

**NEBRA Literature Review:**

**Sources of PFAS in Agricultural Production** v. 1.0

September 2020



**Appendix II**

**Sources of PFAS in Agricultural Production – Compiled Abstracts and Notes**

This appendix is a compilation of the scientific literature reviewed for *Sources of PFAS in Agricultural Production*. It includes a table of contents listing the titles of the papers reviewed. Holding the “Ctrl” key and clicking on the title will bring you to a section of the compilation that will include the title of the paper, it authors, an abstract or summary, and any attendant notes compiled during the paper’s review.

**Note**: The notes and quotes below are selected and rough. Consult the actual published papers for exact details. Do not quote from here.

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1. **PFAS Ambient and Background Concentrations**

## **1.1 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.

**Notes**

* “38 PFOS results ranged from 0.018 to 2.55 *𝜇*g/kg. Forty results were obtained for PFOA, with values ranging from 0.059 to 1.84 *𝜇*g/kg. These PFOS and PFOA soil samples were collected from 21 U.S. states, two U.S. territories, and two Canadian provinces.”
* Based on limited data from four studies, PFOS was detected in freshwater sediments ranging from <0.1 to 2.2 ug/kg. PFOA was frequently undetected but when found concentrations ranged from <0.05 to 0.2 ug/kg.
* For freshwater surface water background 14 studies were reviewed. For PFOS, background ranged from 0.8 to 138 ng/L. These same studies observed mean values (geometric and arithmetic) ranging from 0.26 to 46 ng/L. For PFOA, background ranged from 0.45 to 287 ng/L and mean values (geometric and arithmetic) ranged from 0.65 to 43.4 ng/L.
* For drinking water background, “54 geometric means for PFOS ranged from *<*40 to 43 ng/L and PFOA ranged from *<*20 to 22 ng/L. Individual data results for PFOS ranged from *<*40 to 1,800 ng/L and PFOA ranged from *<*20 to 349 ng/L. Results were reported from 50 U.S. states, two U.S. territories, U.S. District of Columbia, and one U.S. Native American Nation.”
* This paper also reviewed studies reporting on PFOA and PFOS in fish and fish organs.

## **1.2 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.

## **1.3 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.

## **1.4 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.

## **1.5 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, 69 ng 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.

## **1.6 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

## **1.7 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.

**Notes**

“For PFOA, a significant correlation was showed between irrigation water and

agricultural products indicating that maybe the PFOA in agricultural products comes from irrigation

waters.”

## **1.8 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”.

**Notes**

* For aquatic sediments, PFOS was detected in 11 out of 14 samples and the concentration ranged from 0.289 ug/kg up to 27.1 ug/kg
* For surface water, PFOS was detected in 10 out of 14 samples and the concentration ranged from 2.8 ng/L to 102 ng/L

## **1.9 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 conditions change. “PFOS accounted for 55% – 96% of the ΣPFCs, ranging from 4.8 ng g-1 (dw) to 21.7 ng g-1 (dw).”
* 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.

## **1.10 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 conducted 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.

## **1.11 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.

1. **Indirect Sources of PFAS (PFAS sources not directly related to the practice of farming)**

## **2.0 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.

## **2.1 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.

## **2.2 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.

## **2.3 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.

## **2.4 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).

## **2.5 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.

## **2.6 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.

## **2.7 Environmental fate and effects of poly and perfluoroalkyl substances (PFAS)**

Smith, J.W.N., Beuthe, B., Dunk, M., Demeure S., Carmona, J.M.M., Medve, M, Spence, M.L., Pancras, T, Schrauwen, G, Held, T, Baker, M, Ross I. & H. Slenders (2016). Prepared for the Concawe Soil and

Groundwater Taskforce, STF, 33, P62.

**Abstract**

Aqueous Film Forming Foam (AFFF) and Fluoroprotein (FP)/ Film Forming Fluoroprotein Foam (FFFP) foam have been used since the 1960s and 1970s, respectively, for the suppression of class B (flammable liquid) fires at airports, refineries and other major petroleum facilities. In recent years, however, the use of these has been challenged due to concern that certain poly and perfluoroalkyl substances (PFAS) used in their formulation exhibit PBT characteristics (Persistent, Bioaccumulative and Toxic). While alternative PFAS-free foams are now commercially available, concerns have been raised that these may be less effective for fighting large-scale flammable liquid fires and that other issues such as shelf life, compatibility with conventional application equipment and suitability of different materials for storage have not been fully evaluated. It is important that users of class B fire- fighting foams understand and manage both environmental and fire safety aspects of foam use. An assessment of site foam stocks is recommended to ensure that any legacy stocks containing >0.001wt% PFOS (banned for use in the EU since June 2011) are set aside for safe disposal by high temperature incineration. A similar assessment should be completed for foam stocks that may be brought to site from third parties in the event of an emergency. At locations where fluorochemical- based foams have been used for fire- fighting or firefighting training, users should consider how to manage the potential issues. Fire- fighting foams designated “C6” by manufacturers are formulated using PFAS that cannot degrade to form PFOS or PFOA and so these seem of less concern from an environmental standpoint. It should be noted, however, that given the range of compounds present there is still uncertainty about their properties. In addition, low environmental concentration limits have been set for short chain PFAS (i.e. <C6 PFSA; <C7 PFCA) in many EU countries due to their persistence. Where possible, therefore, water containing PFAS- based fire- fighting foam residues should be captured for treatment and not discharged to the environment. This report, which is a review of published literature on the environmental fate and

