

**NEBRA Literature Review:**

**PFAS & Wastewater Residuals** v. 2.0

June 2018, November 2019



**Appendix A**

**Compendium of Abstracts and Notes**

**Introduction**

In researching and preparing the NEBRA PFAS Literature Review, numerous scientific journals and other technical documents were reviewed. Below are the abstracts and notes from all the sources that were reviewed to produce the Literature Review.

The Table of Contents lists each document by title. Holding the “Ctrl” key and clicking on the title will link to that abstract and any accompanying notes.

Table of Contents

[1. PFAS Chemistry and General Information 5](#_Toc26954699)

[1.1 Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins 5](#_Toc26954700)

[1.2 A Never-Ending Story of Per- and Polyfluoroalkyl Substances (PFASs)? 8](#_Toc26954701)

[1.3 Ambient levels of PFOS and PFOA in multiple environmental media 9](#_Toc26954702)

[1.4 A North American and global survey of perfluoroalkyl substances in surface soils: Distribution patterns and mode of occurrence 10](#_Toc26954703)

[1.5 Perfluoroalkyl Acid Characterization in U.S. Municipal Organic Solid Waste Composts 10](#_Toc26954704)

[1.6 Perfluoroalkyl and polyfluoroalkyl substances in consumer products 11](#_Toc26954705)

[1.7 ANALYSIS OF PFASs AND TOF IN PRODUCTS 11](#_Toc26954706)

[1.9 Quantitative determination of perfluoroalkyl substances (PFAS) in soil, water, and home garden produce 13](#_Toc26954707)

[1.10 Pathways of PFOA to the Arctic: variabilities and contributions of oceanic currents and atmospheric transport and chemistry sources 13](#_Toc26954708)

[1.11 Synthesis Paper on Per- and Polyfluorinated Chemical (PFCs) 14](#_Toc26954709)

[1.12 Recently Detected Drinking Water Contaminants: GenX and Other Per- and Polyfluoroalkyl Ether Acids 15](#_Toc26954710)

[1.13 The PFOA substitute GenX detected in the environment near a fluoropolymer manufacturing plant in the Netherlands 15](#_Toc26954711)

[2. PFAS and Wastewater Treatment 16](#_Toc26954712)

[2.1 Review of ‘emerging’ organic contaminants in biosolids and assessment of international research priorities for the agricultural use of biosolids 16](#_Toc26954713)

[2.2 Fate of Pharmaceuticals and Perfluoroalkyl Substance During Source Separated Wastewater Treatment 18](#_Toc26954714)

[2.3 A review of the fate of micropollutants in wastewater treatment plants 19](#_Toc26954715)

[2.4 National inventory of perfluoroalkyl substances in archived U.S. biosolids from the 2001 EPA National Sewage Sludge Survey 20](#_Toc26954716)

[2.5 Sorption of Perfluorinated Compounds onto different types of sewage sludge and assessment of its importance during wastewater treatment 21](#_Toc26954717)

[2.6 Sorption of Perfluorinated Compounds onto different types of sewage sludge and assessment of its importance during wastewater treatment 21](#_Toc26954718)

[2.7 Influence of cations on the partition behavior of perfluoroheptanoate (PFHpA) and perfluorohexanesulfonate (PFHxS) on wastewater sludge 22](#_Toc26954719)

[2.8 An investigation into per- and polyfluoroalkyl substances (PFAS) in nineteen Australian wastewater treatment plants (WWTPs) 22](#_Toc26954720)

[2.9 Physical and Biological Release of Poly- and Perfluoroalkyl Substances (PFASs) from Municipal Solid Waste in Anaerobic Model Landfill Reactors 23](#_Toc26954721)

[2.10 Role of wastewater treatment plant in environmental cycling of poly- and perfluoroalkyl substances 23](#_Toc26954722)

[3. Fate & Transport 24](#_Toc26954723)

[3.1 Perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in soils and groundwater of a U.S. metropolitan area: Migration and implications for human exposure 25](#_Toc26954724)

[3.2 Transport of Perfluorochemicals to Surface and Subsurface Soils 25](#_Toc26954725)

[3.3 Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) in surface waters, sediments, soils and wastewater – A review on concentrations and distribution coefficients 26](#_Toc26954726)

[3.4 Geochemical and Hydrologic Factors Controlling Subsurface Transport of Poly- and Perfluoroalkyl Substances, Cape Cod, Massachusetts 27](#_Toc26954727)

[3.5 Application of WWTP Biosolids and Resulting Perfluorinated Compound Contamination of Surface and Well Water in Decatur, Alabama, USA 27](#_Toc26954728)

[3.6Results of the Analyses of Screening Surface and Well Water Samples from Decatur, Alabama for Selected Perfluorinated Compounds 29](#_Toc26954729)

[3.7 Results of the Analyses of Surface Soil Samples from Near Decatur, Alabama for Fluorinated Organic Compounds 29](#_Toc26954730)

[3.8 Brominated flame retardants and perfluoroalkyl acids in groundwater, tile drainage, soil, and crop grain following a high application of municipal biosolids to a field 30](#_Toc26954731)

[3.9 Subsurface Fate and Transport of Poly- and Perfluoroalkyl 32](#_Toc26954732)

[3.10 Occurrence and Fate of Perfluorochemicals in Soil Following the Land Application of Municipal Biosolids 33](#_Toc26954733)

[3.11 Sources, Fate and Transport of Perfluorocarboxylates 34](#_Toc26954734)

[3.12 Septic systems as sources of organic wastewater compounds in domestic drinking water wells in a shallow sand and gravel aquifer 36](#_Toc26954735)

[3.13 Toxicological relevance of emerging contaminants for drinking water quality 37](#_Toc26954736)

[3.14 Loss and in situ production of perfluoroalkyl chemicals in outdoor biosolids-soil mesocosms 37](#_Toc26954737)

[3.15 6:2 Fluorotelomer alcohol (6:2 FTOH) biodegradation by multiple microbial species under different physiological conditions 37](#_Toc26954738)

[3.16 Desorptive Behavior of Perfluoroalkyl Acids and Perfluoroalkyl Acids Precursors from Aqueous Film-Forming Foaming Impacted Soils and Aquifer 38](#_Toc26954739)

[3.17 Effect of organic carbon, active carbon, calcium ions and aging on the sorption of per- and polyfluoroalkylated substances (PFASs) to soil. 39](#_Toc26954740)

[3.18 Adsorption of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) on alumina: Influence of solution pH and cations 39](#_Toc26954741)

[3.19 Sorption of Perfluoroalkyl and Polyfluoroalkyl Substances (PFASs) by Natural and Anthropogenic Carbonaceous Sorbents 40](#_Toc26954742)

[3.20 Influence of Solution Chemistry on Adsorption of Perfluorooctanesulfonate (PFOS) and Perfluorooctanoate (PFOA) on Boehmite 41](#_Toc26954743)

[3.21 Adsorption behavior of perfluorochemicals (PFCs) on boehmite: influence of solution chemistry 41](#_Toc26954744)

[3.22 Assessment of POP Criteria for Specific Short-Chain Perfluorinated Alkyl Substances 42](#_Toc26954745)

[3.23 Side-chain fluorinated polymer surfactants in aquatic sediment and biosolid-augmented agricultural soil from the Great Lakes basin of North America 42](#_Toc26954746)

[3.24 Experimental and molecular dynamic simulation study of perfluorooctane sulfonate adsorption on soil and sediment components 43](#_Toc26954747)

[3.25 Defluorination of Perfluorooctanoic Acid (PFOA) and Perfluorooctane Sulfonate (PFOS) by Acidimicrobium sp. Strain A6 43](#_Toc26954748)

[3.26 Microbial degradation of polyfluoroalkyl chemicals in the environment: A review 44](#_Toc26954749)

[3.27 Investigation of Levels of Perfluorinated Compounds in New Jersey Fish, Surface Water, and Sediment 45](#_Toc26954750)

[3.28 Removal of Perfluorinated Compounds from Water with Activated Carbon and Redox Treatments 46](#_Toc26954751)

[3.29 Sorption of Poly- and Perfluoroalkyl Substances (PFASs) Relevant to Aqueous Film-Forming Foam (AFFF)-Impacted Groundwater by Biochars and Activated Carbon 46](#_Toc26954752)

[3.30 Stabilization and solidification remediation of soil contaminated with poly- and perfluoroalkyl substances (PFAS) 47](#_Toc26954753)

[3.31 Distribution of Perfluorinated Compounds in Lake Taihu (China): Impact to Human Health and Water Standards 47](#_Toc26954754)

[3.33 PFC-Contaminated Soil and Its Remediation Strategies: A Review 48](#_Toc26954755)

[3.34 Per- and polyfluoroalkyl substances in source and treated drinking waters of the United States 48](#_Toc26954756)

[3.35 Fate and Effects of Poly- and Perfluoroalkyl Substances in the Aquatic Environment: A Review 49](#_Toc26954757)

[3.36 Half-lives of PFOS, PFHxS and PFOA after end of exposure to contaminated drinking water 50](#_Toc26954758)

[3.37 Perfluorinated Chemicals in Surface Waters and Sediments from Northwest Georgia, USA, and Their Bioaccumulation in *Lumbriculus variegatus* 50](#_Toc26954759)

[3.38 Per- and Polyfluoroalkyl Substances in Landfill Leachate: Patterns, Time Trends, and Sources 51](#_Toc26954760)

[4. Plant/Animal Uptake 51](#_Toc26954761)

[4.1 Absorption and Excretion of 14C-Perfluorooctanoic Acid (PFOA) in Angus Cattle (Bos taurus) 52](#_Toc26954762)

[4.2 Absorption, Distribution, and Milk Secretion of the Perfluoroalkyl Acids PFBS, PFHxS, PFOS, and PFOA by Dairy Cows Fed Naturally Contaminated Feed 52](#_Toc26954763)

[4.3 Biochemical Responses and Accumulation Properties of Long-Chain Perfluorinated Compounds (PFOS/PFDA/PFOA) in Juvenile Chickens (Gallus gallus) 53](#_Toc26954764)

[4.4 Comparative tissue and body compartment accumulation and maternal transfer to eggs of perfluoroalkyl sulfonates and carboxylates in Great Lakes herring gulls 53](#_Toc26954765)

[4.5 Depuration kinetics and tissue disposition of PFOA and PFOS in white leghorn chickens (Gallus gallus) administered by subcutaneous implantation 54](#_Toc26954766)

[4.6 Transfer of Perfluorooctanoic Acid (PFOA) and Perfluorooctane Sulfonate (PFOS) From Contaminated Feed Into Milk and Meat of Sheep: Pilot Study 54](#_Toc26954767)

[4.7 Analysis of PFOS, FOSA and PFOA From Various Food Matrices Using HPLC Electrospray Mass Spectrometry 55](#_Toc26954768)

[4.8 Perfluorinated alkylated substances in vegetables collected in four European countries; occurrence and human exposure estimations 55](#_Toc26954769)

[4.9 Perfluorinated Compounds in Greenhouse and Open Agricultural Producing Areas of Three Provinces of China: Levels, Sources and Risk Assessment 56](#_Toc26954770)

[4.10 Carryover of Perfluorooctanoic Acid (PFOA) and Perfluorooctane Sulfonate (PFOS) from Soil to Plants 56](#_Toc26954771)

[4.11 Perfluoroalkyl acid distribution in various plant compartments of edible crops grown in biosolids-amended soils 57](#_Toc26954772)

[4.12 Perfluoroalkyl Acid Uptake in Lettuce (Lactuca sativa) and Strawberry (Fragaria ananassa) Irrigated with Reclaimed Water 57](#_Toc26954773)

[4.13 Uptake of Perfluoroalkyl Acids into Edible Crops via Land Applied Biosolids: Field and Greenhouse Studies 58](#_Toc26954774)

[4.14 The roles of protein and lipid in the accumulation and distribution of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in plants grown in biosolids-amended soils 59](#_Toc26954775)

[4.15 State of the science and meta-analysis of crop uptake of per- and polyfluoroalkyl substances (PFAS) 59](#_Toc26954776)

[4.16 How Reliable Are Field-Derived Biomagnification Factors and Trophic Magnification Factors as Indicators of Bioaccumulation Potential? Conclusions from a Case Study on Per- and Polyfluoroalkyl Substances 60](#_Toc26954777)

[4.17 Uptake of per- and polyfluoroalkyl substances by plants 61](#_Toc26954778)

[4.18 Multiple crop bioaccumulation and human exposure of perfluoroalkyl substances around a mega fluorochemical industrial park, China: Implication for planting optimization and food safety 62](#_Toc26954779)

[4.19 Accumulation of perfluorinated alkyl substances (PFAS) in agricultural plants: A review 63](#_Toc26954780)

[4.20 Uptake of perfluoroalkyl substances and halogenated flame retardants by crops grown in biosolids-amended soils 65](#_Toc26954781)

1. **PFAS Chemistry and General Information**

## **1.1 Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins**

Robert C. Buck, James Franklin, Urs Berger, Jason M Conder, Ian T Cousins, Pim de Voogt, Allan Astrup Jensen, Kurunthachalam Kannan, Scott A. Mabury, and Stefan PJ van Leeuwen, 2011

**Abstract**

The primary aim of this article is to provide an overview of perfluoroalkyl and polyfluoroalkyl substances (PFASs) detected in the environment, wildlife, and humans, and recommend clear, specific, and descriptive terminology, names, and acronyms for PFASs. The overarching objective is to unify and harmonize communication on PFASs by offering terminology for use by the global scientific, regulatory, and industrial communities. A particular emphasis is placed on long-chain perfluoroalkyl acids, substances related to the long-chain perfluoroalkyl acids, and substances intended as alternatives to the use of the long-chain perfluoroalkyl acids or their precursors. First, we define PFASs, classify them into various families, and recommend a pragmatic set of common names and acronyms for both the families and their individual members. Terminology related to fluorinated polymers is an important aspect of our classification. Second, we provide a brief description of the 2 main production processes, electrochemical fluorination and telomerization, used for introducing perfluoroalkyl moieties into organic compounds, and we specify the types of byproducts (isomers and homologues) likely to arise in these processes. Third, we show how the principal families of PFASs are interrelated as industrial, environmental, or metabolic precursors or transformation products of one another. We pay particular attention to those PFASs that have the potential to be converted, by abiotic or biotic environmental

processes or by human metabolism, into long-chain perfluoroalkyl carboxylic or sulfonic acids, which are currently the focus of regulatory action. The Supplemental Data lists 42 families and subfamilies of PFASs and 268 selected individual compounds, providing recommended names and acronyms, and structural formulas, as well as Chemical Abstracts Service registry numbers.

**Notes**

* “The global regulatory community is specifically interested in ‘‘long-chain’’ perfluoroalkyl sulfonic acids (CnF2n+1SO3H, n> or =6, PFSAs) and perfluoroalkyl carboxylic acids (CnF2n+1COOH, n> or =7, PFCAs) and their corresponding anions (USEPA 2009; OECD 2011), which have been shown to be more bioaccumulative than their short-chain analogues (Martin et al. 2003a, 2003b; Conder et al. 2008; Olsen et al. 2009). PFOS and PFOA are the 2 ‘‘long-chain’’ perfluoroalkyl acids most often reported and discussed in the scientific literature.”
* “To avoid any subjectivity associated with these adjectives, we urge scientists to adopt the definition provided by the Organisation for Economic Co-operation and Development (OECD 2011), which stipulates that ‘‘long-chain’’ refers to:

- perfluoroalkyl carboxylic acids with eight carbons and greater (i.e., with 7 or more perfluorinated carbons) and,

- perfluoroalkane sulfonates with six carbons and greater (i.e., with 6 or more perfluorinated carbons).”

* “The telomerization process produces primarily or exclusively linear PFASs, whereas the electrochemical fluorination process produces a mixture of branched and linear isomers.
* Many PFASs are acids and may be present as protonated oranionic forms, or a mixture of both, depending on the pH of the environmental matrix and the compound’s acid dissociation constant (pKa). The pKa values for many of the PFASs (e.g., PFOA) are under review or are unknown, and for simplicity, we will refer to all PFASs with an acid functionality as ‘‘acids,’’ rather than as carboxylates, sulfonates, and so forth, although recognizing that the dissociated forms may well predominate in environmental and human matrices.”
* “Electrochemical fluorination (ECF) is a technology in which an organic raw material (e.g., octane sulfonyl fluoride [OSF], C8H17SO2F) undergoes electrolysis in anhydrous HF, leading to the replacement of all the H atoms by F atoms (Alsmeyer et al. 1994). The free-radical nature of the process leads to C chain rearrangement and breakage, resulting in a mixture of linear and branched perfluorinated isomers and homologues of the raw material, as well as PFCs and other species (Alsmeyer et al. 1994). The ratio of linear to branched perfluorinated C chains formed in the ECF process varies depending on how the process is controlled but is roughly 70% to 80% linear and 20% to 30% branched in the case of the synthesis of PFOS and PFOA.”
* “When a linear telogen and taxogen are employed in the telomerization process, the resulting perfluoroalkyl iodides have exclusively linear perfluoroalkyl chains. If a branched and/or odd C number telogen, e.g., (CF3)2CFI, is employed and reacted with TFE, the resulting product mixture will be branched and/or will contain an odd number of C atoms, despite the incorporation of an even number of taxogen -CF2- units from the TFE.”
* “PFAAs will dissociate to a greater or lesser extent to their anions in aqueous environmental media, soils, or sediments. The protonated and anionic forms have very different physicochemical properties. For instance, the perfluorooctanoate anion is highly water-soluble and has negligible vapor pressure, whereas perfluorooctanoic acid has very low water solubility and sufficient vapor pressure to partition out of water into air (Kaiser et al. 2005; Kaiser et al. 2006; Webster and Ellis 2010; Webster et al. 2010). However, for perfluoroalkyl carboxylic acids, there is an ongoing debate regarding what is the environmentally relevant pKa, with measured and estimated values varying by several log units for PFOA (Burns et al. 2008; Goss 2008; Cheng et al. 2009; Rayne and Forest 2010a).”
* “In addition to their major commercial use as fluoropolymer processing aids and numerous industrial and consumer applications (Kissa 2001; Prevedouros et al. 2006), PFCAs are also the terminal degradation products from abiotic and biotic degradation of certain precursor PFASs. Such precursors include fluorotelomer alcohols (Hagen et al. 1981; Dinglasan et al. 2004; Ellis et al. 2004; Hurley et al. 2004; Wang et al. 2009; Liu et al. 2010), fluorotelomer acrylates (Butt et al. 2009; Butt et al. 2010b), fluorotelomer iodides (Young et al. 2008), fluorotelomer olefins (Nakayama et al. 2007), N-alkyl perfluoroalkane sulfonamides (Tomy, Tittlemier, et al. 2004; Martin et al. 2006; Plumlee et al. 2009), N-alkyl perfluoroalkane sulfonamidoethanols (D’eon et al. 2006; Plumlee et al. 2009), and polyfluoroalkyl phosphates (D’eon and Mabury 2007; Lee et al. 2010).
* “PFCA yields and rates of formation vary depending on the precursor substance and degradation conditions.”
* “Interestingly, coincident with these changes *(reduced production and use of PFOA)*, there have been reports showing significantly increased levels of perfluorobutanoic acid (PFBA) in water (Moeller et al. 2010) and air (Weinberg et al. 2011b) that are most likely associated with the conversion to shorter chain perfluoroalkyl products.”
* “However, the environmental and toxicological significance of PFOS, ubiquitous in the global environment, also results from its presence as an impurity in and formation from perfluorooctane sulfonamido precursor substances (3M Company 1999, 2000a; Lange 2000, 2001; Xu et al. 2004; Boulanger et al. 2005; D’eon et al. 2006; Rhoads et al. 2008; Xie et al. 2009) used in vastly greater quantities (Brooke et al. 2004; Paul et al. 2009).”
* “Shorter perfluoroalkyl chain length products, notably perfluorobutane sulfonyl–based products, have been introduced as alternatives to the previously used compounds with 6 or more perfluorinated carbons, because these shorter chain length substances do not bioaccumulate due to their rapid elimination in multiple organisms tested (Olsen et al. 2009). This substitution is a consequence of the voluntary phase-out and/or subsequent regulatory restriction of PFOS-related substances and certain homologues with 5 to 7 and 9 or 10 perfluorinated C atoms (3M Company 2000b; Federal Register 2006b). Coincident with these changes, reports have shown significantly increased levels of perfluorobutane sulfonic acid (PFBS) in environmental waters, no doubt as a consequence of the conversion to 4-C ECF-derived perfluorobutanesulfonyl products (Eschauzier et al. 2010; Moeller et al.”
* “As reviewed below, the degradation of fluorotelomer-based products is a potential source of PFCAs in the environment.” (pg. 526)
* “One specific use of polyfluoroalkyl phosphoric acid monoesters (monoPAPs) and diPAPs that has led to their widespread presence in the environment is as an approved defoaming adjuvant in pesticide formulations. Approval for this use has now been rescinded (Federal Register 2006a). Recently, diPAPs have been reported detected in human serum at concentrations in some cases comparable to those of PFOA and in WWTP sludge at much greater levels than PFOA (D’eon et al. 2009a; Lee and Mabury 2011).” (pg. 526)
* “Published studies on the aerobic biotransformation of the perfluoroalkane sulfonamido derivatives focus on those compounds having 8 perfluorinated C atoms, in particular N-ethyl perfluorooctane sulfonamidoethanol (EtFOSE), which is ultimately degraded to PFOS.” (pg. 530)
* “Various perfluoroalkyl sulfonamido derivatives have been found in the environment and human samples, whether this is due to industrial or consumer use of these compounds as such, losses during manufacturing operations, presence as ‘‘residuals’’ in other commercial products, or formation as environmental degradation products or metabolites of precursors.” (pg. 531)
* “All the families of perfluoroalkane sulfonamido derivatives discussed above and depicted in Tables 2 and 3 have been found in the environment or in human biota. Those with 8 perfluorinated C atoms are, in general, much more abundant than those with other chain lengths. However, more recently, compounds with 4 such C atoms have also been reported. The medium in which they are detected depends on their physical properties and on their likelihood of being formed there from precursors.” (pg. 531)

## **1.2 A Never-Ending Story of Per- and Polyfluoroalkyl Substances (PFASs)?**

Zhanyun Wang, Jamie C. DeWitt, Christopher P. Higgins, and Ian T. Cousins, 2017

**Abstract**

More than 3000 per- and polyfluoroalkyl substances (PFASs) are, or have been, on the global market, yet most research and regulation continues to focus on a limited selection of rather well-known long-chain PFASs, particularly perfluorooctanesulfonate (PFOS), perfluorooctanoic acid (PFOA) and their precursors. Continuing to overlook the vast majority of other PFASs is a major concern for society. We provide recommendations for how to proceed with research and cooperation to tackle the vast number of PFASs on the market and in the environment.

**Notes**

* “Per- and polyfluoroalkyl substances (PFASs, CnF2n+1−R) refer to a family of chemicals that have been produced since the late 1940s. Due to the strong electronegativity and small atomic size of fluorine, the perfluoroalkyl moiety (CnF2n+1−) imparts enhanced properties to molecules (e.g., stronger acidity, higher surface activity at very low concentrations, stability, and/or water- and oil-repellency) compared to their hydrocarbon counterparts.” (pg. 2508)
* “For example, Place and Field (2012)5 identified 10 subclasses of PFASs in multiple aqueous film forming foam (AFFF) formulations; however, with limited communication between the public and the manufacturers producing PFASs, it is not immediately clear as to whether these PFASs are intended ingredients, residual intermediates, byproducts formed during production, or degradation products.” (pg. 2508)
* “The perfluoroalkyl (CnF2n+1−) and perfluoroether (CnF2n+1−O−CmF2m+1−) moieties are highly persistent under natural conditions.8,18 Even though some PFASs may partially degrade in the environment and biota, they will all ultimately transform into highly stable end products, which are usually the highly persistent perfluoroalkyl or perfluoroalkyl(poly)ether acids (here collectively termed “PFAAs”), for example, PFCAs, PFSAs, PFECAs, and PFESAs.7−9,18 Thus, when assessing and managing PFAAs, all their precursors (which can be challenging to identify7,9) need to be considered as relevant sources and managed as well.” (pg. 2511)
* “The very high persistence of PFAAs leads to poorly reversible exposure to these substances in the global environment and some local/regional environments including groundwater.25 Past and ongoing production and use will lead to the accumulation of PFAAs in the global environment, with very slow mixing/sedimentation to the deep oceans and sedimentation/burial in deep sediments as the only known global environmental sinks (as reviewed in Prevedouros et al. (2006)19).” (pg. 2511)
* “Despite variable kinetics and levels of toxicity in biota, a hallmark response of PFAA exposure is hepatotoxicity. 8,9,27−29 “(pg. 2511*) Our current understanding of PFAS toxicology is incomplete and we currently don’t have the adequate methods for evaluating potential affects across species and life stages.*
* *There are a large number of PFAS compounds many of which are unknown. To identify these unknowns will require “specialized experts” using complex methods and instruments in a resource and time intensive effort.* (pg. 2512)
* *Lack of information on use, product composition, transformations, and decomposition make it difficult to assess ongoing exposure to humans and the environment.* (pg. 2512)
* *Mixture toxicity is generally not considered or understood.* (pg. 2512)
* *Assessing exposure at a site where PFASs have been introduced is difficult because the amount and types of PFAS may not be known and be altered by transformation and transport over time (pg. 2512)*
* *Current treatment technologies are energy intensive and costly. (pg. 2513)*
* *Regarding research recommendations:* “For example, knowledge gained from pharmaceutical research may help to better understand the protein binding and toxicokinetics of some PFASs, and knowledge gained from surfactant research may help to better understand the potential sorption, transport (e.g., on marine aerosols) and bioaccumulation behavior of those PFASs that are fluorosurfactants.”

