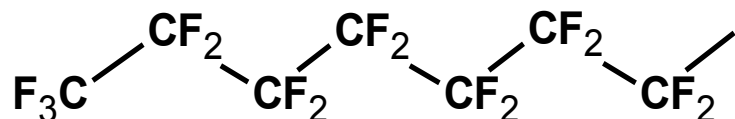


NEBRA Literature Review: PFAS & Wastewater Residuals v. 2.0

June 2018, November 2019



Acknowledgements

This literature review was written by Michael Rainey, M.S. (Northwood, NH) with review and editing by NEBRA staff, Ned Beecher, M.S.

Contents

Background.....	2
Research Concerns & Considerations.....	2
Release, Mobility, and Distribution.....	4
PFAS and Wastewater Treatment.....	5
PFAS in Sewage Sludge.....	5
Land Application of Wastewater Residuals and Soil Impacts.....	7
PFAS Mobility in the Soil and Risk to Groundwater.....	9
Human PFAS Exposure Resulting from Plant and Animal Uptake from Soils Amended with Wastewater Residuals	11
Conclusions and Research Priorities.....	12
Literature Cited.....	14
Appendix A: Compendium of Abstracts & Notes (separate document, 67 pages).....	

Background

During the last several years, the U.S. Environmental Protection Agency (U.S. EPA) and state environmental agencies have become aware of contamination of groundwater by perfluoroalkyl and polyfluoroalkyl substances (PFAS). Frequently, the PFAS contamination in groundwater, and release to the environment in general, is associated with direct release from local industrial sources (use or manufacturing sites) (Zareitalabad et al. 2013) or fire-fighting sites using aqueous fire-fighting foam (AFFF) that contains PFAS. The discovery of PFAS contamination led to the adoption of a life-time drinking water public health advisory by U.S. EPA (70 ng/L or ppt) in May 2016 and stringent drinking water standards by several northeast states.

As regulatory agencies begin to discover the ubiquitous nature of PFAS contamination, there has been speculation about indirect sources. Since municipal wastewater treatment facilities (WWTF) receive domestic and industrial wastes that may potentially contain PFAS, biosolids and effluent are now being scrutinized as indirect sources of PFAS (Hamid and Li 2016, Coggan et al. 2019). Limited research has demonstrated that land application of biosolids in various parts of the country have resulted in PFAS contamination of groundwater at measurable levels (but generally below the public health advisory screening level) (Lindstrom et al., 2011; Sepulvado et al., 2011; Gottschall et al., 2017). In most cases, the groundwater contamination was associated with biosolids from wastewater facilities that had PFAS industrial dischargers (Lindstrom et al., 2011) or high cumulative levels of biosolids applications (Sepulvado et al., 2011). Given that there are industry agreements with U.S. EPA to reduce or eliminate the use and production of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) (Buck et al., 2011), it is not clear if ongoing land application programs constitute a risk to public health from contamination of groundwater through leaching of these two compounds or from PFASs in general. To preserve land application as a viable option for management of wastewater residuals it is necessary to answer the following question:

Does land application of wastewater residuals (paper mill solids, municipal biosolids, etc.) at fertilizer rates with current common regulatory requirements and proper industrial source controls represent a risk to public health from PFAS contamination of groundwater via leaching and/or surface water via runoff?

NEBRA has collected and reviewed peer-reviewed publications, government agency documents, and similar expert information related to this key question. This review evaluates the fate and transport of PFAS movement from production and use sources through the environment and wastewater treatment systems with a focus on wastewater residuals and their recycling. Following is a selected review of the relevant literature.

Research Concerns and Considerations

PFAS are manmade chemicals that have been produced and used since the 1940s. Although not naturally occurring, these compounds are now widely distributed in the environment, including in animal and human tissue. PFAS have been detected widely dispersed across various environmental media and biota in areas not subject to direct release of PFAS (Rankin et al. 2016, Vedagiri et al. 2018). PFAS are frequently detected contaminants in both source water and treated drinking water (Boone et al. 2018) Greater than 3000 PFASs have been used in commerce (Wang et al. 2017). According to the

FluoroCouncil, a global industry council for fluorotechnology, PFAS is used in the electronics, first-responders, oil and gas, military, chemical/pharmaceutical manufacturing, aerospace/defense, automotive, healthcare, alternative energy, semiconductor, building/construction, and outdoor apparel/equipment industries. Given the diverse and extensive list of chemicals included in the term “PFAS”, Buck et al. have proposed a system for naming and classification of PFAS chemicals to bring convention and continuity to research and discussion.

