



Information Update:

Perfluorinated Alkyl Substances (PFAS) in Biosolids

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Note: Abstracts for key relevant published research papers are included in the References.

What are PFASs?

Per- and polyfluoroalkyl substances (PFASs) are a family of synthetic chemical compounds developed more than 60 years ago and used widely in society. They are also called “per- and polyfluorinated alkyl substances.”¹ This family of chemicals is used in household and commercial products that resist heat and chemical reactions and repel oil, stains, grease and water. They include the two most-well-known PFASs:

- PFOA (polyfluorooctanoic acid), which is used in the process of making non-stick cooking surfaces (e.g. Teflon®) and in fire-fighting foams, stain-resistant carpets and furniture fabrics, water resistant clothing, cleaning products, and paper and cardboard food packaging.
- PFOS (perfluorooctane sulfonate), a main ingredient in the fabric treatment Scotchguard® and other stain repellants.

The common chemical structure of this family of compounds involves a chain of bonded carbon and fluorine atoms: C_nF_{2n+1} . The strength of the C-F bond makes these chemicals very stable (persistent) and both lipophobic and hydrophobic (resistant to fats and water, respectively) – which is why they work as stain and water repellants (Buck et al. 2011).

Why are people concerned about PFASs?

Extensive research on PFASs and their potential environmental and public health impacts has been ongoing for 20+ years. Because of decades of use and their mobility in air and water, these chemicals have been found all over the world in waters, soils, wildlife, and people. For example, total concentrations of PFASs in natural precipitation were found to be in the range of 1.4 – 18 parts per billion, or ppb² (Kwok et al., 2010). In the past 15 years, PFASs have been measured in

¹ PFASs are also sometimes called “perfluorinated compounds” (PFCs). This can cause some confusion, because another group of chemicals are also called PFCs: perfluorocarbons (aka fluorocarbons), the infamous ozone-depleting refrigerants and solvents.

² Parts per billion are abbreviated as ppb or ng/g or µg/kg or µg/L. 1 part per billion is the equivalent of 1 second in nearly 32 years. All data presented here are in ppb; some data have been converted to ppb from other units, so that all reported concentrations can be easily compared.

drinking water sources, as well as in homes. Public health authorities have also compiled considerable data from volunteers to determine the levels of PFASs in human blood. PFOA and PFOS concentrations in the blood of chemical plant workers in Alabama averaged 1130 and 910 ppb, respectively. In comparison, the average for the U. S. population was 4 and 17 ppb, respectively, in 2005-06, and 2 and 6 ppb respectively, in 2011-12. (The reduction in blood concentrations is likely caused by reduced use of the chemicals generally.) Recent (2016) investigations around concerns of PFAAs in groundwater in southern NH found average blood levels of 3 – 5 and 5 – 11 ppb, respectively (NH Department of Health & Human Services, 2017).

Some of the PFASs have been shown to have negative health impacts, including causing cancer in animal studies at environmentally relevant concentrations. A study of workers exposed to work-place, higher-than-average levels of PFOA and PFOS found higher levels of prostate and bladder cancers, respectively (Nakayama et al. 2005). However, the most thorough population study to date, involving nearly 70,000 people near Parkersburg, West Virginia, concluded that real-life population exposure near a long-term manufacturing facility resulted in no probable link of PFOA to most cancers, general hypertension, and many other alleged health impacts. They did find probable links to high cholesterol, ulcerative colitis, thyroid disease, testicular and kidney cancers, and pregnancy-induced hypertension. A Center for Disease Control (CDC) review in 2015 found associations between PFOA and decreased birth weight, increased uric acid, and alterations of liver enzymes (Vermont Department of Health, 2016).

PFASs have been found to be highly stable and persistent, even in soils; in comparison, many organic chemical compounds are readily broken down in soils (Higgins, 2014). Their unique properties mean they may or may only moderately sorb (adhere) to organic matter or other soil particles and some can accumulate in soil water and leach to groundwater (Brown, 2014; Higgins et al., 2005). Within the family of PFASs, the degradation rate, solubility, and potential for plant uptake for any specific compound will vary based on its molecular weight, the number of fluorine atoms, etc.

Because of growing concern about potential public health and environmental effects, 3M and other manufacturers and users of the more toxic PFASs have been phasing them out over the past 15 years. Current localized PFOA and PFOS contamination issues around the Northeast are due to legacy releases of these chemicals. The highest levels being found in the environment are near facilities that have made or used these substances.

Why are PFASs in the news now?

In the past two years, in certain localities in Vermont (e.g. North Bennington), New Hampshire (e.g. Merrimack, Pease), and eastern New York (e.g. Hoosick Falls), PFOA and PFOS in particular have been found in drinking water and groundwater. In these highly publicized cases, the locations of the contaminated waters are directly related to manufacturing or utilization sites where PFASs were used and released to the environment over many years.

What limits have been put on PFASs?

In response to recent concerns, state environmental agencies have conducted drinking water, groundwater, and soil sampling and testing to determine the extent of contamination. In addition,

state and federal agencies have conducted updated scientific risk assessments on some of these chemicals, PFOA especially.

In spring of 2016, U. S. EPA reevaluated its drinking water health advisory for PFOA and PFOS and issued a new health advisory level of 0.070 ppb for the combined total of the two compounds – an apparent reduction from the previous EPA advisory. The reduction was caused by a change in the modeling that had assumed only relatively short-term exposure via drinking water; the updated model assumes a lifetime of drinking a significant amount of contaminated water.

The state of Vermont went further and adopted a groundwater quality enforcement standard of 0.020 ppb for PFOA. New Jersey is considering a slightly lower level, 0.014 ppb for PFOA; if it were adopted, it would be the nation's first enforceable drinking water standard (*the EPA advisory level is not an enforcement standard*).