effects of PFAS, has been produced to help Concawe members understand and manage environmental and human health risks associated with current and legacy formulations of PFAS- based class B fire- fighting foams. It describes the main types of PFAS, their use, fate and transport properties, toxicity data, regulation, and gives an overview of chemical analysis and remedial techniques. The report has been reviewed by members of the Concawe Special Taskforce on Soil and Groundwater, and the Emerging Contaminant Working Group of the Network for Industrially Contaminated Land in Europe (NICOLE).

**Notes**

* For complete degradation, PFOS has to be destroyed with high temperature incineration at 1.000 –1.200°C

## **2.8 Wastewater Treatment Plant and Landfills as Sources of Polyfluoroalkyl Compounds to the Atmosphere**

Lutz Ahrens, Mahiba Shoeib, Tom Harner, Sum Chi Lee, Rui Guo, and Eric J. Reiner, April 2011

**Abstract**

Polyfluoroalkyl compounds (PFCs) were determined in air around a wastewater treatment plant (WWTP) and two landfill sites using sorbent-impregnated polyurethane foam (SIP) disk passive air samplers in summer 2009. The samples were analyzed for five PFC classes (i.e., fluorotelomer alcohols (FTOHs), perfluorooctane sulfonamides (FOSAs), sulfonamidoethanols (FOSEs), perfluoroalkyl sulfonic acids (PFSAs), and perfluoroalkyl carboxylic acids (PFCAs)) to investigate their concentration in air, composition and emissions to the atmosphere. ΣPFC concentrations in air were 3-15 times higher within the WWTP (2280-24,040 pg/m3) and 5-30 times higher at the landfill sites (2780-26,430 pg/m3) compared to the reference sites (597-1600 pg/m3). Variations in the PFC pattern were observed between the WWTP and landfill sites and even within the WWTP site. For example, FTOHs were the predominant PFC class in air for all WWTP and landfill sites, with 6:2 FTOH as the dominant compound at the WWTP (895-12,290 pg/m3) and 8:2 FTOH dominating at the landfill sites (1290-17,380 pg/m3). Furthermore, perfluorooctane sulfonic acid (PFOS) was dominant within the WWTP (43-171 pg/m3), followed by perfluorobutanoic acid (PFBA) (55-116 pg/m3), while PFBA was dominant at the landfill sites (101-102 pg/m3). It is also noteworthy that the PFCA concentrations decreased with increasing chain length and that the emissions for the even chain length PFCAs outweighed emissions for the odd chain length compounds. Furthermore, highly elevated PFC concentrations were found near the aeration tanks compared to the other tanks (i.e., primary and secondary clarifier) and likely associated with increased volatilization during aeration that may be further enhanced through aqueous aerosol-mediated transport. ΣPFC yearly emissions estimated using a simplified dispersion model were 2560 g/year for the WWTP, 99 g/year for landfill site 1, and 1000 g/year for landfill site 2. These results highlight the important role of WWTPs and landfills as emission sources of PFCs to the atmosphere.

## **2.9 Results from agricultural soil screening testing for perfluorooctanoic acid (PFOA) in Southern New Hampshire**

N.H. Dept. of Environment Service (NHDES) and N.H. Dept. of Agriculture, Markets, and Food (NHAMF),

August 10, 2016

**Summary**

Over 160 soil samples were collected from 10 farm properties within approximately 5 miles of Saint-

Gobain Performance Plastics’ Merrimack facility to determine if soil contamination is present in

agricultural soil. Preliminary results show PFOA levels ranging from non-detect to 33 parts per billion

in the tested soils; most of the properties tested had levels less than 10 parts per billion. These results

are consistent with results in other states in the Northeast region where PFOA impacted groundwater

has been found. Based on our review of findings from literature studies on PFOA uptake in produce,

the New Hampshire Department of Environmental Services (NHDES) does not see the need for

restrictions on produce grown in these soils, as long as a clean source of water (i.e., with less than 70

parts per trillion of PFOA) is used for irrigation.

