have been shown to
396 be influenced by system conditions. The impact of system conditions on retention and retardation
397 can be accounted for by incorporating distribution coefficients determined for the specific
398 relevant conditions. Note that the model is simplified by assuming that gas-phase transport of
399 compounds in the soil atmosphere is relatively insignificant compared to advective transport in
400 the aqueous phase, such that partitioning to soil atmosphere can be treated as a retention process.
401 In addition, NAPL is assumed to be essentially immobile, and distributed in such a manner that

402 its impact on solid surfaces (e.g., blocking solid-phase adsorption) is minimal. Hence, NAPL is
403 assumed to act as a retention phase for aqueous solute.

404

405 **4. Parameterization for Illustrative Retardation Factor Calculations**

406

407 Measured and estimated values for the relevant distribution coefficients will be used to
408 calculate retardation factors for a representative porous medium. The measured porous-medium
409 properties represent a sandy vadose-zone subsoil composed primarily of quartz with moderately
410 low organic-carbon content. The porous-medium related parameter values used for the
411 calculations are presented in Table 1. A water saturation of 78% is selected for the initial
412 analysis to represent a moderately wet system wherein aqueous-phase advective transport is
413 predominant. The impact of different water saturations will also be examined. A NAPL
414 saturation of 2% is used, representative of a mean value averaged across the entire source zone.
415 This value is representative of measured field-scale values (e.g., Nelson and Brusseau, 1996).
416 The air saturation is 20% given the designated water and NAPL saturations. Air-water and
417 NAPL-water interfacial areas of 80 and 20 cm⁻¹, respectively, are used based on values measured
418 for a sandy subsoil at the corresponding fluid saturations (Brusseau et al., 2007, 2008, 2015).

419 The two primary PFAS of most concern will be examined, PFOS and PFOA. In addition,
420 8:2 fluorotelomer alcohol (FTOH) will be included as a representative precursor of PFOA, given
421 that it can undergo transformation to PFOA (e.g., CONCAWE, 2016). While FTOH has not been
422 reported in published reports of sampled groundwater, it and other select PFAS may transport
423 from facilities via atmospheric processes with subsequent deposition to land (e.g., Ellis et al.,
424 2003; Ahrens, 2011; Shin et al., 2011; Ding and Peijnenburg, 2013). Given FTOH's precursor

425 status and potential for widespread surface distribution, it is relevant to consider its potential
426 transport behavior in soil, as noted by Liu and Lee (2005). It also serves to illustrate the
427 significant differences in transport behavior that exists among the numerous PFAS.

428 Distribution coefficient values used for the calculations are presented in Table 2.
429 Reported K_{ow} values are used as a surrogate for K_{nw} . This is a reasonable first approximation
430 given that both are measures of liquid-liquid partitioning. As noted above, relatively low TCE-
431 water K_{nw} values were reported for PFOA and PFOS for a PFAS mixture. The impact of these
432 lower values will be discussed below. Measured or calculated H values are taken from the
433 literature. Solid-phase sorption is simplified for this assessment by employing the assumption
434 that sorption is governed by hydrophobic interactions, and is correlated to organic carbon. In this
435 case, K_d is calculated as $f_{oc}K_{oc}$, where f_{oc} is the fraction of soil organic carbon and K_{oc} is the OC-
436 normalized sorption coefficient. Representative K_{oc} values are taken from the literature. This
437 simplification is reasonable for the representative porous medium used herein, which has
438 minimal clay-mineral and metal-oxide content. Sorption interactions with clay and oxides would
439 need to be considered for more heterogeneous media. Nonlinear adsorption for PFOA and PFOS
440 is accounted for by employing a Freundlich power term of 0.8, based on values reported in the
441 literature.