New soil screening standards have also been developed. As with drinking water, EPA standards set in the 2000s are much higher than standards adopted recently (see Table 1). Vermont has set the lowest soil screening standard: 300 ppb. NH has set a screening limit of 500 ppb. It is important to emphasize that the soil standards are many orders of magnitude greater from standards for drinking- and groundwaters. *However, to date, soil standards have been set based on risk assessments of potential direct human (e.g. dermal) exposure, not with respect to potential leaching of PFASs to groundwater.*

How do PFASs get into wastewater & biosolids?

In a March 2016 discussion, Professor Sally Brown, PhD (University of Washington) noted that “in the vast majority of treatment works, these compounds can be traced back to people’s homes and the wide range of household products that they are used in.” One research team found that dust in homes and daycare centers in the U. S. contained a median of 142 ppb PFOA and 201 ppb PFOS (Strynar and Lindstrom, 2008). In a review of the literature on trace organic chemicals in biosolids, Hundal et al. (2011) noted that “the most significant human exposure results from ingestion of indoor air and house dust because the largest volume of PFCs (>2.5 million pounds in 2000) is used for indoor applications. Use of PFCs in food contact wrappers and boxes represent another potential source of oral exposure.” For example, microwave popcorn bags *have had* concentrations as high as 300 ppb.

It is the widespread presence of traces of these chemicals in products and homes, as well as in fire-fighting foams and commercial uses, that results in their presence in wastewater and biosolids. The chemistry of wastewater is, after all, a reflection of the chemistry of daily life. In addition, some PFASs are created through the breakdown of more complex molecules, such as polyfluoroalkyl phosphoric acid diesters (diPAPs), which *were* used in greaseproof food wrapping paper, and 2-(N ethylperfluorooctanesulfonamido) acetic acid (N-EtFOSAA) (Higgins et al., 2005).

What levels of PFOA and PFOS have been found in biosolids and biosolids amended soils?

Studies have found PFOA and closely related compounds in biosolids at levels ranging from 5 to 152 ppb. The range for PFOS is 55 to several hundred ppb. A 2016 analysis of a northern New England biosolids compost produced in an area with some known area groundwater contamination found a PFOA concentration of ~8 ppb. See Table 1.

There have been rare cases of direct, substantial industry releases of PFASs into wastewater; these resulted in elevated levels in biosolids. The most prominent example was in the 2000s and involved discharges to the sewer system from a chemical plant near Decatur, AL. The resulting contaminated biosolids were applied to area soils for many years, resulting in soil concentrations of PFOA up to 320 ppb and PFOS up to 410 ppb (Guelfo, 2013). Those Decatur biosolids PFOA concentrations were measured at about 50 – 130 ppb, much higher than typical urban biosolids, such as those from New York City that contained in the range of 5 to 20 ppb. Decatur biosolids PFOS concentrations were measured at about 400 ppb, as compared to New York City biosolids that contained about 30 – 80 ppb (U. S. EPA, 2009). Direct industrial discharges of these chemicals to sewers causes the highest measured concentrations in biosolids; such instances are rare and becoming rarer, as use of the chemicals is reduced.

Typical biosolids application rates and subsequent incorporation and dilution into the soil tend to result in very low concentrations of trace chemicals such as PFASs in soil. An outdoor mesocosm experiment that used a very high biosolids application rate (1 part biosolids to 2 parts soil) found that the highest concentration of PFASs was for PFOA at 24.1 ppb (Venkatesan and Halden, 2014).

The concentrations reported above – even those from highly contaminated sites (e.g. Decatur, AL) – are comparable or much lower than recent New Hampshire and Vermont soil screening standards, which are 500 and 300 ppb for PFOA, respectively. Use of biosolids – even those with exceptionally high, industrially-impacted concentrations – does not appear to create PFAS concentrations of concern *with regards to those soil standards*. However, as noted above, to date, soil standards have been set based on modeling of potential direct human (e.g. dermal) exposure, not with respect to potential leaching of PFASs to groundwater.

What does the research show regarding the fate & impacts of PFASs in biosolids and soils?

When biosolids are applied to soils, they are either disked into the soil or they remain on the surface (surface application is common on perennial crops, such as for hay). Because of their limited ability to sorb (adhere) to soil particles, some of the PFASs may migrate from surface-applied sites in runoff (*Lindstrom et al, 2015*). Or, if the biosolids are incorporated, some PFASs may leach into tile drainage and/or groundwater. Because tile drainage is so close to the actively farmed surface soil layer, it represents a worst-case scenario when it comes to finding trace contaminants. Field studies in biosolids-amended silty-clay agricultural field plots in Ontario found PFOA and PFOS in tile drainage water at *maximum* concentrations of 0.012 ppb (12 ng/L) and 0.017 ppb (17 ng/L), respectively (Gottschall et al., 2010). Compare these concentrations to the most stringent groundwater regulatory limit today, Vermont's limit of 0.020 ppb for PFOA.

However, that and other research (Sepulvado et al., 2011; Xiao et al., 2014) were conducted before the new U. S. EPA drinking water health advisory level³ was established in 2016. That new, dramatically lower drinking water health advisory has led to questions of whether or not typical biosolids applications could contribute to PFAS levels in groundwater in the range of the new health advisory level. This reevaluation depends on many factors and assumptions. What seems to be understood is that shorter-chain PFASs are more likely to leach than are longer-chain PFASs, such as PFOA and PFOS. The shorter-chain PFASs degrade more quickly in soils than do the longer-chain members of the family; for example, the C4 – C8 perfluorinated carboxylates have first-order half-lives of 385-866 days (Venkatesan and Halden, 2014). And, at industrially-impacted sites, research has found increased concentrations of PFOA and PFOS at greater depth, suggesting slow downward leaching and considerable persistence of these chemicals. In addition, Xiao et al. (2014) note that “the transport of PFOS and PFOA is retarded in the vadose zone, but not in the aquifer” and “the groundwater contamination of PFOS and PFOA often follows their release to surface soils by years, if not decades.” Whether such leaching behavior would happen in a typical biosolids application scenario is uncertain.