1. **Direct Sources of PFAS (PFAS sources directly related to farming operations or the practice of farming)**

## **3.1 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).

**Notes**

* Food package-containing composts 1, 4, and 5 had the highest total PFOA + PFOS levels of 7.94−11.5 μg/kg (Table S3). The total PFOA + PFOS range in composts that did not include compostable food packaging (composts 8−10) was 0.54−2.75 μg/kg (Table S3), the highest being from the backyard bin (compost 9), which also included food waste and coffee filters. The source of PFAAs in yard trimmings may come from atmospheric deposition or uptake from contaminated water or applied fertilizers.

## **3.2 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:

**Notes**

* 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.

## **3.3 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].

## **3.4 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 surface 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.

## **3.5 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.”

## **3.6 Guidance on alternatives to perfluorooctane sulfonic acid and its derivatives**

United Nation - Stockholm Convention on Persistent Organic Pollutants, UNEP/POPS/POPRC.6/13/Add.3/Rev.1, Oct. 14, 2011

**“J. Pesticides**

90. *N*-Ethyl perfluorooctane sulfonamide (EtFOSA; sulfluramid; CAS no. 4151-50-2) is both a

surfactant and a pesticide used in tropical areas such as Brazil against termites, cockroaches and other

insects.

91. According to information from the 2006 OECD survey sulfluamid was used in insecticides at a

concentration of 0.01-0.1% at an annual volume of up to 17 tonnes.

92. Fluorosurfactants may also be used as “inert” surfactants (enhancers) in pesticide products. The

two PFOS-related substances potassium *N*-ethyl-*N*-[(heptadecafluorooctyl) sulfonyl] glycinate (CAS

no. 2991-51-7) and 3-[[(heptadecafluorooctyl)sulfonyl]amino]-*N,N,N*-trimethyl 1-propanaminium

iodide (CAS no. 1652-63-7) have been approved in pesticide formulations in the United States.40 Both

chemicals have other uses, for example as cleaning agents. PFOS derivatives were used in pesticides

because they were considered rather inert and non-toxic.

93. PFOS is no longer used to manufacture ant bait or insecticides against beetles and ants in the

European Union, and the United States Environmental Protection Agency cancelled the registration of

sulfluramid in May 2008.41 According to information submitted to the secretariat of the Stockholm

Convention, sulfluramid had been used for pest control (to control cockroaches, white ants and fire

ants) in China, and sulfluramid is used in Brazil in more than 95% of baits for the control of leafcutting

ants, although the amount of PFOS used was not reported.

94. According to the Brazilian delegation, the use of sulfluramid in Brazil prevents damage

corresponding to losses of up to 14.5 % of trees per hectare. The cost of an attack by leaf-cutting ants

is estimated at US$6.7 billion. Other agricultural products likely to suffer costly losses are soybean

and maize. Also, the per-hectare capacity to support livestock is likely to decrease if forage for grazing

is reduced by ants.

95. Currently, the active ingredients registered in Brazil for producing bait to control leaf-cutting

ants are sulfluramid, fipronil and chlorpyrifos. The latter two, however, are considered more acutely

toxic to humans and the environment than sulfluramid. Furthermore, the effectiveness of these

substances has been questioned; thus new alternatives are being studied in Brazil. According to the

Brazilian Annex F information, sulfluramid cannot currently be efficiently replaced in Brazil by any

other registered products commercialized for the same purpose.42 Sulfluramid is the only active ingredient with all the properties necessary for effective functioning as ant bait, which it the only

effective option for controlling leaf-cutting ants.43

96. There are many differences between leaf-cutting ants and exotic ants (urban ants), including in

alimentary behaviour. Such differences explain why certain active ingredients are effective for

controlling urban ants and not for controlling leaf-cutting ants. Fenoxycarb, pyriproxyfen,

diflubenzuron, teflubenzuron, silaneafone, thidiazuron, tefluron, prodrone and methoprene had been

tested for leaf-cutting ants, but they were not effective.44 An adequate insecticide used to formulate

bait for the control of leaf-cutting ants should be lethal at low concentrations, act by ingestion and

present a delayed toxic action. Additionally, it should be odorless and non-repellent, so as to be

dispersed by trophallaxis to most workers in the colony.45 Since 1958, over 7,500 chemical

compounds for ant control have been studied in many countries. Fewer than 1% of those

7,500 compounds have shown promise.46”