PFAS, as a group of chemicals, have properties that make them very useful in modern society. The strong electronegativity and small atomic size of fluorine creates a very strong bond with carbon atoms giving PFAS molecules some unique properties compared to other halogenated hydrocarbons. PFAS molecules, particularly perfluoroalkyl acids (PFAA), are thermally and chemically stable and resistant to degradation in the environment. They are repellent to water and oils/fats but have an affinity for proteins and have high surface activity at low concentrations (Zareitalabad et al. 2013; Wang et al. 2017). PFAS molecules can be strongly acidic and likely to ionize in solution (Buck et al. 2011; Wang et al. 2017). At the soil pH typically maintained for successful agriculture, the anionic form of perfluorocarboxylic acids (PFCA) will predominate. For example, PFOA will generally be found in the environment as the perfluorooctanoate form (PFO) ion (Prevedouros et al. 2006). PFO is more soluble and has a lower vapor pressure than PFOA, which can volatilize from water into the atmosphere (Prevedouros et al. 2006; Buck et al. 2011). This suggests that ionized PFAS compounds in the soil or soil solution will be soluble and susceptible to leaching. Vapor pressure, bioaccumulation, and soil-water partitioning are strongly correlated with carbon chain length. Longer-chain PFAS have lower vapor pressure and are more strongly retained in the soil and in animal tissue (Prevedouros et al. 2006; Gebbink and Letcher 2011). Since longer-carbon-chain PFAA are more strongly retained in the soil, plant uptake favors shorter chain PFAS (Blaine et al. 2014). Until relatively recently, most research and regulatory attention has focused on PFOA and PFOS; but, as these compounds are removed from commerce, research has broadened to include shorter-chain PFAA and their precursor compounds. The presence and increasing background concentrations of shorter alkyl-chain PFAS such as perfluorobutanoic acid (PFBA) and perfluorobutane sulfonic acid (PFBS) have been observed as longer-chain PFAS products are removed from commerce (Buck et al. 2011). PFAS chemicals such as the ammonium salt of hexafluoropropylene oxide–dimer acid (GenX) and other perfluoroalkyl ether acids (PFEA) are receiving increased scrutiny as chemical manufactures use them as replacements for PFOA and other long-chain PFAS (Hopkins et al. 2018, Brandsma et al. 2018). Some of these unique properties are what make PFAS so attractive in commerce and problematic in the environment.

Not only is PFAS a large and diverse group of chemicals, but individual PFAS-based materials can contain several subclasses of PFAS within the same product. Historically, four methods have been used to synthesize PFCAs: electrochemical fluorination (ECF), fluorotelomer iodide oxidation, fluorotelomer olefin oxidation, and fluorotelomer iodide carboxylation (Prevedouros et al. 2006). Obviously, each method would utilize different raw materials and produce different end-products. Even using a common synthesis method, manufacturers may use different raw materials resulting in different products. Over time, synthesis methods have been changed and refined. PFAS-based products can be complex mixtures containing the intended end-product, unreacted raw materials or intermediate chemicals, and unintended byproducts. Even the intended products may be mixtures of chemical analogues and homologues (Prevedouros et al. 2006; Wang et al. 2017). It has been suggested that certain “finger-print” patterns in carbon-chain length and branching could be used to identify sources and transport pathways (Prevedouros et al. 2006). Although some PFAS compounds are considered persistent in the environment, it has been well established that certain precursor compounds will degrade both biotically and abiotically to very stable and persistent PFAAs (Wang et al. 2017), such as PFOA.

Degradation and transport of volatile precursors such as fluorotelomer alcohols (FTOH) may be the source of long-chain PFAS in remote regions (Prevedouros et al. 2006). There is a myriad of these PFAS precursors, including fluorotelomer alcohols, fluorotelomer acrylates, fluorotelomer iodides, fluorotelomer olefins, N-alkyl perfluoroalkane sulfonamides, N-alkyl perfluoroalkane sulfonamidoethanols, and polyfluoroalkyl phosphates (Buck et al. 2011). The type and amount of PFAA acids produced by precursor transformations in the environment are dependent on the type of precursors and environmental conditions (Buck et al., 2011, Kim et al., 2013). For example, degradation of certain complex fluorotelomer alcohol (FTOH) molecules was observed in forest soils but not in agricultural soils presumably because of the higher fungal biomass present in forest soils (Liu and Avendaño, 2013). FTOH generally degrade to resistant PFAA of the same carbon-chain length. However, defluorination and mineralization of the carbon-chain have been observed especially for shorter-chain FTOH molecules (Liu and Avendaño, 2013). Although the presence of PFAS precursors and their potential transformation into PFAAs complicates PFAS research, an understanding of transformation pathways and kinetics may also provide additional clues about PFAS sources and fate in the environment (Wang et al. 2017).

Release, Mobility, and Distribution

It has been well established that PFAS are widely produced and used in our modern society. Unfortunately, production and use have resulted in release to the environment. Prevedouros et al. estimate historic global emissions of 3,200 to 7,300 metric tons with the majority resulting from fluoropolymer manufacture and use. Some emissions are direct intentional releases, such as the use of PFAS in aqueous film forming foams (AFFF) used in fire-fighting (Weber et al. 2017). Other emissions are inadvertent releases from the production and use of consumer products. GenX and PFOA have been detected in grass and leaf samples as far as three kilometers from a fluoropolymer manufacturing facility (Brandsma et al. 2018). In a field 10 kilometers away from a fluorochemical industrial park in China, the soil concentration for the sum of 12 PFAS compounds ranged from 2.09 ng/g to 3.75 ng/g or parts per billion (ppb) (Liu et al. 2019).