And many additional factors influence the trace levels found in groundwater, including, but not limited to:

- the widespread distribution of traces of these compounds in the environment, resulting in background soil levels being in the same range as proposed calculated soil screening levels (Xiao et al., 2014);
- the variety of transport and distribution factors (e.g. aerial transport) that make it difficult to determine the source of contamination at any particular site;
- the uncertain extent to which the organic matter and other properties of biosolids reduce leaching potential;
- the fact that calculations and results behind public health advisories depend on the appropriateness of embedded conservative assumptions; and
- the fact that manufacture and use of PFASs is diminishing, meaning that current and future biosolids will contain lower levels than older biosolids on which much of the research data is based.

When it comes to research findings regarding plant uptake of PFASs, there is a pattern similar to that for groundwater. Those with shorter chains are more mobile and can pass through cell walls into plants. A study using biosolids impacted by industrial discharges of PFASs mixed 1 part biosolids to 10 parts soil resulted in PFOA and PFOS levels in lettuce of 195 and 185 ppb, respectively. However, higher levels (~250 ppb) of the shorter chain PFBA and PFPeA were found (Blaine et al., 2013; Higgins, 2014). The longer-chain versions are less easily taken up by plants. Bioaccumulation of short-chain PFASs (PFBA and PFPeA) has been measured in greenhouse studies in lettuces and tomatoes (Blaine et al., 2013). *It is important to note that past greenhouse and pot studies of other biosolids contaminants (e.g. heavy metals, pharmaceuticals) have dramatically overestimated plant uptake in actual field conditions.*

³ An EPA health advisory level is not a regulatory standard. Rather, it is an "informal technical guidance" designed to "provide information for public health officials or other interested groups on pollutants associated with short-term contamination incidents." The health advisory involves many conservative assumptions to provide exceeding protection from a lifetime's consumption of significant quantities of drinking water.

While use of high application rates of industrially-contaminated biosolids may result in measurable levels of some PFASs in some produce, typical municipal biosolids used at normal application rates are unlikely to do so. “PFAS levels measured in lettuce and tomato grown in field soil amended with only a single application of biosolids (at an agronomic rate for nitrogen) were predominantly below the limit of quantitation (LOQ). In addition, corn (*Zea mays*) stover, corn grains, and soil were collected from several full-scale biosolids-amended farm fields. At these fields, all PFASs were below the LOQ in the corn grains and only trace amounts of PFBA and PFPeA were detected in the corn stover” (Blaine et al., 2013). Their conclusion: “These data suggest that edible crops grown in soils conventionally amended for nutrients with biosolids (that are not impacted by PFAS industries) are unlikely a significant source of long-chain PFAS exposure to humans.”

Brown (2014) summarized this as well: “Plant uptake from biosolids amended soils was only demonstrated in extreme cases – with high contaminant biosolids or extraordinary loading rates.”

Conclusions

Wastewater and biosolids reflect what we use in our daily lives and living spaces. PFASs have been widely used in many different products over many decades and are found widely in homes, products, and the environment. Research suggests that, in the 2000s at least, 95% of the general U. S. population had measurable levels of PFOA, PFOS, and related compounds in their blood. Fortunately, the data indicate that, when use of any of these chemicals is reduced, blood levels decrease (Kato et al., 2011). The primary route of human exposure is through exposure to products containing these chemicals (or their precursors), household air and dust, *and, in some cases, drinking water.*

“Land application of biosolids may release trace levels of PFCs into the agricultural soils but it doesn’t seem to be a major source of human exposure” (Hundal et al., 2011).

The one current area of concern is whether biosolids-applied PFASs may leach from soils and contribute to elevated levels of PFASs in groundwater. This potential concern has been elevated because the current drinking water health advisory level for PFOA and PFOS is set at a dramatically lower concentration.

Biosolids managers and wastewater treatment plant operators should evaluate potential sources of biosolids contamination, including potential industrial discharges of PFASs. They can apply industrial pretreatment and pollution prevention to further reduce the levels of PFASs in their final biosolids product. Testing and knowing biosolids concentrations is recommended.

Acknowledgements

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Table 1: Measured levels of PFOA and PFOS in various media compared to advisory & regulatory limits.

Concentrations in...	PFOA (ppb)	PFOS (ppb)
...Biosolids (ppb):		
Higgins et al., 2005	5 – 152 (total perfluorocarboxylates, not just PFOA) Detection limits of 0.7 – 2.2	55 – 3370 (total perfluoroalkyl sulfonates, not just PFOS)
Sepulvado et al., 2011		80 – 219 (range)
Tests of EPA samples from 32 states & DC in 2001 (Venkatesan and Halden, 2013)	34 (average) 11.8 - 70.3 (range)	403 (average) 308 – 618 (range)
a northern New England biosolids compost, 2016	8.3	
...Soils		
Advisory & Regulatory Limits <i>(based on direct (e.g. dermal) exposure, not potential impacts on groundwater)</i>		
U. S. EPA Soil Screening Level, 2009	16,000	6,000
Minnesota soil reference value, in effect in 2012	2100	2100
New Hampshire soil screening level, June 2016	500 (S-1, young child residential) 4300 (S-2, maintenance worker)	
Vermont preliminary soil screening level, March 2016	300	
Test results (ppb):		
Control soil (Venkatesan and Halden, 2014)	0.1 – 0.5 (range)	
Garden control soils (MN Dept.	0.36 (median)	1.4 (median)

