Post-wildfire soil and aquifer contamination: A review

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ABSTRACT

The need to understand the effects of wildfire and post-fire contamination of soil and groundwater has grown as a result of the expansion of the extent and severity of wildfires around the world. In addition to their direct hazards, wildfires can also contribute to human and environmental health concerns due to secondary contamination, e.g., wildfire suppression such as aqueous film-forming foams (AFFF) can release per- and polyfluoroalkyl substances (PFAS) into the soil, which are very mobile, toxic, and persistent. Both direct seepage through the topsoil and biotransformation of fluorotelomers (FTs) determine the fate of PFAS in soils and aquifers. Research has indicated that phase partitioning behavior, such as sorption to soils and sediments, controls the fate and transport of chemicals in the environment. According to various studies, the main soil or sediment characteristics that control PFAS’ sorption behavior include organic carbon (OC), pH, index cations, and ionic strength. However, neither OC, pH, nor clay-content alone could explain the sorption behavior of PFAS. More research is needed to help to understand the role of co-contaminants on the sorption behavior of PFAS, the role of surface charge on the sorption of PFAS, and on a wider range of PFAS chain compounds in the future. This paper aims to review the fate and transport of PFAS and identify the areas of research need.

Keywords: per- and polyfluoroalkyl substances, wildfire, post-fire, contaminant, aqueous film-forming foams.

1 INTRODUCTION

In addition to the direct impact of wildfires on human lives and health, wildfires can leave various direct and indirect impacts on soil and its ecosystem. The need to understand the effects of wildfire on soil, including its contaminating effect, is growing as a result of expanding wildfire seasons and regions across the U.S. and the globe. Fire and fire suppression after wildfires both result in harmful impacts on the environment. Aqueous film-forming foam (AFFF) is a popular and effective firefighting foam used to suppress wildfires. AFFF is a mix of foaming agents and fluorinated surfactants. Per- and Polylfluoroalkyl substances (PFAS) are the active ingredients in these fluorinated surfactants. PFAS consist of a broad group of perfluoroalkyl and polyfluoroalkyl substances. This group contains diverse categories and classes unified by the presence of a perfluoroalkyl group but differing in ionic, cationic, and zwitterionic species (Barzen-Hansong et al., 2017). These compounds have notable uses such as imparting oil, water repellency in consumer products, and reducing surface tension in firefighting foams (Houtz et al., 2016). The polyfluorinated compounds in AFFF and their polyfluorinated intermediated products are known as perfluoroalkyl acid (PFAA) precursors, also referred to simply as precursors. Figure 1 shows two types of PFAS, Perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA), the most manufactured and investigated PFAA compounds (Houtz et al., 2016). PFAS typically have a carbon-fluorine tail and a nonfluorinated head consisting of a polar functional group. The tail is described as hydrophobic while the head is polar and hydrophilic (ITRC, 2018).

![Fig. 1. The tail and head structure of PFOS and PFOA molecules. Adapted from fig. 1 by ITaC, 2018.](https://doi.org/10.3208/jgssp.v09.cpeg004)

PFAS contribute to the contamination of the soil and aquifers and have been released into the environment for over 50 years (Houde et al. 2011). PFAS, including perfluorooctane sulfonic acid (PFOS), perfluorooctanoic acid (PFOA), and many other chemicals, are usually detectable in sediment and groundwater media. Because PFAS are very stable, they have been utilized in many products. Nowadays, scientists pay more attention to
PFAS and their fate in and effects on the environment. This is due to PFAS’ resistance to degeneration, their bioaccumulation properties, and toxicity and hazard for humans and living organisms (Martin et al., 2003). Several studies have shown that PFAS can pollute soil, sediments, and surface- and groundwater during the use of firefighting AFFFs (Backe et al., 2013; Munoz et al., 2017), but it is obvious that data and research about the fate and transport of PFAS are not by any means complete and still require more research. PFAS can be released into the environment through direct (their formation cycle) and indirect (alteration of their precursors) sources, i.e., they have point (industrial sites) and nonpoint sources (Buck et al., 2011). The fate of PFAS consists of their partitioning, transport (advection, dispersion, and diffusion), and transformation. Various partitioning processes have a significant role in determining and understanding the PFAS transport. Because of the heterogeneity of the subsurface environment, understanding the fate and transport of PFAS requires consideration of several partitioning mechanisms. PFAS have surfactant properties, which make them different from other contaminants (Oliver et al., 2013), which is why the prediction of their behavior in the soil is difficult (Bräunig et al., 2017). Most research on the fate and behavior of PFAS in the environment has focused on the transport, remediation, and source of these contaminations on a small fraction (PFOS and PFAS) of these compounds (Miyake et al., 2007). Xiao (2017) reviewed recent research focused on the fate and behavior, existence, and identification of novel PFAS in groundwater. Xiao (2017) concluded that studies regarding the fate of novel PFAS in rivers, aquifer, drinking water, and during treatment methods are very limited. Barzen-Hanson et al. (2017) focused on the sorption of anionic, cationic, and zwitterionic novel PFAS, which exist in AFFF. They showed that the sorption of cationic and zwitterionic compounds, due to both hydrophobic and electrostatic behavior, and the sorption of anionic substances that are controlled by hydrophobic interaction are very complex and it is not possible to be predicted by soil characteristic. Mejia-Avendaño et al. (2020) also claimed that the fate and transport of cationic and zwitterionic compounds are not well understood.