## **3.7 Survey of PFOS, PFOA and other perfluoroalkyl and polyfluoroalkyl substances**

Danish Environmental Protection Agency, Environmental Project No. 1475, 2013

Carsten Lassen, Allan Astrup Jensen, Alexander Potrykus, Frans Christensen, Jesper Kjølholt, Christian Nyande Jeppesen, Sonja Hagen Mikkelsen, Sally Innanen

**Notes**

* In Denmark, the authors estimate a minimum of 180 kg of PFAS was used in pesticides in 2007. By 2012, usage of PFAS in pesticides was eliminated.
* This document notes the use of PFOS and its derivatives in the formulation of pesticides.
* “The mono- and di-substituted perfluorinated phosphonic acids (mono-PFPAs and di-PFPAs) are a new class of fluorinated acids, high volume chemicals (surfactants) used. as wetting agent in waxes and coatings and as defoaming additives in pesticides, among other uses” pg. 100
* “Sulfluoramid is used in some countries as an active sub-stance and surfactant in pesticide products for termites, cockroaches and other insects. Other fluoro-surfactants may be used as “inert” surfactants in other pesticide products.” pg. 131
* “In the past, perfluorooctane sulfonic acid and its derivatives have been used for a wide range of products and processes. Among these uses are pesticides, plumbing fluxing agent, medical applications and devices, flame retardants, coatings and coating additives, adhesives as well as uses in rubber and plastics, upholstery, and the leather and carpet industries.” pg. 71

## **3.8 Fluorinated Surfactants and Repellents, 2nd ed.**

Erik Kissa, Surfactant Science Series, Volume 97, Marcel Dekker, Inc., New York, 2001

*Herbicides and Insecticides* p.367

“The nonionic fluorinated surfactants tested by Sakakibara et al. [ 1921 exhibited hardly any herbicidal activity. Hence, selected fluorinated surfactants can be used safely as dispersants and adjuvants for agricultural chemicals. When compared to hydrocarbon surfactants, fluorinated surfactants are more powerful wetting agents for leaves (e.g., wheat leaves) [193].

Fluorinated surfactants are used in insecticide formulations to aid wetting and penetration of the insecticide into the insect. Insecticidal aerosols may contain an insecticide, solvent, and a fluorinated surfactant. An insecticide formulated with a fluorinated surfactant and dimethyl ether as the solvent is readily absorbed by insects [194]. Some fluorinated surfactants are insecticides in their own right, affecting the common housefly and the carmine mite [192]. The mechanism of insecticidal activity appears to be suffocation of the insect by the adsorbed fluorinated surfactant.

p. 351. The relatively high price of fluorinated surfactants limits their use to applications where hydrocarbon-based surfactants are inadequate. Usually, fluorinated surfactants are cost-effective because their high price is compensated by the low concentration needed. Sometimes, as little as 50-150 ppm of the surfactant may be adequate. The fluorinated surfactants cost typically about 10 times more than silicones and 100 times more than hydrocarbon surfactant. However, fluorinated surfactants are about 10 times more effective than silicones and 50-100 times more effective than hydrocarbon surfactants. In some applications, a mixture of a fluorinated surfactant and a hydrocarbon-based surfactant is more cost-effective or performs better than either one alone.

## **3.9 The Perfluorochemicals in Homes and Gardens Study (PIHGS): Implications for human exposure assessment**

D. Scher, J. Kelly, C. Huset, R. Hoffbeck, K. Souther, E. Hansen, J. Korinek, R. Messing, and V. Yingling. Minnesota Department of Health, St. Paul, MN, 2014

**Conclusions**

•The continued presence of PFBA in water used for garden irrigation contributes to higher levels of PFBA in home-grown produce.

•PIHGS and other studies highlight the high leaching potential and high plant uptake rate of shorter-chain PFCs. In comparison, PFOS and PFOA in soil are not readily translocated through plants.

•At homes unaffected by groundwater contamination, detectible levels in soil, produce, and dust provide further evidence of the widespread occurrence of PFCs.

•Recent studies emphasize growing concern for human exposure to PFCs beyond PFOS and PFOA due to substitution of longer-chain PFCs by shorter-chain compounds in industrial processes. More studies of PFC movement through environmental and human food chains are needed to identify shifting exposure patterns.

•Based on increased exposure concerns, more research on the toxicity of PFC compounds other than PFOA and PFOS is warranted.

1. **Potential Impacts to Farm Products**

## **4.1 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 (<0.03 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.