Once released, PFAS have been shown to be very mobile in the environment. PFAS can be dispersed over long distances via atmospheric transport and ocean currents (Stemmler and Lammel 2010). Some PFAS, depending on their specific chemical properties, can move in the atmosphere within the gaseous phase or associated with soils/dust, airborne particles, and aerosols (Prevedouros et al. 2006; Xiao et al. 2013). The solubility of many PFAS also allows these chemicals to move to groundwater and surface water and ultimately to the oceans. Prevedouros et al. (2006) conclude that the majority of PFO released to the environment is contained within the earth's oceans. This suggests that a significant portion of all PFAS released may also be in the oceans and available for widespread dispersal by ocean currents.

The mobility and persistence of PFAS, coupled with its common use in commerce, have made these compounds ubiquitous in the environment and biota including human blood (Clarke and Smith, 2011; Grandjean and Clapp 2014). Analyses of a wide variety of consumer products show detectable and sometimes significant levels of various PFAS (Kotthoff et al. 2015, Borg and Ivarsson 2017). Inevitably, these chemicals find their way into society's waste collection, treatment, and disposal systems.

PFAS and Wastewater Treatment

The pervasiveness and persistence of PFAS in commerce and the environment suggests that these chemicals will be discharged to wastewater treatment facilities (WWTF) at low levels for a long time (Clarke and Smith 2011). Of course, PFAS loading to a WWTF can significantly increase if an industrial source (manufacturing or use) is a discharger. Although research related to PFAS and wastewater treatment have looked at a variety of PFAS compounds, the bulk of the data involves PFOA and PFOS. Influent PFAS loading can be variable both in composition and concentration. Past research found PFOA and PFOS to be the most abundant PFAS in wastewater influent with average concentrations in the 5-50 ng/L or part per trillion (ppt) range (Margot et al. 2015). According to Hamid and Li (2016), PFOA and PFOS are still two of the most frequently detected PFAS in wastewater. One “worst-case” study found influent concentrations of 470 ng/L, 640 ng/L, and 61,205 ng/L for PFOS, PFOA, and perfluorooctanesulfonamide (PFOSA), respectively (Koch 2015). The total sum of PFAS concentrations in influent for commonly monitored PFAS compounds is usually in the range 30-150 ng/L (Margot et al. 2015). In a survey of 19 Australian WWTFs, the average total PFAS concentration found in wastewater for 21 chemicals from four different classes of PFAS compounds was 110 ng/L (Coggan et al. 2019).

Treatment/removal of PFAS during conventional secondary wastewater treatment is negligible (Hamid and Li 2016). Removal efficiencies are generally less than 5% (Margot et al. 2015). Anaerobic digestion, both mesophilic and thermophilic, also has demonstrated little removal of PFAS (Koch 2015, Hamid and Li 2016). Removal of PFAS from wastewater is mainly from sorption onto wastewater solids. Some PFAS compounds, such as PFOH, can be volatilized and transported off-site (Hamid and Li 2016). Longer carbon-chain (>6 C) tend to adsorb to solids and are removed in the sewage sludge, while shorter chain compounds remain in wastewater and are discharged with effluent (Koch, 2015; Hamid and Li, 2016). PFAS sorption in secondary wastewater treatment plants is an organic matter partitioning process (Zareitalabad et al. 2013). Field studies at WWTFs have yielded average organic carbon partitioning coefficients ($\log K_{oc}$) of 3.7 for PFOA and 4.2 for PFOS (Zareitalabad et al. 2013). These partitioning coefficients suggest a strong potential for these two compounds to be sorbed to organic matter and removed in the sludge. Lower pH favors PFAS sorption (Koch, 2015). However, effluent mean concentrations for PFOA (13 ng/L) and PFOS (12 ng/L) are frequently reported as not significantly different than influent levels (Margot et al. 2015). Zareitalabad et al. (2013) reported median effluent concentrations for PFOA and PFOS of 24 ng/L and 13 ng/L, respectively. Occasionally, effluent concentrations for these compounds and PFCA in general exceed influent concentrations (Clarke and Smith 2011, Hamid and Li 2016, Coggan et al. 2019). Similarly, PFAS concentrations have been observed to increase through sludge treatment and processing (Hamid and Li 2016). A concurrent reduction in the concentration of certain precursor PFAS compounds across the waste treatment process suggests that biodegradation transforms these precursors into the more stable and persistent PFOA and PFOS, thereby increasing the concentration of these compounds in the effluent (Koch 2015, Hamid and Li 2016).

PFAS in Sewage Sludge

Given the lack of PFAS degradation during wastewater treatment and ability to partition between the aqueous and solid phases, a portion of PFAS loading to WWTFs will ultimately reside in the sludge generated by a facility. Which specific compounds and their final concentration in sludge is determined by multiple factors, including PFAS sources contributing to the collection system, wastewater

characteristics, wastewater treatment process, and sludge treatment/handling. Wastewater and sludge treatment are complex biochemical processes, and although generalizations can be made about PFAS fate within a facility, the only reliable way to assess sludge quality relative to PFAS contamination is through testing.