Understanding the fate and behavior of novel PFAS can help to predict their unknown environmental risks and dangers. This paper briefly reviews the research on the fate and transport of novel PFAS released into the environment as a result of wildfires.

2 FLOW AND TRANSFORMATION MECHANISMS OF PFAS

Dauchy et al. (2019) attempted to determine the depth to which PFAS can penetrate the soil. They evaluated the seepage of four classes of PFAS into the soil (PFSA, PFCA, PFOS precursors, and FTs). The results of their study and observations of other studies confirmed that it is difficult to determine the fate of PFAS in soil and groundwater because it depends on both PFAS flow and their transformation.

2.1 Flow mechanisms

In addition to partitioning, the transport mechanism (advection, dispersion, and diffusion) is important in the fate of PFAS. Advection can strongly influence the transport of PFAS, but it does not affect contaminant concentration (ITRC, 2018). Dispersion disperses the contaminants in different directions due to changes in flow velocity. The concentration-gradient driven flow, which can move the contaminant molecules into areas with a lower concentration, is referred to as diffusion (ITRC, 2018). Although the diffusion in aquifer is hard to measure in some cases, it can contribute to the penetration process (Baduel et al., 2015).

2.2 Transformation mechanisms

PFAS transformation includes biotic (living) and abiotic (nonliving) transformation, which can lead to other harmful chemicals. Hatton et al. (2018) showed that due to transformation, PFAS compounds found in the groundwater are considerably different from those in AFFF. Perfluoroalkyl acids (PFAAs) such as PFOA and PFAS can form from both biotic and abiotic transformation of polyfluorinated precursors. PFAAs are very stable, difficult to degraded, and mobile in the subsurface. This fact along with PFAAs’ low sorption results in their accumulation in aquifers (Hatton et al., 2018). Because emerging PFAS have properties different from other contaminants, there are limited data regarding their transformation and, in general, their fate and transport.

3 FATE AND TRANSPORT OF PFAS

As discussed in the Introduction section, the mechanism of partitioning, transport, and transformation within soils and aquifers has a significant role in determining and understanding the PFAS’ fate and transport. Hydrophobic and lipophobic effects (Anderson et al., 2016; Xiao et al., 2017), electrostatic interactions (Zhao et al., 2014), and interfacial behaviors (Brusseau, 2018) are partitioning mechanisms that affect PFAS. Du et al. (2014) have shown that electrostatic and hydrophobic interactions likely control the sorption behavior of PFAS more than other interactions. Some PFAS are more mobile, and they exist in the solute phase due to their low $K_d$ (sorption partitioning coefficient), determined by:

$$K_d = C_s/C_w$$

where $C_s$ and $C_w$ are the PFAS concentrations in sediment and water, respectively. However, some PFAS with high $K_d$ are more likely to be absorbed by soil and become immobile. Li et al. (2018) reviewed studies to assess the effects of soil properties on the sorption
behavior of PFAS. Their review focused on the effects of clay content (due to interfacial interaction), pH, and organic carbon (OC) due to hydrophobic partitioning on the sorption behavior of PFAS. The main soil properties that control the sorption behavior of PFAS and mitigate their transport within source zones, based on Li et al. (2018), are as follows.

1. **Organic carbon (OC):** There are studies (Ahrens et al., 2014; Chen et al., 2013; You et al., 2010) that indicated the existence of a strong relation between the sorption of PFAS and OC. These studies used the Freundlich equation (Equation 2) to formulate sorption isotherms.

   \[ C_s = K_F/C_w^n \]  
   \[ K_D = K_F * C_w^{(n-1)} \]  

where \( K_F \) is the Freundlich sorption coefficient, and \( n \) provides an indication of the nonlinearity. \( K_D \) is calculated using the following formula.