of Health), 2005 (n=6)	0.29 – 0.54 (range)	0.93 – 2.1 (range)
Garden soils at homes with known water contamination (MN Dept. of Health), 2005 (n=34)	0.73 (median) 0.11 – 3.0 (range)	2.9 (median) 0.57 – 12 (range)
Soil in Minneapolis/St. Paul, MN metropolitan area with historic industrial uses & releases of PFASs (Xiao et al., 2009)	8	12.2
Soils in Hoosick Falls, NY (2016)	Non-detect to 21	
NH soils within 5 miles of a Merrimack plastics manufacturing facility that used PFASs	up to 33 (maximum of 160 samples, n = 160)	
VT soils near plastics manufacturing facility in No. Bennington (VT Agency of Natural Resources, 2016)	Non-detect to 45	
Decatur, AL biosolids site after years of manufacturer discharge to the biosolids production wastewater facility (U.S. EPA, 2009)	50 - 320 (range, n=25)	30 – 410 (range, n=25)
Biosolids amended soil (Sepulvado et al, 2011)		2 – 483 (range)
...Soil water (ppb):		
Gottschall et al., 2010, tile drainage water	0.012 (maximum, = 12 ng/L)	0.017 (maximum, = 17 ng/L)
...Groundwater		
Advisory & Regulatory Limits:		

U. S. EPA Health Advisory for drinking water, short term, 2009	0.4	0.2
U. S. EPA Health Advisory for drinking water, 2016	0.07 combined total for PFOA and PFOS	
Maine CDC, 2014	0.1	
Minnesota MDH, 2008	0.3	
Vermont <i>interim</i> groundwater quality standard, 2016	0.02	
Test results (ppb):		
Suffolk County, NY drinking water wells (Lerner, 2016)		0.33, 0.53
Scottsdale, AZ drinking water (Lerner, 2016)		0.2, 0.23
At grounds of plastics manufacturing facility, Merrimack, NH (2016)	non-detect to 1.6 (n = 195)	
Near OH plastics manufacturing facility (as quoted in NJ Drinking Water Quality Institute, 2016)	up to 4	
At grounds of plastics manufacturing facility, Hoosick Falls, NY (2015)	up to 18 (maximum)	
...Produce		
Advisory & Regulatory Limits:		
U. S. EPA human subchronic interim oral dose (2009, per Higgins, 2014)	80 ng PFOA intake / kg body weight / day 5600 ng PFOA intake /day for a 70 kg person	200 ng PFOS intake / kg body weight / day 14,000 ng PFOS intake /day for a 70 kg person
Test results (ppb):		
Produce grown in 10 parts soil to 1 part industrially-contaminated	~200 (in lettuce)	~75 (in lettuce)

biosolids (dry weight ratio) – 5 to 10 times a typical application rate (Blaine et al., 2013 & 2014)	~10 (in tomato) up to 67 (in radish root)	Non-detect (in tomato)
Produce grown with typical municipal biosolids (Blaine et al., 2013)	~20 (in lettuce) Non-detect (in tomato)	~100 (in lettuce) Non-detect (in tomato)
Produce grown in garden control soils (MN Dept. of Health), 2005 (n=47)	Non-detect to 0.043 (range, 6% detects)	Non-detect to 0.029 (range, 6% detects)
Produce grown in garden soils at homes with known water contamination (MN Dept. of Health), 2005 (n=232)	Non-detect to 0.26 (range, 13% detects)	Non-detect to 0.38 (range, 8% detects)
Grains and grasses grown on biosolids amended soils (Yoo et al., 2009)		1.2 – 20.4 (range)

References

Abstracts are included for those references related to PFASs in biosolids, soils, and crops.

Blaine, A.C.; C.D. Rich; L.S. Hundal; C. Lau; M.A. Mills; K.M. Harris; and C.P Higgins. 2013. Uptake of perfluoroalkyl acids into edible crops via land applied biosolids: Field and greenhouse studies *Environ. Sci. Technol.*

Abstract: The presence of perfluoroalkyl acids (PFAAs) in biosolids destined for use in agriculture has raised concerns about their potential to enter the terrestrial food chain via bioaccumulation in edible plants. Uptake of PFAAs by greenhouse lettuce (*Lactuca sativa*) and tomato (*Lycopersicon lycopersicum*) grown in an industrially impacted biosolids-amended soil, a municipal biosolids amended soil, and a control soil was measured. Bioaccumulation factors (BAFs) were calculated for the edible portions of both lettuce and tomato. Dry weight concentrations observed in lettuce grown in a soil amended (biosolids:soil dry weight ratio of 1:10) with PFAA industrially contaminated biosolids were up to 266 and 236 ng/g for perfluorobutanoic acid (PFBA) and perfluoropentanoic acid (PFPeA), respectively, and reached 56 and 211 ng/g for PFBA and PFPeA in tomato, respectively. BAFs for many PFAAs were well above unity, with PFBA having the highest BAF in lettuce (56.8) and PFPeA the highest in tomato (17.1). In addition, the BAFs for PFAAs in greenhouse lettuce decreased approximately 0.3 log units per CF2 group. A limited-scale field study was conducted to verify greenhouse findings. The greatest accumulation was seen for PFBA and PFPeA in both field-grown lettuce and tomato; BAFs for PFBA were highest in both crops. PFAA levels measured in lettuce and tomato grown in field soil amended with only a single application of biosolids (at an agronomic rate for nitrogen) were predominantly below the limit of quantitation (LOQ). In addition, corn (*Zea mays*) stover, corn grains, and soil were collected from several full-scale biosolids-amended farm fields. At these fields, all PFAAs were below the LOQ in the corn grains and only trace amounts of PFBA and PFPeA were detected in the corn stover. This study confirms that the bioaccumulation of PFAAs from biosolids-amended soils depends strongly on PFAA concentrations, soil properties, the type of crop, and analyte.