## **4.2 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)

## **4.3 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)

## **4.4 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)

## **4.5 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.

**Notes**

* Concentrations of PFAS food in produce were generally low.
* Perfluoroalkyl sulfonic acids (PFSAs) were generally not detected with exception of PFOS in spinach.
* The detectable concentrations of PFOA varied between 8 and 121 ng/kg fw in the vegetable species analysed.
* The authors conclude that in general human exposure to PFAS from vegetables is low.
* “The existing guidelines on tolerable daily intakes of two PFAS in the EU have been derived by the EFSA in 2008. EFSA recommends a maximal total daily intake (TDI) of 1,500 ng/kg b.w./day for PFOA and for PFOS, 150 ng/kg b.w./day. The intake estimation for PFOA via vegetables and potatoes available in Europe calculated in the present study for adults and children are about four orders of magnitude lower than the recommended EFSA TDI.” (European Food Safety Authority -EFSA)
* These data are limited, and further study is warranted.

## **4.6 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.

## **4.7 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.

## **4.8 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.

## **4.9** **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.

## **4.10 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. The paper cites sources detailing high soil concentrations of PFOA and PFOS in Germany and the U.S. resulting from the use of sewage sludge
* 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 proximity to point sources (airports, fire-training locations, industrial use or production 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.”

## **4.11 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).”

## **4.12 U.S. Food & Drug Administrative Webpage (**[**https://www.fda.gov/food/chemicals/and-polyfluoroalkyl-substances-pfas**](https://www.fda.gov/food/chemicals/and-polyfluoroalkyl-substances-pfas)**) - Per and Polyfluoroalkyl Substances (PFAS)**

**Content current as of:** 12/20/2019

“The FDA is focused on:

* Assessing foods for PFAS from environmental contamination; and
* Reviewing the limited authorized uses of PFAS in food contact applications.
* “When analyzing food that may contain PFAS because of environmental contamination, the FDA has used the Environmental Protection Agency’s reference doses (RfD) for perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), of 0.02 μg/kg bw/day as an appropriate toxicity reference value.”
* “The results posted today show that out of 88 foods, one sample—tilapia— had a detectable level of perfluorooctane sulfonate (PFOS), which is a type of PFAS. This is the same PFAS that was detected in the two samples with detectable levels—ground turkey and tilapia— reported in the first round of testing in foods collected for the TDS. Both sample sizes are limited and cannot be used to draw definitive conclusions. Based on the best available current science, the FDA has no indication that PFOS levels found in the limited sampling from these TDS data sets present a human health concern.”
* “Overall, [our findings](https://www.fda.gov/food/chemicals/and-polyfluoroalkyl-substances-pfas) did not detect PFAS in the vast majority of the foods tested. In addition, based on the best available current science, the FDA does not have any indication that these substances are a human health concern, in other words a food safety risk in human food, at the levels found in this limited sampling. These data give our scientists a benchmark to use as we continue our critical work studying this emerging area of science.”
* FDA work does consider food packaging when assessing PFAS risk in the food supply.
* **“Bottled Water, 2016:** Samples of domestic and imported carbonated and non-carbonated bottled water were collected at retail locations in the Washington, D.C. metropolitan area and analyzed for PFAS. The samples included: purified, artesian, spring, mineral, and carbonated waters. None of the 30 samples had detectable levels of PFAS. This sample size is limited and cannot be used to draw definitive conclusions.”
* **“Seafood, 2013:** Fish and shellfish samples from 13 species of fresh and saltwater fish from across the country were analyzed for PFAS. Eleven of the 46 samples had detectable levels of PFAS. This sample size is limited and cannot be used to draw definitive conclusions. Based on the best available current science, the FDA has no indication that these substances at the levels found in the limited sampling present a human health concern.”
* “To ensure that food contact substances used in packaging, cookware, and food processing equipment are safe for their intended use, the FDA conducts a rigorous review of scientific data prior to their authorization. Prior to 2000, the FDA authorized the use of food contact substances through the food additive petition process, which resulted in a regulation establishing safe conditions of use in Title 21 of the Code of Federal Regulations. Since 2000, the FDA authorizes the use of food contact substances through the Food Contact Notification (FCN) program. The [Inventory of Effective Food Contact Substance (FCS) Notifications](https://www.accessdata.fda.gov/scripts/fdcc/?set=FCN) is a publicly available database of all uses of food contact substances authorized through the FCN program.”
* “Certain PFAS are currently authorized for use in specific applications related to their non-stick and grease, oil, and water-resistant properties. Whether these PFAS migrate to food depends on the molecular structure of the PFAS and the conditions of use. For example, the PFAS used in non-stick coatings on cookware and sealing gaskets for food processing equipment do not migrate to food. However, PFAS used to make oil- and water-resistant coatings on paper food packaging have the potential to migrate to food. The specific authorized uses for PFAS in food packaging take into consideration this potential for migration and these authorized uses are limited to ensure safe levels of exposure.”
* “The FDA reviews updated scientific information on food contact substances as it becomes available. The agency can revoke food contact authorizations when scientific data demonstrate that the authorized uses of a food contact substance are no longer safe. In addition, the FDA can also work with industry to remove food contact substances from the market through voluntary agreements.”
* “For example, in 2011, the FDA obtained voluntary agreements with the manufacturers of certain “long-chain” PFAS compounds authorized under food contact notifications to remove those substances from food contact applications. “Long-chain” and “short-chain” refer to the number of carbon atoms in the molecular structure of a subset of PFAS. In 2016, the FDA revoked the regulations that authorized the remaining uses of these long-chain PFAS in food packaging.”
* “Newer studies suggest that “short-chain” PFAS (i.e., carbon chain length is less than 8 atoms long), may also pose a risk to human health. To better understand the potential health effects of these PFAS the FDA is collaborating with the National Toxicology Program. This, along with emerging information from the U.S Environmental Protection Agency, the Centers for Disease Control and Prevention, and the Agency for Toxic Substances and Disease Registry will inform any future action on the authorizations for the short-chain PFAS in the manufacturing of components for use in food packaging.”