## **1.3 Ambient levels of PFOS and PFOA in multiple environmental media**

Usha K. Vedagiri, Richard H. Anderson, Heather M. Loso, and Catherine M. Schwach, 2018

**Abstract**

Making remediation and risk management decisions for widely-distributed chemicals is a challenging aspect of contaminated site management. The objective of this study is to present an initial

evaluation of the ubiquitous, ambient environmental distribution of poly- and perfluoroalkyl substances (PFAS) within the context of environmental decision-making at contaminated sites. PFAS are anthropogenic contaminants of emerging concern with a wide variety of consumer and industrial sources and uses that result in multiple exposure routes for humans. The combination of widespread prevalence and low screening levels introduces considerable uncertainty and potential costs in the environmental management of PFAS.

PFAS are not naturally-occurring, but are frequently detected in environmental media independent of site-specific (i.e., point source) contamination. Information was collected on background and ambient levels of two predominant PFAS, perfluorooctane sulfonate and perfluorooctanoate, in North America in both abiotic media (soil, sediment, surface water, and public drinking water supplies) and selected biotic media (human tissues, fish, and shellfish). The background or ambient information was compiled from multiple published sources, organized by medium and concentration ranges, and evaluated for geographical trends and, when available, also compared to health-based screening levels. Data coverage and quality varied from wide-ranging and well-documented for soil, surface water, and serum data to more localized and less well-documented for sediment and fish and shellfish tissues and some uncertainties in the data were noted. Widespread ambient soil and sediment concentrations were noted but were well below human health-protective thresholds for direct contact exposures. Surface water, drinking water supply waters (representing a combination of groundwater and surface water), fish and shellfish tissue, and human serum levels ranged from less than to greater than available health-based threshold values. This evaluation highlights the need for incorporating literature-based or site-specific background into PFAS site evaluation and decision-making, so that source identification, risk management, and remediation goals are properly focused and to also inform general policy development for PFAS management.

## **1.4 A North American and global survey of perfluoroalkyl substances in surface soils: Distribution patterns and mode of occurrence**

Keegan Rankin, Scott A. Mabury, Thomas M. Jenkins, and John W. Washington, 2016

**Abstract**

The distribution of 32 per/polyfluoroalkyl substances (PFASs) in surface soils was determined at 62 locations representing all continents (North America n ¼ 33, Europe n ¼ 10, Asia n ¼ 6, Africa n ¼ 5,

Australia n ¼ 4, South America n ¼ 3 and Antarctica n ¼ 1) using ultra performance liquid chromatography tandem mass spectrometry (UPLC-MS/MS) systems. Quantifiable levels of perfluoroalkyl carboxylates (PFCAs: PFHxA-PFTeDA) were observed in all samples with total concentrations ranging from 29 to 14,300 pg/g (dry weight), while perfluoroalkane sulfonates (PFSAs: PFHxS, PFOS and PFDS) were detected in all samples but one, ranging from <LOQ-3270 pg/g, confirming the global distribution of PFASs in terrestrial settings. The geometric mean PFCA and PFSA concentrations were observed to be higher in the northern hemisphere (930 and 170 pg/g) compared to the southern hemisphere (190 and 33 pg/g). Perfluorooctanoate (PFOA) and perfluorooctanesulfonate (PFOS) were the most commonly detected analytes at concentrations up to 2670 and 3100 pg/g, respectively. The sum of PFCA homologues of PFOA commonly were roughly twice the concentration of PFOA. The PFCA and PFSA congener profiles were similar amongst most locations, with a few principal-component statistical anomalies suggesting impact from nearby urban and point sources. The ratio of even to odd PFCAs was consistent with the atmospheric oxidation of fluorotelomer-based precursors previously observed in laboratory and environmental studies. Given the soils were collected from locations absent of direct human activity, these results suggest that the atmospheric long-range transport (LRT) of neutral PFASs followed by oxidation and deposition are a significant source of PFCAs and PFSAs to soils.

## **1.5 Perfluoroalkyl Acid Characterization in U.S. Municipal Organic Solid Waste Composts**

Youn Jeong Choi, Rooney Kim Lazcano, Peyman Yousefi, Heather Trim, and Linda S. Lee, 2019

**Abstract**

Composting the organic fraction of municipal solid waste (OFMSW) creates a nutrient rich soil amendment and reduces the amounts of wastes going to landfills or incineration. However, the occurrence and fate of persistent and challenging per- and polyfluoroalkyl substances (PFAS) in OFMSW composts have not been well studied. The loads and leachability of 17 perfluoroalkyl acids (PFAAs) were analyzed in nine OFMSW commercial composts and one backyard compost. PFAA loads ranged from 28.7 to 75.9 μg/kg for OFMSW composts that included food packaging and from 2.38 to 7.60 μg/kg for composts that did not include food packaging. Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate (PFOS) were detected in all composts; however, OFMSW composts were dominated by short-chain PFAAs (>64%) and perfluoroalkyl carboxylates (PFCAs, >68%), particularly the C6 PFCA. The total oxidizable precursor assay indicated the presence of PFAS precursors in three OFMSW composts for which 6:2 fluorotelomer sulfonate and 6:2 dipolyfluoroalkyl phosphate ester were identified. Of the total PFAA load in the composts, 25−49% was released to porewater (∼1 g/2 mL). PFAA porewater concentrations versus PFAA loads as well as organic carbon-normalized sorption coefficients versus the number of PFAA CF2 units are strongly correlated (R2 > 0.85).

## **1.6 Perfluoroalkyl and polyfluoroalkyl substances in consumer products**

Matthias Kotthoff, Josef Müller, Heinrich Jürling, Martin Schlummer, and Dominik Fiedler, 2015

**Abstract**

Perfluoroalkyl and polyfluoroalkyl substances (PFAS) are used in a wide range of products of all day life.

Due to their toxicological potential, an emerging focus is directed towards their exposure to humans. This study investigated the PFAS load of consumer products in a broad perspective. Perfluoroalkyl sulfonic acids (C4, C6–C8, C10-PFSA), carboxylic acids (C4–C14-PFCA) and fluorotelomer alcohols (4:2, 6:2; 8:2 and 10:2 FTOH) were analysed in 115 random samples of consumer products including textiles (outdoor materials), carpets, cleaning and impregnating agents, leather samples, baking and sandwich papers, paper baking forms and ski waxes. PFCA and PFSA were analysed by HPLC-MS/MS, whereas FTOH were detected by GC/CI-MS. Consumer products such as cleaning agents or some baking and sandwich papers show low or negligible PFSA and PFCA contents. On the other hand, high PFAS levels were identified in ski waxes (up to about 2000 μg/kg PFOA), leather samples (up to about 200 μg/kg PFBA and 120 μg/kg PFBS), outdoor textiles (up to 19 μg/m2 PFOA) and some other baking papers (up to 15 μg/m2 PFOA). Moreover, some test samples like carpet and leather samples and outdoor materials exceeded the EU regulatory threshold value for PFOS (1 μg/m2). A diverse mixture of PFASs can be found in consumer products for all fields of daily use in varying concentrations. This study proves the importance of screening and monitoring of consumer products for PFAS loads and the necessity for an action to regulate the use of PFASs, especially PFOA, in consumer products.

## **1.7 ANALYSIS OF PFASs AND TOF IN PRODUCTS**

Daniel Borg and Jenny Ivarsson, 2017

**Summary**

Per- and polyfluorinated substances (PFASs) make up a large group of man-made highly fluorinated substances that have been used in industrial and consumer applications for more than six decades. For the last twenty years PFASs have received increasing attention from scientists and regulators following their detection in wildlife and humans globally. It is today recognized that some PFASs are extremely persistent, bioaccumulative and toxic. There are thousands of PFASs on the global market and for many of these there is little information publicly available regarding their potential to affect human health and the environment.

This study is a follow-up of a NORAP (Nordic Risk Assessment Project) project from 2015 where 29 samples of different household products were analysed for 22 PFASs. The result of that study showed that all 29 products contained PFASs and that 12 of the 22 PFASs that were analysed for were detected. Here we have further analysed the products from the study in 2015 together with additional analysis of product types known to contain PFASs or suspected to contain PFASs. Since the targeted PFASs analysis of individual PFAS likely will not display the total PFASs-content of the products, we have analysed them for their total organic fluorine (TOF) content. The results of the TOF-analyses can be used to demonstrate to what extent the PFASs in the targeted analyses comprise the total organic fluorine content and thus provide an estimate of our knowledge about the use of PFASs in the products.

In total 17 new product samples collected in 2016 were in this project analysed for 19 individual PFASs as well as TOF. In addition, 27 samples from the 2015-project were re-analysed for TOF and eight textile samples collected in 2015 for a monitoring project by the Swedish Chemicals Agency were analysed for 22 individual PFASs as well as TOF.

The result of the targeted PFAS analyses of products collected in 2016 showed that PFASs is widely used in these products. PFASs were detected in 16 of the 17 products. All of these contained perfluorooctanoic acid (PFOA) which was the most frequently detected PFAS. Perfluorinated carboxylic acids (PFCA) was the most commonly detected subgroup. Of the perfluorinated sulfonic acids (PFSAs) only perfluorooctane sulfonate (PFOS) was detected, present in one sample. Among the fluorotelomer alcohols (FTOHs) only 6:2 FTOH was found. No fluorotelomer acrylates (FTAs), perfluorooctane sulphonamides (FOSAs) or perfluorooctane sulfonamidoethanols (FOSEs) were detected. Overall, the levels of PFCAs and PFSAs were in the low μg/m2 and μg/l range in the products and the levels of 6:2 FTOH were in the μg/m2 range in food packaging and mg/l range in waterproofing products and one polish.

The result of the targeted PFAS analysis of textiles collected in 2015 showed that 6 out of 8 products contained PFASs. The most commonly detected PFAS was PFBA. Overall the levels of PFCAs were in the low μg/m2 range and the level of 6:2 FTOH in the mg/m2 range. No sample contained PFSAs, FTAs, FTSs, FOSAs or FOSEs. The TOF analysis suffered some methodological problems. The method originally developed for TOF-analysis of paper and packaging experienced problems with the analysis of waterproofing treatment sprays and waxes. The TOF-concentrations in the successfully analysed samples spanned over several orders of magnitude for the products collected 2014, 2015 and 2016, respectively, from μg/m2 to g/m2, μg/l to mg/l, and μg/kg to g/kg. The products containing highest concentration of TOF were dental floss (310 g/kg), non-stick baking ware (1.7 g/m2) and table cloth (0.9 g/m2). The comparisons between the sums of detected PFASs to the TOF concentrations showed that for most samples the analysed PFAS constituted only a very minor part of the TOF (below or far below 1%). Some samples had TOF concentrations below the limit of detection, of which some did not detect PFASs in the targeted analyses, indicating that these products may be free of PFASs.

This study, important for the understanding of sources for human and environmental exposure to PFASs via consumer products, show that PFASs are widely used in all analysed product types. The large gap between the TOF and the sum of all targeted PFAS analysed illustrate large data gaps on which PFASs that are being used. Further, there is a need for improved TOF-analysis and a follow-up of the study after the implementation of the PFOA restriction would be valuable.

1.8 PFAS Toxicology - What is Driving the Variation in Drinking Water Standards?

Christy A. Barlow, Ph.D., Cynthia A. Boyd, CHMM, Megan J. Kemp, MSPH, and Kimberly A. Hoppe Parr, Ph.D., 2019

**Abstract**

The growing awareness of per- and polyfluoroalkyl substances (PFAS) in drinking water throughout the U.S is driving the demand for technically defendable, risk-based drinking water standards. In May 2016, the U.S. Environmental Protection Agency (EPA) issued lifetime health advisory levels of 70 parts per trillion (ppt) individually or for the sum of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), as guidance. In February 2019, the EPA decided to move forward with the development of a PFOA and PFOS maximum contaminant level (MCL) process as part of their National PFAS Action Plan under the Safe Drinking Water Act. In the absence of federally-developed enforceable standards, individual states are using their authority to develop and enforce drinking water standards and guidelines. This has resulted in a wide variation of PFAS drinking water guidelines and standards across State and Federal agencies. This variation is related to limited and developing knowledge regarding the critical health effects associated with PFAS exposure over time and largely reflects discordant risk assessment principles and practices among the regulatory agencies. Specifically, the differences in these recommended limits reflect selection of different critical health effects, target populations, uncertainty factors, and additional relative source contribution (RSC) used to derive state specific drinking water

criteria. In this technical review, we examine the body of toxicological research being used by individual states and other developed nations to establish allowable exposure levels for individual PFAS compounds in humans. The primary focus of the discussion will be the points of departure in the development of these standards. Until the EPA issues enforceable health-based drinking water MCLs or action criteria for individual PFAS, State agencies may be required by statute or even stakeholder pressure to assess and issue their own drinking water guidelines. Based on the factors reviewed in this paper, we recommend that the EPA, as well as other State agencies, consider 1) the clinical relevance of more recently identified critical health endpoints; 2) the recent criticisms of physiologically-based

pharmacokinetic (PBPK) modeling and its effect on the derivation of the human equivalent dose (HED); 3) the representativeness of exposure factors and overly conservative uncertainty factors being considered by State agencies; and 4) the potential potency differences among individual PFAS and the effects of different PFAS in a mixture. The development of any MCL or drinking water guideline should be based on robust science and risk-based criteria and should consider all relevant societal costs including a robust cost-benefit analysis.

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## **1.9 Quantitative determination of perfluoroalkyl substances (PFAS) in soil, water, and home garden produce**

Carin A. Huset and Kitrina M. Barry, 2018

**Abstract**

This data article includes details on the simple and efficient analytical methods used to measure perfluoroalkyl substances (PFASs) in water, soil, and produce from home gardens in Minnesota. PFASs in water were analyzed via direct injection. PFASs were extracted from homogenized soil using sonication, and from produce using dispersive solid phase extraction. Isotope dilution was used for quantitation in all methods. The method performance parameters and quality control measures are described. The methods described are applicable for a PFAS ranging from C4-C8 and the produce method was used on a wide variety of produce. For further details and experimental findings, please refer to the article “Occurrence of perfluoroalkyl substances (PFAS) in garden produce at homes with a history of PFAS-contaminated drinking water” The key benefits of this method are:

* This method adapts dispersive solid phase extraction for the analysis of PFAS in produce.
* The method can be used to analyze PFAS ranging from 4 to 8 carbons in a variety of produce types.

## **1.10 Pathways of PFOA to the Arctic: variabilities and contributions of oceanic currents and atmospheric transport and chemistry sources**

I. Stemmler and G. Lammel, 2010

**Abstract**

Perfluorooctanoic acid (PFOA) and other perfluorinated compounds are industrial chemicals in use for

decades which resist degradation in the environment and seem to accumulate in polar regions. Transport of PFOA was modeled using a spatially resolved global multicompartment model including fully coupled three-dimensional ocean and atmosphere general circulation models, and two-dimensional top soil, vegetation surfaces, and sea ice compartments. In addition to primary emissions, the formation of PFOA in the atmosphere from degradation of 8:2 fluorotelomer alcohol was included as a PFOA source. Oceanic transport, delivered 14.8±5.0 (8–23) t a−1 to the Arctic, strongly influenced by

changes in water transport, which determined its interannual variability. This pathway constituted the dominant source of PFOA to the Arctic. Formation of PFOA in the atmosphere led to episodic transport events (timescale of days) into the Arctic with small spatial extent. Deposition in the polar region

was found to be dominated by wet deposition over land, and shows maxima in boreal winter. The total atmospheric deposition of PFOA in the Arctic in the 1990s was ~1 t a−1, much higher than previously estimated, and is dominated by primary emissions rather than secondary formation.

**Notes**

* This study is a modeling exercise explaining pathways of PFOA transport to the artic and long-distance dispersal in general.
* Great storage of the PFAS environmental burden in the ocean rather than in the atmosphere explains the greater total PFAS deposition by ocean currents than atmospheric currents.

## **1.11 Synthesis Paper on Per- and Polyfluorinated Chemical (PFCs)**

OECD Environment Directorate: Environmental, Health & Safety Div. (2013)

**Background, Aim, and Scope**

Per- and polyfluorinated chemicals (PFCs)c, or more specifically per- and polyfluoroalkyl substances (PFASs), are a large group of chemicals that have been used since the 1950s as ingredients or intermediates of surfactants and surface protectors for assorted industrial and consumer applications. During the last decade, several PFASs have been recognised as highly persistent, potentially bioaccumulative and toxic. In addition, many PFASs have been detected globally in the environment, biota, humans and food items. Initially, most attention was given to perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), two PFAS chemicals found commonly in the environment, biota and human and most studied with regard to toxicity and ecotoxicity. Lately, more attention has also been given to other PFASs.

Since 2000, there has been an increasing interest in OECD and non-OECD countries in this particular category of chemicals, and there has been a trend towards restricting the use of long-chain PFASs (for a definition of this term, see the Terminology section) at the international and national level. While some data is available showing the levels and temporal trends of some PFASs in the environment, there remains a critical need for more information on PFASs on both the technical and policy levels, particularly in developing countries. The objective of this document is to provide an overview of the current understanding of PFASs, particularly long-chain PFASs, regarding their major historical and current uses, scientific information about their relevance for human health and the environment (sources to the environment, human exposure, environmental fate and potential adverse effects on humans), alternatives and regulatory approaches.

This document has been prepared by the OECD/UNEP Global PFC Group, which brings together experts from developed and developing countries in governments, academia, industry and NGOs (information on the Group see box 1 and on the website: http://www.oecd.org/ehs/pfc/). The Group’s activities aim to support the implementation of resolutions II/5 and III/ of the International Conference on Chemicals Management. These resolutions encourage the “development, facilitation and promotion in an open, transparent and inclusive manner of national and international stewardship programmes and regulatory approaches to reduce emissions and the content of relevant perfluorinated chemicals (PFCs) of concern in products and to work towards global elimination, where appropriate and technically feasible.”

## **1.12 Recently Detected Drinking Water Contaminants: GenX and Other Per- and Polyfluoroalkyl Ether Acids**

Zachary R. Hopkins, Mei Sun, Jamie C. Dewitt, and Detlef R.U. Knappe, 2018

**Abstract**

For several decades, a common processing aid in the production of fluoropolymers was the ammonium salt of perfluorooctanoic acid (PFOA). Because PFOA is persistent, bioaccumulative, and toxic, its production and use are being phased out in the United States. In 2009, the US Environmental Protection Agency stipulated conditions for the manufacture and commercial use of GenX, a PFOA replacement. While GenX is produced for commercial purposes, the acid form of GenX is also generated as a byproduct during the production of fluoromonomers. The discovery of high concentrations of GenX and related perfluoroalkyl ether acids (PFEAs) in the Cape Fear River and in finished drinking water of more than 200,000 North Carolina residents required quick action by researchers, regulators, public health officials, commercial laboratories, drinking water providers, and consulting engineers. Information about

sources and toxicity of GenX as well as an analytical method for the detection of GenX and eight related

PFEAs is presented. GenX/PFEA occurrence in water and GenX/PFEA removal by different drinking water

treatment processes are also discussed.

**Notes**

* GenX and other perfluoroalkyl ether acids (PFEA) are PFOA replacements in the production of fluoropolymers.
* Wide-spread contamination of drinking water in North Carolina suggests that PFAS replacement chemicals such as GenX will be receiving public and regulatory attention.

## **1.13 The PFOA substitute GenX detected in the environment near a fluoropolymer manufacturing plant in the Netherlands**

S.H. Brandsma, J.C. Koekkoek, M.J.M. van Velzen, and J. de Boer, 2018

**Abstract**

The ban on perfluorooctanoic acid (PFOA) has led to the production and use of alternative fluorinated

compounds such as GenX. Limited information is available on the occurrence of this PFOA substitute. In

this pilot study, we investigated the presence of GenX in/on grass and leaf samples collected near a

fluoropolymer manufacturing plant in the Netherlands and in drinking water produced from surface and

surface-water influenced groundwater intake points within 25 km from the plant. GenX was detected in/

on all grass and leaf samples collected within 3 km north-east from the plant, with levels ranging from 1

to 27 ng/g wet weight (ww) and 4.3-86 ng/g ww, respectively. The PFOA levels in/on grass and leaves

were lower, ranging from 0.7 to 11 ng/g ww and 0.9-28 ng/g ww, respectively. A declining concentration gradient of GenX and PFOA with increasing distance from the plant was observed, which suggests that the plant is a point source of GenX and was a point source for PFOA in the past. In all drinking water samples, GenX and PFOA were detected with levels ranging from 1.4 to 8.0 ng/L and 1.9-7.1 ng/L, respectively. The detection of GenX, which is only used since 2012, in/on grass and leaves and in drinking water indicates that GenX is now distributed through the environment. The presence of GenX and PFOA in/on grass and leaves within 3 km north-east of the plant also suggests that these chemicals could also be present on the locally grown food in gardens around the factory.

**Notes**

* Detection of GenX on vegetation within 3 kilometers and in local surface and groundwater demonstrate the mobility of PFAS replacement chemicals.

1. **PFAS and Wastewater Treatment**

## **2.1 Review of ‘emerging’ organic contaminants in biosolids and assessment of international research priorities for the agricultural use of biosolids**

Bradley O. Clarke, Stephen R. Smith, 2011

**Abstract**

A broad spectrum of organic chemicals is essential to modern society. Once discharged from industrial,

domestic and urban sources into the urban wastewater collection system they may transfer to the residual solids during wastewater treatment and assessment of their significance and implications for beneficial recycling of the treated sewage sludge biosolids is required. Research on organic contaminants (OCs) in biosolids has been undertaken for over thirty years and the increasing body of evidence demonstrates that the majority of compounds studied do not place human health at risk when biosolids are recycled to farmland. However, there are 143,000 chemicals registered in the European Union for industrial use and all could be potentially found in biosolids. Therefore, a literature review of ‘emerging’ OCs in biosolids has been conducted for a selection of chemicals of potential concern for land application based upon human toxicity, evidence of adverse effects on the environment and endocrine disruption. To identify monitoring and research priorities the selected chemicals were ranked using an assessment matrix approach. Compounds were evaluated based upon environmental persistence, human toxicity, evidence of bioaccumulation in humans and the environment, evidence of ecotoxicity and the number and quality of studies focused on the contaminant internationally. The identified chemicals of concern were ranked in decreasing order of priority: perfluorinated chemicals (PFOS, PFOA); polychlorinated alkanes (PCAs), polychlorinated naphthalenes (PCNs); organotins (OTs), polybrominated diphenyl ethers (PBDEs), triclosan (TCS), triclocarban (TCC); benzothiazoles; antibiotics and pharmaceuticals; synthetic musks; bisphenol A, quaternary ammonium compounds (QACs), steroids; phthalate acid esters (PAEs) and polydimethylsiloxanes (PDMSs). A number of issues were identified and recommendations for the prioritisation of further research and monitoring of 'emerging' OCs for the agricultural use of biosolids are provided. In particular, a number of ‘emerging’ OCs (PFOS, PFOA and PCAs) were identified for priority attention that are environmentally persistent and potentially toxic with unique chemical properties, or are present in large concentrations in sludge, that make it theoretically possible for them to enter human and ecological food-chains from biosolids-amended soil.