Historically, the PFAS most frequently detected in sludge and at the highest concentrations were PFOA and PFOS (Clarke and Smith 2011). The preponderance of historical PFAS sludge analytical results report data for these two compounds. Table 1 shows selected data sets for PFOA and PFOS over time, including recent data compiled by NEBRA and the NH Department of Environmental Services. The results in the first row of Table 1, reported by Lindstrom et al. (2011), are for a single sample collected from the Decatur, Alabama WWTF, a facility impacted by an industrial PFAS manufacturer and whose land-applied sludge was the source of PFAS groundwater contamination at several area farms (Lindstrom et al. 2011). As would be expected, WWTFs with PFAS industrial dischargers have higher concentrations of PFAS in their sludge (Clarke and Smith 2011; Lindstrom et al. 2011). However, the presence of PFOA and PFOS in sludge from facilities without industrial input underscores the importance of domestic sources of PFAS (Clarke and Smith 2011). Other studies reporting on PFAS in sludge have observed no significant differences between rural and urban WWTFs, but have observed seasonal variations in PFAS concentrations (Clarke and Smith 2011).

Table 1. Data Comparison of PFOA and PFOS over time

Study	Year(s) of Testing	PFOA (ng/g)	PFOS (ng/g)	Data Type
Lindstrom et al., 2011	1999-2001	244	3000	single data point
Venkatesan & Halden, 2013	2001	34	403	average
Clarke & Smith, 2011	2001-2008	37	196	median
Sepulvado et al., 2011	2004-2007	8-68	80-219	range
Gottschall et al. 2016	2009	1.6	7.2	single data point
Zareitalabad et al., 2013	2013	37	69	median
NEBRA/DES Data	2017	6.7	34	average
Coggan et al. 2019	2017	2.6	14	average

Table 2 shows three data sets for nine perfluoroalkyl acids (PFAA) frequently detected in sludge. Within this list are shorter carbon-chain PFAS (i.e. perfluorobutanoic acid (PFBA), perfluorobutanesulfonic acid (PFBS), etc.) which may be substitutes for PFOA and PFOS since their phase-out starting in 2002 (Buck et al. 2011). These data sets span the time from 2001 to 2017. There has been speculation that PFOA and PFOS concentrations in various media would decrease with an accompanying increase in short-chain PFAA. Although limited and not statistically valid, the data in Tables 1 and 2 seem to confirm this supposition, especially relative to reductions in PFOS concentrations. However, other studies have concluded that, at least for the time frame from 2001 to 2007, there was no statistically significant changes in PFOS or overall PFAS concentrations in sludge (Venkatesan & Halden 2013; Sepulvado et al. 2011).

Table 2. Data Comparison of Nine Perfluoroalkyl Acids (PFAA) in Sludge from Three Data Sets

Compound	Venkatesan & Halden 2013 ng/g (2001 averages)	Gottschall et al. 2016 ng/g (2009 data point)	NEBRA/DES Data ng/g (2017 averages)
PFBA	2	<0.4	34.6
PFPeA	3.5	1.2	22.5
PFHxA	6.2	1.5	11.0
PFHpA	3.4	<0.4	1.1
PFOA	34	1.6	6.7
PFNA	9.2	19	2.6
PFBS	3.4	22	5.7
PFHxS	5.9	<0.7	13.3
PFOS	403	7.2	34

As PFAS research related to wastewater residuals progresses, increasing attention is focused on PFAS other than PFOA and PFOS. Target analyte lists for sludge analysis have expanded to include PFAS with branched alkyl chains, perfluorinated side-chain polymers, and various PFAA precursor compounds. Monitoring for these other PFAS will be necessary to answer questions about PFAS fate and transport in the environment (Wang et al. 2017, Hamid and Li, 2016). Degradation and transformation of these more complex molecules may explain the continued presence and stable concentrations of PFOA, PFOS, and other PFAA in wastewater residuals and other environmental media even as the use of PFOA, PFOS, and other PFAA is discontinued.

Land Application of Wastewater Residuals and Soil Impacts

Given the presence of PFAS in wastewater residuals and the persistence of these chemicals in the environment, it is safe to assume that the recycling of wastewater residuals via land application will result in measurable PFAS contamination of the receiving soils. Table 3 shows soil concentrations for PFOA and PFOS following land application of biosolids from three studies. The data from Zareitalabad et al. (2013) are for background soil concentrations derived from limited data from around the world. Washington et al. (2009) reported on samples collected for six agricultural fields that received biosolids from the Decatur, Alabama WWTF for at least 12 years. This facility was known to receive wastewater from PFAS industrial dischargers. Sepulvado et al. (2011) reported data on short-term plots receiving biosolids for three years at total cumulative loading rates of up to 178 Mg/ha dry weight (DW) and long-term plots receiving applications for up to 32 years at cumulative loading rates up to 2218 Mg/ha. Although the biosolids used in this study were not impacted by PFAS industrial discharge, the cumulative loading rates are high and represent a “worst case” especially for the long-term plots (Sepulvado et al. 2011). Gottschall et al. (2016) detected the PFOA and PFOS concentrations shown in Table 3 after a one-time application of 22 Mg/ha.