442 To our knowledge, K_{ai} and K_{ni} values have not yet been reported for PFAS. They can be
443 determined by analyzing measured surface tension or interfacial tension data, which is the
444 standard method for measuring K_{ai} and K_{ni} . The surface excess Γ (mol/cm²) is related to aqueous
445 phase concentration (C) using the Gibbs equation (e.g., Adamson 1982):

446
$$\Gamma = -\frac{1}{RT} \cdot \frac{\partial \gamma}{\partial C} = K_1 \cdot C \quad (6)$$

447 where K_i represents the interfacial adsorption coefficient (in our case K_{ai} or K_{ni}), γ is the
448 interfacial tension (dyn/cm), C represents the aqueous phase concentration (mol/cm³), and R is
449 the gas constant (erg/mol °K). In the absence of excess electrolyte, a correction factor of $\frac{1}{2}$ is
450 applied to equation 6. Surface tension data have been reported for PFOA by several investigators
451 (Downes et al., 1995; Lopez et al., 2005; Vecitis et al., 2008; Lunkenheimer et al., 2015), and the
452 results are consistent among the studies. Data reported by Vecitis et al. (2008) are used to
453 calculate K_{ai} values for PFOS and PFOA as these were the sole data available for PFOS. The
454 data were re-plotted and regressed to determine K_{ai} (Figure 1). Note that these data were
455 measured for pure water. Thus, the resultant K_{ai} values may vary somewhat from what would be
456 measured for an aqueous solution containing electrolytes (e.g., groundwater). Interface
457 adsorption data for fluorotelomers is very scarce, with the only data reported for 8:2 FTOH (Li et
458 al., 2006; Rontu and Vaida, 2007). Conversion of the interface uptake coefficient reported by Li
459 et al. (2006) results in a K_{ni} value of approximately 0.0005 cm. This is in the range of values
460 reported for various polar organic compounds (Kim et al., 1998; Costanza and Brusseau, 2000).
461 In the absence of NAPL-water interfacial tension data for PFOA and PFOS, the K_{ni} value will be
462 set equal to K_{ai} . This is a reasonable first approximation, supported by the similarity of K_{ni} and
463 K_{ai} values measured for a common surfactant used as an interfacial partitioning tracer, SDBS
464 (Brusseau et al., 2007, 2008, 2010). However, it is possible that K_{ni} and K_{ai} values for PFAS may
465 exhibit greater disparity given their unique physicochemical properties.

466

467

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469

470 **5. Assessing the Contribution of Retention Processes to Retardation**

471 **5a. Results**

472 Individual process-specific retardation factor (R) values are calculated and reported in
473 Table 3 for each PFAS, along with the total R for the combined retention from all processes. The
474 fractions of total retention associated with each retention process are also reported. For both
475 PFOA and PFOS, the retardation factors for sorption are of sufficient magnitude to have a
476 significant impact on migration potential. This is consistent with prior analyses reported in the
477 literature. Retention associated with partitioning to the soil atmosphere is negligible, as would be
478 anticipated given the small H values. Partitioning to bulk NAPL contributes similar magnitudes
479 of retention to that of solid-phase sorption. Finally, retention associated with adsorption at the
480 air-water and NAPL-water interfaces is observed to be quite large for both PFOA and PFOS.
481 Specifically, interfacial adsorption comprises approximately 65% of total retention for both
482 compounds. Additionally, air-water interface adsorption alone accounts for approximately 50%
483 of total retention. These results illustrate the significance of interfacial adsorption on PFOA and
484 PFOS retention for this example system.

485 Quite different results are obtained for 8:2 FTOH. Adsorption to fluid-fluid interfaces is
486 minimal, which is expected given the much lower surface activity of FTOH compared to PFOS
487 and PFOA. Partitioning to the soil atmosphere is relatively small. However, this could be
488 significant under conditions wherein vapor-phase transport is relevant. The retardation factor for
489 sorption is relatively large, signifying small migration potential. By far the largest source of
490 retention is partitioning to bulk NAPL, contributing ~98% of total retention. Comparison of the
491 results between PFOA/PFOS and FTOH serves to illustrate the significant differences in

492 retention behavior that may be anticipated for the various PFAS as a function of their specific
493 physicochemical properties.