## **4.13 PFAS in paper and board for food contact - options for risk management of poly- and perfluorinated substances**

Trier, Xenia; Taxvig, Camilla; Rosenmai, Anna Kjerstine; Pedersen, Gitte Alsing, 2017

**Summary:**

“Poly- and perfluorinated alkyl substances, PFASs, are widely used substances including applications in food contact materials (FCMs) of paper and board. The substances have been found to be highly persistent, bioaccumulative and toxic, and recently some long-chain PFASs have begun being regulated or phased out. However, they have been replaced with a wide range of fluorinated alternatives that are less examined but of potential similar concern. Food is estimated to be a main source of human exposure to PFASs. However, due to the data gap in research on toxicity and exposure to these compounds, it is difficult to perform a risk assessment of individual substances, and to assess which sources are the most relevant for human exposure and hence the most effective to regulate.

The purpose of the Nordic workshop was to:

* create an overview of the use of PFASs in FCMs of paper and board, the toxicity of the different substances, and the migration of the substances from paper and board into food
* provide an overview of whether appropriate risk assessments of fluorinated substances exist and can form the basis for specific regulations or recommendations
* provide an overview of whether analytical methods suitable for analysing and regulating the substances in food simulants and/or food are available
* discuss the possibility and structure of national regulations or Nordic recommendations for PFASs in FCM of paper and board.

In conclusion of the workshop a risk management to reduce the total content of organically bound fluorine in paper and board FCMs was proposed.

As a subsequent follow-up, a level for a Danish recommended limit on total organic fluorine in paper and board FCMs was suggested by the National Food Institute, DTU Food, in 2016. The limit value should take a possible background level of fluorinated chemicals present in the paper into account. Due to higher background levels in the paper and board FCMs than originally expected and uncertainties of the analytical method, the level of the recommended limit value and the analytical method for its determination are currently under revision.”

## **4.14 Perfluorinated Compounds, Polychlorinated Biphenyls, and Organochlorine Pesticide Contamination in Composite Food Samples from Dallas, Texas, USA**

Arnold Schecter, Justin Colacino, Darrah Haffner, Keyur Patel, Matthias Opel, Olaf Päpke, and Linda Birnbaum, June 2010

**Notes**

Objectives: The objective of this article is to extend our previous studies of persistent organic pollutant (POP) contamination of U.S. food by measuring perfluorinated compounds (PFCs), organochlorine pesticides, and polychlorinated biphenyls (PCBs) in composite food samples. This study is part of a larger study reported in two articles, the other of which reports levels of poly­brominated diphenyl ethers and hexabromocyclododecane brominated flame retardants in these composite foods [Schecter et al. 2010. Polybrominated diphenyl ethers (PBDEs) and hexabromocyclodecane (HBCD) in composite U.S. food samples, Environ Health Perspect 118:357–362].

Methods: In this study we measured concentrations of 32 organochlorine pesticides, 7 PCBs, and 11 PFCs in composite samples of 31 different types of food (310 individual food samples) pur­chased from supermarkets in Dallas, Texas (USA), in 2009. Dietary intake of these chemicals was calculated for an average American.