Blaine, A.C.; C.D. Rich, E.M. Sedlacko; L.S. Hundal; K. Kumar; C. Lau, M.A. Mills, K.M. Harris, and C.P Higgins. 2014. Perfluoroalkyl acid distribution in various plant compartments of edible crops grown in biosolids-amended soils. *Environ. Sci. Technol.* 48(14): 7858-65.

Abstract: Crop uptake of perfluoroalkyl acids (PFAAs) from biosolids-amended soil has been identified as a potential pathway for PFAA entry into the terrestrial food chain. This study compared the uptake of PFAAs in greenhouse-grown radish (*Raphanus sativus*), celery (*Apium graveolens* var. *dulce*), tomato (*Lycopersicon lycopersicum*), and sugar snap pea (*Pisum sativum* var. *macrocarpon*) from an industrially impacted biosolids-amended soil, a municipal biosolids-amended soil, and a control soil. Individual concentrations of PFAAs, on a dry weight basis, in mature, edible portions of crops grown in soil amended with PFAA industrially impacted biosolids were highest for perfluorooctanoate (PFOA; 67 ng/g) in radish root, perfluorobutanoate (PFBA; 232 ng/g) in celery shoot, and PFBA (150 ng/g) in pea fruit. Comparatively, PFAA concentrations in edible compartments of crops grown in the municipal biosolids-amended soil and in the control soil were less than 25 ng/g. Bioaccumulation factors (BAFs) were calculated for the root, shoot, and fruit compartments (as applicable) of all crops grown in the industrially impacted soil. BAFs were highest for PFBA in the shoots of all crops, as well as in the fruit compartment of pea. Root-soil concentration factors (RCFs) for tomato and pea were independent of PFAA chain length, while radish and celery RCFs showed a slight decrease with increasing chain length. Shoot-soil concentration factors (SCFs) for all crops showed a decrease with increasing chain length (0.11 to 0.36 log decrease per CF2 group). The biggest decrease (0.54-0.58 log decrease per CF2 group) was seen in fruit-soil concentration factors (FCFs). Crop anatomy and PFAA properties were utilized to explain data trends. In general, fruit crops were found to accumulate fewer long-chain PFAAs than shoot or root crops presumably due to an increasing number of biological barriers as the contaminant is transported throughout the plant (roots to shoots to fruits). These data were incorporated into a preliminary conceptual framework

for PFAA accumulation in edible crops. In addition, these data suggest that edible crops grown in soils conventionally amended for nutrients with biosolids (that are not impacted by PFAA industries) are unlikely a significant source of long-chain PFAA exposure to humans.

Brown, Sally. 2014. "New Initials," discussion of Univ. of Washington/NBMA abstracts. Available from NEBRA.

Brown, Sally. 2016. "Source Identification – Perfluorinated Compounds," discussion of Univ. of Washington/NW Biosolids research abstracts. March. Available from NEBRA.

R. C. Buck, James Franklin, U. Berger, Jason M. Conder, I. T. Cousins, P. de Voogt, Allan Astrup Jensen, K. Kannan, S. A. Mabury, and S. P. J. van Leeuwen. 2011. Per-fluoroalkyl and poly-fluoroalkyl substances in the environment: Terminology, classification, and origins. *Integrated Environmental Assessment and Management*, 7(4):513-541.

Chen, H., et al. (2012). "PFOS and PFOA in influents, effluents, and biosolids of Chinese wastewater treatment plants and effluent-receiving marine environments." *Environmental Pollution* 170(0): 26-31.

Abstract: Concentrations of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in influents, effluents and sludges were investigated by analyzing the samples from twelve wastewater treatment plants (WWTPs) in China. The highest concentrations of PFOS and PFOA in influents were found to occur in municipal and industrial WWTPs, respectively. Relative to PFOS and PFOA concentrations in influents, elevated concentrations were observed in effluents from WWTPs applying anaerobic, Anoxic, and aerobic wastewater treatment process. Importantly, application of previously reported organic carbon normalized partition coefficients (KOC) derived from sediment-based sorption experiments appear to underestimate the PFOS and PFOA levels in biosolids quantified in the current study. PFOS and PFOA levels in effluents were found to be approximately 27 and 2 times higher than those detected in the effluent-receiving seawater, respectively. However, their levels in this area of seawater haven't exceeded the provisional short-term health advisories in drinking water issued by U.S. EPA yet.