494

495 **5b. Condition Dependency of the Retention Processes**

496 The illustrative application presented above was developed using a single set of system
497 variables for generally idealized conditions. As discussed in the prior sections, retention by the
498 various processes is influenced by numerous factors. Hence, it is important to discuss the
499 condition dependency of the retardation factors reported in Table 3. Factors that may influence
500 the values include aqueous PFAS concentration, porous-medium conditions such as fluid
501 saturation, and water-chemistry properties (ionic strength, salt composition, co-contaminants). In
502 addition, some of these may change with time or space.

503 Air-water partitioning and NAPL-water partitioning are linear mass-transfer processes
504 under normal conditions. Therefore, the magnitudes of the associated distribution coefficients
505 reported in Table 2 are independent of PFAS concentration. Thus, the calculated R values apply
506 irrespective of the PFAS concentration present. For this assessment, sorption was treated as a
507 nonlinear process for PFOA and PFOS, and thus the associated R values are a function of
508 concentration. Fluid-fluid interface adsorption coefficients are strongly nonlinear, as seen
509 through examination and application of equation 6. The K_{ai} and K_{ni} values used for the analysis
510 presented in Table 3 are based on an aqueous PFAS concentration of 0.1 mg/L. This represents
511 an approximate median groundwater concentration for ranges of values reported in the literature
512 (cf., Cousins et al., 2016). Lower concentrations would result in larger K_{ai} and K_{ni} values,
513 leading to larger contributions of interface adsorption to retention, and vice versa. The effect of
514 aqueous PFOS concentration on K_{ai} values and resultant R values for air-water interface

515 adsorption and solid-phase adsorption is illustrated in Table 4. The magnitude of the R for air-
516 water interfacial adsorption is observed to differ by a factor of ~200 over a concentration range
517 from 0.01 to 10 mg/L. The contribution of solid-phase adsorption is observed to be greater than
518 that of air-water interfacial adsorption at aqueous PFOS concentrations near and greater than 1
519 mg/L.

520 For a given porous medium, bulk density, porosity, and f_{oc} are presumed to be constants
521 for most conditions (although site activities may induce changes). Conversely, fluid saturations
522 are condition dependent and can vary over a wide range. Changes in fluid saturation control the
523 magnitudes of the fluid volumes and fluid-fluid interfacial areas, which affects the associated
524 magnitudes of PFAS retention. Thus, the magnitude of the calculated R values will depend upon
525 fluid saturation. This is illustrated in Figure 2, where the R for air-water interface adsorption is
526 observed to increase to 140 as water saturation decreases to 0.4. For this analysis, A_{ai} was
527 assumed to be a linear function of S_w . However, total A_{ai} is actually a nonlinear function of S_w ,
528 particularly at lower S_w (e.g., Or and Tuller, 1999; Kim et al., 1999; Peng and Brusseau, 2005;
529 Brusseau et al., 2007). Hence, the increase in R for air-water interface adsorption may in fact be
530 greater than illustrated, especially for S_w lower than 0.4.

531 The calculations presented above were produced for an idealized system treating each
532 PFAS as the sole constituent of concern in solution. However, it is likely that many PFAS
533 constituents will be present in solution at most sites. In addition, other contaminants such as
534 solvents, fuel constituents, salts, non-PFAS surfactants, and metals may also be present. The
535 presence of co-contaminants is likely to have impacts on the magnitudes of PFAS partitioning to
536 the various phases. For example, competitive and/or cooperative sorption effects may influence
537 solid-phase adsorption. This is illustrated by the results presented by Guelfo and Higgins (2013),

538 who examined the impact of co-contaminants on the sorption of several PFAS. As noted above,
539 the interfacial activity of PFAS has been shown to be influenced by water chemistry properties
540 such as ionic composition (Downes et al., 1995) and the presence of co-occurring PFAS
541 compounds (Vecitis et al., 2008). In addition, the presence of co-contaminants can affect surface
542 wettability, which can influence fluid configuration and distribution, and thereby alter interfacial
543 adsorption. The preceding demonstrates that it is critical to assess the potential impact of co-
544 contaminants on the various retention processes.