**Excerpt from Clarke and Smith, 2011**

“2.10. Perfluorochemicals (PFCs), p. 238

Perfluorochemicals (PFCs) are a family of anthropogenic chemicals that have been used since the late 1950s to make products resistant to heat, oil, stains, grease and water. Common applications include nonstick cookware, breathable membranes for clothing, stain-resistant carpets and fabrics, components of fire fighting foam, surfactants and other industrial applications (US EPA, 2008). They have been used in many industry sectors, including the aerospace, automotive, building/construction, chemical processing, electronics, semiconductors, and textile industries (US EPA, 2008).

PFCs are persistent and widely dispersed in the environment (Giesy and Kannan, 2001; Kannan et al., 2001). Accumulation of PFCs has been detected in ocean animals, such as birds and mammals, and in human tissues throughout the world (Olsen et al., 2003; Kannan et al., 2004). The human and environmental toxicological response to such exposure is not known, but could include endocrine disruption (Lau et al., 2004).

The chemical structures of PFCs make them very resistant to degradation in the environment; the carbon–fluorine bonds are extremely strong and are stronger relative to other commonly used

halogens viz., bromine and chlorine. Consequently, perfluorocarbon chains do not readily biodegrade and any biodegradation may be limited to attached hydrocarbon moieties. The two most common groups of PFCs that are measured and detected in environmental matrices are:

• Perfluoroalkyl sulphonates (PFASs) — perfluorooctane sulphonate (PFOS), perfluorohexane sulphonate (PFHxS), perfluorooctanesulphonamide (PFOSA)

• Perfluoroalkyl carboxylates (PFACs) — perfluorooctanoic acid (PFOA), perflurorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), perfluorododecanoic acid (PFDoDA)

PFASs and PFACs are synthetic chemicals that do not occur naturally in the environment (US EPA, 2008). They are employed as a base chemical in the preparation of fluoropolymers and upon degradation can release the environmentally persistent monomers (Boulanger et al., 2005).

Directive 2006/122/EC (EPCEU, 2006) places restrictions on the marketing and use of PFOS and there are also voluntary reductions on PFOA although it is still manufactured. PFOS is also under review for possible identification as a WFD Priority Substance or PHS (EPCEU, 2008). The EU is currently assessing PFOA and, whilst there are no restrictions in place in the EU at present, a ban could be imposed in the future. However, these substances have been extensively used in the built environment and therefore could represent a significant, long-term diffuse input into wastewater and sludge.

The earliest available report of PFCs in sewage sludge is a study of sludges collected from six USA cities (3M Environmental Laboratory, 2001). PFOS and PFOA were the most common PFCs present and were detected in all samples analysed at the low μg kg−1 dw range (Table 3). A sludge sample was tested from a WWTP serving a fluorochemical manufacturer and this correlated with substantial increases in PFOS (2980 μg kg−1 dw) and PFOA (173 μg kg−1 dw) concentrations. This study demonstrated that PFCs, in particular PFOS and PFOA, are likely to be present in sludge in Western countries where PFCs are manufactured and used. Domestic sources are also likely to be a major contributor of PFCs in sewage sludge.

Other studies in the USA (Schultz et al., 2006; Sinclair and Kannan, 2006; Loganathan et al., 2007) and Europe (Bossi et al., 2008) report similar concentration ranges. No differences in PFC levels were apparent in sludges from urban and rural WWTPs, however, major seasonal variations in concentrations were observed (Loganathan et al., 2007). Whilst PFCs have been investigated at WWTPs in other countries (Alzaga and Bayona, 2004; Boulanger et al., 2005), sewage sludge concentrations have mainly been reported in the US. This is largely a consequence of the analytical difficulties associated with quantification of PFCs in sewage sludge matrices.

Mass balance studies of PFCs at WWTP commonly report higher mass loadings of PFOA and PFOS in WWTP effluent compared to raw influent (Schultz et al., 2006; Sinclair and Kannan, 2006; Loganathan et al., 2007). This suggests the degradation of other fluorinated organic compounds (i.e. fluoropolymers) into PFOA and PFOS may take place during wastewater treatment (Loganathan et al., 2007). Field investigations have demonstrated that PFCs in sludge-amended soil can be mobilized by rainfall (Gottschall et al., 2010).”

## **2.2 Fate of Pharmaceuticals and Perfluoroalkyl Substance During Source Separated Wastewater Treatment**

Alina Koch, Dept. of Aquatic Sciences and Assessment, Master’s Thesis, Uppsala, Sweden

**Abstract**

In the past decade, water reuse and nutrient recycling of wastewater has gained more attention as sustainable water cycle management solutions, driven by the increasingly noticeable resource restrictions of the 21st century. One of these possible solutions is source separated treatment of latrine or blackwater for nutrient recovery. However, one major issue of wastewater recycling are micropollutants released into the environment, which can affect ecosystems and human health. This study investigated the fate and removal efficiency of two emerging groups of micropollutants, pharmaceutically active compounds (PhACs) and perfluoroalkyl substances (PFASs), in two source separating wastewater treatments. The first treatment investigated was laboratory-based anaerobic degradation of latrine under mesophilic (37 °C) and thermophilic (52 °C) conditions. The second was a full-scale blackwater treatment, including wet composting and sanitation with urea. Occurrences and concentrations in different steps of the treatments of 29 PhACs and 26 PFASs in the liquid and solid phase of latrine and blackwater were determined.

The results showed high environmental concentrations of PhACs in latrine and blackwater with values up to hundred *μ*g L-1 and *μ*g g-1 dry weight (d.w.) in the liquid and solid phase, respectively. The concentrations measured in latrine and blackwater were higher than those found in conventional wastewater effluents, due to lower dilution. The average removal rates of PhACs were 45 % under mesophilic and 31 % under thermophilic conditions of latrine and a slightly higher removal rate was determined in blackwater, 49 %. Some compounds showed close to complete removal, such as most antibiotics (up to 100 %, n=4). The majority of PFASs were not detected and the ones detected showed low environmental concentrations in the range of low ng L-1 and ng g-1 d.w. in the liquid and solid phase, respectively. In the removal analysis, increased concentrations have been found for PFASs in mesophilic treatment (in average 24 %), possibly due to degradation of PFAS precursors, and a low average removal rate in the thermophilic experiment (in average 4 %). No evaluation could be made about the fate of PFASs in blackwater, due to no significant concentrations measured. It is concluded that latrine and blackwater are no major sources of PFASs and therefore do not represent a major threat to the environment.

The removal efficiency of the two source separated treatments revealed moderate to low removal rates for PhACs and PFASs. But since the occurrence of PFASs in latrine and blackwater is low, their removal might not have to be considered in the source separated wastewater such as latrine and blackwater. Regarding the PhACs additional advance treatments might be necessary or efforts to find a better suitable treatment technique need to be made, as the treated end-product of blackwater is reused as fertilizer in agricultural fields

**Notes**

* Several studies detected PFASs at concentration up to some hundreds ng L-1 and some thousands in ng g-1 d.w., in untreated wastewater e.g. concentrations of 470 ng L-1, 640 ng L-1 and 61205 ng L-1 for PFOS, PFOA and PFOSA, respectively were detected (Arvaniti and Stasinakis, 2015). In sewage sludge, PFOS has been determined with up to 7300 ng g-1 d.w., which makes it the most dominant compound (Arvaniti and Stasinakis, 2015).
* In general compounds with a long carbon chain (> C6) tend to partition onto the solid phase and compounds with a short chain occur most likely in the liquid phase (Ahrens and Bundschuh, 2014). The review Arvaniti and Stasinakis (2015) reported that PFDoA, PFTeDA, PFHpS, PFDS and PFOSA were detected in solid phases, whereas mainly PFHpA, PFOA, PFNA and PFHxS were found in the liquid phase. (p. 7-8)
* Lower pH favors sorption onto wastewater solids
* During conventional wastewater treatment most monitoring studies reported that during secondary treatment (biological) the removal of PFASs seems inconsistent (Arvaniti et al., 2012, Stasinakis et al., 2013, Schultz et al., 2006). Other studies found that specific PFAS concentrations in treated wastewater are higher compared to concentration measured in wastewater influent (Loganathan et al., 2007, Arvaniti et al., 2012, Stasinakis et al., 2013), indicating that they were transformed via biodegradation of precursor compounds. Biodegradation and sorption can be important mechanisms concerning PFASs removal during wastewater treatment (Wang et al., 2011, Wang et al., 2005, Sinclair and Kannan, 2006).

## **2.3 A review of the fate of micropollutants in wastewater treatment plants**

Jonas Margot, Luca Rossi, David A. Barry and Christof Holliger

***Perfluorinated Compounds*** (one section of a larger very relevant document, p. 19)

Perfluorinated compounds (PFCs) are a large family of synthetic chemicals used in many types of household products that utilize their properties of creating *water-repellent*, *grease-repellent*, *and dirt-repellent* *surfaces.* They are for instance used in nonstick cookware (polytetrafluoroethylene (PTFE) known as Teflon), water-proofing sprays, Gore-Tex clothing, stain- or water-resistant textiles (clothes, carpets, tablecloths, upholstered furniture), some cosmetics (nail polish, eye make-up), floor polish and waxes, window cleaners, degreasers, or paper packages for oily foodstuffs (pizza and pop-corn boxes).133 PFCs are a complex group of organic compounds characterized by a carbon chain in which all hydrogen atoms have been replaced by fluorine atoms. This characteristic makes PFCs very persistent in the environment and nondegradable. The PFC perfluorooctane sulfonicacid (PFOS) was classified as a persistent organic pollutant in the Stockholm convention and as a priority hazardous substance in the EU due to its very high persistence in the environment, its bioaccumulation potential and its toxicity. Its use is now restricted in many countries and its production, as well as its concentration in wastewater, have decreased drastically in recent years.134 The PFC perfluorooctanoic acid (PFOA) has also recently received more attention due to its toxic and eco-toxic properties and its high persistence.135 PFOA and PFOS are among the most abundant PFCs observed in raw municipal wastewaters, with average concentrations around 5–50 ng L−1. The sum of the concentrations of the most common PFCs is usually reported in the range of 30–150 ng L−1. PFCs are usually not significantly removed (*<*5%) in WWTPs (despite variable removal efficiencies).67*,*136–138 Concentrations in WWTP effluents are thus relatively similar those in the influents (12–13 ng L−1 for PFOA and PFOS, Table 1). Despite these very low effluent concentrations, PFOS is still present at a level 20 times higher than its European EQS for surface waters (0.65 ng L−1)126 and may persist for a very long time in the environment.

## **2.4 National inventory of perfluoroalkyl substances in archived U.S. biosolids from the 2001 EPA National Sewage Sludge Survey**

Arjun K. Venkatesan and Rolf 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 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.

**Excerpt from p.416**

Ten out of thirteen PFASs analyzed were consistently detected in all composite biosolids samples except for PFBA, PFHpA, and PFBS (Table 2). The most abundant PFAS in biosolids was PFOS, detected at a concentration of 403±127 ng/g dw, followed by PFOA (34±22 ng/g dw). The remaining eleven PFASs ranged between 2 and 26 ng/g dw (Table 2) and the mean total concentration of PFASs (\_PFAS) detected in the five composite samples was 539± 224 ng/g dw. The levels detected in U.S. biosolids are more than an order of magnitude higher than levels detected in sewage sludge samples collected from Spain and Germany [35]. For comparison purposes, the national baseline levels of PFASs detected in this study were plotted with levels reported in other studies for sludge samples collected from U.S. WWTPs (Fig. 1). It must be noted that the concentrations reported in the present study represent samples collected at 94 WWTPs from across the U.S., whereas previously reported values were limited to specific study locations and a maximum of 11 WWTPs. The levels of PFASs from other studies plotted in Fig. 1 are for sludge samples collected in the U.S. between 2004 and 2007 (except for one in 1998). Whereas, the biosolids samples analyzed in this study were collected by U.S. EPA between February and March 2001, which was during the phase out period of PFOS and perfluorooctanesulfonyl fluoride (POSF) related products by the 3M Company between 2000 and 2002. PFAS emission during manufacturing process has reduced since then in the U.S. [36] and hence their current concentrations in biosolids are expected to be lower. However, interestingly the mean concentration of PFASs detected in this study were not significantly different (p > 0.05) to concentrations reported in sludge samples collected between 2004 and 2007 (except for one collected in 1998) in U.S., years after 3M discontinued its industrial production of PFOS and related compounds. A similar observation was also reported for PFAS levels in human serum samples during the 2003–2004 NHANES survey [2]. The survey reported the prevalence of PFASs in more than 98% of the people analyzed even after the phase-out in production by 3M. Even though the current producers are committed to reducing emissions of PFASs, it is suggested that there still exist other direct and indirect sources of PFASs in the U.S. [2].

## **2.5 Sorption of Perfluorinated Compounds onto different types of sewage sludge and assessment of its importance during wastewater treatment**

Arvaniti et al. 2014

**Abstract**

The distribution coefficient (Kd) and the organic carbon distribution coefficient (KOC) were determined for four Perfluorinated Compounds (PFCs) to three different types of sludge taken from a conventional Sewage Treatment Plant (STP). Batch experiments were performed in six different environmental relevant concentrations (200 ng L-1 to 5 μg L-1) containing 1 g L-1 sludge. Kd values ranged from 330 to 6015, 329 to 17432 and 162 to 11770 L Kg-1 for primary, secondary and digested sludge, respectively.

The effects of solution’s pH, ionic strength and cation types on PFCs sorption were also evaluated. Sorption capacities of PFCs significantly decreased with increased pH values from 6 to 8. Furthermore, the divalent cation (Ca2+) enhanced PFCs sorption to a higher degree in comparison with the monovalent cation (Na+) at the same ionic strength. The obtained Kd values were applied to estimate the sorbed fractions of each PFC in different stages of a typical STP and to calculate their removal through treated wastewater and sludge. In primary settling tank, the predicted sorbed fractions ranged from 3% for Perfluorooctanoic acid (PFOA) to 55% for Perfluoroundecanoic acid (PFUdA), while in activated sludge tank and anaerobic digester sorption was more than 50% for all target compounds. Almost 86% of initial PFOA load is expected to be detected in treated wastewater; while Perfluorodecanoic acid (PFDA), PFUdA and Perfluorooctanesulfonate (PFOS) can be significantly removed (>49%) via sorption to primary and excess secondary sludge. In anaerobic digester, the major part (>76%) of target PFCs is expected to be sorbed to sludge, while almost 3% of initial PFOA load will be detected in sludge leachates.

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## **2.7 Influence of cations on the partition behavior of perfluoroheptanoate (PFHpA) and perfluorohexanesulfonate (PFHxS) on wastewater sludge**

Wang, F., Shih, K., Ma, R., and Li, X., 2015

**Abstract**

The effects of different cations on the sorption behavior of PFHpA and PFHxS on two types of sludge were investigated in this study. The sodium and potassium ions did not significantly affect PFHpA and PFHxS sorption on different sludge. For calcium and magnesium, the sorption amount of PFAS increased with calcium and magnesium concentration increasing from 1 to 30 mM and then decreased with those

increasing from 30 to 100 mM. The sorption level of PFHxS or PFHpA greatly increased with increasing

Al3+ and Fe3+ cation concentrations due to the strong sorption and coagulation effects by the formation

of aluminum hydroxide (or ferric hydroxide) colloids or precipitates. After the organics in sludge has been removed by thermal treatment, the PFAS sorption on sludge was greatly reduced. Such finding indicated that sorption to organic matter is more important for anionic PFASs than adsorption to mineral surfaces. However, due to the higher content of biological organics, a secondary activated sludge has higher affinity toward PFAS species than chemically enhanced primary treatment sludge. It indicated that the organic types in sludge were also crucial to the sorption levels of PFASs by sludge.

## **2.8 An investigation into per- and polyfluoroalkyl substances (PFAS) in nineteen Australian wastewater treatment plants (WWTPs)**

Timothy L. Coggan, Damien Moodie, Adam Kolobaric, Drew Szabo, Jeff Shimeta, Nicholas D. Crosbie, Elliot Lee, Milena Fernandes, and Bradley O. Clarke, 2019

**Abstract**

Quantifying the emissions of per- and polyfluoroalkyl substances (PFAS) from Australian wastewater treatment plants (WWTP) is of high importance due to potential impacts on receiving aquatic ecosystems. The new Australian PFAS National Environmental Management Plan recommends 0.23 ng L\_1 of PFOS as the guideline value for 99% species protection for aquatic systems. In this study, 21 PFAS from four classes were measured in WWTP solid and aqueous samples from 19 Australian WWTPs. The mean P21PFAS was 110 ng L\_1 (median: 80 ng L\_1; range: 9.3–520 ng L\_1) in aqueous samples and 34 ng g\_1 dw (median: 12 ng g\_1 dw; range: 2.0–130 ng g\_1 dw) in WWTP solids. Similar to WWTPs worldwide, perfluorocarboxylic acids were generally higher in effluent, compared to influent. Partitioning to solids within WWTPs increased with increasing fluoroalkyl chain length from 0.05 to 1.22 log units. Many PFAS were highly correlated, and PCA analysis showed strong associations between two groups: odd chained PFCAs, PFHxA and PFSAs; and 6:2 FTS with daily inflow volume and the proportion of trade waste accepted by WWTPs (as % of typical dry inflow). The compounds PFPeA, PFHxA, PFHpA, PFOA, PFNA, and PFDA increased significantly between influent and final effluent. The compounds 6:2

FTS and 8:2 FTS were quantified and F–53B detected and reported in Australian WWTP matrices. The compound 6:2 FTS was an important contributor to PFAS emissions in the studied Australian WWTPs, supporting the need for future research on its sources (including precursor degradation), environmental fate and impact in Australian aquatic environments receiving WWTP effluent.

## **2.9 Physical and Biological Release of Poly- and Perfluoroalkyl Substances (PFASs) from Municipal Solid Waste in Anaerobic Model Landfill Reactors**

B. McKay Allred, Johnsie R. Lang, Morton A. Barlaz, and Jennifer A. Field, 2015

**Abstract**

A wide variety of consumer products that are treated with poly- and perfluoroalkyl substances (PFASs) and related formulations are disposed of in landfills. Landfill leachate has significant concentrations of PFASs and acts as secondary point sources to surface water. This study models how PFASs enter leachate using four laboratory-scale anaerobic bioreactors filled with municipal solid waste (MSW) and operated over 273 days. Duplicate reactors were monitored under live and abiotic conditions to evaluate influences attributable to biological activity. The biologically active reactors simulated the methanogenic conditions that develop in all landfills, producing ∼140 mL CH4/dry g refuse. The average total PFAS leaching measured in live reactors (16.7 nmol/kg dry refuse) was greater than the average for

abiotic reactors (2.83 nmol/kg dry refuse), indicating biological processes were primarily responsible for leaching. The low-level leaching in the abiotic reactors was primarily due to PFCAs ≤C8 (2.48 nmol/kg dry refuse). Concentrations of known biodegradation intermediates, including methylperfluorobutane sulfonamide acetic acid and the n:2 and n:3 fluorotelomer carboxylates, increased steadily after the onset of methanogenesis, with the 5:3 fluorotelomer carboxylate becoming the single most concentrated PFAS observed in live reactors (9.53 nmol/kg dry refuse).

## **2.10 Role of wastewater treatment plant in environmental cycling of poly- and perfluoroalkyl substances**

Hanna Hamid and Loretta Y. Li, 2016

**Abstract**

The role of wastewater treatment plants (WWTP) in environmental cycling of poly- and perfluoroalkyl substances (PFASs) through aqueous effluent, sludge and air emission has been critically reviewed here. Understanding the role of WWTPs can provide better understanding of global cycling of persistent PFASs and assist in formulating relevant environmental policies. The review suggests that WWTP effluent is a major source of perfluoroalkyl acids (PFAAs) in surface water. Land application of biosolids (treated sludge) has shown preferential bioaccumulation of short chain (<C7) PFAAs in various plant compartments, leading to possible contamination of the food cycle. Elevated air concentration (1.5 to 15 times) of ΣPFASs have been reported at the aeration tanks on WWTP sites, compared to reference sites not contaminated with WWTP emission. The air emission of neutral PFASs has important implications

considering the long-range transport and subsequent degradation of neutral compounds leading to the occurrence of recalcitrant PFAAs in pristine remote environments. Research gap exist in terms of fate of polyfluroalkyl compounds (neutral PFASs) during wastetwater treatment and in aquatic and terrestrial environment. Considering the wide range of commercially available PFASs, measuring only perfluorocarboxylic acid (PFCA) and perfluorosulfonic acid (PFSA) can lead to underestimation of the total PFAS load derived from WWTPs. Knowledge of the various pathways of PFAS from WWTPs to receiving environments, outlined in this study, can help in adopting best possible management practices to reduce the release of PFASs from WWTPs.

**Notes**

* Despite phase-out, PFOA and PFOS are still the most frequently detected PFAA in wastewater.
* Few studies have intensively investigated the fate of PFAS during conventional and/or advanced wastewater treatment.
* Primary settling seems to provide little or no removal of PFAS.
* Variable, poor, and negative treatment has been observed in secondary treatment processes. The increase in PFAA concentration in secondary effluent is attributed to the degradation of precursor compounds.
* Different types of treatment processes can result in the evolution of different amounts of PFAA during treatment. Increased (i.e. higher summer temperatures) or prolonged (increased HRT) microbial activity seems to be the primary factor for increased concentrations of PFAS across the treatment process.
* WWTF can be a significant source of PFAS contamination to surface water. The detection of PFAS in freshwater biota has been well documented in the literature. In general, the concentration of PFAAs has been observed to increase with increasing trophic level in the food chain in riverine ecosystems.
* Occasionally, increases in the concentrations of PFAS have been observed moving downstream from WWTF. This suggests that PFAS precursors are discharged in the wastewater effluent and degrade to the more stable PFCA forms further downstream.
* There is little information about the fate of PFAS during sludge treatment. PFAS seem to increase after anaerobic and aerobic digestion for three potential reasons: 1) degradation of precursor compounds, 2) decrease of volatile solids during digestion, and 3) increased sorption capacity of the digested sludge. Also, even chain-length PFCA seem to predominate digested sludge. Long-chained PFAS such as PFNA, PFDA and perfluorododecanoic acid (PFDoA), and PFUnDA are more likely to be detected in wastewater solids than in wastewater or effluent.
* Incineration was shown to reduce long-chain PFAS 2- to 10-fold.
* One, limited study showed a reduction in PFAS between dewatered sludge and thermally-dried sludge.
* Air concentrations of PFAS at WWTFs can exceed ambient air at reference sites by a factor of 1.5 to 15. FTOHs were found to be dominant, accounting for 60 – 90% of total PFAS measured in activated sludge system. The distribution of PFAS chemicals can change significantly depending on the treatment process. For example, PFAA can account for >70% of total PFAS for lagoon systems.

1. **Fate & Transport**

## **3.1 Perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in soils and groundwater of a U.S. metropolitan area: Migration and implications for human exposure**

Feng Xiao, Matt F. Simcik , Thomas R. Halbach, and John S. Gulliver, 2014

**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 (2009e2013), 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.

## **3.2 Transport of Perfluorochemicals to Surface and Subsurface Soils**

Feng Xiao, John Gulliver, and Matt Simcik (Xiao et al., 2013)

**Abstract**

Perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA), as persistent organic pollutants, are

ubiquitously present in the environment, and have been detected in human blood and breast milk at concentrations of concern to health and environmental regulators. This project aims to identify the PFOS/PFOA contamination sources, contaminant release mechanisms, and migration pathways from contaminated soils. Soil samples at different depths along and perpendicular to a U.S. highway were collected, and both compounds were regularly quantified in all of our surface soils samples (0.2–125.7 ng/g dry soil weight). The results of the surveying and sampling program and subsequently geo-statistical modeling with the aid of a Geographic Information System (GIS) identified two hot spots, and supported wind as the primary transport carrier causing the mitigation of contaminated soils from the hot spots to off-site soils. The observations indicate that PFOS and PFOA contamination is not contained to a few hot spots, but is migrating with wind and traffic to other locations. This proposed soil-to-soil migration pathway appears to be an important and heretofore overlooked migration mechanism of PFOS and PFOA from contaminated spots. We also studied their occurrence and fate in subsurface

soil samples, and found a general increase in concentrations with the depth at which soil samples were collected, indicating that the contamination is also migrating toward the groundwater table.