Results: Contamination varied greatly among chemical and food types. The highest level of pesti­cide contamination was from the dichlorodiphenyltrichloroethane (DDT) metabolite *p*,*p*´‑dichlorodiphenyldichloroethylene, which ranged from 0.028 ng/g wet weight (ww) in whole milk yogurt to 2.3 ng/g ww in catfish fillets. We found PCB congeners (28, 52, 101, 118, 138, 153, and 180) primarily in fish, with highest levels in salmon (PCB-153, 1.2 ng/g ww; PCB-138, 0.93 ng/g ww). For PFCs, we detected perfluorooctanoic acid (PFOA) in 17 of 31 samples, ranging from 0.07 ng/g in potatoes to 1.80 ng/g in olive oil. In terms of dietary intake, DDT and DDT metabolites, endo­sulfans, aldrin, PCBs, and PFOA were consumed at the highest levels.

Conclusion: Despite product bans, we found POPs in U.S. food, and mixtures of these chemicals are consumed by the American public at varying levels. This suggests the need to expand testing of food for chemical contaminants.

1. **PFAS Regulatory Standards Potentially Impacting Agriculture**

## **5.1** **EPA’s Per- and Polyfluoroalkyl Substances (PFAS) Action Plan**

EPA 823R18004 | February 2019 | [www.epa.gov/pfas](http://www.epa.gov/pfas)

**Executive Summary**

Per- and polyfluoroalkyl substances (PFAS) are a group of synthetic chemicals that have been in use since the 1940s. PFAS are found in a wide array of consumer and industrial products. PFAS manufacturing and processing facilities, facilities using PFAS in production of other products, airports, and military installations are some of the contributors of PFAS releases into the air, soil, and water. Due to their widespread use and persistence in the environment, most people in the United States have been exposed to PFAS. There is evidence that continued exposure above specific levels to certain PFAS may lead to adverse health effects (USEPA 2016a, 2016b, ATSDR 2018a).

The EPA will continue to partner with other federal agencies, states, tribes, and local communities to protect human health and, where necessary and appropriate, to limit human exposure to potentially harmful levels of PFAS in the environment. The EPA is leading the national effort to understand PFAS and reduce PFAS risks to the public through implementation of this Action Plan and through active engagement and partnership with other federal agencies, states, tribes, industry groups, associations, Throughout recent engagements, the EPA heard clearly the public’s desire for immediate action to address potential human health and economic impacts from PFAS in the environment.

This Action Plan describes the EPA’s approach to identifying and understanding PFAS, approaches to addressing current PFAS contamination, preventing future contamination, and effectively communicating with the public about PFAS. The Action Plan describes the broad actions the EPA has underway to address challenges with PFAS in the environment, including next steps on the four PFAS management actions the EPA announced at the May 2018 National Leadership Summit. The four actions announced at the Summit were:

• Initiating steps to evaluate the need for a maximum contaminant level (MCL) for perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS);

• Beginning the necessary steps to propose designating PFOA and PFOS as “hazardous substances” through one of the available federal statutory mechanisms1;

• Developing groundwater cleanup recommendations for PFOA and PFOS at contaminated sites;

• Developing toxicity values or oral reference doses (RfDs)2 for GenX chemicals3 and perfluorobutane sulfonic acid (PFBS).

In addition to these significant actions, the EPA’s PFAS Action Plan identifies more short-term and long-term actions that are currently being implemented to understand and address PFAS. Short-term actions include:

• Developing new analytical methods and tools for understanding and managing PFAS risk;

• Promulgating Significant New Use Rules (SNURs) that require EPA notification before chemicals are used in new ways that may create human health and ecological concerns; and

• Using enforcement actions to help manage PFAS risk, where appropriate.

Short-term actions are generally taking place or expected to be completed within two years. The Action Plan also sets out long-term regulatory and research approaches the EPA will pursue to reduce exposures and to understand the potential human health and environmental risks associated with PFAS. Actions classified as long-term, such as multi-step research initiatives or regulatory actions, are generally expected to take more than two years. Some long-term actions may result in intermediate steps and products that can help to reduce PFAS exposures and protect public health.

Ecological risks are of great concern to many stakeholders due to the widespread distribution and persistence of PFAS in the environment and the wide variety of PFAS chemicals for which environmental fate and transport is currently uncharacterized. While this Action Plan focuses mainly on human health, characterizing potential ecological impacts and risks are important areas of work for the EPA.

Table 1 below summarizes the key actions the EPA is taking to assist states, tribes, and communities in addressing PFAS. These activities are intended to address challenges identified though stakeholder input during the PFAS National Leadership Summit, multiple community engagements, and through the public docket (see Appendices B and C for summaries of stakeholder input).

In addition to the highlighted action items in Table 1, the EPA continues to make progress on developing tools and expanding the body of scientific knowledge needed to understand and effectively manage risk from PFAS, including developing PFAS analytical methods, evaluating treatment and remediation techniques for PFAS, understanding the exposure from various environmental media, and evaluating human health impacts of additional PFAS. These activities are described in more detail in Appendix A.