Table 3. PFOA and PFOS Concentrations in Soil

Study	PFOA Concentration (ng/g)	PFOS Concentration (ng/g)
Washington et al., 2009	50-320	30-410
Sepulvado et al., 2011: Short-term plots Long-term plots		2-11 5-483
Gottschall et al. 2016	0.12-0.83	Below detection - 0.4
Zareitalabad et al., 2013	0.124	0.472

Clearly, land application of biosolids, especially applications that involve biosolids impacted by PFAS industrial discharges or high cumulative loading, will increase PFOA and PFOS concentrations above the typical background contamination levels found in agricultural soils. Generally, PFAS concentrations in biosolids-amended soil will be determined by biosolids PFAS quality (composition and quantity) and residuals cumulative loading rate (Sepulvado et al. 2011; Lindstrom et al. 2011). Sepulvado et al. (2011) have observed a statistically significant positive correlation between individual PFAS concentrations in the soil and cumulative biosolids loading rate for biosolids of relatively consistent quality. The correlation is described by the following regression:

$$[\text{PFC}] = m * \text{LR} \quad \text{where:}$$

[PFC] = the concentration of individual PFAS compounds in the soil (ng/g)

m = slope of the regression for individual PFAS compounds (ng/g per Mg/ha dry weight),

LR = cumulative biosolids loading rate (Mg/ha dry weight)

This correlation is particularly strong for long-chain PFAS (>C₈), with these PFAS compounds frequently detected at the highest concentrations after land application in surface soils (Lindstrom et al. 2011). Short-chain PFAS (<C₈) may be abundant in surface soils if the land applied residuals also have high concentrations of these compounds. For short-chain PFAS, the correlation between surface soil concentrations and cumulative loading weakens as the post-application time increases (Lindstrom et al. 2011). A microcosm study by Venkatesan and Halden (2014) reported relatively rapid loss of short-chain PFCA (C8-C4) and calculated first order half-lives in soil-biosolids mixtures ranging between 385 to 866 days. The less frequent detection and lower relative abundance of short-chain PFAS is attributed to their greater mobility within the soil profile (Sepulvado et al, 2011; Lindstrom et al. 2011). Although less mobile, long-chain compounds such as PFOA and PFOS have been detected at decreasing concentrations down to a depth of 120 cm at sites receiving long-term biosolids applications (Sepulvado et al. 2011).

Observations and/or predictions concerning the specific compounds and their concentrations in soil following residuals land application are complicated by transformation/degradation of certain PFAS. Although PFAA such as PFOA and PFOS are very stable and persistent in the environment, numerous studies have reported on the transformation/degradation of PFAS products and synthesis intermediates or byproducts. Collectively, this large group of chemicals demonstrating the potential for transformation under ambient conditions have been dubbed “PFAS precursors” of simply “precursors”. These transformations have been observed in the soil following land application of biosolids (Washington et al. 2009; Sepulvado et al. 2011; Gottschall et al. 2016). Transformations result in reduced soil concentrations of the parent compound and the production of a more stable PFAA (for example PFOA or PFOS) and concurrent concentration increases in the product compound. Spatial and temporal occurrence of these transformations within the soil profile, as well as their reaction rate, are affected by a myriad of factors, both biotic and abiotic (Wang et al. 2017, Kim et al. 2013, Liu and Avendaño 2013). As long-

chain PFAS use is reduced or eliminated, PFAS chemical production processes change with a resulting change in potential PFAS precursors and eventual transformation end-products in the soil (Wang et al. 2017, Chu and Letcher, 2017). Changing PFAS product chemistry coupled with limited understanding of PFAS transformations are confounding factors in determining PFAS composition and concentrations in the soil following land application (Wang et al. 2017, Liu and Avendaño 2013).

PFAS Mobility in the Soil and Risk to Groundwater

The mobility of PFAS in soil and potential risk for groundwater contamination have been demonstrated in the literature (Xiao et al. 2014; Zareitalabad et al. 2013). PFAS contamination in groundwater from sources such as AFFF and septic systems has been demonstrated (Weber et al. 2017; Schaidler et al. 2016). More than a decade of land application of biosolids impacted by industrial discharges resulted in PFAS groundwater contamination exceeding federal health guidelines (Lindstrom et al., 2011). Land application of biosolids not impacted by PFAS dischargers at high annual and cumulative loading rates has resulted in detectable levels of PFAS moving down through the soil profile and entering groundwater, but not at levels exceeding most health guidelines (Sepulvado et al. 2011; Gottschall et al. 2016).

Evaluating the risk to groundwater from land application of wastewater residuals hinges on an understanding of the factors that affect PFAS mobility. The literature suggests the following factors are the most important in determining PFAS mobility:

- 1) PFAS carbon-chain length/molecule size,
- 2) Absorption onto soil organic matter and other soil constituents,
- 3) Soil textural class/mineral composition, and
- 4) Soil solution chemistry.