## **3.3 Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) in surface waters, sediments, soils and wastewater – A review on concentrations and distribution coefficients**

P. Zareitalabad, J. Siemens, M. Hamer, W. Amelung, 2013

**Abstract**

The sorption of perfluorinated compounds (PFCs) to soils and sediments determines their fate and distribution in the environment, but there is little consensus regarding distribution coefficients that should be used for assessing the environmental fate of these compounds. Here we reviewed sorption coefficients for PFCs derived from laboratory experiments and compared these values with the gross distribution between the concentrations of PFCs in surface waters and sediments or between wastewater and sewage sludge. Sorption experiments with perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) suggest that their sorption can be described reasonably well as a partitioning-like process with an average log Koc of approximately 2.8 for PFOA and 3.0 for PFOS. However, median concentrations in sediments (PFOA, 0.27 ng g\_1; PFOS, 0.54 ng g\_1) or sewage

sludge (PFOA, 37 ng g\_1; PFOS, 69ng g\_1) in relation to median concentrations in surface water (PFOA,

3 ng l\_1; PFOS,3 ng l\_1) or wastewater treatment effluent (PFOA, 24 ng l\_1; PFOS,11 ng l\_1), suggest that effective log Koc distribution coefficients for the field situation maybe close to 3.7 for PFOA and 4.2 for PFOS. Applying lab-based log Koc distribution coefficients can therefore result in a serious overestimation of PFC concentrations in water and in turn to an underestimation of the residence time of PFOA and PFOS in contaminated soils. Irrespective of the dissipation kinetics, the majority of PFOA and PFOS from contaminated soils will be transported to groundwater and surface water bodies.

**Notes**

* Half of the surface water concentrations of PFOA reported in the literature fall within a rather low range between 0.8 and 13 ng/L with a median concentration of 3.1 ng/L and concentrations exceeding 100 ng/L are likely a sign of a point source. PFOS concentrations in surface water are similar with a median value of 3.2 ng/L. p. 728-729
* As expected, concentrations of PFOA in effluents of wastewater treatment plants (WWTPs) tended to exceed concentrations in surface water by approximately a factor of 12. P.729
* The ratio of reported PFOA concentrations in sewage sludge (and some samples of solids suspended in wastewater) in relation to effluent concentrations is much higher than the ratio of sediment concentrations in relation to surface water concentrations. This observation is probably at least partly related to the higher organic carbon contents of sewage sludge compared with the organic carbon contents of sediments. P. 729
* The ‘‘global average’’ Kd that we could calculate from the median concentrations of PFOA in WWTP effluent of 24 ng/L and sewage sludge (37 ng/g) equals 1535 l/kg (logKd = 3.2). Considering an average dry matter organic carbon content of 31% for sewage sludge gives a global average logKOC of 3.7, which is surprisingly similar to that calculated for sediments. P.729-730
* Concentrations of PFOS in WWTP effluent exceed concentrations in surface water by a factor of four and median sludge concentrations are even two orders of magnitude larger than sediment concentrations (Fig. 1). ‘‘Global average’’ logKd and KOC values for sewage sludge are thus 3.8 and 4.3, respectively. The difference in logKoc between PFOS and PFOA for sewage sludge hence fits in with the 0.5–0.8 log units increase of the distribution coefficient per CF2-group. P.730
* Overall, the field-based distribution coefficients of Ahrens et al. (2010), Kwadjik et al. (2010) and Labadie and Chevreuil (2011) as well as our ‘‘global’’ distribution coefficients are consistently larger than distribution coefficients derived from laboratory batch experiments, which suggests that sorption of PFOA and PFOS under field conditions might be stronger than would be estimated from lab experiments, e.g. because of much smaller concentrations encountered in the field and the principally non-linear nature of sorption isotherms that is not reflected in laboratory batch experiments conducted at higher concentrations, and/or because ageing and sorption hysteresis in general enhances the binding of older contaminations in environmental samples. P.730
* Although data derived from laboratory sorption experiments with PFOA and PFOS can be successfully described with logKoc distribution coefficients with surprisingly small variability, field-based observations of PFOA and PFOS concentrations in surface waters, sediments, wastewater treatment effluent and sewage sludge suggest that lab-based distribution coefficients potentially underestimate sorption of both compounds under field conditions. This underestimation can lead to a much too optimistic forecast of the rate of removal of PFOA and PFOS from soil with harvested biomass and drainage and in turn to a much longer residence time of these compounds in contaminated soils, e.g. following the phasing out of their production. This longer residence time would also result into an increased cumulative transfer of PFOA and PFOS from soils into crops. Nevertheless, the majority of soil contaminations with PFOA and PFOS will eventually drain to ground and surface water bodies.

## **3.4 Geochemical and Hydrologic Factors Controlling Subsurface Transport of Poly- and Perfluoroalkyl Substances, Cape Cod, Massachusetts**

Andrea K. Weber, Larry B. Barber, Denis R. LeBlanc, Elsie M. Sunderland, and

Chad D. Vecitis (Weber et al., 2017)

**Abstract**

Growing evidence that certain poly- and perfluoroalkyl substances (PFASs) are associated with

negative human health effects prompted the U.S. Environmental Protection Agency to issue

lifetime drinking water health advisories for perfluorooctanoic acid (PFOA) and perfluorooctane

sulfonate (PFOS) in 2016. Given that groundwater is a major source of drinking water, the main

objective of this work was to investigate geochemical and hydrological processes governing the

subsurface transport of PFASs at a former fire training area (FTA) on Cape Cod, Massachusetts,

where PFAS-containing aqueous film-forming foams were used historically. A total of 148

groundwater samples and 4 sediment cores were collected along a 1,200-m-long downgradient

transect originating near the FTA, and analyzed for PFAS content. The results indicate that

unsaturated zones at the FTA and at hydraulically downgradient former domestic wastewater

effluent infiltration beds both act as continuous PFAS sources to the groundwater despite 18 and

20 years of inactivity, respectively. Historically different PFAS sources are evident from

contrasting PFAS composition near the water table below the FTA and wastewater-infiltration

beds. Results from total oxidizable precursor assays conducted using groundwater samples

collected throughout the plume suggest that some perfluoroalkyl acid precursors at this site are

transporting with perfluoroalkyl acids.

## **3.5 Application of WWTP Biosolids and Resulting Perfluorinated Compound Contamination of Surface and Well Water in Decatur, Alabama, USA**

Andrew B. Lindstrom, Mark J. Strynar, Amy D. Delinsky, Shoji F. Nakayama, Larry McMillan, E. Laurence Libelo, Michael Neill, and Lee Thomas, March 23, 2011

**Abstract**

Perfluorinated chemicals (PFCs) such as perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate (PFOS) have been produced and used in a wide range of industrial and consumerproducts for many decades. Their resistance to degradation has led to their widespreaddistribution in the environment, but little is known about how humans become exposed. Recentstudies have demonstrated that the application of PFC contaminated biosolids can have important effects on local environments, ultimately leading to demonstrable human exposures. This manuscript describes a situation in Decatur, Alabama where PFC contaminated biosolids from a local municipal waste water treatment facility that had received waste from local fluorochemical facilities were used as a soil amendment in local agricultural fields for as many as twelve years. Ten target PFCs were measured in surface and groundwater samples. Results show that surface and well water in the vicinity of these fields had elevated PFC concentrations, with 22% of thesamples exceeding the U.S. Environmental Protection Agency’s Provisional Health Advisorylevel for PFOA in drinking water of 400 ng/L. Water/soil concentration ratios as high as 0.34 for perfluorohexanoic acid, 0.17 for perfluoroheptanoic acid, and 0.04 for PFOA verify decreasingmobility from soils with increasing chain length while indicating that relatively high transport from soils to surface and well water is possible.

**Notes**

* 51 water samples collected: 6 private drinking water wells, 13 wells used for other purposes (livestock, watering, etc.), and 32 surfaces waters These samples were collected from 21 separate farms that had received application of fluorochemical industry impacted biosolids (Figure 1). In most cases the water sources were either on or within 500 m of a biosolid applied field. Farms ranged in size from 9 – 308 hectares, with a total area of more than 2000 hectares receiving WWTP biosolids for as long as 12 years.
* Of the 51 unique field samples collected, PFOA was detected in 29 (57%) of the samples at concentrations ranging from < LOQ to a high of 11,000 ng/L, with 11 samples out of 51 (22%) above the PHA level of 400 ng/L. Two additional samples (389 and 397 ng/L) were not appreciably different from the PHA. PFOA occurred in two drinking water samples: W54PW at 2,070 ng/L and WP14PW at 594 ng/L. PFOS was measured in 15 samples (29%) at concentrations ranging from < LOQ to a high of 151 ng/L, but all concentrations were below the 200 ng/L PHA level. PFOS was measured in two drinking water samples: W11PW at 12.0 ng/L and W14PW at 14.1 ng/L.
* Of the 51 samples, 42 (82%) had at least one target compound at concentrations above the LOQ. Five of the target compounds were measured in more than half of the samples, with PFBA in 39 samples (77%), PFHxA and PFOA in 29 (57%), PFBS in 27 (53%), and PFPeA in 26 (51%). PFNA was detected in 10 (20%) samples with the highest concentration being 286 ng/L and PFDA was detected in 6 (12%) samples with a high value of 838 ng/L. Neither compound was observed in drinking water samples.
* Long chain compounds (>C8) were rarely detected in well water.
* Well water tended to have higher and more variable concentrations of the shorter chain compounds (≤ C8) in comparison to surface water samples, suggesting greater mobility of the low molecular weight materials. This is consistent with the data presented in Figure S3 which show the correlations between dry metric tons of biosolids applied per hectare and PFC concentrations in water samples from adjacent ponds, streams, or wells. Only concentrations of the shorter chain compounds were significantly related to biosolids application rates, with PFOA (r = 0.49, *p* <0.010), PFHxA (r = 0.46, *p* < 0.05), PFPA (r = 0.30, *p* < 0.05), and PFBA (r = 0.57, *p* < 0.001).
* In a study of soils from a subset of these Decatur fields, Washington et al. found PFOS from 30– 410 ng/g and PFOA from 50 - 320 ng/g, but the highest level contaminants were PFDA and perfluorododecanoic acid, which ranged from 130 – 990 ng/g and from 30 – 530 ng/g, respectively [14]. Moreover, the 10:2 and 12:2 fluorotelomer alcohols (FTOHs) were found at concentrations from <5.6 - 166 ng/g and 2 -133 ng/g, respectively [15]. These FTOHs are known to break down or be metabolized to corresponding carboxylic acids. Washington et al. also found that PFCAs in these fields were significantly related to total mass of biosolids applied, with longer chain PFCAs more highly correlated with total mass applied, whereas shorter chain PFCAs were more highly correlated with the time since last application of biosolids. Both observations suggest long chain materials persist in the soil longer and that shorter chain materials may be more mobile.
* There was a statistically significant correlation for the ratio of well/surface water concentrations (ng/ml) to nearby soil concentrations (ng/g). The ratio was low for long chain compounds (>C8) suggesting limited mobility for these compounds.

## **3.6 Results of the Analyses of Screening Surface and Well Water Samples from Decatur, Alabama for Selected Perfluorinated Compounds**

Andrew B. Lindstrom, Mark J. Strynar, Amy D. Delinsky, Larry McMillan

Human Exposure and Atmospheric Sciences Division National Exposure Research Laboratory U. S. Environmental Protection Agency Research Triangle Park, NC 27711

May 2009

Table 8 summarizes all of the data from the field samples. Samples W01PW, W11PW, W22PW, W54PW, W62PW, and W14PW were identified by Region 4 personnel as samples from wells used for drinking water (indicated in Table 8). Of the 51 unique field samples collected (duplicates excluded), PFOA was detected in 29 (57%) of the samples. The PFOA concentrations ranged from < LOQ to a high of 11,000 ng/L, with 11 samples out of 51 (22%) above 400 ng/L and two samples had concentrations (389 ng/L and 397 ng/L), which are not significantly different from the 400 ng/L Provisional Health Advisory level. PFOA occurred in two drinking water samples: W54PW at 2,070 ng/L and WP14PW at 594 ng/L. PFOS was measured in 15 samples (29%) at concentrations ranging from < LOQ to a high of 151 ng/L; all PFOS concentrations were below the 200 ng/L Provisional Health Advisory level. PFOS was measured in two drinking water samples: W11PW at 12.0 ng/L and W14PW at 14.1 ng/L. Of the 51 samples, 42 (82%) had at least one target compound at concentrations above the LOQ. Five of the target compounds were measured in more than half of the samples, with C4 in 39 samples (77%), both C6 and PFOA in 29 (57%), PFBS in 27 (53%), and C5 in 26 (51%). The C9 acid was detected in 10 (20%) samples with the highest concentration being 286 ng/L. The C10 acid was detected in 6 (12%) samples with a high value of 838 ng/L. Neither compound was measured in the drinking water samples. It should be noted again that this method was optimized for performance in the 200 ng/L to 400 ng/L range to allow for accurate comparison with the Provisional Health Advisories for PFOS and PFOA. Concentrations of PFCs in samples listed as being below the LOQ have not been reported, but should not be assumed to be zero.

**3.7 Results of the Analyses of Surface Soil Samples from Near Decatur, Alabama for Fluorinated Organic Compounds**

Ecosystem Research Division Principal Investigator for Analyses: John W. Washington

Science and Ecosystem Support Division Principal Investigator for Sampling: Mike Neill

Sample Analyses: John W. Washington, Ph.D., J. Jackson Ellington, Ph.D. EPA/ORD/NERL/ERD, Hoon Yoo, Ph.D. NRC-EPA/ORD/NERL/ERD, Thomas M. Jenkins, Ph.D., SSA-EPA/ORD/NERL/ERD

July 2009

**Abstract**

In March 2009, soil samples were collected from six agricultural fields near Decatur, Alabama area where sludge from the Decatur Utilities had been applied for more than 12 years. Two soil samples were also collected at one background field, an area where sludge had not been applied. These samples were analyzed for a variety of perfluorinated chemicals (PFCs) and fluorotelomer alcohols (FTOHs). Samples from five of the sludge-applied fields had soil concentrations of PFCs and selected FTOHs exceeding the background sample levels. The soil samples from one field where sludge had been applied at relatively limited rates had levels similar to the background field samples.

Key findings include:

• Perfluorooctanoic acid (PFOA) levels ranged from 50-320 ng/g soil (or parts per billion, ppb), two to three orders of magnitude above background

• Perfluorooctane sulfonate (PFOS) levels ranged from 30-410 ng/g soil (ppb), one to two orders of magnitude above background

• Perfluorodecanoic acid (PFDA or C10) levels ranged from 130-990 ng/g (ppb) and perfluorododecanoic acid (PFDoA or C12) levels ranged from 30-530 ng/g (ppb). Levels for these two PFCs were the highest observed, both at least two orders of magnitude above background

• 8:2 FTOH levels ranged from 4-80 ng/g (ppb), one to two orders of magnitude above background. (8:2 FTOH can degrade to PFOA)

• 10:2 FTOH levels ranged from 4-150 ng/g (ppb) and 12:2 FTOH levels ranged from 2-160 ng/g (ppb), one to three orders of magnitude above background. 10:2 FTOH and 12:2 FTOH (which can degrade to PFDA and PFDoA, respectively) were the highest FTOHs generally observed.

**Discussion**

These sample analysis results indicate that the majority of the Decatur soils in the land application area have concentrations of numerous PFCs and FTOHs above the background levels. In general, the highest mass-basis concentrations of the perfluorocarboxylic acids were the C8 through the C12 acids, particularly the even-chained C8, C10 and C12 acids; values commonly fell in the 100-800 ng/g range. Among the analyzed sulfonates, only PFOS was detected, with mass-basis concentrations falling in the same general range as the C8 through C12 carboxylic acids.

For the fluorotelomer alcohols in the land application areas, the 8:2 through the 12:2FTOHs generally measured at the highest concentrations; values commonly fell in the 10-100 ng/g range. In addition to measuring the commonly reported even-chained FTOHs (e.g., 8:2, 10:2, 12:2), the odd-chained secondary (sec) FTOHs (e.g., 7:2s, 9:2s, and 11:2s) were detected. Only the 7:2s-FTOH has been reported in peer-reviewed literature to our knowledge, and was interpreted as being a degradation product of 8:2FTOH (Ellington et. al., 2009a). Our working hypothesis is that these other FTOHs are degradation products of the respective homologues of 8:2FTOH.

## **3.8 Brominated flame retardants and perfluoroalkyl acids in groundwater, tile drainage, soil, and crop grain following a high application of municipal biosolids to a field**

N. Gottschall, E. Topp, M. Edwards, M. Payne, S. Kleywegt, D.R. Lapena, 2016

**Abstract**

Dewatered municipal biosolids (DMB) were applied at a rate of 22 Mg dw ha−1 to an agricultural field in fall 2008. Concentrations of polybrominated diphenyl ethers (PBDEs; BDE-47, -99, -100, -153, -154, -183, -197, -207, -209), other brominated flame retardants (BFRs; HBB, PBEB, DBDPE, BTBPE) and perfluoroalkyl acids (PFAAs; PFHxS, PFOS, PFDS, PFOSA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFTA) were monitored in tile drainage, groundwater (2 m, 4mand 6mdepth), soil cores (0–0.3m) pre- and post-application, DMB aggregates incorporated into the soil post-application, and in wheat (Triticum spp.) planted post-application. Several compounds were detected in soil and water pre-application and on a reference field plot. PBDEs, other BFRs and PFAAs were detected in tile drainage and 2 m groundwater throughout the post-application study period; a few PBDEs were also detected sporadically at lower depths in groundwater. Some of these compounds had not been detected pre-application, while some exceeded reference field plot/pre-application levels (some significantly (p<0.05) in tile drainage); both cases indicating biosolid-based water contamination. In DMB aggregates, several PBDE congeners were found to have dissipated exponentially, with reductions N90% in many of them within 1 year post-application. Exponential dissipation of other BFRs and PFAAs in DMB aggregates were not significant. No PBDEs, other BFRs, or PFAAs were detected in wheat grain.

**Notes**

Perfluoroalkyl acids (PFFAs) (ng g−1dw) – Concentration of dewater municipal biosolids (DMB) used

Perfluorobutanoic acid (PFBA) <0.4

Perfluoropentanoic acid (PFPeA) 1.2

Perfluorohexanoic acid (PFHxA) 1.5

Perfluoroheptanoic acid (PFHpA) <0.4

Perfluorooctanoic acid (PFOA) 1.6

Perfluorononanoic acid (PFNA) 19

Perfluorodecanoic acid (PFDA) 7.2

Perfluoroundecanoic acid (PFUnA) 2.7

Perfluorododecanoic acid (PFDoA) 3.6

Perfluorobutane sulfonate (PFBS) 22

Perfluorohexane sulfonate (PFHxS) <0.7

Perfluorooctane sulfonate (PFOS) 7.2

Perfluorooctane sulfonamide (PFOSA) 0.5

* The site was land applied one time at a rate 22 Mg/ha DW (9.8 T/A DW).
* Actual biosolids aggregates incorporated in the soil did not show a decreasing trend in detectable PFAA concentrations over time.
* Surface soil cores had detectable levels of long chain PFAA (PFOA, PFOS, PFNA, and PFDA), but shorter chained PFAA were more sporadically detected at low ng/g levels. Soil cores at 0.3-0.6 m and 0.6-0.9 m had no detectable levels of PFAA.
* There were no statistically significant increases in PFAA concentration in GW post biosolids application but pattern of PFAA detections suggest some biosolids based impacts to GW.
* PFAA were detected in tile drainage after biosolids application but the increases were not statistically significant, but again the detection pattern suggests an impact from biosolids.
* No PFAAs were detected in wheat grain samples.
* While this study could not estimate PFAA dissipation rates, other studies have observed half-lives of 8 mon. to 3 yr. The dissipation was mainly influenced by compound mobility through the soil profile.
* This study also showed evidence of precursor transformation especially in the increase of some PFAA at the end of the study period.
* This study concluded that although PFAA was detected in GW and tile drainage, concentrations did not approach toxicity thresholds for aquatic life.
* Tile drainage PFAA concentrations did not exceed typical WWTF effluent PFAS concentrations.
* PFOA and PFOS levels did not exceed Canadian screening level or USEPA PHA levels.

## **3.9 Subsurface Fate and Transport of Poly- and Perfluoroalkyl**

Jennifer L. Guelfo, 2013

**Abstract**

Poly and perfluoroalkyl substances (PFASs) are fluorinated chemicals that have been the focus of many recent studies because of their widespread use, persistence, bioaccumulative potential, toxicity, and distribution in the environment. Because of their unique properties, PFASs are used in a wide variety of products including food paper packaging products, stain repellants, nonstick coatings, and fire fighting foams. Releases of PFASs to the environment and impact to groundwater has occurred through land application of biosolids as well as through use of firefighting foams known as aqueous film-forming foam (AFFF). Because of the potential risk associated with exposure to these compounds, it is important to understand their subsurface fate and transport.

The present study investigated the occurrence and fate of PFASs from land-applied municipal biosolids by evaluating the levels, mass balance, desorption, and transport of per-fluoroalkyl acids (PFAAs) and PFAA precursors in soils receiving application of municipal biosolids at various loading rates. PFOS was the dominant PFAS in both biosolids and biosolids-amended soil. Concentrations of PFASs in soil increased linearly with increasing biosolids loading rate, enabling development of a model for predicting PFAS soil levels based on cumulative biosolids loading rates. Mass balance calculations showed a loss of PFAA precursors in soil relative to the mass applied in biosolids, suggesting precursor transformation. Laboratory desorption experiments indicated that the leaching potential of PFASs

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 PFAAs from biosolids-amended soils. Trace levels of PFAAs 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 PFAAs in soils amended with municipal biosolids.

This study also investigated PFAA sorption to multiple soils in the presence of nonaqueous

phase liquid (NAPL) and nonfluorinated AFFF surfactants. Sorption of small-chain PFAAs did not follow the chain-length dependent trend observed for longer chain-length PFAAs. NAPL and nonfluorinated AFFF surfactants all had varying impacts on sorption on longer chain (>6 CF2 groups) PFAAs. The primary impact of NAPL was observed in low *foc* soil where Freundlich n-values increased when NAPL was present. Impacts of nonfluorinated AFFF surfactants varied with surfactant and soil. In general, the anionic surfactant sodium decyl sulfate (SDS) had chain-length dependent impacts on sorption. Increases in sorption were noted for the smallest compounds and these increases diminished in magnitude with increasing chain length. An amphoteric surfactant, n,n-dimethyldodecylamine

n-oxide(AO), significantly increased sorption for the longer chain PFAAs in a positively charged soil. Changes in sorption caused by SDS and AO may be due to mixed hemimicelle formation, competitive sorption, or changes to PFAA solubility. Short-chain PFAA sorption generally increased in the presence of NAPL, SDS, and AO. These results demonstrate detailed site-specific information will likely be needed to model PFAA transport at AFFF-impacted sites.

Finally, column studies in multiple solid phases were used to understand 1-D advective transport of PFAAs with respect to the equilibrium batch sorption data. Overall, behavior was chain-length dependent, though short chain PFAA behavior was again notable, confirming equilibrium studies. Comparison of equilibrium and column sorption results showed the potential for nonequilibrium behavior, particularly in soils with appreciable organic carbon content and for longer chain PFAAs. Nonequilibrium was confirmed to be the result of rate-limited sorption. Mass transfer coefficients were fitted from the data and found to vary with organic carbon content. This may be due to intraparticle diffusion into the organic matter matrix.

This study initiates an understanding of the subsurface fate and transport of PFASs at

the equilibrium and 1-dimensional scales. Additional research is needed to understand how these results translate to larger scales towards the end goal of reliable site characterization and remediation of PFASs.