The relation between the sorption of PFAS and OC has been expressed via figures relating \( K_D \) and the sediment OC content fraction (\( F_{OC} \)). Based on Figure 2), studies (such as Milinovic et al., 2015; Chen et al., 2012) claimed that organic carbon can control the sorption of PFAS. However, the study results of Barzen-Hanson et al. (2017) demonstrated that the sorption process is more complex than what can only be calculated using soil characteristics. This was consistent with most other findings in the literature. However, Wang et al. (2020) assessed the partitioning behavior of PFAS and claimed that OC does not have a significant effect on the partitioning behavior of PFAS. Therefore, the OC content cannot be considered as the only factor that affects the sorption behavior of PFAS.

![Fig. 2. Relation between fraction of OC content and sorption of PFOA and PFOS (adapted from figure by Milinovic et al., 2015).](image)

2. **pH:** Like OC, there are different results regarding the impact of pH on the sorption of PFAS. Despite that no direct exclusive physical relation between pH and sorption has been developed, researchers often attempted to relate the two using empirical linear models. Deng et al. (2012), Wang et al. (2012), and Yu et al. (2008) observed that, like other anionic contaminants, the sorption of anionic PFAS decreased as a result of increasing pH. On the other hand, You et al. (2010) and Zhou et al. (2013) showed that the sorption of PFAS in presence of Ca\(^{2+}\) or Mg\(^{2+}\) increased with increasing pH while Milinovic et al. (2015) and Kwadijk et al. (2013) indicated that there is not a demonstrable relation between pH and sorption of PFAS.

3. **Index cations and ionic strength:** Cations can control the fate of anionic PFAS in soil. Chen et al. (2012) assessed the effect of cations such as K\(^+\), Ca\(^{2+}\), Na\(^+\), and Mg\(^{2+}\). They observed the increase of sorption due to increasing the concentration of Ca\(^{2+}\) and Mg\(^{2+}\) but found K\(^+\) has no significant impact on sorption (Figure 3). Through another review of previous research, Li et al. (2018) concluded that there is no significant relation between the sorption of PFOA and PFOS with Ca\(^{2+}\) and/or with Na\(^+\). In addition, changes in ionic strength lead to a change in pH, and it is hard to determine which parameter has a role in sorption (Higgins and Luthy, 2006).

![Fig. 3. Effects of monovalent and divalent metal cations' concentration on sorption coefficient (\( K_d \)) of PFOA (adapted from figure by Chen et al., 2012).](image)

4. **Clay content, cation exchange capacity (CEC), and anion exchange capacity (AEC):** There are very few studies that evaluated the role of clay content, but they mostly demonstrate a strong relation between clay content and sorption of some PFAS (Li et al., 2018). CEC and AEC are the capacity of soil to hold cations and anions, respectively. Mejia-Avendaño et al. (2020) observed that increasing the CEC value leads to an increase in cationic PFAS sorption. This can be justified based on the fact that high CEC can be translated to the availability of more cationic space (i.e., hole) within clays’ microstructure (i.e., fundamental mineral unit blocks), which means more space for PFAS sorption. In contrast, the anion exchange capacity (AEC) can affect anionic compounds (Li et al., 2018). However, there is still not enough information regarding CEC and AEC.

Hence, the sorption behavior of PFAS is a compounded mechanism and cannot be explained only
using one factor. There is usually a correlation between soil characteristics, e.g., it is probable to find higher contents of OC in clay textured soils (Li et al., 2018). Therefore, to better understand the sorption behavior of PFAS, it is necessary to focus on several soil characteristics simultaneously.

4 CONCLUSIONS

The review in this paper resulted in the conclusion that phase-partitioning behaviors, such as sorption to soils and sediments, transport, and transformation, control the fate, transport, and behavior of PFAS within the soil environment. Major soil/sediment components that control sorption behavior include organic carbon (OC), pH, index cations and their ionic strength, clay content, and cation or anion exchange capacity (CEC or AEC). However, the sorption behavior of PFAS is complex and can be explained by only a combination of OC, pH, and clay content. Despite existing studies, there are still numerous unknowns, and specifically, there is a need for more research to understand the role of co-contaminants on the sorption behavior of PFAS and the role of surface charge on the sorption of PFAS. In addition, more research is needed on a wider range of PFAS chain compounds.

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