Environmental Council of States. 2016. New Jersey develops tight standard for PFOA in drinking water. Accessed 9/29/16 at <http://www.ecos.org/news-and-updates/new-jersey-develops-tight-standard-for-pfoa-in-drinking-water/>

Gottschall, E, E. Topp, M. Edwards, P. Russell, M. Payne, S. Kleywegt, W. Curnoe, and D.R. Lapan. 2010. Polybrominated diphenyl ethers, perfluorinated alkylated substances, and metals in tile drainage and groundwater following applications of municipal biosolids to agricultural fields. *Sci. Total Environ.* 408: 873-883

Abstract: Polybrominated diphenyl ethers (PBDEs), perfluorinated alkylated substances (PFAS), and metals were monitored in tile drainage and groundwater following liquid (LMB) and dewatered municipal biosolid (DMB) applications to silty-clay loam agricultural field plots. LMB was applied (93,500 L ha⁻¹) in late fall 2005 via surface spreading on un-tilled soil (SSLMB), and a one-pass aerator based pre-tillage prior to surface spreading (AerWay SSD) (A). The DMB was applied (8 Mg dw ha⁻¹) in early summer 2006 on the same plots by injecting DMB beneath the soil surface (DI), and surface spreading on un-tilled soil (SSDMB). Key PBDE congeners (BDE-47, -99, -100, -153, -154, -183, -209) comprising 97% of total PBDE in LMB, had maximum tile effluent concentrations ranging from 6 to 320 ng L⁻¹ during application-induced tile flow. SSLMB application-induced tile mass loads for these PBDE congeners were significantly higher than those for control (C) plots (no LMB) (p < 0.05), but not A plots (p > 0.05). PBDE

mass loss via tile (0–2 h post-application) as a percent of mass applied was ~ 0.04–0.1% and ~ 0.8–1.7% for A and SSLMB, respectively. Total PBDE loading to soil via LMB and DMB application was 0.0018 and 0.02 kg total PBDE ha⁻¹ yr⁻¹, respectively. Total PBDE concentration in soil (0–0.2 m) after both applications was 115 ng g⁻¹ dw, (sampled 599 days and 340 days post LMB and DMB applications respectively). Of all the PFAS compounds, only PFOS (max concentration = 17 ng L⁻¹) and PFOA (12 ng L⁻¹) were found above detectable limits in tile drainage from the application plots. Mass loads of metals in tile for the LMB application-induced tile hydrograph event, and postapplication concentrations of metals in groundwater, showed significant (p < 0.05) land application treatment effects (SSLMB > A > C for tile and SSLMB and A > C for groundwater for most results). Following DMB application, no significant differences in metal mass loads in tile were found between SSDMB and DI treatments (PBDE/PFAS were not measured). But for many metals (Cu, Se, Cd, Mo, Hg and Pb) both SSDMB and DI loads were significantly higher than those from C, but only during < 100 days post DMB application. Clearly, pre-tilling the soil (e.g., A) prior to surface application of LMB will reduce application-based PBDE and metal contamination to tile drainage and shallow groundwater. Directly injecting DMB in soil does not significantly increase metal loading to tile drains relative to SSDMB, thus, DI should be considered a DMB land application option.

Guelfo, Jennifer L. 2013. Subsurface Fate and Transport of Poly- and Perfluoroalkyl Substances. PhD Dissertation, Colorado School of Mines, Thesis Advisor: C. Higgins

Harrad, S., C.A. DeWit, M.A.Abdallah, C. Bergh, J. A. Björklund, A. Covaci, P.O. Darnerud, J.DeBoer, M. Diamond, S. Huber, P. Leonards, M. Mandalakis, C. Ostman, L. Småstuen Haug, C. Thomsen, and T.F. Webster Indoor contamination with hexabromocyclododecanes, polybrominated diphenyl ethers, and perfluoroalkyl compounds: An important exposure pathway for people? *Environ. Sci. Tech.* 2010 44: 3221-3231

Abstract: This review underlines the importance of indoor contamination as a pathway of human exposure to hexabromocyclododecanes (HBCDs), polybrominated diphenyl ethers (PBDEs), and perfluoroalkyl compounds (PFCs). There is ample evidence of substantial contamination of indoor dust with these chemicals and that their concentrations in indoor air exceed substantially those outdoors. Studies examining the relationship between body burden and exposure via indoor dust are inconsistent; while some indicate a link between body burdens and PBDE and HBCD exposure via dust ingestion, others find no correlation. Likewise, while concentrations in indoor dust and human tissues are both highly skewed, this does not necessarily imply causality. Evidence suggests exposure via dust ingestion is higher for toddlers than adults. Research priorities include identifying means of reducing indoor concentrations and indoor monitoring methods that provide the most “biologically- relevant” measures of exposure as well as monitoring a wider range of microenvironment categories. Other gaps include studies to improve understanding of the following: emission rates and mechanisms via which these contaminants migrate from products into indoor air and dust; relationships between indoor exposures and human body burdens; relevant physicochemical properties; the gastrointestinal uptake by humans of these chemicals from indoor dust; and human dust ingestion rates.

Higgins, C.P., J.A. Field, C.S. Criddle, and R.G. Luthy. 2005. Quantitative Determination of Perfluorochemicals in Sediments and Domestic Sludge. *Environ. Sci. Technol.* 39:3946-3956

Abstract: Perfluorochemicals (PFCs) are the subject of increasingly intense environmental research. Despite their detection both in biota and in aqueous systems, little attention has been paid to the possible presence of this class of compounds in solid environmental matrixes. The limited available data indicate that some PFCs such as perfluorooctane sulfonate (PFOS) may strongly sorb to solids, and sewage sludge is widely suspected as a major sink of PFCs entering municipal waste streams. A quantitative analytical method was developed that consists of liquid solvent extraction of the analytes from sediments and sludge,

cleanup via solid-phase extraction, and injection of the extracts with internal standards into a high-performance liquid chromatography (HPLC) system coupled to a tandem mass spectrometer (LC/MS/MS). The limits of detections of the method were analyte and matrix dependent, but ranged from 0.7 to 2.2 ng/g and 0.041 to 0.246 ng/g (dry weight) for sludge and sediment, respectively. A demonstration of the method was performed by conducting a limited survey of domestic sludge and sediments. The concentration of PFCs in domestic sludge ranged from 5 to 152 ng/g for total perfluorocarboxylates and 55 to 3370 ng/g for total perfluoroalkyl sulfonyl-based chemicals. Data from a survey of San Francisco Bay Area sediments suggest widespread occurrence of PFCs in sediments at the low ng/g to sub-ng/g level. Furthermore, substances that may be transformed to PFOS, such as 2-(N ethylperfluorooctanesulfonamido) acetic acid (N-EtFOSAA) and 2-(N-methylperfluorooctanesulfonamido) acetic acid (N-MeFOSAA), are present in both sediments and sludge at levels often exceeding PFOS.