## **3.10 Occurrence and Fate of Perfluorochemicals in Soil Following the Land Application of Municipal Biosolids**

Jennifer G. Sepulvado, Andrea C. Blaine, Lakhwinder S. Hundal, and Christopher P. Higgins, 2011

**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.

**Notes**

* Land application of “typical biosolids” will result in detectable levels of PFAS in agricultural soils.
* On short-term plots (3 consecutive years) with a range of loading rates of up to 178 Mg/ha DW (79 T/A dw, within normal agronomic rates), PFOS concentrations in the soil ranged from 2-11 ng/g DW. Although the second most abundant compound in biosolids, MeFOSAA was < 4 ng/g in soil, suggesting transformation.
* On Long-term plots (32 yrs., up to 2218 Mg/ha) and general application plots (1-20 yrs., 47-1654 Mg/ha), PFOS soil concentrations were the highest with a range of 5.5-483 ng/g. One plot receiving a single application in 1988 had a PFOS soil concentration of 5.5 ng/g.
* Long-term control plots showed low cross-contamination of 1ng/g or less for PFAS except PFOS which had concentrations up to 96 ng/g.
* Observed a statistically significant positive correlation between individual PFAS concentrations in the soil and cumulative biosolids load rate. The correlation is described by the following regression:

[PFC] = m \* LR 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)

* The authors cautioned the accuracy of this expression as a predictive tool may be compromised by variability in PFAS biosolids concentrations over time.
* This study showed evidence of PFAS precursor transformations with significant increases (300% to 2000%) of PFBS in the soil over what would be predicted by PFBS concentration in biosolids and biosolids loading rates.
* Analysis of soil cores from long term plots showed PFAS concentrations decreased with depth, but were detected at the lowest depth interval analyzed (120 cm, ~4 ft.)
* The authors attributed movement through the profile to leach (rather preferential flow) for three reasons: 1) consistent PFAS concentrations with depth in control plots, 2) statistically significant correlations between soil PFAS correlation and biosolids loading in the bottom soil core layers, and 3) the ratio of surface soil PFAS concentrations to PFAS concentration in lowest soil core layer decreased with increasing carbon-chain length. This also confirms the greater mobility of short-chain PFAS
* Worst-calculations (5-10 years agronomic applications in 3 yrs.) using Koc (determined this study and other studies) suggest soil pore water PFAS concentration would exceed the EPA PHA for PFOA and PFOS (400 ng/L and 200 ng/L respectively at the time of the study).
* The authors finally conclude: “the risk of groundwater impact from biosolids-borne PFCs is uncertain and will depend heavily on soil type and PFC concentrations in biosolids.”

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## **3.11 Sources, Fate and Transport of Perfluorocarboxylates**

Konstantinos Prevedouros, Ian Cousins, Robert Buck and Stephen Korzeniowski, 2006

**Abstract**

This review describes the sources, fate, and transport of perfluorocarboxylates (PFCAs) in the environment, with a specific focus on perfluorooctanoate (PFO). The global historical industry-wide emissions of total PFCAs from direct (manufacture, use, consumer products) and indirect (PFCA impurities and/or precursors) sources were estimated to be 3200-7300 tonnes. It was estimated that the

majority (~80%) of PFCAs have been released to the environment from fluoropolymer manufacture and use. Although indirect sources were estimated to be much less important than direct sources, there were larger uncertainties associated with the calculations for indirect sources. The physical-chemical properties of PFO (negligible vapor pressure, high solubility in water, and moderate sorption

to solids) suggested that PFO would accumulate in surface waters. Estimated mass inventories of PFO in various environmental compartments confirmed that surface waters, especially oceans, contain the majority of PFO. The only environmental sinks for PFO were identified to be sediment burial and transport to the deep oceans, implying a long environmental residence time. Transport pathways for PFCAs in the environment were reviewed, and it was concluded that, in addition to atmospheric transport/degradation of precursors, atmospheric and ocean water transport of the PFCAs themselves could significantly contribute to their long-range transport. It was estimated that 2-12 tonnes/year of PFO are transported to the Artic by oceanic transport, which is greater than the amount estimated to result from atmospheric transport/degradation of precursors.

**Notes**

* “PFCAs and their potential precursors are of increasing scientific and regulatory (*4*) interest because they have been found globally in wildlife and in humans (*5*-*15*).” p.32
* “PFCAs have been manufactured as salts by four distinct synthesis routes, namely: electrochemical fluorination (ECF), fluorotelomer iodide oxidation, fluorotelomer olefin oxidation, and fluorotelomer iodide carboxylation.” p.32
* “From 1947 through 2002, the ECF process (*16*) was used worldwide to manufacture the majority (80-90% in 2000) of ammonium perfluorooctanoate (APFO).” p. 32
* “PFO emissions from the largest ECF production plant, located in the United States, were reported to be approximately 20 t (5-10% of total annual production) in 2000, roughly 5% discharged to air and 95% to water (*21*). The estimated historical (1951-2004) industry-wide global emissions from APFO manufacture are between 400 and 700 t.”
* “By 2002, the principal worldwide APFO manufacturer by the ECF process discontinued external sales and ceased production leaving only a number of relatively small producers in Europe and in Asia (*22*). New APFO production capacity based on >99% pure perfluorooctyl iodide commenced in the United States in late 2002 with reported annual releases of approximately 50 kg per year to air (*23*). With the termination of U.S. ECF-based manufacture, current and future U.S. releases from APFO manufacture have been dramatically reduced from many t per year to kg per year. As a result, global APFO manufacturing emissions have decreased from about 45 t in 1999 to about 15 t in 2004 and to an expected 7 t in 2006 (*20*).” p. 34
* “PFCAs have been used for over fifty years as processing aids in the manufacture of fluoropolymers such as polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF) (*28*).“ p. 34.
* **“Indirect Sources of PFCAs.** Perfluorooctyl sulfonyl-based (POSF) products made by the ECF process contained PFCA impurities (*55*-*58*). Further, fluorotelomer-based products may contain trace levels of PFCAs (<1-100 ppm) as unintended reaction byproducts (*59*). Investigations to determine the environmental fate through the life cycle (manufacture, use, and disposal) of these two different material classes have revealed that there are potential transformation pathways by which some raw materials from each class may degrade to form PFCAs in the environment (*60*-*65*).” p. 35
* Low pka values indicate that both PFOA and PFO- will be present in the environment but that PFO- will predominate with increasing dissociation with higher pH. Undissociated PFCA will have higher vapor pressures than dissociated forms and vapor decreases with increasing C-chain length. Volatility from water (Henry’s law constant) will be higher from PFOA than PFO-. p. 37
* Soil-Water partitioning coefficients are strongly correlated with organic matter content in the soil. Adsorption in the soil organic matter is related to C-chain length. Higher C-chain length are more strongly adsorbed.
* Bioconcentration increases with increase C-chain length. P.38
* PFO- in the atmosphere is expected to be associated with aerosols either dissolved in water vapor or as part of the organic phase. P.38
* “PFOA is expected to dissociate in the environment almost entirely to PFO-. PFO- has negligible vapor pressure, a high solubility in water, and moderate sorption to solids. Based on these properties, accumulation in surface waters is expected. Limited environmentally relevant physical-chemical properties and partitioning data prohibit the application of classical fate models based on partitioning in the air/water/octanol system (*97*).” P.38
* Open ocean concentrations of PFO- were generally in range of 0.015 to 0.439 ng/L. p.38
* For freshwater, PFO- concentrations were in the range of 0.1 to 10 ng/L. p.38
* Fresh and coastal water sediment concentrations of PFO-were taken to be in the 20 to 500 pg/g range away from point sources. p.38
* This paper suggests that the majority of the PFO- historically release is contained in the ocean. P.39
* The degradation and transport (both air and ocean) of volatile precursor chemicals such as FTOHs have been hypothesized as the main source of long-chain PFCAs in remote regions such as the Arctic (*63*, *84*). P.39
* Patterns in chain lengths and the branching of PFCAs in environmental samples may provide clues to their sources and transport pathways. P.40

## **3.12 Septic systems as sources of organic wastewater compounds in domestic drinking water wells in a shallow sand and gravel aquifer**

Laurel A. Schaider , Janet M. Ackerman, Ruthann A. Rudel, 2016

**Abstract**

Domestic drinking water wells serve 44 million people in the US and are common globally. They are often located in areas served by onsite wastewater treatment systems, including septic systems, which can be sources of biological and chemical pollutants to groundwater. In this study we tested 20 domestic drinking water wells in a sand and gravel aquifer on Cape Cod, Massachusetts, USA, for 117 organic wastewater compounds (OWCs) and for inorganic markers of septic system impact. We detected 27 OWCs, including 12 pharmaceuticals, five per- and polyfluoroalkyl substances (PFASs), four organophosphate flame retardants, and an artificial sweetener (acesulfame). Maximum concentrations of several PFASs and pharmaceuticals were relatively high compared to public drinking water supplies in the US. The number of detected OWCs and total concentrations of pharmaceuticals and of PFASs were positively correlated with nitrate, boron, and acesulfame and negatively correlated with well depth. These wells were all located in areas served exclusively by onsite wastewater treatment systems, which are likely the main source of the OWCs in these wells, although landfill leachate may also be a source. Our results suggest that current regulations to protect domestic wells from pathogens in septic system discharges do not prevent OWCs from reaching domestic wells, and that nitrate, a commonly measured drinking water contaminant, is a useful screening tool for OWCs in domestic wells. Nitrate concentrations of 1 mg/L NO3-N, which are tenfold higher than local background and tenfold lower than the US federal drinking water standard, were associated with wastewater impacts from OWCs in this study.

## **3.13 Toxicological relevance of emerging contaminants for drinking water quality**

Merijn Schriks, Minne B. Heringa, Margaretha M.E. van der Kooi, Pim de Voogt,

Annemarie P. van Wezel, 2009

**Abstract**

The detection of many new compounds in surface water, groundwater and drinking water raises considerable public concern, especially when human health based guideline values are not available it is questioned if detected concentrations affect human health. In an attempt to address this question, we derived provisional drinking water guideline values for a selection of 50 emerging contaminants relevant for drinking water and the water cycle. For only 10 contaminants, statutory guideline values were available. Provisional drinking water guideline values were based upon toxicological literature data. The

maximum concentration levels reported in surface waters, groundwater and/or drinking water were compared to the (provisional) guideline values of the contaminants thus obtained, and expressed as Benchmark Quotient (BQ) values. We focused on occurrence data in the downstream parts of the Rhine and Meuse river basins. The results show that for the majority of compounds a substantial margin of safety exists between the maximum concentration in surface water, groundwater and/or drinking water and the (provisional) guideline value. The present assessment therefore supports the conclusion that the majority of the compounds evaluated pose individually no appreciable concern to human health.

## **3.14 Loss and in situ production of perfluoroalkyl chemicals in outdoor biosolids-soil mesocosms**

Arjun K. Venkatesan and Rolf U. Halden, Environ Res. 2014 Jul; 132: 321-327

**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), perfluorononaoate (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.

## **3.15 6:2 Fluorotelomer alcohol (6:2 FTOH) biodegradation by multiple microbial species under different physiological conditions**

Myung Hee Kim & Ning Wang & Kung Hui Chu, Published online Aug. 2, 2013

**Abstract**

Factors affecting microbial aerobic biodegradation of 6:2 fluorotelomer alcohol [6:2 FTOH, F(CF2)6CH2CH2OH] were investigated using three alkane-degrading bacteria (Mycobacterium vaccae JOB5, Pseudomonas oleovorans, and Pseudomonas butanovora) and one fluoroacetate-degrading bacterium (Pseudomonas fluorescens DSM 8341). In the presence of formate (an external reducing energy source), P. fluorescens DSM 8341 produced perfluorobutanoic acid by removing three –CF2– groups from 6:2 FTOH. Only P. fluorescens DSM 8341 transformed 5:3 acid to 4:3 acid and perfluoropentanoic acid. However, formate showed no effects on the degradation rates, patterns, or transformation products of 6:2 FTOH by M. vaccae JOB5. When dicyclopropylketone (an alkane hydroxylase inducer) or formate was added, P. oleovorans rapidly degraded 6:2 FTOH and produced PFPeA. In the presence of lactate, P. butanovora degraded 6:2 FTOH slowly but produced diverse metabolites. Our results demonstrate that the extent and mechanisms of 6:2 FTOH biotransformation are affected by strain types, enzyme inducers, and levels of reducing energy.

## **3.16 Desorptive Behavior of Perfluoroalkyl Acids and Perfluoroalkyl Acids Precursors from Aqueous Film-Forming Foaming Impacted Soils and Aquifer**

Azzolini, D.C., 2014

**Abstract**

Aqueous film-forming foams (AFFFs) have been used to fight hydrocarbon fuel fires and

for firefighter training at a number of U.S. military sites. As a result, soils, aquifer materials,

and groundwater near these firefighter training sites can be contaminated with a broad

suite of poly- and perfluorinated substances (PFASs), including many perfluoroalkyl acids

(PFAAs). Though plumes resulting from such activities are well documented, the extent to

which surface soils can serve as long term sources of both PFAAs and PFASs remains unclear.

To this end, 14 day infinite sink batch desorption experiments were conducted to measure the

desorption behavior of PFAAs and PFAA precursors using four field-contaminated surface

soils and two subsurface aquifer materials collected at two AFFF-impacted sites. The desorption

of precursors to eight different perfluorocarboxylates (PFCAs) from these materials

was measured through use of the recently-developed total oxidizable precursor (TOP) assay.

PFAA and PFAA precursor desorption data were modeled using either a two-compartment

or a one-compartment kinetic model. PFCAs and perfluorosulfonates (PFSAs) showed similar

desorption rates for equivalent perfluorinated carbon chain lengths, and both showed

decreasing desorption rates with increasing perfluorinated chain length. PFAA precursors

desorbed more slowly than PFAAs from the contaminated materials; all PFAAs could be

modeled with a single fast desorbing compartment while many PFAA precursors required an

additional, slower compartment containing up to 96% of precursor mass with desorption rate

constants 3 to 15 times smaller than in the fast desorbing compartment. PFAAs had larger

fast desorption rate constants than PFAA precursors with average values of 2.27 and 1.65

(day-1), respectively. Noteable differences in desorption rate were also observed between the

six sediment samples. Despite slower desorption rates, PFAA precursors may still constitute

a significant portion of potentially mobile PFASs at sites impacted by AFFF use.

## **3.17 Effect of organic carbon, active carbon, calcium ions and aging on the sorption of per- and polyfluoroalkylated substances (PFASs) to soil.**

Schedin, E., November 2013

**Abstract**

Per- and polyfluoroalkylated substances (PFASs) are a large group of organic chemicals that

have gained an increased attention during recent years. Many of the compounds have shown

to be persistent, toxic and bioaccumulating and they are found in water, soils, sediments,

biota, animals and humans across the globe. The effects of PFASs to humans and animals are

still being debated. It is suspected that the compounds can be carcinogenic, disrupt different

hormone systems and have other severe effects.

The main transport pathways of PFASs to soil are applied PFAS based firefighting foam, soil

improvers and waste from industries producing PFASs or PFAS based products. Once the

PFASs find their way to the soil the risk for leaching to drinking water supplies and aquatic

ecosystems becomes some of the issues of great concern. In order to be able to evaluate the

potential leakage of PFASs from different contaminated soils it is important to know how the

PFASs interact with the soil matrix and what parameters that affects these interactions.

The objective of this study was to investigate the influence of organic carbon (OC), Ca2+ ions

and active carbon (AC) on the n of PFCAs and PFSAs to soil. The PFCAs examined were

PFHxA, PFOA, PFNA, PFDA, PFUnDA, PFOcDA, PFHxDA and PFOcDA and the PFSAs

examined were PFBS, PFHxS, PFOS and PFDS. Batch experiments were performed on soils

with varying concentrations of TOC, Ca2+ and AC. The samples were spiked with PFAS

native standard solution containing the 12 target PFASs. All studied parameters showed a

positive influence on the sorption of PFASs to soil. The AC was found to have the highest

influence on the sorption. The OC was however found to be the most important soil parameter

influencing the sorption of PFASs to soil. In order to investigate the influence of aging on the

sorption of PFASs, batch experiments were also conducted on soils from four different PFAS

contaminated sites. The results showed that the aging positively influenced the strength of the

interactions between PFASs and soil.

The organic carbon normalized distribution coefficients (*Koc*) showed a positive correlation

with the carbon chain length of the PFAS molecules and also with the substitution of a

carboxylic group with a sulfonic group. The log *Koc* values calculated in this study decreased

in the following order PFDS (log *Koc* 3.8±0.3) > PFOS > (log *Koc* 2.8±0.3) > PFUnDA (log

*Koc* 3.2±0.2) > PFDA (log *Koc* 2.7±0.1) > PFNA (log *Koc* 2.0±0.1) > PFHxS (log *Koc* 1.9±0.1)

> PFOA (log *Koc* 1.8±0.3) > PFHxA (log *Koc* 1.6 ±0.3) > PFBS (log *Koc* 1.5±0.2). The log *Koc*

values found in this study were within the range of previously reported log *Koc* values.

## **3.18 Adsorption of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) on alumina: Influence of solution pH and cations**

Wang, F. and Shih, K., Available online 15 March 2011

**Abstract**

The persistent nature of perfluorochemicals (PFCs) has attracted global concern in recent years. Perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) are the most commonly found PFC compounds, and thus their fate and transport play key roles in PFC distribution in the natural environment. As most solid phases in natural water contain alumina, an investigation of PFOS and PFOA adsorption behavior on alumina should prove useful in evaluating the environmental impact of this type of persistent pollutant. Systematic experiments were carried out in this study to investigate the adsorption behavior of PFOS and PFOA onto alumina. The results of adsorption kinetics on alumina show that it takes 48 h to reach equilibrium. The adsorption isotherms reveal maximum adsorption capacities of 0.252 mg/m2 for PFOS and 0.157 mg/m2 for PFOA at pH ¼ 4.3, with the difference primarily due to their different functional groups. An increase in pH leads to a decrease in PFOS and PFOA adsorption on alumina, which may be attributed to the reduction in electrostatic interaction. The adsorption of both PFOS and PFOA decreases with an increase in ionic strength for all four types of cations (Na+, K+, Mg2+, and Ca2+), due to the compression of the electrical double layer. Furthermore, the results also indicate that both Ca2+ and Mg2+ can form bridges with PFOA anions in solution, whereas only PFOS can be bridged by Ca2+ due to the higher covalent nature of magnesium.

## **3.19 Sorption of Perfluoroalkyl and Polyfluoroalkyl Substances (PFASs) by Natural and Anthropogenic Carbonaceous Sorbents**

Zhi, Y., March 2017

**Abstract**

As a large number of perfluoroalkyl and polyfluoroalkyl substances (PFASs) has been extensively used in industrial and consumer products, many of these species are detected in the global environment and biota, including some carcinogenic ones. Perfluorooctane sulfonic (PFOS) and carboxylic acids (PFOA) are examples of PFASs currently subject to strict regulatory and scientific scrutiny. There are many other analogous compounds, such as those used in aqueous film-forming foams (AFFFs), for which environmental fate and effect are little known. In addition, high chemical stability and hydrophilicity of PFASs pose challenges to effective treatment and mitigation of those present in groundwater and drinking water sources. The objective of this research was to elucidate interactions between PFASs and naturally occurring and engineered carbonaceous materials, the knowledge base needed for PFAS risk assessment and treatment.

The research first examined the interactions between commercial adsorbents with two most prominent PFAS species (PFOA and PFOS), to identify the ways in which water treatment efficiency for the PFASs can be improved. The study assessed the sorption of PFOS and PFOA onto as-received and surface-modified carbonaceous adsorbents using single-solute batch sorption experiments, and the main carbon characteristics controlling the uptake of PFASs were identified. Adsorbent surface chemistry played a more important role in controlling the extent of uptake than physical properties. High carbon surface basicity was closely linked to high PFOS and PFOA affinity. Prior to any modification of the carbon materials, synthetic polymer-based Ambersorb and activated carbon fibers were the most effective adsorbents due to their basic character. Surface modification, more so with ammonia gas treatment than with high-temperature thermal treatment, greatly improved sorption of PFOS and PFOA by wood-based carbons and activated carbon fibers.

The research then focused on the role that soil organic matter (SOM) and pyrogenic carbonaceous materials (PCMs) played in determining the transport potential of a range of perfluoroalkyl acids (PFAAs) and their chemical precursors (PrePFAAs). A novel dynamic HPLC-based column method was developed to determine distribution coefficients (*Koc*) between SOM and water at various conditions. PrePFAAs with betaine, sulfonamide betaine, and quaternary amine functional groups exhibit higher *Koc* values than the PFAAs with the same perfluoroalkyl chain length. Calcium ion had a positive impact on the sorption of anionic PFAAs to SOM while showing a negative impact on the PrePFAAs. Moreover, an increase in pH reduced sorption of all the PFASs to SOM.

In comparison, sorption of PFASs to PCMs (charcoal and soot) was stronger and less linear than SOM, indicating that PCMs could be a more significant sink to PFASs in the firefighting training sites where regular releases of AFFFs resulted in PFAS pollution of soil and groundwater. The role of PCMs was more pronounced than SOM at lower aqueous concentrations without an attenuation effect. Additionally, apparent sorption-desorption hysteresis exhibited by PCMs was sorbate-specific, and the soot had the highest hysteresis among all the sorbents.

These findings illustrate the importance of considering the surface chemistry of adsorbents, along with solution chemistry when investigating PFAS uptake by carbonaceous materials of different origins. Furthermore, the results obtained emphasize the need to evaluate the interactions between PrePFAAs and PCMs, in the efforts to delineate the behaviours of PFASs in soil and groundwater impacted by AFFFs, as well as to decide remediation strategies.

## **3.20 Influence of Solution Chemistry on Adsorption of Perfluorooctanesulfonate (PFOS) and Perfluorooctanoate (PFOA) on Boehmite**

Wang, F. and Shih, K., 2012

**Abstract**

The persistent nature of perfluorochemicals (PFCs) has attracted global concern in recent years. Perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) are the most commonly found

PFC compounds, and thus their fate and transport play key roles in PFC distribution in the natural environment. The kinetic behavior of PFOS or PFOA on boehmite consists of a fast adsorption process

followed by a slow adsorption process which may be attributed to the slow transport of PFOS or PFOA into the boehmite pore surface. The adsorption isotherms estimated the maximum adsorption capacities of PFOS and PFOA on boehmite as 0.877 μg/m2 and 0.633 μg/m2, with the difference primarily due to their different functional groups. The increase of solution pH led to a moderate decrease of PFOS and PFOA adsorption, owing to the increase of ligand exchange reactions and the

decrease of electrostatic interactions. The presence of NaCl in solution demonstrated negative effects for PFOS and PFOA adsorption on boehmite surfaces, with potential mechanisms being electrical double layer compression, competitive adsorption of chloride.

## 3.21 Adsorption behavior of perfluorochemicals (PFCs) on boehmite: influence of solution chemistry

Shih, K. and Wang, F., 2013

**Abstract**

With global distribution, persistence nature, and strong bioaccumulation, the fate and transport of

perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) in natural environment have recently attracted strong attentions. As boehmite is a common form of hydrated aluminum oxide existing in soils and sediments, this study successfully revealed the adsorption behavior of PFOS and PFOA on boehmite and the influence from solution chemistry. The results of kinetic experiments show that the adsorption equilibrium can be achieved within 48 hours and the boehmite surface is generally receptive to PFOS and PFOA adsorption. The adsorption isotherms estimated the maximum adsorption capacities of PFOS and PFOA on boehmite to be 0.877 μg/m2 and 0.633 μg/m2, respectively. The increase of pH can lead to a moderate decrease of PFOS and PFOA adsorption, owing to the increase of ligand exchange reaction and the decrease of electrostatic interaction. With the compression of electrical double layers, the competitive adsorption from the other ions and the Ca2+ bridging effect between perfluorochemicals have demonstrated their negative influence for PFOS and PFOA adsorption on boehmite surface. Finally, humic acid (HA) also showed significant retardant effects on the sorption of perfluorooctanesulfonate (PFOS) and perfluorobutanesulfonate (PFBuS) on boehmite.

## **3.22 Assessment of POP Criteria for Specific Short-Chain Perfluorinated Alkyl Substances**

Ramboll Environ, December 6, 2016

**p. 2, Executive Summary**

Since 2013, several studies have been published on the environmental fate of the short chain PFAS of interest, including studies related to the degradation potential of the methacrylate polymer, fluorotelomer alcohol, fluorotelomer acrylate, and fluorotelomer methacrylate. Additionally, researchers have continued to measure 6:2 FTOH and PFHxA in remote environments, including the Arctic. Since 2013, additional information has also been published on the health hazards associated with 6:2 FTOH and PFHxA, particularly related to the substantiation of a NOAEL based on rat/mouse studies. Lastly, researchers have looked into the ecotoxicity and bioaccumulation potential of PFHxA. These new data are generally supportive of the primary conclusions reached in Ramboll Environ’s initial report; none of the short chain PFAS evaluated in the study meet the Stockholm Convention POP criteria. In fact, as shown in Table 1.1, none of these substances meet more than one criterion.