The influence of carbon chain length has been observed repeatedly in the literature evaluating PFAS mobility, regardless of the original source of PFAS contamination. Lindstrom et al. (2011) reported that, even at high PFAS loading rates to the soil, long-chain (>C8) were rarely detected in groundwater, while concentrations of shorter-chain compounds were higher in surface and well water. Statistically significant correlations have been observed between short-chain PFAA concentrations in groundwater and biosolids cumulative loading (Lindstrom et al 2011). Sepulvado et al. (2011) demonstrated that PFOA and PFOS do move through the profile, but more slowly than short-chain PFAS. It has been suggested that PFOA and PFOS detection in groundwater may follow contamination of surface soils by years and possibly decades (Xiao et al. 2014). The literature also suggests that PFAA precursors may move through the soil at a slower rate than PFAA (Azzolini 2014). Molecular size/weight and functional groups attached to the carbon chain also appear to affect PFAS mobility (Azzolini 2014). In particular, the sulfonate functional group (SO_3^-) in PFSA has a greater affinity for solids than the carboxylate group (COO^-) in PFCA (Pan et al. 2010, Lasier et al. 2011, Sorengard et al. 2019).

Although carbon-chain length is obviously an important component of PFAS mobility, the relationship between chain length and absorption/desorption from soil organic matter is the key factor determining PFAS movement. Sorption behavior over wide concentration gradients is not linear and is best described by Freundlich or Langmuir isotherms (Zareitalabad et al. 2013). Various studies have attempted to characterize linear portions of partitioning curves for specific compounds by calculating organic carbon-water partition coefficients ($\log K_{oc}$) (Sepulvado et al. 2011). Sepulvado et al. (2011) show a positive correlation between carbon-chain and $\log K_{oc}$. Higher partition coefficients indicate

stronger sorption to soil organic matter with log K_{oc} increasing 0.5 to 0.8 log units for each additional CF₂ group (Zareitalabad et al. 2013). Table 4 shows variability in reported log K_{oc} values reported in the literature.

Table 4. Log K_{oc} Values Reported in the Literature

Study	PFOA (log K_{oc})	PFOS (log K_{oc})
Zareitalabad et al. 2013		
Average from published data	2.8	3.0
Field-based data	3.7	4.2
Sepulvado et al. 2011		
Lab-based values	2.3	3.34
Previous study	2.06	2.57

Some of this variability has been explained as resulting from deviations between laboratory derived-values and those observed in the field (Zareitalabad et al., 2013). However, variability is evident between K_{oc} values derived by the same methods, suggesting that other factors beyond sorption to organic matter influence PFAS mobility. Using different K_{oc} values can result in vastly different estimates of PFAS retention or, conversely, release from the soil (Zareitalabad et al. 2013).

K_{oc} values are typically derived by experimental determinations of soil sorption coefficients (K_d) and then correcting for the organic carbon content of the soil (Zareitalabad et al. 2013; Sepulvado et al. 2011). This assumes that all PFAS absorption involves the soil organic matter. However, the literature does indicate that other soil factors can have significant influence on PFAS equilibria (Zareitalabad et al. 2013). Sorption of PFAS is dependent on the complex interactions of soil solids, both mineral and organic, and the soil solution and its attendant effects on the electrostatic forces of the soil matrix (Zareitalabad et al. 2013). For example, different minerals within the soil mineral fraction can have different sorption capacities (Zareitalabad et al. 2013; Wank and Shih 2011; Shih and Wang 2013). Likewise, organic matter in the soil is complex in composition, and it has been proposed that different components of organic matter have different sorption capacities (Zhang et al. 2015; Wang et al. 2015). For example, PFOA is more likely to bind to proteinaceous organic matter as compared to more lignin-based components (Liu and Avendaño 2013). In addition, the specific surface area of a soil influences sorption capacity (Zareitalabad et al., 2013). Consequently, differences in soil textural classes are a factor to be considered. In terms of soil solution chemistry, pH and cationic strength (calcium, magnesium, sodium, potassium, iron, aluminum) can influence sorption of PFAS. Increasing pH, especially in the 6-8 range, will decrease PFAS sorption in soil and biosolids (Wank and Shih 2011; Zhi 2017; Wang and Shih 2012; Arvaniti et al. 2014; Shih and Wang 2013). Increases in soil solution cations appears to decrease PFAS sorption to the soil mineral fraction (Wank and Shih 2011; Wang and Shih 2012; Shih and Wang 2013). If organic matter is a component of the sorbent, then cations, especially divalent and trivalent ions, can have a positive impact on PFAS sorption in biosolids and soil (Schedin 2013; Zhi 2017; Wang et al. 2015; Arvaniti et al. 2014). Also, there is some evidence that over time certain PFAS compounds may become more permanently bound in the soil matrix (Liu and Avendaño 2013, Schedin 2013). Some of these soil attributes can and do change over relatively short spatial and temporal spans. For example, land application of alkaline stabilized biosolids is intended to rapidly add organic matter and raise pH and calcium concentrations in the soil. There is likely to be some concurrent change in PFAS sorption capacity in the soil. Whether the change is positive, negative, or negligible is uncertain considering that certain components of that lime-stabilized biosolids can have opposite effects on sorption. Given the complexity of sorption reactions and the potential for change in relevant soil parameters over time and

space, the use of K_{oc} from the literature may result in inaccurate estimates of fugitive PFAS from land application sites.