545 The system conditions may change with time, which may influence retention. For
546 example, water saturations may change relatively rapidly with a precipitation-infiltration-
547 redistribution event. Changes in S_w would lead to changes in the magnitudes of air-water
548 interfacial area, which would result in changes in the magnitude of air-water interfacial
549 adsorption. This in turn would cause redistribution of PFAS among the phases. Natural or
550 remediation-induced changes to system conditions may occur, thereby altering retention. For
551 example, site remediation activities may induce changes in the composition and/or physical
552 properties of the NAPL, which can alter its configuration and distribution, thereby influencing
553 retention. Site perturbations may also affect properties of the PFAS mixture, the porous medium,
554 and water chemistry, all of which may influence retention.

555 Accounting for the impacts of the complexities discussed above is feasible, albeit likely
556 difficult in many cases. The impact of water-chemistry properties and the presence of co-
557 contaminants would ideally be addressed by measuring distribution coefficients for the specific
558 system of interest (i.e., using site groundwater, with all relevant constituents present). The impact
559 of changes in water or NAPL saturation on magnitudes of interfacial area can be accounted for

560 using the correlations that are available in the literature relating interfacial area to porous-
561 medium properties (texture) and fluid saturation.

562 An alternative or supplemental approach for characterizing multi-process retention under
563 specific site conditions would be to conduct tracer tests using a suite of conservative and
564 partitioning tracers (Brusseau et al., 1997). For example, to delineate NAPL partitioning versus
565 NAPL-water interfacial adsorption, one would use a tracer that partitions to bulk NAPL (with
566 minimal interfacial adsorption) and another tracer that adsorbs at the interface (with minimal
567 bulk partitioning) (e.g., Annable et al., 1998b; Brusseau et al. 2003). Similarly, specific tracers
568 can be selected to characterize solid-phase adsorption, air-water partitioning, and air-water
569 interfacial adsorption (e.g., Nelson and Brusseau, 1996; Annable et al., 1998a; Cain et al., 2000;
570 Brusseau et al., 2003; Costanza-Robinson et al., 2013).

571

572 **6. Conclusion**

573 Currently, solid-phase adsorption is the sole retention process considered for published
574 conceptual and mathematical models of PFAS transport and fate in the subsurface. However,
575 specific physicochemical properties of PFAS impart a potential propensity to partition to other
576 retention phases. A comprehensive conceptual model is proposed for PFAS retention and
577 retardation to account for these additional retention processes. It includes: (i) solid-phase
578 adsorption, (ii) adsorption at the air-water interface, (iii) partitioning to the soil atmosphere, (iv)
579 adsorption at the NAPL-water interface, and (v) absorption by NAPL. An assessment of the
580 relative magnitudes and significance of these retention processes was conducted for three
581 representative PFAS for a representative, idealized system.

582 The results showed that adsorption to air-water and NAPL-water interface was a primary
583 source of retention for both PFOA and PFOS, contributing approximately 65% of total retention
584 for the example system. Additionally, air-water interface adsorption alone accounted for ~50%
585 of total retention. This assessment represents a first-order analysis of these factors, given the use
586 of a single system and simplified conditions. Clearly, the specific magnitudes of R reported
587 apply solely to the specific system investigated. The magnitudes and relative significance of the
588 various retention processes will depend upon conditions of each specified system of interest.
589 However, the parameter values employed were obtained primarily from measured data sets,
590 providing confidence in the general validity of the overall results indicating the potential
591 significance of interfacial adsorption. For example, the values used for the K_{ai} were determined
592 from measured surface-tension data, which is the standard method for its determination. The
593 values used for A_{ai} were obtained from reported measured data from prior works. Hence, both
594 parameters used to determine the magnitude of air-water interfacial adsorption originate from
595 measured data.

596 While simplified conditions were employed in the analysis, the potential impacts of more
597 complex system conditions were discussed. These factors can be accounted for by measuring the
598 distribution coefficients under conditions representative of the particular subsurface environment
599 of concern. In addition, partitioning tracer tests serve as a means by which to characterize multi-
600 process retention under site-specific field conditions.