## **3.23 Side-chain fluorinated polymer surfactants in aquatic sediment and biosolid-augmented agricultural soil from the Great Lakes basin of North America**

Shaogang Chu, Robert J. Letcher, Available online 27 July 2017

**Abstract**

Side-chain fluorinated polymer surfactants are the main components of fabric protector sprays and used extensively on furniture and textiles. The composition of these commercial protector products has changed, but there is currently a total dearth of information on these novel fluorinated polymers in the environment. Using a developed analytical approach, two complementary studies examined the distribution of Scotchgard™fabric protector components in aquatic sediment and in agricultural soils where wastewater treatment plant (WWTP) sourced biosolid application occurred, and in samples from sites in the Laurentian Great Lakes basin of North America. The main components in the pre- and post-2002 Scotchgard™ fabric protectors were identified by MS/MS and Q-TOF-MS to contain a perfluorooctane sulfonamide (S1) and perfluorobutane sulfonamide (S2) based sidechain, respectively, and bonded to a polymer backbone. In fifteen sediment samples collected in 2012–2013 from western Lake Erie and Saginaw Bay (Lake Huron), S1 was in all sediment samples (0.18 to 461.59 ng/g dry weight (d.w.)); S2 was in 80% of the sediment samples (b0.03 to 24.08 ng/g d.w.). Thirteen soil samples were collected (2015) from a biosolid applied and two non-biosolid applied farm field sites in southern Ontario (Canada). S1 was detected in 100% of the soil samples from biosolid-augmented agricultural sites (mean 236.36 ng/g d.w.; range 41.87 to 622.46 ng/g d.w.), and at concentrations much greater than in the aquatic sediment samples. The concentration of S1 and S2 in soil and sediment samples were also much greater than the total concentration of other per-and poly-fluoroalkyl substances (PFASs) that were measured.

## **3.24 Experimental and molecular dynamic simulation study of perfluorooctane sulfonate adsorption on soil and sediment components**

Zhang, R., Yan, W., and Jing, C., 2015

**Abstract**

Soil and sediment play a crucial role in the fate and transport of perfluorooctane sulfonate (PFOS) in the environment. However, the molecular mechanisms of major soil/sediment components on PFOS adsorption remain unclear. This study experimentally isolated three major components in soil/sediment: humin/kerogen, humic/fulvic acid (HA/FA), and inorganic component after removing organics, and explored their contributions to PFOS adsorption using batch adsorption experiments and molecular dynamic simulations. The results suggest that the humin/kerogen component dominated the PFOS adsorption due to its aliphatic features where hydrophobic effect and phase transfer are the primary adsorption mechanism. Compared with the humin/kerogen, the HA/FA component contributed less to the PFOS adsorption because of its hydrophilic and polar characteristics. The electrostatic repulsion

between the polar groups of HA/FA and PFOS anions was attributable to the reduced PFOS adsorption. When the soil organic matter was extracted, the inorganic component also plays a non-negligible role because PFOS molecules might form surface complexes on SiO2 surface. The findings obtained in this study illustrate the contribution of organic matters in soils and sediments to PFOS adsorption and provided new perspective to understanding the adsorption process of PFOS on micro-interface in the environment.

## **3.25 Defluorination of Perfluorooctanoic Acid (PFOA) and Perfluorooctane Sulfonate (PFOS) by Acidimicrobium sp. Strain A6**

Shan Huang and Peter R. Jaffé, 2019

**Abstract**

Incubations with pure and enrichment cultures of Acidimicrobium sp. strain A6 (A6), an autotroph that

oxidizes ammonium to nitrite while reducing ferric iron, were conducted in the presence of PFOA or PFOS at 0.1 mg/L and 100 mg/L. Buildup of fluoride, shorter-chain perfluorinated products, and acetate was observed, as well as a decrease in Fe(III) reduced per ammonium oxidized. Incubations with hydrogen as a sole electron donor also resulted in the defluorination of these PFAS. Removal of up to 60% of PFOA and PFOS was observed during 100 day incubations, while total fluorine (organic plus fluoride) remained constant throughout the incubations. To determine if PFOA/PFOS or some of their degradation products were metabolized, and since no organic carbon source except these PFAS was added, dissolved organic carbon (DOC) was tracked. At concentrations of 100 mg/L, PFOA/PFOS were the main contributors to DOC, which remained constant during the pure A6 culture incubations. Whereas in the A6 enrichment culture, DOC decreased slightly with time, indicating that as defluorination of PFOS/PFOA occurred, some of the products were being metabolized by heterotrophs present in this culture. Results show that A6 can defluorinate PFOA/PFOS while reducing iron, using ammonium or hydrogen as the electron donor.

## **3.26 Microbial degradation of polyfluoroalkyl chemicals in the environment: A review**

Jinxia Liu and Sandra Mejia Avendaño, 2013

**Abstract**

Polyfluoroalkyl chemicals containing perfluoroalkyl moieties have been widely used in numerous industrial and commercial applications. Many polyfluoroalkyl chemicals are potential perfluoroalkyl acid (PFAA) precursors. When they are released to the environment, abiotic and microbial degradation of non-fluorinated functionalities, polyfluoroalkyl and perfluoroalkyl moieties can result in perfluoroalkyl carboxylic (PFCAs) and sulfonic acids (PFSAs), such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS). These highly persistent and ubiquitously detected PFAAs are the subjects of many regulations and actions due to their toxic profiles. In order to confidently evaluate the environmental fate and effects of these precursors and their links to PFSAs and PFCAs, we present the review into the environmental biodegradability studies carried out with microbial culture, activated sludge, soil and sediment in the past decade. First, we propose that the knowledge gap caused by the lack of direct detection of precursor chemicals in environmental samples can be bridged by laboratory investigations of important precursors such as fluorotelomer-based compounds and perfluoroalkane sulfonamido derivatives. Then we evaluate the experimental setups and methodologies, sampling and sample preparation methods, and analytical techniques that have been successfully applied. Third, we provide the most updated knowledge on quantitative and qualitative relationships between precursors and PFSAs or PFCAs, microbial degradation pathways, half-lives of precursors, defluorination potential, and novel degradation intermediates and products. In the end, we identify knowledge gaps and suggest research directions with regard to future biodegradation studies, environmental monitoring and ecotoxicological assessment of perfluoroalkyl and polyfluoroalkyl chemicals.

**Notes**

* Biodegradability of PFAS precursors in soil is variable and can be dependent on soil type and origin. “For instance, toluene-2,4-di-(8:2 FTOH urethane) [FTU, (CH3)C6H3(NHC(O)OCH2- CH2C8F17)2] did not degrade in an agricultural soil, but showed significant degradation in a forest soil, which presumably had higher fungal biomass (Dasu, 2011).”
* PFOA is generally consider the end product of 8:2 FTOH biodegradation. However, other stable end products such as PFHpA and PFHxA are produced when one or two carbons are mineralized from the C-chain.
* C-chain length reduction has been observed during the aerobic biodegradation of 6:2 FTOH in sludge to PFPeA and PFBA.
* Fluorotelomer alcohols are expected have a greater tendency to defluorinated with decreased molecular size (4:2 FTOH > 6:2 FTOH > 8:2 FTOH).
* Anaerobic degradation (as observed in an WWTP digester) of fluorotelomer alcohols is likely to produce polyfluoroalkyl acids.
* “Biodegradability of polyfluoroalkyl chemicals is largely owing to its non-fluorinated functionality, whose breakdown precedes the breakdown of the perfluorinated carbons, if the later occurs. In contrast, perfluoroalkyl chemicals in general resist biotransformation and defluorination under natural conditions.”
* While PFOA and PFOS are resistant to degradation under natural conditions, they do degrade to shorter-chain PFAS in catalyzed enzymatic digestion systems in the lab.
* Over time a portion of PFAS compounds or degradation products can be become irreversibly bound in soils. There is some evidence that this binding may be catalyzed by microbial activity. More temporary binding to soil organic matter can be depended on the composition of the organic matter. For example, PFOA is more likely to bind to proteinaceous organic matter as compared to more lignin-based components.
* “Drawn on the studies performed so far on a number of precursors(as summarized in Table 1), it has been demonstrated that the half-life of precursors, degradation kinetics and quantitative contributions to PFAAs vary dramatically, and depend on both chemical structures and environmental conditions, such as the size of the perfluoroalkyl chain, the type of internal chemical linkage connecting to non-fluorinated functionalities, the type of non-fluorinated functionality, molecular size, type of microbes or microcosms and other environmental factors (e.g. temperature).”

## **3.27 Investigation of Levels of Perfluorinated Compounds in New Jersey Fish, Surface Water, and Sediment**

Sandra M. Goodrow, Ph.D., Bruce Ruppel, Lee Lippincott, Ph.D., and Gloria B. Post, Ph.D., D.A.B.T., 2018

**Executive Summary**

Per- and polyfluorinated substances (PFAS) are used in the manufacture of useful products that impart stain resistance, water resistance, heat resistance and other desirable properties. PFAS are also used in various Aqueous Film Forming Foams (AFFF) that are used in fire-fighting. These substances are in wide use today, found at industrial sites that use or manufacture them and at military bases, airports and other areas known for fire-fighting activities. A subset of PFAS, perfluorinated compounds (PFCs), have fully fluorinated carbon chains as their backbone, and their extremely strong carbon-fluorine bonds makes them very resistant to degradation. When released to the environment, PFCs persist indefinitely and can travel distances from their source in surface water, groundwater, or in the atmosphere. PFAS are considered “emerging contaminants” because additional information on their presence and toxicity to ecosystems and humans continues to become available.

The Division of Science, Research and Environmental Health (DSREH) performed an initial assessment of 13 PFAS, all of which are perfluorinated compounds (PFCs), at 11 waterways across the state. Fourteen surface water and sediment samples and 94 fish tissue samples were collected at sites along these waterways. The sites were selected based on their proximity to potential sources of PFAS and their likelihood of being used for recreational and fishing purposes. The sampling sites are located within Passaic, Middlesex, Ocean, Burlington, Gloucester, and Salem Counties.

All surface water samples contained detectable levels of at least four PFAS. The lowest total PFAS in surface water was in the Cohansey River, with Horicon Lake and Echo Lake having the second and third lowest total PFAS, respectively. The highest total level of PFAS was found in Little Pine Lake, near the Joint Base McGuire-Dix-Lakehurst, with Mirror Lake and Pine Lake ranking the second and third highest, respectively. Consistent with the known characteristics of preferential partitioning of longer chain PFCs to sediment and shorter chain PFCs to the water column, the PFAS detected in surface water were those with a carbon chain length of nine carbons or less.

Ten of the 14 sites where sediment samples were collected had detectable levels of at least one, and up to eight, PFAS. Pine Lake had the highest total PFAS concentration (30.93 ng/g) in the sediment, with the majority being perfluorooctane sulfonate (PFOS), the eight-carbon chain sulfonate. Echo Lake (West Milford in Passaic County), often used as a New Jersey “background” site, had no detectable levels of PFAS in the sediment. All detectable PFAS in the sediment were compounds with six or more carbons (i.e. PFHxS and longer carbon chain length).

One to three individual fish from two to four species (three each of three species at most sites) were collected and analyzed at each site. The average detectable concentrations (non-detects were not included in the averaging of the tissue concentrations) of the individual PFAS showed that all species at all sites were impacted by one or more PFAS compounds. These contaminants are “proteinophilic” (e.g. bind to muscle tissue in the fillets) and do not bioaccumulate in the fatty tissue like other persistent organic pollutants frequently found in fish (e.g. PCBs, dioxins). In general, the sites with identified sources and detectable levels of PFAS in surface water and sediment had higher levels of PFAS in the fish tissue, with the samples from Pine Lake and Little Pine Lake having the highest detected concentrations.

This report includes preliminary fish consumption advisories for three PFAS – PFNA, PFOA and PFOS - based on current New Jersey Reference Doses established for each of these compounds. While these preliminary advisories provide the reader with an early indication of potential outcomes, it is emphasized that the advisories have not been finalized as of this writing and should only be viewed as potential benchmarks for evaluating the data. Based on the preliminary advisories, all of the 11 sites would have some level of fish consumption guidance ranging from “one meal per week” to “do not eat”.

## **3.28 Removal of Perfluorinated Compounds from Water with Activated Carbon and Redox Treatments**

O.S. Arvaniti, H.R. Andersen, Y.H. Hwang, M.G. Antoniuo, G.M. Gatidou, N.S. Thomaidis, and A.S. Stasinakis, 2013

**Abstract**

Perfluorinated compounds (PFCs) consist by a hydrophobic perfluorinated carbon tail and a hydrophilic ionic headgroup. Because of their unique structure, PFCs have a wide variety of applications including active ingredient in fire fighting foams, impregnation for food packing and waterproof breathable fabrics and the producing of teflon. Recently, the research interest for these compounds has been increased due to their recalcitrance, strong bioaccumulation and potential toxicity. While the occurrence of PFCs have been well documented in Sewage Treatment Plants (STPs) all over the world, however there is few data for their removal. The aim of this work was to investigate the removal of 6 PFCs (C5, C8 to C11 carboxylic acids and C8 sulfonic acid) in water using a) activated carbon (Powdered Activated Carbon; PAC, Granular Activated Carbon; GAC), b) advanced oxidation processes such as: UV/H2O2, UV/S2O82- and c) reductive treatments based on nanoscale Zero Valent Iron (nZVI). The percentage removal was calculated for each target compound using the above techniques.

## **3.29 Sorption of Poly- and Perfluoroalkyl Substances (PFASs) Relevant to Aqueous Film-Forming Foam (AFFF)-Impacted Groundwater by Biochars and Activated Carbon**

Xin Xiao, Bridget A. Ulrich, Baoliang Chen, and Christopher P. Higgins, 2017

**Abstract**

Despite growing concerns about human exposure to perfluorooctanoate (PFOA) and perfluorooctanesulfonate (PFOS), other poly- and perfluoroalkyl substances (PFASs) derived from aqueous film-forming foams (AFFFs) have garnered little attention. While these other PFASs may also be present in AFFF-impacted drinking water, their removal by conventional drinking-water treatment is poorly understood. This study compared the removal of 30 PFASs, including 13 recently discovered PFASs, from an AFFF-impacted drinking water using carbonaceous sorbents (i.e., granular activated carbon, GAC). The approach combined laboratory batch experiments and modeling: batch sorption

data were used to determine partition coefficients (Kd) and calibrate a transport model based on intraparticle diffusion-limited sorption kinetics, which was used to make forward predictions

of PFAS breakthrough during GAC adsorption. While strong retention was predicted for PFOS and PFOA, nearly all of the recently discovered polyfluorinated chemicals and PFOS-like PFASs detected in the AFFF-impacted drinking water were predicted to break through GAC systems before both PFOS and PFOA. These model breakthrough results were used to evaluate a simplified approach to predicting PFAS removal by GAC using compound-specific retention times on a C18 column (RTC18). Overall, this study reveals that GAC systems for the treatment of AFFF-impacted sources of water for PFOA and PFOS likely

achieve poor removal, when operated only for the treatment of PFOS and PFOA, of many unmonitored PFASs of unknown toxicity.

## **3.30 Stabilization and solidification remediation of soil contaminated with poly- and perfluoroalkyl substances (PFAS)**

Mattias Sorengard, Dan B. Kleja, Lutz Ahrens, 2019

**Abstract**

Remediation methods for soils contaminated with poly- and perfluoroalkyl substances (PFASs) are urgently needed to protect the surrounding environment and drinking water source areas from pollution. In this study, the stabilization and solidification (S/S) technique was tested on aged PFAS-contaminated soil that were artificially spiked with 14 PFAS. To further reduce leaching of PFASs in S/S-treated soil, seven different additives were tested at 2% concentration: powdered activated carbon (PAC), Rembind®, pulverized zeolite, chitosan, hydrotalcite, bentonite, and calcium chloride. Standardized leaching tests on S/S-treated soil revealed that leaching of 13 out of 14 target PFASs (excluding perfluorobutane sulfonate (PFBA)) was reduced by, on average, 70% and 94% by adding PAC and Rembind®. Longer-chained PFASs such as perfluorooctane sulfonate (PFOS), which is considered persistent, bioaccumulative and toxic, were stabilized by 99.9% in all S/S treatments when PAC or Rembind® was used as an additive. The S/S stabilization efficiency depended on PFAS perfluorocarbon chain length and functional group, e.g., it increased on average by 11–15 % per CF3-moeity and was on average 49% higher for the perfluorosulfonates (PFSAs) than the perfluorocarboxylates (PFCAs). Overall, the S/S treatment with active carbon-based additives showed excellent performance in reducing leaching of PFASs, without marked loss of physical matrix stability.

## **3.31 Distribution of Perfluorinated Compounds in Lake Taihu (China): Impact to Human Health and Water Standards**

Gang Pan, Qin Zhou, Xuan Luan, and Q. Shiang Fu, 2010

**Abstract**

The distribution in water and sediment, the sources/sinks and the risk of perfluorinated compounds (PFCs) in Lake Taihu, China were investigated. The total PFCs concentration was 164 to 299 ng L-1 in water and 5.8 to 35 ng g-1 (dw) in sediment. The highest concentrations of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in water were 29.2 ng L-1 and 136 ng L-1. PFOS was largely associated with sediment, whereas short chain PFCs predominated in water. The partition coefficient (*K*d) was positively correlated with the organic carbon fraction (ƒoc) for PFOS but not for the other PFCs. The organic carbon normalized partition coefficient (*K*oc) increased by 0.51 log units for each additional CF2 moiety from perfluoro-butanesulfonate (PFBS) to PFOS. For the same chain length but different functional groups, the log *K*oc of PFOS was 1.35 units higher than PFOA. PFOS exhibited the highest affinity for sediment through the partition mechanism, and ƒoc affected the sediment as a sink of PFOS. Although there was no immediate health impact by the intake of the water alone, the consumption of aquatic products may cause potential health risks for animals/humans on the time scale of months to years. The relationship between the concentration, water-sediment distribution, bioaccumulation and toxicity should be considered in determining the water standards of PFCs.

**Notes**

* PFSAs clearly have a stronger affinity for sediments than PFCA.
* Kd and Koc values determined in this study were comparable to those reported in other research.
* Sediments act as a PFOS sink and may also buffer PFOS concentration in the water column as condition change.
* This paper, as in other research, suggested that characteristics of the sediment particles (mineral composition) and the associated aqueous phase influence PFAS partitioning. Decreasing pH and increasing salinity may enhance PFAS partitioning into solids.

## **3.33 PFC-Contaminated Soil and Its Remediation Strategies: A Review**

Yuan Yao, Tanja U. Sack, Konstantin Volchek, and Carl E. Brown, 2015

**Abstract**

This literature review summarizes the current state of knowledge on soil contamination with perfluorinated compounds (PFCs) along with information on remediation strategies. The paper discusses PFC presence, levels, sources, and fate in soil and emphasizes the current lack of feasible technologies available for PFC-contaminated soil remediation. The bulk of search into PFC remediation focuses on treatment in aqueous systems, which does not translate well to soil- or sediment-based environmental decontamination. Although evidence suggests that aqueous film-forming foams (AFFF) are composed of hundreds of diverse fluorinated surfactants, perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid seem to dominate the vast majority of studies concerning remediation techniques. Possible soil remediation techniques include excavation and landfilling, soil flushing, soil washing, chemical immobilization, encapsulation, vitrification, incineration, and in-situ oxidation have been assessed and their performance and costs have been compared. Most of the technologies, especially emerging technologies such as in-situ persulfate oxidization, need further testing to evaluate their effectiveness for PFC treatment and determine whether their full-scale application is feasible. It is believed that a complete destruction of PFCs would be the best long-term strategy and would facilitate reclamation of contaminated land for agriculture and residential use.

## **3.34 Per- and polyfluoroalkyl substances in source and treated drinking waters of the United States**

J. Scott Boone, Craig Vigo, Tripp Boone, Christian Byrne, Joseph Ferrario, Robert Benson,

Joyce Donohue, Jane Ellen Simmons, DanaW. Kolpin, Edward T. Furlong, Susan T. Glassmeyer, 2018

**Abstract**

Contaminants of emerging concern (CECs), including per- and polyfluoroalkyl substances (PFAS), are of interest to regulators, water treatment utilities, the general public and scientists. This study measured 17 PFAS in source and treated water from 25 drinking water treatment plants (DWTPs) as part of a broader study of CECs in drinking water across the United States. PFAS were quantitatively detected in all 50 samples, with summed concentrations of the 17 PFAS ranging from <1 ng/L to 1102 ng/L. The median total PFAS concentration was 21.4 ng/L in the source water and 19.5 ng/L in the treated drinking water. Comparing the total PFAS concentration in source and treated water at each location, only five locations demonstrated statistically significant differences (i.e. P<0.05) between the source and treated water. When the perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) concentrations in the treated drinking water are compared to the existing US Environmental Protection Agency's PFOA and PFOS drinking water heath advisory of 70 ng/L for each chemical or their sum one DWTP exceeded the threshold. Six of the 25 DWTPs were along two large rivers. The DWTPs within each of the river systems had specific PFAS profiles, with the three DWTPs from one river being dominated by PFOA, while three DWTPs on the second river were dominated by perfluorobutyric acid (PFBA).

**Notes**

* PFAS detection frequencies in this study were higher than in third monitoring round conduct under the federal unregulated contaminant monitoring rule (UCMR).
* Only 5 of 25 DWTPs showed a significant reduction in PFAS between source water and treated drinking water.
* GAC may provide some removal of long-chain PFAS. GAC removal efficiency is best correlated to frequency of GAC replacement.

## **3.35 Fate and Effects of Poly- and Perfluoroalkyl Substances in the Aquatic Environment: A Review**

Lutz Ahrens and Micro Bundschuh, 2014

**Abstract**

Polyfluoroalkyl and perfluoroalkyl substances (PFASs) are distributed ubiquitously in the aquatic environment, which raises concern for the flora and fauna in hydrosystems. The present critical review focuses on the fate and adverse effects of PFASs in the aquatic environment. The PFASs are continuously emitted into the environment from point and nonpoint sources such as sewage treatment plants and atmospheric deposition, respectively. Although concentrations of single substances may be too low to cause adverse effects, their mixtures can be of significant environmental concern. The production of C8 based PFASs (i.e., perfluorooctane sulfonate [PFOS] and perfluorooctanoate [PFOA]) is largely phased out; however, the emissions of other PFASs, in particular short-chain PFASs and PFAS precursors, are increasing. The PFAS precursors can finally degrade to persistent degradation products, which are, in particular, perfluoroalkane sulfonates (PFSAs) and perfluoroalkyl carboxylates (PFCAs). In the environment, PFSAs and PFCAs are subject to partitioning processes, whereby short-chain PFSAs and PFCAs are mainly distributed in the water phase, whereas long-chain PFSAs and PFCAs tend to bind to particles and have a substantial bioaccumulation potential. However, there are fundamental knowledge gaps about the interactive toxicity of PFAS precursors and their persistent degradation products but also interactions with other natural and anthropogenic stressors. Moreover, because of the continuous emission of PFASs, further information about their ecotoxicological potential among multiple generations, species interactions, and mixture toxicity seems fundamental to reliably assess the risks for PFASs to affect ecosystem structure and function in the aquatic environment.

**Notes**

* This paper discusses our current understanding of the introduction, transportation, partitioning, and transformation of PFAS in aquatic ecosystems.
* The paper also looks at exposure, bioaccumulation and toxicity of PFAS in aquatic organisms.
* Finally, the paper identifies knowledge gaps regarding ecotoxicology.
* The overall conclusion of the paper seems to be that there is currently insufficient knowledge to judge the impacts of PFAS on aquatic ecosystems.

## **3.36 Half-lives of PFOS, PFHxS and PFOA after end of exposure to contaminated drinking water**

Ying Li, Tony Fletcher, Daniel Mucs, Kristin Scott, Christian H Lindh, Pia Tallving,

Kristina Jakobsson, 2017

**Abstract**

**Background:** Municipal drinking water contaminated with perfluorinated alkyl acids had been distributed to one-third of households in Ronneby, Sweden. The source was firefighting foam used in a nearby airfield since the mid-1980s. Clean water was provided from 16 December 2013.