Human PFAS Exposure Resulting from Plant and Animal Uptake from Soils Amended with Wastewater Residuals

The presence of PFAS in foods for human consumption has been well established (Smith 2001; Herzke et al. 2013; Genualdi and deJager, 2019). The uptake of PFAS by plants grown in contaminated soil or consumption of these plants as animal feed has long been recognized as a potential contributor of PFAS to the human diet (Perez et al. 2017, Ghisi et al. 2018, Liu et al. 2019). Numerous studies have documented the uptake of PFAS from contaminated soil, including biosolids-amended soil (Stahl et al. 2008; Zhang et al. 2016; Blaine et al, 2014; Blaine et al. 2014A; Blaine et al. 2013; Wen et al. 2016, Navarro et al. 2017). The literature has explored the transfer of PFAS from the soil into plants and animals, including the bioaccumulation in specific plant and animal tissues. The factors that influence plant uptake and accumulation are (Ghisi et al. 2018):

- 1) PFAS concentrations in the soil,
- 2) PFAS chain length and functional groups,
- 3) Plant species/organ, and
- 4) Soil organic matter content.

The predominant factor controlling plant uptake of individual PFAS and total PFAS is the concentration in the soil (Stahl et al. 2008; Blaine et al. 2014; Blaine et al. 2014A; Blaine et al. 2013). For example, Blaine et al. (2014) reported PFOA and PFBS concentrations ranging from 67 ng/g to 232 ng/g in the edible portions of plants grown on “industrially impacted biosolids”. In the same study, the concentrations of all individual PFAS were less than 25 ng/g for crops grown on the control soil as well as biosolids amended-soil that was not industrially impacted. A study using reclaimed water as a source of PFAS showed a linear increase in plant PFAA content with increasing PFAA soil concentrations applied (Blaine et al. 2014A). However, some studies have observed a reduction (non-linear response) in bioconcentration factors for certain PFAS at higher soil concentrations suggesting that PFAS uptake may be inhibited at very high soil concentrations (Ghisi et al. 2018).

As with most PFAS biochemical/chemical interactions, carbon-chain length influences plant uptake from the soil. Plant uptake shows an inverse relationship with carbon chain length, with a statistically significant correlation between decreasing bioaccumulation factors and increasing carbon-chain length (Blaine et al. 2014; Blaine et al. 2014A; Blaine et al. 2013, Gobelius 2016, Liu et al. 2019). PFAS functional groups also influence plant uptake. It appears the PFCAs (e.g. PFOA) have a higher potential to bioaccumulate than perfluoroalkyl sulfonic acids (e.g. PFOS) (Stahl et al. 2008; Blaine et al. 2014A; Wen et al. 2016; Perez et al. 2017, Gobelius 2016, Liu et al. 2019).

Plant uptake compared to soil concentrations is also moderated by plant species and the plant organ (root, shoot, fruit, leaves, etc.). Numerous studies have shown plant uptake of PFAS is variable across plant species as well as plant organs within the same species (Stahl et al. 2008; Blaine et al. 2014, Blaine et al. 2014A; Blaine et al. 2013; Wen et al. 2016). For PFOA and PFOS, PFAS bioaccumulation appears to decrease with translocation through the plant from roots to shoots to fruit/plant storage organs (Stahl et al. 2008; Blaine et al. 2014; Blaine et al. 2013; Wen et al. 2016). Again, carbon-chain influences

the distribution of PFAS within plants. The highest concentrations of long-chain (>C6) PFAS are usually found in the roots while short-chain (C4-C6) are more likely to accumulate in above-ground plant organs (Navarro et al. 2017, Ghisi et al. 2018). For specific chemicals, distribution within the plant is highly dependent on plant species (Ghisi et al. 2018). For some species, edible portions of plants, such as fruits and grains, will have lower PFAS levels than leaves and shoots (Blaine et al. 2014, Liu et al. 2019, Ghisi et al. 2018). For radishes, lettuce, and celery grown on highly contaminated soils, the edible portions of the plant accumulated the most PFAS (Ghisi et al. 2018). Also, PFAS functional groups will influence plant uptake of PFAS. PFCA (carboxylate group) are more readily accumulated by plants than PFSA (sulfonate group) (Gobelius 2016, Ghisi et al. 2018, Navarro et al. 2017, Blaine et al. 2014A). It has been suggested that the process of absorption through the root system is different for PFOA and PFOS and this difference influences uptake and translocation (Navarro et al. 2017). Interestingly, Wen et al. (2016) suggest that the variability of uptake between species and translocation within a plant may be explained by the proportion of protein and lipid content. Higher protein content favors uptake and translocation, while higher lipid content inhibits those processes (Liu et al. 2019).

As discussed above, soil organic matter content is likely the predominant factor controlling PFAS sorption in the soil. Higher organic matter content in soil inhibits uptake of PFAS and reduces plant bioaccumulation (Blaine et al. 2014A, Ghisi et al. 2018). This suggests that PFAS added to agricultural soils due to biosolids land application would be less available for plant uptake (Ghisi et al. 2018). Logically, other soil parameters (pH, soil type, etc.) that influence PFAS sorption will also affect plant uptake (Blaine et al. 2013; Perez et al. 2017).