601 The results of this initial assessment indicate that we may anticipate significant retention
602 of PFAS by these additional processes under certain conditions. For example, the total R values
603 for PFOS and PFOA, which account for all potential sources of retention, were approximately 4-
604 10 times larger than the R values for solid-phase adsorption alone. As discussed above, several

605 recent studies have indicated that PFAS present in the vadose zone is a primary, long-term
606 source of groundwater contamination. Thus, the results of the present study suggest specifically
607 that air-water interface adsorption should be considered when assessing PFAS transport and fate
608 in the vadose zone. In addition, the potential for NAPL-water partitioning and NAPL-water
609 interfacial adsorption interactions should be considered for sites with NAPL present.

610 In cases wherein one or more of the additional retention processes are relevant,
611 retardation of PFAS in source areas may be significantly greater than what is typically estimated
612 based on the assumption of solid-phase adsorption as the sole retention mechanism. This has
613 significant ramifications for example for accurate determination of the migration potential and
614 magnitude of mass flux to groundwater. In addition, calculations of contaminant mass residing in
615 source zones would also be influenced by the existence of these additional retention processes,
616 with the potential for significant underestimation. Both of these elements have critical
617 implications for risk assessment and remedial-action decision-making. Based on these results,
618 additional investigation of the impact of these retention processes on PFAS transport is
619 warranted.

620

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625

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Table 1. Properties of representative porous medium.

Property	Value
Bulk density (g/cm ³)	1.5
Porosity	0.333
Fraction of soil organic carbon	0.002
Water saturation	0.78
Air saturation	0.2
NAPL saturation	0.02
Volumetric water content	0.26
Volumetric air content	0.067
Volumetric NAPL content	0.0067
Air-water interfacial area (cm ⁻¹)	80
NAPL-water interfacial area (cm ⁻¹)	20

Table 2. Distribution coefficients.

Coefficient	Value	Source
<i>PFOA</i>		
K _{oc}	108	mean of values reported by ref a and b ^a
H	0.002	compiled value from Ding and Peijnenburg (2013)
K _{nw} [K _{ow}]	83	Jing et al. (2009)
K _{ai} , K _{ni} (cm) ^b	0.0234	analysis of Vecitis et al. (2008) data
<i>PFOS</i>		
K _{oc}	568	mean of values reported by ref a and b ^a
H	0.002	compiled value from Ding and Peijnenburg (2013)
K _{nw} [K _{ow}]	282	Jing et al. (2009)
K _{ai} , K _{ni} (cm) ^b	0.0755	analysis of Vecitis et al. (2008) data
<i>FTOH</i>		
K _{oc}	13490	Liu and Lee (2005)
H	3.8	Goss et al. (2006)
K _{nw} [K _{ow}]	380189	Carmosini and Lee (2008)
K _{ai} , K _{ni} (cm) ^b	0.0005	analysis of Li et al. (2006) data

^aRef a: Higgins and Luthy, 2006, ref b: Milinovic et al., 2015.

^bCalculated for an aqueous PFAS concentration of 0.1 mg/L.

Table 3. Process-specific and Total Retardation Factors

Retention Process^a	PFOA	PFOS	FTOH
Sorption	3.0 (15) ^b	11.4 (22)	157 (2)
Air-water Partitioning	1.0 (0)	1.0 (0)	2.0 (0)
Air-water Interfacial Adsorption	8.2 (55)	24.4 (50)	1.2 (0)
NAPL-water Partitioning	3.1 (16)	8.2 (15)	9749 (98)
NAPL-water Interfacial Adsorption	2.8 (14)	6.9 (12)	1.0 (0)
Total Retardation Factor	14.1	47.9	9906
$R_{total}/R_{sorption}$	4.7	4.2	63

^aRetardation factors for individual retention processes are calculated using the relevant process-specific equations. An R value of 1 denotes no retention.

^bPercentage of total retention associated with each retention process (rounded), calculated as $(R_i - 1)/(R_t - 1) * 100$, where R_i and R_t are the process-specific and total retardation factors, respectively.