**Objective:** To determine the rates of decline in serum perfluorohexane sulfonate (PFHxS), perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA), and their corresponding half-lives.

**Methods:** Up to seven blood samples were collected between June 2014 and September 2016 from 106

participants (age 4–84 years, 53% female).

**Results:** Median initial serum concentrations were PFHxS, 277 ng/mL (range 12–1660); PFOS, 345 ng/mL

(range 24–1500); and PFOA, 18 ng/mL (range 2.4–92). The covariate-adjusted average rates of decrease in serum were PFHxS, 13% per year (95% CI 12% to 15%); PFOS, 20% per year (95% CI 19% to 22%); and PFOA, 26% per year (95% CI 24% to 28%). The observed data are consistent with a first-order elimination model. The mean estimated half-life was 5.3 years (95% CI 4.6 to 6.0) for PFHxS, 3.4 years (95% CI 3.1 to 3.7) for PFOS and 2.7 years (95% CI 2.5 to 2.9) for PFOA. The interindividual variation of half-life was around threefold when comparing the 5th and 95th percentiles. There was a marked sex difference with more rapid elimination in women for PFHxS and PFOS, but only marginally for PFOA.

**Conclusions:** The estimated half-life for PFHxS was considerably longer than for PFOS and PFOA. For PFHxS and PFOS, the average half-life is shorter than the previously published estimates. For PFOA the half-life is in line with the range of published estimates.

## **3.37 Perfluorinated Chemicals in Surface Waters and Sediments from Northwest Georgia, USA, and Their Bioaccumulation in *Lumbriculus variegatus***

Peter J. Lasier, John W. Washington, Sayad M. Hassan and Thomas M. Jenkins, 2011

**Abstract**

Concentrations of perfluorinated chemicals (PFCs) were measured in surface waters and sediments from the Coosa River watershed in northwest Georgia, USA, to examine their distribution downstream of a suspected source. Samples from eight sites were analyzed using liquid chromatography-tandem mass spectrometry. Sediments were also used in 28-d exposures with the aquatic oligochaete, Lumbriculus variegatus, to assess PFC bioaccumulation. Concentrations of PFCs in surface waters and sediments increased significantly below a land-application site (LAS) of municipal/industrial wastewater and were further elevated by unknown sources downstream. Perfluorinated carboxylic acids (PFCAs) with eight or fewer carbons were the most prominent in surface waters. Those with 10 or more carbons predominated sediment and tissue samples. Perfluorooctane sulfonate (PFOS) was the major homolog in contaminated sediments and tissues. This pattern among sediment PFC concentrations was consistent among sites and reflected homolog concentrations emanating from the LAS. Concentrations of PFCs in oligochaete tissues revealed patterns similar to those observed in the respective sediments. The tendency to bioaccumulate increased with PFCA chain length and the presence of the sulfonate moiety.

Biota-sediment accumulation factors indicated that short-chain PFCAs with fewer than seven carbons may be environmentally benign alternatives in aquatic ecosystems; however, sulfonates with four to seven carbons may be as likely to bioaccumulate as PFOS.

**Notes**

* This study reinforces the concept that wastewater effluents and residuals from POTWs impacted by PFAS industrial discharges can be a significant point-sources for PFAS release to the environment.
* Partitioning of PFAS between surface water, sediment, and aquatic worm tissue showed that Perfluorinated carboxylic acids (PFCAs) with eight or fewer carbons were the most prominent in surface waters and that those with 10 or more predominated sediment and worm tissue.
* As demonstrated in other research the propensity to bioaccumulate increased with carbon chain length and the presence of the sulfonate functional group.
* Concentration of PFAS in worm tissue reflected concentrations in surrounding sediments.
* Short-chain PFCAs (<C6) may be preferable to longer-chain PFCA in terms of retention in the environment and bioaccumulation, but short-chained perfluorinated sulfonic acids (PFSA) were similar to PFOS in their tendency to bioaccumulate.

## **3.38 Per- and Polyfluoroalkyl Substances in Landfill Leachate: Patterns, Time Trends, and Sources**

Jonathan P. Benskin, Belinda Li, Michael G. Ikonomou, John R. Grace, and Loretta Y. Li, 2012

**Abstract**

Concentrations and isomer profiles for 24 per- and polyfluoroalkyl substances (PFASs) were monitored over 5 months (February−June, 2010) in municipal landfill leachate. These data were used to assess the role of perfluoroalkyl acid (PFAA) precursor degradation on changes in PFAA concentrations over time. The influence of total organic carbon, total suspended solids, pH, electrical conductivity (EC), leachate flow rates, and meteorological data (precipitation, air temperature) on leachate PFAS concentrations

was also investigated. Perfluoropentanoate and perfluorohexanoate were typically the dominant PFASs in leachate, except for March−April, when concentrations of perfluorooctane sulfonate, perfluorooctanoate, and numerous PFAA-precursors (i.e., (N-alkyl) perfluorooctane sulfonamides and fluorotelomer carboxylic acids) increased by a factor of 2−10 (∼4 μg/L to ∼36 μg/L ΣPFASs). During this time, isomer profiles of PFOA became increasingly dominated by the linear isomer, likely from transformation of linear, telomer-manufactured precursors. While ΣPFAA-precursors accounted for up to 71% of ΣPFASs (molar basis) in leachate from this site, leachate from a second landfill displayed only low concentrations of precursors (<1% of ΣPFASs). Overall, degradation of PFAA-precursors and changes in leachate pH, EC, and 24-h precipitation were important factors controlling PFAS occurrence in leachate. Finally, 8.5−25 kg/yr (mean 16 kg/yr) of ΣPFASs was estimated to leave the landfill via leachate for subsequent treatment at a wastewater treatment plant.

**Notes**

* Some of the factors (i.e. pH and ionic concentrations) controlling PFAS mobility in the soil also seems to apply in landfills.
* This paper also suggests that landfill leachate can be a significant sources of PFAS for POTWs accepting leachate for treatment.

1. **Plant/Animal Uptake**

## **4.1 Absorption and Excretion of 14C-Perfluorooctanoic Acid (PFOA) in Angus Cattle (*Bos taurus*)**

Sara J. Lupton, Janice K. Huwe, David J. Smith, Kerry L. Dearfield, and John J. Johnston, Published: December 22, 2011

**Abstract**

Perfluoroalkyl substances (PFASs), such as perfluorooctanoic acid (PFOA), are environmentally persistent industrial chemicals often found in biosolids. Application of these biosolids to pastures raises concern about the accumulation of PFOA in the edible tissues of food animals. Because data on the absorption, distribution, metabolism, and excretion (ADME) of PFOA in cattle were unavailable, a study was conducted to determine pharmacokinetic parameters following a single oral exposure (1 mg/kg body weight of 14C-PFOA) in four Lowline Angus steers. Radiocarbon was quantified in blood, urine, and feces for 28 days and in tissues at the time of slaughter (28 days) by liquid scintillation counting (LSC) or by combustion analysis with LSC with confirmation by liquid chromatography−tandem mass spectrometry (LC-MS/MS). 14C-PFOA was completely absorbed and excreted (100.7 ± 3.3% recovery) in the urine within 9 days of dosing. The plasma elimination half-life was 19.2 ±3.3 h. No 14C-PFOA-derived radioactivity was detected in edible tissues. Although PFOA was rapidly absorbed, it was also rapidly excreted by steers and did not persist in edible tissues, suggesting meat from cattle exposed to an acute dose of PFOA is unlikely to be a major source of exposure to humans. (Lupton et al., 2011)

## **4.2 Absorption, Distribution, and Milk Secretion of the Perfluoroalkyl Acids PFBS, PFHxS, PFOS, and PFOA by Dairy Cows Fed Naturally Contaminated Feed**

Janine Kowalczyk, Susan Ehlers, Anja Oberhausen, Marion Tischer, Peter Furst, Helmut Schafft, and Monika Lahrssen-Wiederholt, Published: February 27, 2013

**Abstract**

The transfer of the perfluoroalkyl acids (PFAAs) perfluorobutanesulfonate (PFBS), perfluorohexanesulfonate (PFHxS), perfluorooctanesulfonate (PFOS), and perfluorooctanoate (PFOA) from feed into tissue and milk of dairy cows was investigated. Holstein cows (n = 6) were fed a PFAA-contaminated feed for 28 days. After the PFAA-feeding period, three cows were slaughtered while the others were fed PFAA-free feed for another 21 days (depuration period). For PFAA analysis plasma, liver, kidney, and muscle tissue, urine, and milk were sampled and analyzed using high-performance liquid chromatography (HPLC) with tandem mass spectrometry (MS/MS). The average daily intake of dairy cows was 3.4 ± 0.7, 4.6 ± 1.0, 7.6 ± 3.7 and 2.0 ± 1.2 μg/kg body weight (bw) for PFBS, PFHxS, PFOS, and PFOA, respectively. Overall, PFBS, PFHxS, PFOS, and PFOA showed different kinetics in dairy cows. In plasma, concentrations of PFBS (mean = 1.2 ± 0.8 μg/L) and PFOA (mean = 8.5 ± 5.7 μg/L) were low, whereas PFHxS and PFOS continuously increased during the PFAA-feeding period up to maximal concentrations of 419 ± 172 and 1903 ± 525 μg/L, respectively. PFOS in plasma remained constantly high during the depuration period. PFOS levels were highest in liver, followed by kidney, without significant differences between feeding periods. The highest PFHxS levels were detected in liver and kidney of cows slaughtered on day 29 (61 ± 24 and 98 ± 31 μg/kg wet weight (ww)). The lowest PFAA levels were detected in muscle tissue. At the end of the feeding study, cumulative secretion in milk was determined for PFOS (14 ± 3.6%) and PFHxS (2.5 ± 0.2%). The other two chemicals were barely secreted into milk: PFBS (0.01 ± 0.02%) and PFOA (0.1 ± 0.06%). Overall, the kinetics of PFOA were similar to those of PFBS and substantially differed from those of PFHxS and PFOS. The very low concentration of PFBS in plasma and milk, the relatively high urinary excretion, and only traces of PFBS in liver (0.3 ± 0.3 μg/kg ww) and kidney (1.0 ± 0.3 μg/kg ww) support the conclusion that PFBS does not accumulate in the body of dairy cows. (Kowalczyk et al., 2013)

## **4.3 Biochemical Responses and Accumulation Properties of Long-Chain Perfluorinated Compounds (PFOS/PFDA/PFOA) in Juvenile Chickens (*Gallus gallus*)**

Leo W. Y. Yeung, Eva I. H. Loi, Vicky Y. Y. Wong, Keerthi S. Guruge, Noriko Yamanaka, Nobuhiko Tanimura, Jun Hasegawa, Nobuyoshi Yamashita, Shigeru Miyazaki, and Paul K. S. Lam

Published online: January 8, 2009

**Abstract**

One-day-old male chickens were exposed via oral gavage to mixtures of perfluorooctane sulfonate (PFOS), perfluorooctanoate (PFOA), and perfluorodecanoate (PFDA) at either a low dose (0.1 mg/kg body weight [b.w.]) or a high dose (1.0 mg/kg b.w.), or a saline/ethanol vehicle control, three times a week for 3 weeks. After 3 weeks of exposure, half of the chicks were sacrificed and the other half were allowed to depurate for a further 3 weeks. No dose-dependent statistically significant differences in body/organ weights were observed among treatment and control groups after 3 weeks of exposure or after three 3 of depuration. Neither 15 histological nor 14 measured plasma biochemical parameters were significantly different in chicks from the exposed groups and vehicle controls. PFOS, PFDA, and PFOA concentrations in blood/liver/kidney samples were measured throughout the exposure and depuration periods at different time intervals. PFOS and PFDA accumulated at much higher concentrations than PFOA during the experimental periods. Interestingly, PFOS and PFDA accumulation patterns in the blood were similar during the exposure and depuration periods. The half-lives for each PFC at the 0.1 and 1.0 mg/ kg doses were, respectively, approximately 15 and 17 days for PFOS, 11 and 16 days for PFDA, and 3.9 and 3.9 days for PFOA. PFDA accumulation in organs was greater than or similar to that of PFOS: the liver was the main target during exposure and the blood was the main reservoir during depuration. These results indicate that exposure to a 1.0-mg mixture of PFOS/PFDA/PFOA/kg b.w. has no adverse effect on juvenile chickens. (Yeung et al. 2009)

## **4.4 Comparative tissue and body compartment accumulation and maternal transfer to eggs of perfluoroalkyl sulfonates and carboxylates in Great Lakes herring gulls**

Wouter A. Gebbink, and Robert J. Letcher, October 12, 2011

**Abstract**

The comparative accumulation of C4-C15 perfluorinated sulfonates (PFSAs) and carboxylates (PFCAs), and several precursors (e.g., perfluorooctane sulfonamide, N-methyl-FOSA, and fluorotelomer unsaturated acids and alcohols) was examined in tissues (liver, brain, muscle, and adipose), plasma/red blood cells (RBCs) and whole egg clutches (yolk and albumen) of female herring gulls collected in 2010 from Chantry Island, Lake Huron of the Laurentian Great Lakes. Highest mean ∑PFSA concentrations were in yolk, followed by adipose, liver, plasma, muscle, RBCs, and brain. Highest mean ∑PFCA concentrations were in yolk, followed by brain, plasma, liver, RBC, adipose and muscle. PFOS accounted for >88% of ∑PFSA in all samples; the liver, plasma/RBCs, muscle and adipose PFCA patterns were dominated by C8-C11 PFCAs, whereas C10-C15 PFCAs in brain and yolk. Among PFSAs and PFCAs there is tissue-specific accumulation, which could be due to a number of pharmacokinetic processes. (Gebbink and Letcher, 2011)

## **4.5 Depuration kinetics and tissue disposition of PFOA and PFOS in white leghorn chickens (*Gallus gallus*) administered by subcutaneous implantation**

Hoon Yoo, Keerthi S. Guruge, Noriko Yamanaka, Chihiro Sato, Osamu Mikami, Shigeru Miyazaki, Nobuyoshi Yamashita, and John P. Giesy, online November 19, 2007

**Abstract**

Elimination kinetics and tissue disposition of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate (PFOS) in male chickens (Gallus gallus) was determined following exposure by subcutaneous implantation. Chickens were exposed to two levels of PFOA or PFOS for 4 wk and then allowed to depurate for an additional 4 wk. These exposures did not cause any statistically significant changes in body index, clinical biochemistry or histology among treatments relative to the controls (p>0.05), except that concentrations of total cholesterol and phospholipids were less in chickens exposed to PFOS. The elimination rate constant for PFOA (0.150±0.010 d-1) was approximately six-fold greater than that of PFOS (0.023±0.004 d-1). The greatest concentrations of PFOA and PFOS were found in kidney and liver, respectively. The organ to blood ratio of PFOS concentration was increased after the whole experiment, indicating the importance of organ partitioning of PFOS in elimination kinetics. The depuration half-life of PFOA (t1/2 =4.6 d) and PFOS (t1/2=125 d) in chickens was calculated. (Yoo et al., 2007)

## **4.6 Transfer of Perfluorooctanoic Acid (PFOA) and Perfluorooctane Sulfonate (PFOS) From Contaminated Feed Into Milk and Meat of Sheep: Pilot Study**

Janine Kowalczyk, Susan Ehlers, Peter Furst, Helmut Schafft, and Monika Lahrssen-Wiederholt, Published online: March 28, 2012

**Abstract**

A pilot study was performed with dairy sheep to generate the first data on the transfer of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) from feed into food of animal origin. Corn silage was cultivated on cropland in Lower Saxony in Germany where, as a result of illegal waste disposal in 2006, farmland was contaminated with perfluorinated alkylacids (PFAAs). Two sheep were exposed by way of PFAA-contaminated corn silage to PFOS (1.16 and 1.45 ug/kg body weight [bw]/d, respectively) and PFOA (0.43 and 0.53 ug/kgbw/d) during a period of 21 days. During the PFAA-feeding period, PFOS levels in plasma increased continuously to maximum concentration of 103 and 240 lg/L for sheep 1 and sheep 2, respectively. The PFOA plasma concentration remained low (sheep 1 = 3.3 ± 2.2 ug/L; sheep 2 = 15.6 ± 8.3 ug/L). Data indicate that urinary excretion is the primary clearance route for PFOA (sheep 1 = 51 %; sheep 2 = 55 %), whereas PFOS excretion by way of urine could not be quantified. The highest PFOS excretion (4 to 5 %) was detected in faeces. PFOS was also excreted at higher levels than PFOA by way of milk. During a period of 21 days, a total PFOS transfer into milk ≤2 % was calculated. Overall, total excretion of PFOS was significantly lower compared with that of PFOA (PFOS 6 %; PFOA 53 to 56 %). PFOS levels in sheep 1 and sheep 2 were highest in liver (885 and 1,172 ug/kg weight wet [ww], respectively) and lowest in muscle tissue (24.4 and 35.1 ug/kg ww, respectively). PFOA levels in muscle tissue were low for sheep 2 (0.23 ug/kg ww) and not detectable after the PFAA free feeding period in sheep 1. A slight background load of PFOS in liver (1.5 µg/kg ww) and kidney (0.3 ug/kg ww) was detected in sheep 3 (control). (Kowalczyk et al., 2010)

## **4.7 Analysis of PFOS, FOSA and PFOA From Various Food Matrices Using HPLC Electrospray Mass Spectrometry**

Karen Smith, June 21, 2001

The Multi-City Study was originally designed by Battelle Memorial Institute (Columbus,

OH), to obtain preliminary data about the presence of fluorochemicals in foods and in

drinking water to understand the potential sources of human exposure. The Multi-City

Study paired each of three cities having manufacturing or commercial use of

fluorochemical products (test cities) with three cities that do not (control cities).

Information on residues in selected foods was obtained from analyses of food samples

collected in a market basket study. The market basket sampling of the original Multi-

City Study design was implemented by Pace Analytical Services, Inc., Minneapolis, MN.

The samples were analyzed for PFOS, PFOA, and FOSA by Centre Analytical

Laboratories, Inc., State College, PA.

The distributions of the PFOS, PFOA, and FOSA residue data by food and city category

reveal similar patterns of residue concentrations in the control and test cities for each type

of food. A total of 12 samples were found to contain levels of fluorochemical residues

above the limit of quantification. Of the 12 samples with measurable fluorochemical

residue levels, eight were samples collected in test cities.

Measurable quantities of PFOS were found in five samples: four whole milk samples

(three from test cities) and a ground beef sample (test city). PFOS residues found in the

foods ranged from non-quantifiable levels to 0.852 ng/g.

Measurable quantities of PFOA were found in seven samples: two ground beef samples

(neither from test cities); two bread samples (one from a test city); two apple samples

(both from test cities); and one green bean sample (from a test city). PFOA residue levels

ranged from non-quantifiable levels to 2.35 ng/g. A value of 14.7 ng/g was found for

PFOA in a bread sample from a control city, but was considered “suspect” by Centre Analytical.

## **4.8 Perfluorinated alkylated substances in vegetables collected in four European countries; occurrence and human exposure estimations**

Dorte Herzke, Sandra Huber, Lieven Bervoets, Wendy D’Hollander, Jana Hajslova, Jana Pulkrabova, Gianfranco Brambilla, Stefania Paola De Filippis, Stefanie Klenow, Gerhard Heinemeyer, and Pim de Voogt, Published online: May 19, 2013

**Abstract**

The human diet is recognised as one possible major exposure route to the overall perfluorinated alkylated substances (PFAS) burden of the human population, resulting directly from contamination of dietary food items, as well as migration of PFAS from food packaging or cookware. Most European countries carry out national monitoring programs (food basket studies) to monitor contamination with pollutants. Usually, for PFASs, non-coordinated approaches are used in Europe, since food basket studies are mainly carried out by national authorities following national requirements and questions, making comparisons between different countries difficult. A harmonised sampling campaign collecting similar food items in a uniform procedure enabling direct comparison between different regions in Europe was designed. We selected four countries (Belgium, Czech Republic, Italy and Norway), representing the four regions of Europe: West, East, South and North. In spring 2010 and 2011, 20 different types of vegetables were sampled in Belgium, Czech Republic, Italy and Norway. Perfluorinated carboxylic acids (PFCAs) were the main group of detected PFASs, with perfluorinated octanoic acid (PFOA) as the most abundant PFCA (with exception of samples from Czech Republic), followed by perfluorinated hexanoic acid and perfluorinated nonanoic acid. Dietary intake estimates for PFOA show only low human exposure due to vegetable consumption for adults and children, mostly governed by high intake of potatoes.

## **4.9 Perfluorinated Compounds in Greenhouse and Open Agricultural Producing Areas of Three Provinces of China: Levels, Sources and Risk Assessment**

Yanwei Zhang, Dongfei Tan, Yue Geng, Lu Wang, Yi Peng, Zeying He, Yaping Xu

and Xiaowei Liu,Published: December 10, 2016

**Abstract**

Field investigations on perfluoroalkyl acid (PFAA) levels in various environmental matrixes were reported, but there is still a lack of PFAA level data for agricultural environments, especially agricultural producing areas, so we collected soil, irrigation water and agricultural product samples from agricultural producing areas in the provinces of Liaoning, Shandong and Sichuan in China. The background pollution from instruments was removed and C4–C18 PFAAs were detected by LC-MS/MS. The concentrations of PFAAs in the top and deep layers of soil were compared, and the levels of PFAAs in different agricultural environments (greenhouses and open agriculture) were analyzed. We found the order of PFAA levels by province was Shandong > Liaoning > Sichuan. A descending trend of PFAA levels from top to deep soil and open to greenhouse agriculture was shown and perfluorobutanoic acid (PFBA) was considered as a marker for source analysis. Bean vegetables contribute highly to the overall PFAA load in vegetables. A significant correlation was shown between irrigation water and agricultural products. The EDI (estimated daily intake) from vegetables should be of concern in China.

## **4.10 Carryover of Perfluorooctanoic Acid (PFOA) and Perfluorooctane Sulfonate (PFOS) from Soil to Plants**

T. Stahl, J. Heyn, H. Thiele, J. Huther, K. Failing, S. Georgii, and H. Brunn, published online Dec. 27, 2008

**Abstract**

Within the scope of a joint project to study soil-to-plant carryover of polyfluorinated compounds (PFCs), five cultivated plants (spring wheat, oats, potatoes, maize, and perennial ryegrass) were sown or planted in Mitscherlich pots. Six variants per species were used, each with a different concentration level of PFOA and PFOS (from 0.25 to 50 mg/kg as aqueous solution) to detect possible concentration dependence in the transfer of these two PFCs from soil to plant. PFOA and PFOS were detected by liquid chromatography-tandem mass spectrometry after appropriate sample preparation (partial drying, mincing, homogenizing, extraction). Since PFOA and PFOS presently represent the most widely studied PFCs, they are classified as ‘‘leading compounds.’’ The results show that concentrations of PFOA/PFOS in the plants vary greatly, depending on the concentrations applied to the soil. PFOA values were higher than PFOS values in all plants except potatoes, in which these differences could be quite substantial. From the results presented here it can be seen that uptake and storage are much more intensive in the vegetative portion of the plant than relocation in the storage organs. This is particularly evident from the comparison of concentrations found in the grain and ear and those in the straw or rest of the plant in spring wheat, oats, and maize. Transfer from ‘‘soil to crops’’ provides a possible explanation for the presence of PFCs in foodstuffs and in human body fluids such as blood, plasma, serum, or breast milk. The aim of the present study was to determine whether a statistically significant, concentration- dependent carryover of PFOA and PFOS in crop plants can take place, which would provide a potential entrance point for these substances into the food chain.

## **4.11 Perfluoroalkyl acid distribution in various plant compartments of edible crops grown in biosolids-amended soils**

Blaine, A., C. Rich, E. Sedlacko, L. Hundal, K. Kumar, C. Lau, Marc A. Mills, Kimberly M. Harris, AND C. Higgins. Perfluoroalkyl acid distribution in various plant compartments of edible crops grown in biosolids-amended soils. ENVIRONMENTAL SCIENCE & TECHNOLOGY. American Chemical Society, Washington, DC, 48(14):7858-65, (2014).

**Description**

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.