As would be expected, PFAS adsorption and excretion is variable across animal species and within tissue compartments within a species. Liver, kidneys, and blood plasma tend to accumulate higher PFAS concentrations than muscle tissue (Lupton et al. 2011; Kowalczyk et al. 2013; Gebbink and Letcher, 2011; Yoo et al. 2007; Kowalczyk et al., 2012). Unlike other persistent organic contaminants, PFAS compounds do not seem to accumulate in fatty tissue (Goodrow et al. 2018). PFAS carbon-chain length and functional group play a role in accumulation, as well as the route (urine, feces, etc.) and rate of elimination from animal tissue. Longer carbon-chains and sulfonate functional groups (e.g. PFOS) favor retention in animal tissues, while shorter carbon chains and carboxylate functional groups (e.g. PFOA) correlate with faster elimination (Kowalczyk et al. 2013; Gebbink and Letcher 2011; Yoo et al. 2007; Kowalczyk et al. 2012). For example, Yoo et al. (2007) report a depuration (elimination) half-life for PFOA and PFOS in chickens of 4.6 days and 125 days, respectively. Although not the primary route of excretion, PFAS excretion in milk was reported, with the highest concentrations for compounds having longer carbon-chains and/or sulfonate functional groups (Kowalczyk et al. 2013; Kowalczyk et al. 2012). Rates of excretion in milk were reported as percentages of cumulative PFAS intake for individual compounds (Kowalczyk et al. 2013; Kowalczyk et al. 2012). Consequently, concentrations in milk would depend on the exposure/intake by the animal. Field studies involving aquatic species seem to confirm the general observations about carbon-chain length and functional group on animal bioaccumulation of PFAS compounds (Goodrow et al. 2018, Lasier et al. 2011),

The literature provides ample evidence that land application of wastewater residuals can contribute to PFAS in the human diet through the direct consumption of crops or consumption of animal products tainted by residuals through animal feed or water (Perez et al. 2017, Ghisi et al. 2018, Navarro et al. 2017). However, because the rates of plant uptake are minimal, there is no evidence to date that shows exposure from plant uptake is significant and impacts human health, although further study is needed (Lupton et al. 2011; Kowalczyk et al. 2013; Blaine et al. 2014; Perez et al. 2017). Significant exposure to

the general public through diet seems particularly unlikely given the very small proportion of nationwide crop production fertilized by amendment with wastewater residuals compared to production associated with chemical fertilizers and manure. Since federal harvesting restrictions frequently make it impractical to use biosolids on food crops for direct human consumption, the potential exposure from residuals use is decreased further.

Conclusions and Research Priorities

The foregoing discussion of the scientific literature pertaining to PFAS suggests multiple avenues for fugitive emissions to the environment and potential human exposure. Certainly, emissions from the production of these chemicals or their use in manufacturing of other products accounts for high exposure for local populations. The mobility and persistence of PFAS results in more diffuse, long-term exposure for wider populations. The general population also experiences PFAS exposure through their use of consumer products. Diffuse, long-term PFAS presence in the environment and commerce ensure that PFAS will be discharged to society's waste management systems such as landfills and wastewater treatment facilities. The focus of the above discussion was the potential for PFAS to be released to the environment via the land application of wastewater residuals and evaluation of land application as a pathway for human exposure through the contamination of groundwater and/or surface water and uptake by plants and animals. Are the exposures associated with land application significant compared to the other direct and indirect exposures suggested above? Are the concentrations detected in groundwater, surface water, plants, and animal products impacted by land application sufficient to exceed health guidelines?

Except for worst-case scenarios, the literature does not show clear cases of excessive human exposure associated with the use of wastewater residuals in agriculture (Lindstrom et al. 2011; Zhang et al. 2016; Blaine et al., 2014). Some studies demonstrate human PFAS exposure from the use of residuals not impacted by industrial discharge, but suggest that such exposure may be insufficient to affect human health (Gottschall et al. 2016; Blaine et al. 2014, Lupton et al. 2011; Kowalczyk et al. 2013). At this time, the scientific literature does not provide a clear and unequivocal answer to our original question:

Does land application of wastewater residuals (paper mill solids, municipal biosolids, etc.) at fertilizer rates with current common regulatory requirements and proper industrial source controls represent a risk to public health from PFAS contamination of groundwater via leaching and/or surface water via runoff?

Further, part of the answer to this question involves the regulations and guidelines adopted by the local regulatory authorities. Zareitalabad et al. (2013) suggest that the majority of PFOA and PFOS in the soil will eventually reach groundwater and surface water. If the rate of release is slow enough, concentrations in the groundwater may not exceed drinking water standards. However, if the local standards for PFOA and PFOS are sufficiently stringent, then any release to groundwater may be cause for concern. Regulations regarding residuals application rates (e.g. P-index, mineralization rates, etc.) and setback distances (e.g. depth to groundwater, surface water buffers, etc.) can affect loading of PFAS to the soil and ultimately the likelihood that residuals applications will affect groundwater as well as plant and animal uptakes to the degree that human health is a concern. In addition, local climate and soils types influence PFAS mobility and the potential for these chemicals to reach human receptors. The role of local factors (regulations and environmental conditions) in formulating an answer to our question strongly suggests that the best answer will come from research conducted locally.

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