Table 4. Impact of aqueous PFOS concentration on K_{ai} and R values for air-water interfacial adsorption (R_{aw}), solid-phase adsorption (R_s), and the sum of the two (R_t).

Concentration (mg/L)	K_{ai} (cm)	R_{aw}	R_s	R_t
10	0.0007	1.2	5.1	5.4
1	0.0076	3.3	7.6	9.9
0.1	0.0755	24.3	11.4	34.7
0.01	0.755	234	17.5	250

K_{ai} values were calculated using equation 6 and the regression data from Figure 2.

Figure Captions

Figure 1. Surface tension measurements for PFOA and PFOS over relevant concentration range.

PFOA regression: $\gamma = -0.276 \cdot \ln(C) + 74.2$, $r^2 = 0.972$; PFOS regression: $\gamma = -0.737 \cdot \ln(C) + 74.3$, $r^2 = 0.89$. Raw data from Vecitis et al. (2008).

Figure 2. Impact of water saturation on PFOS retardation factors for solid-phase adsorption, air-water interface adsorption, and the sum of the two (total).

Figure 1

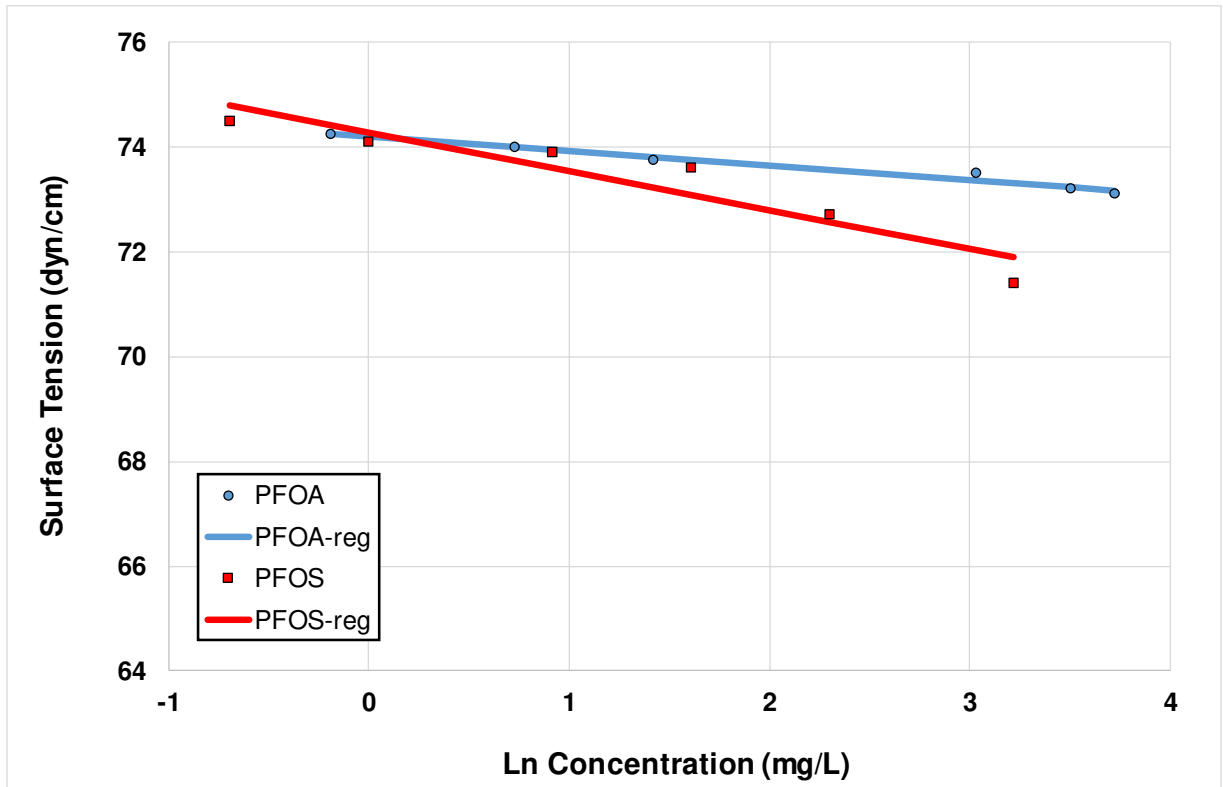
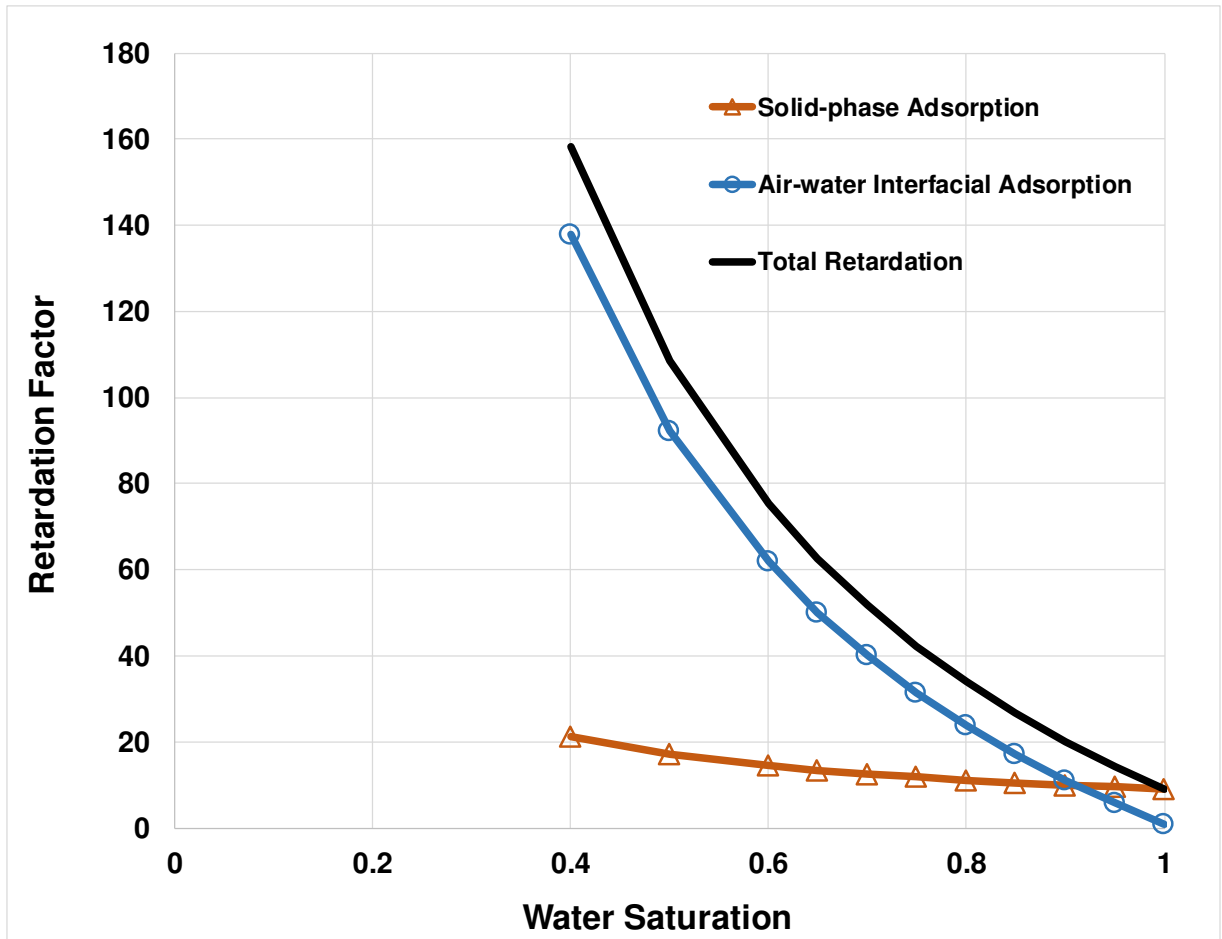


Figure 2



Graphical Abstract