1 There are multiple statutory mechanisms available to designate PFAS as CERCLA hazardous substances, including CERCLA, RCRA, TSCA, CWA, and CAA.

2 A reference dose is an estimate of the amount of a chemical a person can ingest daily over a lifetime (chronic RfD) or less (subchronic RfD) that is unlikely to lead to adverse health effects.

3hexafluoropropylene oxide (HFPO) dimer acid and its ammonium salt

**Key EPA Actions Addressing PFAS-Related Challenges**

• Expand toxicity information for PFAS

• Develop new tools to characterize PFAS in the environment

• Evaluate cleanup approaches

• Develop guidance to facilitate cleanup of contaminated groundwater

• Use enforcement tools to address PFAS exposure in the environment and assist states in enforcement activities

• Use legal tools such as those in TSCA to prevent future PFAS contamination

• Address PFAS in drinking water using regulatory and other tools

• Develop new tools and materials to communicate about PFAS

## **5.2 The second webinar in Geosyntec’s PFAS Webinar Series on Tuesday, April 14, 2020 (PFAS Toxicology and Risk Assessment: State of the Science).** In the event you missed this webinar, or if you would like to revisit some of the slides, you can **access a recording** at [https://vimeo.com/407719091](http://r20.rs6.net/tn.jsp?f=001xPaVDQF0Rd4KJZAdeur-HQFI2Vpo8mOaIdXnYmnpuQxt8By0jSuFauWCSFA8_KxX6aLBvYh_Tk1dHJF8PsaIp_DDyW3mOKbrL5eJLhF_-OqnSgXuHHaFT1WZc83MGMyU0mhjGZUBkzi6UBmiZJLHzA==&c=aMkiCMysEl0YvaOoXGA-ec8MTZONnDeIArQxmthcd-otnqOSns8F4Q==&ch=fc6pFFBcFUbbrfN5K8wOyxh-2uaOlzyrkwAJKh_YGIG5iCvlGVgYrw==" \t "_blank) (Password: geosyntecPFAS). Kristin Bridges, Ph.D.; Jason Conder, Ph.D.; and Jennifer Arblaster

Slide 22 – The greatest ecological risk (aquatic ecosystem, offsite groundwater) is offsite from the original contamination source.

Slide 28 – Shows a wide range of PFOS screening values (< 1 ng/L to > 10 ug/L) for aquatic life adopted around the world. Australia has developed aquatic life screening standards that encompass ambient concentration ranges for PFOS.

Slide 29 – Most of the PFOS aquatic screening values are in the 1 to 10 ug/L range, much higher than the drinking water standards. These screening values might not factor into concerns about PFAS in groundwater but may be a consideration for NPDES permitting.

Slide 30 – Using current wildlife toxicity reference values for PFOS, traditional ecological models derive aquatic sediment screening levels of 10-30 ug/kg. The slide suggests that ambient soil concentrations are in the 1-10 ug/kg range.

Slide 32 – For some sites, ecological risk standards/guidelines may be more stringent that standards to protect human health, especially for aquatic birds exposed to aquatic sediments.

## **5.3 Maine Department of Agriculture, Conservation and Forestry – Per- and Polyfluoroalkyl Substances (PFAS)**

“Is Maine Milk Safe?

* In 2016, PFAS chemicals were found to be present at unsafe levels in the milk of a Maine dairy farm that had historically applied biosolids and papermill residuals to its fields. In 2017, the Maine Center for Disease Control & Prevention created an Action Threshold for milk to determine when milk is considered adulterated. That Action Threshold is 210 ng/L.
* To determine the safety of Maine’s current overall milk supply:
  + DACF completed a state-wide retail milk survey in June 2019 of Maine-produced fluid pasteurized milk. The results demonstrated that all samples were below the laboratory reporting level of 50 ng/L. The survey focused on Maine-produced milk that is either bottled in-state or is bottled out of state but sold in-state. Twenty-six samples were taken throughout the state to ensure broad geographic representation and population centers.
  + DACF estimates that this sampling captured 75% of all milk sold in Maine.
  + The Department also tested three commercial dairy farms, two with a history of biosolid and/or paper mill residual applications and which had soil samples that exceeded DEP’s screening levels for PFOA and/or PFOS. The third farm was near the farm that had tested high for PFOS in 2016. Milk sampled from all three farms were also below the lab’s reporting level of 50 ng/L.
  + Based on the retail milk survey and these three individual farm results, DACF has high confidence in the safety of Maine-produced milk.”