Higgins, Christopher P. 2014. Potential for perfluoroalkyl acid bioaccumulation in food crops. Colorado School of Mines presentation, Sept. 8, 2014. Accessed 9/26/16 at https://www.eiseverywhere.com/file_uploads/73e144b03e7f8593de17b6a3cce443c9_PFAAsHigginsForDistribution.pdf

Hundal, L. S.; K. Kumar; N. Basta; and A.E. Cox. 2011. Evaluating Exposure Risk To Trace Organic Chemicals In Biosolids. *BioCycle*: 52 (8), p. 31.

From this article: “Perfluorochemicals (PFCs), especially perfluorooctane sulfonates (PFOS) and perfluorooctanoic acid (PFOA), have been used in industrial and consumer products since the 1950s. PFOA is also used in the production of Teflon and Gore-Tex. PFCs can be released into the environment from the manufacture of fluorinated chemicals and losses from PFCs-treated PCCPs and eventually enter the wastewater stream. PFOA and PFOS were the most prominent PFCs detected in indoor air, house dust and biosolids (Table 2). They are also detected in low concentrations in the blood of wildlife and humans around the world. Both PFOA and PFOS have been shown to be toxic and persistent in the environment (Delinsky et al., 2010).

“Exposure of PFOA and PFOS to developing fetus and infants is of particular concern because they are found in breast milk and have the ability to cross the placenta barrier. Exposure to PFOS and PFOA may result from the intake of contaminated food, including fish and water. The most significant human exposure results from ingestion of indoor air and house dust because the largest volume of PFCs (>2.5 million pounds in 2000) is used for indoor applications. Use of PFCs in food contact wrappers and boxes represent another potential source of oral exposure. PFOA is present in microwave popcorn bag paper at amounts as high as 300 µg/kg. According to the U.S. Food and Drug Administration, microwavable popcorn bags alone could account for about 20 percent of the PFOA levels measured in an individual consuming 10 bags of popcorn a year (Renner, 2006).

“Ingestion of house dust and inhalation of indoor air are the major pathways for PFOS and PFOA exposure to toddlers and children because they spend greater than 90 percent of their time indoors, exhibit the highest hand-to-mouth frequency and may ingest 100 to 200 mg/day of dust. Land application of biosolids may release trace levels of PFCs into the agricultural soils but it doesn’t seem to be a major source of human exposure.”

Kato, K. L-Y Wong, L.T. Jia, Z. Kuklenyik, and A.M. Calafat. 2011. Trends in Exposure to Polyfluoroalkyl Chemicals in the U.S. Population: 1999-2008. *Environ. Sci. Technol.*

Abstract: Since 2002, practices in manufacturing polyfluoroalkyl chemicals (PFCs) in the United States have changed. Previous results from the National Health and Nutrition Examination Survey (NHANES) documented a significant decrease in serum concentrations of some PFCs during 1999- 2004. To further assess concentration trends of perfluorooctane sulfonate (PFOS), perfluorooctanoate (PFOA), perfluorohexane sulfonate (PFHxS), and perfluorononanoate (PFNA), we analyzed 7876 serum samples

collected from a representative sample of the general U.S. population ≥12 years of age during NHANES 1999-2008. We detected PFOS, PFOA, PFNA, and PFHxS in more than 95% of participants. Concentrations differed by sex regardless of age and we observed some differences by race/ethnicity. Since 1999-2000, PFOS concentrations showed a significant downward trend, because of discontinuing industrial production of PFOS, but PFNA concentrations showed a significant upward trend. PFOA concentrations during 1999-2000 were significantly higher than during any other time period examined, but PFOA concentrations have remained essentially unchanged during 2003-2008. PFHxS concentrations showed a downward trend from 1999 to 2006, but concentrations increased during 2007-2008. Additional research is needed to identify the environmental sources contributing to human exposure to PFCs. Nonetheless, these NHANES data suggest that sociodemographic factors may influence exposure and also provide unique information on temporal trends of exposure.

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New Hampshire Department of Health & Human Services. 2017. Preliminary Results of the PFC Blood Testing Program for the Pease Tradeport and Southern New Hampshire Communities. Division of Public Health Services.
<http://www.dhhs.nh.gov/dphs/pfcs/blood-testing.htm>

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Sepulvado, J. G., et al. 2011. Occurrence and Fate of Perfluorochemicals in Soil Following the Land Application of Municipal Biosolids. *Environmental Science & Technology*