## **4.12 Perfluoroalkyl Acid Uptake in Lettuce (Lactuca sativa) and Strawberry (Fragaria ananassa) Irrigated with Reclaimed Water**

Andrea C. Blaine, Courtney D. Rich, Erin M. Sedlacko, Katherine C. Hyland, Cecil Stushnoff, Eric R. V. Dickenson, and Christopher P. Higgins, Published: November 11, 2014 (cited as 2014A)

**Abstract**

Using reclaimed water to irrigate food crops presents an exposure pathway for persistent organic contaminants such as perfluoroalkyl acids (PFAAs) to enter the human food chain. This greenhouse study used reclaimed water augmented with varying concentrations (0.2−40 μg/L) of PFAAs, including perfluorocarboxylates (C3F7COO− to C8F17COO−) and perfluorosulfonates (C4F9SO2O−, C6F13SO2O−, C8F17SO2O-), to investigate potential uptake and concentration−response trends in lettuce (Lactuca sativa) and strawberry (Fragaria ananassa). In addition, studies were conducted to evaluate the role of soil organic carbon concentrations on plant uptake of PFAAs. PFAA concentrations in lettuce leaves and strawberry fruit were measured for each aqueous PFAA concentration applied. PFAA plant concentrations increased linearly with the aqueous concentration for all PFAAs, with PFCAs bioaccumulating to a greater degree than PFSAs in the edible portions of the tested plants. Chain-length-dependency trends were evident in both lettuce shoot and strawberry fruit, with decreasing concentrations associated with increasing chain length. Perfluorobutanoate (PFBA) and perfluoropentanoate (PFPeA), both short-chain PFAAs (<8 carbon chain length), accumulated

the most compared with other PFAAs tested in the edible parts of both lettuce and strawberry. PFAA concentrations in strawberry root and shoot were also measured at selected PFAA aqueous concentrations (0.4, 4, and 40 μg/L). Short-chain perfluorocarboxylates were the dominant fraction in the strawberry fruit and shoot compartments, whereas a more even distribution of all PFAAs appeared in the root compartment. Lettuce grown in soils with varying organic carbon contents (0.4%, 2%, 6%) was used to assess the impact of organic carbon sorption on PFAA bioaccumulation. The lettuce grown in soil with the 6% organic carbon content had the lowest bioaccumulation of PFAAs. Bioaccumulation factors for lettuce were correlated to carbon chain length of PFAAs, showing approximately a 0.4 to 0.6 log decrease per CF2 group. This study confirms that PFAAs can enter and bioaccumulate in food crops irrigated with reclaimed water. Bioaccumulation potential depends on analyte functional group and chain length, concentration in the reclaimed water, and organic carbon content of the soil.

## **4.13 Uptake of Perfluoroalkyl Acids into Edible Crops via Land Applied Biosolids: Field and Greenhouse Studies**

Andrea C. Blaine, Courtney D. Rich, Lakhwinder S. Hundal, Christopher Lau, Marc A. Mills, Kimberly M. Harris, and Christopher P. Higgins, Published: November 8, 2013

**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.

## **4.14 The roles of protein and lipid in the accumulation and distribution of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in plants grown in biosolids-amended soils**

Bei Wen, Yali Wu, Hongna Zhang, Yu Liu, Xiaoyu Hu, Honglin Huang,

Shuzhen Zhang, Available online 2 July 2016

**Abstract**

The roles of protein and lipid in the accumulation and distribution of perfluorooctane sulfonate (PFOS)

and perfluorooctanoate (PFOA) in seven species of plants from biosolids-amended soils were investigated. The PFOS and PFOA root concentration factors (Croot/Csoil) ranged from 1.37 to 4.68 and 1.69 to 10.3 (ng/groot)/(ng/gsoil), respectively, while the translocation factors (Cshoot/Croot) ranged from 0.055 to 0.16 and 0.093 to 1.8 (ng/gshoot)/(ng/groot), respectively. The PFOS and PFOA accumulations in roots correlated positively with root protein contents (P < 0.05), while negatively with root lipid contents (P < 0.05). These suggested the promotion effects of protein and inhibition effects of lipid on root uptake. The translocation factors correlated positively with the ratios between protein contents in shoots to those in roots (P < 0.05), showing the importance of protein on PFOS and PFOA translocation. This study is the first to reveal the different roles of protein and lipid in the accumulation and distribution of PFOS and PFOA in plants.

## **4.15 State of the science and meta-analysis of crop uptake of per- and polyfluoroalkyl substances (PFAS)**

Angela L. Perez, Cayla Poteete, Fian Louie, Lindsey Garner, and Paul K. Scott, August 21, 2017

Exposures to PFASs through the consumption of vegetables has been hypothesized to be a non-negligible source of PFASs intake (Herzke et al. 2013; Domingo 2012; Halldorsson et al. 2012; Braun et al. 2016; Vieira et al. 2013). Agricultural soil PFAS input sources may vary, but are generally thought to originate from biosolids (Lu et al. 2012), aerial deposition (Stemmler and Lammel 2010; Wallington et al. 2006; Paustenbach et al. 2006), and irrigation water (Blaine et al. 2014). Crop uptake of PFASs has been reported in corn, wheat, potato, oats, carrots, and cucumbers that were grown in PFASs-spiked soils (Blaine et al. 2013; Stahl et al. 2009; Lechner and Knapp 2011; Yoo et al. 2011). Yoo et al. reported a transfer of PFASs to grass from industrially contaminated biosolid- amended soils (Yoo et al. 2011). To our knowledge, there are no published reports of crop uptake of PFASs using municipal biosolids with detected PFAS.

**Results and discussion**

We captured over 140 data points, of which approximately 50% were comprised of human edible plants or crops intended for livestock consumption. Over 85% of all data points were for either shoots (e.g. celery shoot, wheat shoot) or aerial plant components (e.g. Bermuda grass, corn grain, corn stover, Kentucky blue grass, lettuce leaves, maize kernel, maize straw, maize ears, oat grain, oat straw, pea fruit, perennial wheatgrass, pumpkin stalk, pumpkin flower, pumpkin leaf, pumpkin fruit, tall fescue, tomato fruit, wheat grain, and wheat straw). The remainder were components below ground surface (e.g. potato tuber, potato peel, radish root, pumpkin root, wheat root). Bioaccumulation factors (BAFs), defined as the PFAS concentration in plant divided by the PFAS concentration in soil, for the current data set ranged from 0 to 6.20 for PFOA and 0 to 0.98 for PFOS.

Limited data were available for other, shorter carbon chain PFASs, with the exception of PFHxA (perfluorohexanoic acid and PFHxS (perfluorohexanesulfonic acid). BAF for PFHxA and PFHxS ranged from 0.12 - >10.0 (median 2.47) and 0.006 to 2.9 (median 0.40), respectively. PFHxS has an elimination half-life in humans of several years and has been widely detected in serum samples in the United States and Australia (Calafat et al. 2007; Kärrman et al. 2006). Across all PFASs of variable carbon chain length, serum concentrations of many PFAS have decreased since 2000; however, PFNA (perfluorononanoic acid) serum concentrations have inexplicably increased (Anderson et al. 2008). No studies were located that reported plant concentrations of PFNA or BAFs.

Our analyses showed that PFASs accumulate in crops for human or livestock consumption. However, the BAFs represent a wide range that does not seem to follow a linear dose response. Field site- and chemical-specific physico-chemical factors undoubtedly play a large role in the resulting BAFs. Collectively, these results indicate that the long-term use of PFAS-containing irrigation or biosolids as a soil amendment may result in human intake of PFASs through consumption of crops or consumption of meat or milk fed to livestock who consumes these crops. Further studies will investigate the implications for human health risk as a result of consuming crops, meat, or milk that contain PFASs.

## **4.16 How Reliable Are Field-Derived Biomagnification Factors and Trophic Magnification Factors as Indicators of Bioaccumulation Potential? Conclusions from a Case Study on Per- and Polyfluoroalkyl Substances**

J. Franklin, 2015

**Abstract**

This review examines the usefulness of the metrics BMF (biomagnification factor) and TMF (trophic magnification factor), derived from field measurements of the levels of contaminants in naturally occurring biota, for characterizing the bioaccumulation potential (“B”) of chemicals. Trophic magnification factor and BMF values greater than 1.0 are often considered to be the most conclusive indicators of B status, and the TMF criterion has been referred to as the “gold standard” for B categorization. Although not wishing to dispute the theoretical primacy of field-derived BMFs and TMFs as B metrics, we make the case that, in practice, the study-to-study (and even within-study) variability of the results is so great that they are of very restricted usefulness for assessing B status, at least in the case of the per- and polyfluoroalkyl substances (PFASs), on which we focus here. This conclusion is based on an analysis of the results of 24 peer-reviewed studies reporting field-derived BMFs or TMFs for 14 PFASs, for which BMF values often range over several orders of magnitude from <<1.0 to >>1.0,

sometimes even in the same study. For TMFs, the range is a factor of approximately 20 for the most intensely studied PFASs (perfluorooctanoic acid [PFOA] and perfluorooctanesulfonic acid [PFOS]).We analyze the possible causes for such variability: To some extent it results from the differing ways in which the metrics are expressed, but most of the scatter is likely attributable to such factors as nonachievement of the tacitly assumed steady-state conditions, uncertainties in the feeding

ecology, the impact of metabolism of precursor compounds, and so forth. As more trustworthy alternatives to field-derived BMFs and TMFs, we suggest the implementation of dietary BMF studies performed under strictly controlled conditions on aquatic, terrestrial, and avian species, as well as the consideration of measured elimination half-lives, which have been demonstrated to be directly related to BMF values.

**Notes**

* Does this make the studies of plant and animal uptake less reliable?
* Table 2 shows how variable field determination of biomagnification factors (BMF=[X]predator/[X]prey) is.
* Factors that lead to variability are of two types: 1) definitional variations for BMF and TMF, and 2) factors related to the organism studied and the subject chemical (pg. 12)
* The BMF definition assumes a steady-state concentration has been achieved in the organisms studied. This assumption is frequently erroneous and almost impossible to verify (pg. 14).
* Poorly understood or misinterpreted feeding ecology can also lead to variability in the BMF calculation. Example: Not accounting for bears eating human garbage containing PFAS compounds.
* Other possible sources of error include contaminant variability based on age, sex, or size as well as other biological or ecological factor, metabolism of precursors, variations in BMF with trophic level

## **4.17 Uptake of per- and polyfluoroalkyl substances by plants**

Laura Gobelius, 2016

**Abstract**

The extensive use of per- and polyfluoroalkyl substances (PFASs) as surfactants in, for example textiles,

cookware and aqueous firefighting foams (AFFFs) during the last decades has resulted in widespread

environmental contamination. Due to the persistent and bioaccumulative characteristics of PFASs, they

are ubiquitously found in the environment, wildlife and humans. Currently, the knowledge of remediation techniques for environments contaminated with PFASs is limited. Therefore, this study aims at evaluating the potential of plant uptake of 26 different PFASs from contaminated soils and groundwater. Arlanda airport, Sweden’s biggest airport, has a fire training facility that is suffering from severe PFAS contamination due to former regular practices with PFAS-containing AFFFs for safety purposes. Samples from different plant species, namely silver birch (*Betula pendula*), Norway spruce (*Picea abies*), bird cherry (*Prunus padus*), mountain ash (*Sorbus aucuparia*), ground elder (*Aegopodium podagraria*), long beechfern (*Phegopteris connectilis*) and wild strawberry (*Fragaria vesca*), surface soil and groundwater were taken near the fire training site to assess the accumulation potential and eligibility of selected plants for phytoremediation. In comparison to typical background levels, elevated ΣPFAS levels were detected in soil and groundwater ranging from 16-156 ng g-1 dry weight (dw) and 1,200 and 34,000 ng L-1, respectively. The plants showed a high variability of concentrations with highest ΣPFAS concentrations in vegetative compartments, particularly the foliage. Birch leaves exceeded all other sampled tissues and species with a maximum of ΣPFAS 327 ng g-1 dw, followed by spruce needles with 222 ng g-1 dw. The leaves and twigs of mountain ash were generally the least contaminated (<10 ng g-1 dw), while the other twigs had concentrations of up to 76 ng g-1 dw (birch). Interestingly, the annual ground cover plants were highly contaminated and accumulated high amounts of PFASs. The bioconcentration factors (BCFs; plant/soil ratios) were found to be as high as 143,700 for 6:2 FTSA (birch leaves), which turned out to have the highest accumulation potential in plants. Moreover, the BCFs were highest for short-chained C3-C5 perfluoroalkyl carboxylic acids (PFCAs; median ~0.9) and decreased for the longer chained C7-C9 PFCAs (~0.4), while being lowest for the long-chained C6-C8 perfluoroalkane sulfonic acids (PFSAs; ~0.2). In conclusion, silver birch, Norway spruce, bird cherry and long beechfern seem promising candidates for phytoremediation of PFASs.

**Notes**

* PFAS were found in all species involved in the study, but concentrations were variable among plant tissues. The highest concentrations were found in vegetative tissue, especially foliage, rather than storage tissues. PFAS concentrations decreased from ““shoots to roots”: leaves > twigs/stems > trunk > roots.”
* Whole plant uptake was extremely species specific.
* BCFs increased in the following manner: short-chained (C3-C5) PFCA > long-chained (C7-C9) PFCA > long-chained (C7-C9) PFSA.
* Several species showed promise for phytoremediation with silver birch demonstrating the greatest propensity for uptake and accumulation of PFAS.

## **4.18 Multiple crop bioaccumulation and human exposure of perfluoroalkyl substances around a mega fluorochemical industrial park, China: Implication for planting optimization and food safety**

Zhaoyang Liu, Yonglong Lua, Xin Song, Kevin Jones, Andrew J. Sweetman, Andrew C. Johnson, Meng Zhang, Xiaotian Lua, Chao Su, 2019

**Abstract**

Perfluoroalkyl substances (PFASs) have become a recognized concern due to their mobility, persistence, ubiquity and health hazards in the environment. In this study, ten types of vegetables and three types of grain crops were collected in two open-air fields with different distances (0.3 km, 10 km) from a mega fluorochemical industrial park (FIP), China. Bioaccumulation characteristics of PFASs in light of crop types and organs were explored, followed by analyzing human exposure and risks to local residents with different age groups and dietary habits. Elevated levels of ΣPFASs were found nearby the FIP ranging from 79.9 ng/g to 200 ng/g in soils and from 58.8 ng/g to 8085 ng/g in crops. Perfluorooctanoic acid (PFOA) was the predominant PFAS component in soil; while shorter-chain perfluoroalkyl carboxylic acids (PFCAs), especially perfluorobutanoic acid (PFBA), were the major PFAS contaminants in multiple crops, resulting from their bioaccumulation preference. Depending on the crop types, the bioaccumulation factors (BAFs) of ΣPFASs for edible parts varied from 0.36 to 48.0, and the highest values were found in shoot vegetables compared with those in fruit vegetables, flower vegetables, root vegetables and grain crops. For typical grains, the BAFs of ΣPFASs decreased in the order of soybean (Glycine max (Linn.) Merr.), wheat (Triticum aestivum L.) and corn (Zea mays L.), possibly related to their protein and lipid

content. Among specific organs in the whole plants, leaves exhibited the highest BAFs of ΣPFASs compared with corresponding roots, stems, husks or grains. With increasing carbon chain lengths of individual PFCAs (C4-C8), the logarithm of their BAFs for edible parts of various crops showed a linear decrease (0.1–1.16 log decrease per CF2 unit), and the largest decrease was observed in grains. Human exposure to PFOA via the consumption of contaminated crops represents a health risk for local residents, especially for low-age consumers or urban consumers with higher vegetable diet. Implications for planting optimization and food safety were provided aiming to reduce health hazards of PFASs.

**Notes**

* In a field 10 Km away from a fluorochemical industrial park, the soil concentration for the sum of 12 PFAS compounds (∑PFAS) ranged from 2.09 ng/g to 3.75 ng/g. For the same field, the range of the ∑PFAS in crops was 1.36 ng/g to 63.4 ng/g.
* PFOA was more likely to remain in the soil, while short-chain PFCA such as PFBA were more likely to be taken up by crops.
* Bioaccumulation factors (BAFs) for edible portions of various crops (10 vegetables and 3 grains) ranged from 0.36 to 48.0 and the BAFs were highest for shoots as compared to flowers, fruit, roots or grain.
* An inverse correlation between carbon chain length and BAFs for edible portions of crops was observed. This decrease was largest for grain crops.
* In grain crops, BAFs decreased in the following order: Glycine max (Linn.) Merr.), wheat (Triticum aestivum L.) and corn (Zea mays L.). This variability in BAF is possibly related to their protein and lipid content.
* For individual crop species, leaves showed the highest BAFs compared to the roots, stems, husks or grains of the same species.
* The authors concluded that eating vegetables grown near the fluorochemical industrial park represents a health risk especially to the young and those who have a higher than average dietary consumption of vegetables.

## **4.19 Accumulation of perfluorinated alkyl substances (PFAS) in agricultural plants: A review**

Rossella Ghisi, Teofilo Vamerali, and Sergio Manzetti, 2018

**Abstract**

PFASs are a class of compounds that include perfluoroalkyl and polyfluoroalkyl substances, some of the most persistent pollutants still allowed - or only partially restricted - in several product fabrications and industrial applications worldwide. PFASs have been shown to interact with blood proteins and are suspected of causing a number of pathological responses, including cancer. Given this threat to living organisms, we carried out a broad review of possible sources of PFASs and their potential accumulation in agricultural plants, from where they can transfer to humans through the food chain. Analysis of the literature indicates a direct correlation between PFAS concentrations in soil and bioaccumulation in plants. Furthermore, plant uptake largely changes with chain length, functional group, plant species and organ. Low accumulations of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) have been found in peeled potatoes and cereal seeds, while short-chain compounds can accumulate at high levels in leafy vegetables and fruits. Significant variations in PFAS buildup in plants according to soil amendment are also found, suggesting a particular interaction with soil organic matter. Here, we identify a series of challenges that PFASs pose to the development of a safe agriculture for future

generations.

**Notes**

* The literature supports the conclusion that plants in the human diet are a potential source of PFAS contributing to the human body burden.
* The literature demonstrates that landfills and WWTFs can be significant sources of PFAS in surface waters.
* Fire-training areas and airports can release very high amounts of PFAS to groundwater and surface water.
* Use of contaminated groundwater or surface water for irrigation can represent a significant source of contamination to soils and therefore plants grown on those soils.
* The use of sewage sludge as a soil conditioner/fertilizer can contribute to soil PFAS contamination.
* Other industrial wastes used as soil amendments can also add to soil PFAS contamination.
* The use of PFAS as an emulsifier in phytosanitary product formulations may also contribute to the presence of these substances in the above-ground edible parts of vegetables (Lassen et al., 2012).
* Aerial transport of PFAA and precursors that are volatile or particle-bound can be absorbed by plant leaves directly or add to soil concentrations.
* The differences between species uptake might be related to differences in protein content or differences in the roots systems (composition and surface area).
* “The amount of water transpired during growth has also been suggested to account for different uptakes and translocation capabilities among crops (Blaine et al., 2014a; 2014b). Therefore, all the climatic parameters influencing stomatal opening, such as irradiance, temperature and humidity, can influence plant uptake of perfluorinated compounds.”
* In cereal plants, PFAS concentrations were generally higher in the straw portion than the grain.
* A field study looking at PFAS uptake of PFAS from biosolids-amended soils shows that biosolids can be an important source of PFAS contamination in agriculture. The same study showed the importance of organic matter in limiting PFAS uptake.
* Observed uptake of PFAS can be highly variable between experiments. These authors recommend comparing BCF between studies as a more comprehensive parameter.
* For one study, PFBA had the highest BCF among all PFAS. The BCF for PFBA was significantly higher at the lowest soil concentration. It has been suggested that plants may adapt to higher PFAS soil concentrations or that there is some interaction between PFAS molecules that inhibits uptake at higher soil concentrations.
* For lettuce, celery, and radish grown on industrially impacted biosolids, PFAS increased in concentrations from roots to the above ground plant organs. The highest concentrations were in the edible portions of the plants.
* “This clearly shows that the amount of PFASs accumulated from biosolid-treated soils by the same plant species depends on the kind of sludge utilized, not only with respect to the total and individual concentrations of these pollutants, but also because different biosolids have different effects on the availability and/or uptake of individual PFASs by plants. Blaine et al. (2013) hypothesized that differences in the bioavailability of PFAAs may also be due to the different nature of the organic carbon of the two kinds of biosolids.”
* “Gellrich et al. (2012) found strong adsorption of PFASs to sewage sludge, which they attributed to its high organic carbon content.”
* Higher temperatures (increased transpiration) and higher salinity (partitioning in organic components of roots) can increase plant absorption of PFAS.
* The mobility and bioavailability of PFAS may be enhanced when delivered to soil by irrigation as compared to soil amendment with biosolids.
* Soil and sediment interactions with PFAS are complex and can’t generally be correlated to a single soil property.
* Current research suggests that PFAS in agricultural soils results mainly from the use contaminated irrigation water, industrially-impacted biosolids or other residuals, or transportation manufacturing or use sites.
* “PFASs are absorbed by plants to different extents according to their concentrations, chain lengths, functional group, plant species and variety, growth media (hydroponics vs. soil), and soil and biosolid characteristics. In particular, the abundance and characteristics of soil organic matter are considered one of the most important factors. Once inside the plants, partitioning among organs depends on species, and, particularly, on functional group and chain length. The C4–C6 compounds, which have recently replaced C8 PFOA and PFOS in many industrial processes, appear to accumulate particularly in leaves and fruits, whereas the compounds with higher chain lengths tend to be more concentrated in roots.”

## **4.20 Uptake of perfluoroalkyl substances and halogenated flame retardants by crops grown in biosolids-amended soils**

Irene Navarro, Adrián de la Torre, Paloma Sanz, Miguel Ángel Porcel, Javier Pro, Gregoria Carbonell, and María de los Ángeles Martínez, 2017

**Abstract**

The bioaccumulation behavior of perfluoroalkyl substances (PFASs) and halogenated flame retardants (HFRs) was examined in three horticultural crops and earthworms. Two species, spinach (Spinacia oleracea) and tomato (Solanum lycopersicum L.), were grown in field soil amended with a single application of biosolids (at agronomic rate for nitrogen), to represent the scenario using commercial biosolids as fertilizer, and the third crop, corn (Zea mays) was grown in spiked soil (~50 mg PFOS/kg soil, ~5 mg Deca-BDE/kg soil and a mixture of both, ~50 mg PFOS and ~5 mg Deca-BDE/kg soil) to represent a worst-case scenario. To examine the bioaccumulation in soil invertebrates, earthworms (Eisenia andrei) were exposed to the spiked soil where corn had been grown. PFASs and HFRs were detected in the three crops and earthworms. To evaluate the distribution of the compounds in the different plant tissues, transfer factors (TFs) were calculated, with TF values higher for PFASs than PBDEs in all crop plants: from 2 to 9-fold in spinach, 2 to 34-fold in tomato and 11 to 309-fold in corn. Bioaccumulation factor (BAF) values in earthworms were also higher for PFASs (4.06 ± 2.23) than PBDEs (0.02 ± 0.02).

**Notes**

* Within a tomato plant species, PFOS and long-chain PFCA tended to remain in the roots, while short-chain (C4 – C6) were more likely to be transferred to above-ground plant organs. This has been observed in other studies involving tomato, zucchini and cabbage (Felizeter et al., 2014), corn (Krippner et al., 2014), wheat (Wen et al., 2014) and lettuce (Felizeteret al., 2012).
* “In general, small and more apolar molecules can be dissolved in the lipid phase of the cell membrane and pass through it more easily. Several properties are decisive so as to a molecule could diffuse through a membrane: polarity, molecular size, functional groups and the position of the functional groups within the molecule (Krippner et al., 2014). Organic compounds could be taken up via passive (i.e apoplastic) process, which involves simple and facilitated diffusion, and/or active (i.e. symplastic) process, depending on the properties, the concentration of the compounds and the plant species (Zhan et al., 2010). The mechanism of PFOS and PFOA uptake by corn was examined by Wen et al. (2013). According to that, uptake of PFOS is carrier-mediated passive process, which may be conducted via aquaporins and anion channel in root cell membranes. They demonstrated that corn absorption of PFOS and PFOA may follow different pathways. PFOS and PFOA are PFASs, with similar perfluoroalkyl tail of varying chain length and different polar head group (sulfonate for PFOS and carboxylate for PFOA).”