Abstract: The recent implementation of soil and drinking water screening guidance values for two perfluorochemicals (PFCs), perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS) by the U.S. Environmental Protection Agency (EPA), reflects the growing concerns regarding the presence of these persistent and bioaccumulative chemicals in the natural environment. Previous work has established the potential risk to the environment from the land application of industrially contaminated biosolids, but studies focusing on environmental risk from land application of typical municipal biosolids are lacking. Thus, the present study investigated the occurrence and fate of PFCs from land-applied municipal biosolids by evaluating the levels, mass balance, desorption, and transport of PFCs in soils receiving application of municipal biosolids at various loading rates. This study is the first to report levels of PFCs in agricultural soils amended with typical municipal biosolids. PFOS was the dominant PFC in both biosolids (80 - 219 ng/g) and biosolids-amended soil (2 - 483 ng/g). Concentrations of all PFCs in soil increased linearly with increasing biosolids loading rate. These data were used to develop a model for predicting PFC soil concentrations in soils amended with typical municipal biosolids using cumulative biosolids loading rates. Mass balance calculations comparing PFCs applied vs those recovered in the surface soil interval indicated the potential transformation of PFC precursors. Laboratory desorption experiments indicated that the leaching potential of PFCs decreases with increasing chain length and that previously derived organic-carbon normalized partition coefficients may not be accurate predictors of the desorption of long-chain PFCs from biosolids-amended soils. Trace levels of PFCs were also detected in soil cores from biosolids-amended soils to depths of 120 cm, suggesting potential movement of these compounds within the soil profile over time and confirming the higher transport potential for short-chain PFCs in soils amended with municipal biosolids.

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Venkatesan, A. K. and R. U. Halden, 2013

Abstract: Using liquid chromatography tandem mass spectrometry, we determined the first nationwide inventories of 13 perfluoroalkyl substances (PFASs) in U.S. biosolids via analysis of samples collected by the U.S. Environmental Protection Agency in the 2001 National Sewage Sludge Survey. Perfluorooctane sulfonate [PFOS; 403 ± 127 ng/g dry weight (dw)] was the most abundant PFAS detected in biosolids composites representing 32 U.S. states and the District of Columbia, followed by perfluorooctanoate [PFOA; 34 ± 22 ng/g dw] and perfluorodecanoate [PFDA; 26 ± 20 ng/g dw]. Mean concentrations in U.S. biosolids of the remaining ten PFASs ranged between 2 and 21 ng/g dw. Interestingly, concentrations of PFOS determined here in biosolids collected prior to the phase-out period (2002) were similar to levels reported in the literature for recent years. The mean load of Σ PFASs in U.S. biosolids was estimated at 2749–3450 kg/year, of which about 1375–2070 kg is applied on agricultural land and 467–587 kg goes to landfills as an alternative disposal route. This study informs the risk assessment of PFASs by furnishing national inventories of PFASs occurrence and environmental release via biosolids application on land.

Venkatesan, A.K. and R. U. Halden. 2014. Loss and in situ production of perfluoroalkyl chemicals in outdoor biosolids-soil mesocosms. *Environ Res.* Jul; 132: 321–327. Accessed 9/23/16: <http://www.ncbi.nlm.nih.gov/pmc/articles/PMC4122524/>

Abstract: An outdoor mesocosm study was conducted in Baltimore, Maryland, to explore the fate of thirteen perfluoroalkyl substances (PFASs) over the course of three years in biosolids/soil mixtures (1:2) exposed to ambient outdoor conditions. Analysis by liquid chromatography tandem mass spectrometry showed perfluorooctanoate (PFOA) to be the most abundant analyte found early in the soil weathering experiment at 24.1 ng/g dry weight (dw), followed by perfluoroundecanoate (PFUnDA) and perfluorodecanoate (PFDA) at 18.4 and 17.4 ng/g dw, respectively. Short-chain perfluorinated carboxylates (PFCAs; C₄-C₈) showed observable loss from biosolids/soil mixtures, with experimentally determined first-order half-lives in soil ranging from 385 to 866 days. Perfluorooctane sulfonate (PFOS), perfluorononanoate (PFNA) and PFUnDA levels in biosolids/soil mixtures remained stable, while other long-chain PFCAs [PFDA, perfluorododecanoate (PFDoDA)] and perfluorooctane sulfonamide (PFOSA) levels increased over time, presumably due to the breakdown of unidentified precursors in a process analogous to that reported previously for wastewater treatment plants. This study informs risk assessment initiatives by furnishing data on the environmental persistence of PFASs while also constituting the first report on *in situ* production of long-chained PFASs in terrestrial environments.

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Vermont Department of Health. 2016. PFOA Exposure & Health Studies. Fact sheet. March 16, 2016. See also: <http://www.c8sciencepanel.org/>.

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Xiao, F.; M. Simcik; T. R. Halbach; and J. S. Gulliver. 2014. Perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in soils and groundwater of a U.S. metropolitan area: Migration and implications for human exposure. *Water Research*, 72:

Abstract: Perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) are emerging anthropogenic compounds that have recently become the target of global concern due to their ubiquitous presence in the environment, persistence, and bioaccumulative properties. This study was carried out to investigate the migration of PFOS and PFOA in soils and groundwater in a U.S. metropolitan area. We observed elevated

levels in surface soils (median: 12.2 ng PFOS/g dw and 8.0 ng PFOA/g dw), which were much higher than the soil-screening levels for groundwater protection developed in this study. The measured levels in subsurface soils show a general increase with depth, suggesting a downward movement toward the groundwater table and a potential risk of aquifer contamination. Furthermore, concentrations of PFOS and PFOA in monitoring wells in the source zone varied insignificantly over 5 years (2009-2013), suggesting limited or no change in either the source or the magnitude of the source. The analysis also shows that natural processes of dispersion and dilution can significantly attenuate the groundwater contamination; the adsorption on aquifer solids, on the other hand, appears to have limited effects on the transport of PFOS and PFOA in the aquifer. The probabilistic exposure assessment indicates that ingestion of contaminated groundwater constitutes a much more important exposure route than ingestion of contaminated soil. Overall, the results suggest that (i) the transport of PFOS and PFOA is retarded in the vadose zone, but not in the aquifer; (ii) the groundwater contamination of PFOS and PFOA often follows their release to surface soils by years, if not decades; and (iii) the aquifer can be a major source of exposure for communities living near point sources.