In this issue of PFAS Alerts...

2019 continues to present a high volume of publications and regulatory developments on PFAS. In this issue, about 35 citations with abbreviated abstracts are presented. See the *Special Highlights* section for the most notable citations.

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Special Highlights

NHANES releases its' 2019 updated tables for human exposure to environmental chemicals.

CDC; January 2019

The updated tables include exposure data

for 12 PFAS (PFOS, PFOA, PFNA, PFHxS, PFHpA, PFDoA, PFDA, PFBS, perfluorooctane sulfonamide [PFOSA], ethyl perfluorooctane sulfonamido acetic acid [EtFOSAA], methyl perfluorooctane sulfonamido acetic acid [MeFOSAA], PFUnDA), and include data from the most recent 2015-2016 survey period. Geometric mean serum levels of PFOA, PFOS, PFDA, and PFNA in the total U.S. population have continued to decline from the previous survey period.

Maine creates special task force to study the impacts of PFAS. March 6, 2019

The task force was formed by an executive order issued by Governor Janet Mills, and is tasked with 1) identifying sites in Maine with PFAS contamination; 2) investigating the effects of PFAS on fish and marine organisms; and 3) take steps to implement treatment options.

Michigan Department of Environmental Quality (MDEQ) finalizes state-wide testing: Fluorochemicals found in 10% of Michigan's drinking water sources, but none above the USEPA Health Advisory. MDEQ; February 25, 2019

MDEQ assessed state-wide levels of PFAS in over 1,100 public water systems. Detectable levels of PFAS were present in 119 systems, or approximately 10%. Of the 10% of water systems with detectable levels of PFAS, 3% had total PFAS levels between 10 to 70 parts per trillion (ppt), and the remaining detections were below 10 ppt. Michigan's Scott Dean said in a statement that up to 40 contaminated sites may warrant cleanup.

Policy and Regulation

The Biomonitoring California Program has Expanded its Designated Chemical List to Include Additional PFAS. Biomonitoring California. 2019

The expanded list now includes ~60 PFAS, including GenX, ADONA, a large suite of short and long FTs, linear and branched PFOA and PFOS isomers, and short- and long-chain PFCAs and PFSAs.

New Hampshire Introduced SB 257 into the State Senate to Limit AFFF Use. New Hampshire State Legislature. 2019

The bill restricts the sale and use of PFAScontaining class B firefighting foams in New Hampshire. The bill would allow the state to fine any manufacturer that knowingly manufactures or sells class B foams in which PFAS was intentionally added. If passed by the senate, the bill would take effect January 1, 2020. Additional bills limiting AFFF use have also recently been introduced in Georgia, Kentucky, and Michigan.

California to Survey Airports, Landfills, Wells for Contaminants.

Bloomberg News. 2019

Based on survey data, California officials estimate that 3.5 million Californians are exposed to levels of PFAS above the USEPA Health Advisory limit. To understand the widespread contamination, California officials have announced that they will begin sampling at manufacturing facilities, refineries, WWTPs, and areas affected by wildfires in 2017 and 2018. The timeframe of the new sampling program has not yet been announced. New Mexico Environmental Defense Department Sues Air Force Over PFAS Contaminated Groundwater. <u>USDC:</u> March 5, 2019

The suit alleges that firefighting foams used at Air Force bases in New Mexico contaminated groundwater with fluorinated chemicals. Some of the groundwater is used as supply water for livestock, including a dairy farm.

Fate and Transport

Multi-compartment Distribution of PFAS in an Urban Catchment System.

H. Chen, M. Reinhard, T. Yin...; Water Res. 2019

The fate and distribution of 21 PFAS in an urban water body were determined. Longer chain PFAS (C>11) were predominantly found sorbed to suspended particulate matter and sediment, while short chain PFAS were predominantly found in the dissolved phase. Levels of PFAS were higher in porewater than in surface water. Field-derived distribution coefficients were higher than laboratory estimated values, and sorption isotherms estimated in the lab did not correlate well with field measurements. The authors suggest that laboratory-based results for PFAS distribution should be used with caution.

Contamination of Groundwater with PFAS from Legacy Landfills in an Urban Redevelopment Precinct.

E. Hepburn, C. Madden, D. Szabo,...; Environ. Pollut. 2019

Levels of 17 PFAS were measured in groundwater from 13 sampling sites in close proximity to legacy landfills in an Australian re-development precinct. PFOA, PFOS, PFHxS, and PFBS were detected at all sites. PFOA and PFHxA levels were found to be positively correlated with landfill leachate

indicators such as ammonia and bicarbonate, while the ratio of PFOA to sum PFAAs was positively correlated with groundwater ammonia levels. The authors suggest the PFOA/ Σ PFAAs ratio in groundwater may be a useful indicator of landfill-derived PFAAs.

Fate of a PFAA Mixture in an Agricultural Soil Studied in Lysimeters.

M.S. McLachlan, S. Felizeter, M. Klein;...; Chemosphere. 2019

The environmental fate of C4-C14 PFCAs and two PFSAs in soil was investigated in a field lysimeter experiment. Soil levels of all PFAAs decreased over the growing season, however, levels of short-chain PFAAs decreased more rapidly than levels of long-chain PFAAs. Levels of PFAAs in drainage water from were inversely correlated with chain-length. For C11-C14, decreases in soil levels were primarily due to the formation of nonextractable residues, whereas leaching into drainage water was the primary removal process for other PFAAs.

Remediation – In Situ

Efficient Removal of PFAS from Water using a Regenerable Magnetic Activated Carbon. (MAC).

P. Meng, X. Fang, A. Maimaiti...; *Chemosphere*. 2019

Ultrafine MAC consisting of Fe_3O_4 and powder activated carbon (PAC) was developed for the removal of PFAS from water. Optimized MAC consisted of a 1:3 ratio of Fe_3O_4 to PAC, with adsorption capacities of 1.6, 0.9, 0.3, and 0.2 mmol/g PFOS, PFOA, PFHxS, and PFBS, respectively. The spent MAC could easily be regenerated via methanol treatment, and be re-used up to 5 additional times, with stable adsorption capacities after 3 reuse cycles.

Study Demonstrates Effective Removal of PFAS from Soil.

W. DiGuiseppi, R. Richter, M. Riggle; *The Military Engineer*. 2019

Bench-scale studies in which PFAS contaminated soil was heated to temperatures of 250-700°C for 50 minutes to 8 days demonstrate thermal desorption may be a viable option for treating AFFF-impacted sites. The lowest effective temperature for removal of PFAS was 350°C and required 2 days of treatment to remove 99.4% of 29 different PFAS. The authors indicate that in situ treatment of soil at this temperature is feasible, and could be coupled to a vapor extraction system to capture volatilized PFAS.

Analytical Chemistry

Identification and Quantification of PFOSA Isomers by Liquid Chromatography-tandem Mass Spectrometry (LC-MS/MS).

<u>G. Shan, L. Yang, J. Zhao,...; *J. Chromatogr.* <u>A.</u>2019</u>

A LC-MS/MS method was developed to detect and quantify 6 branched PFOSA isomers. The developed method was then used to quantify all 6 isomers in spiked fish blood. The method detection limits ranged from 0.1 to 1 pg/g for blood samples, demonstrating that the method has potential to be utilized for detection of PFOSA in complex matrices.

Rapid Separation of Isomeric PFAS by Highresolution Differential Ion Mobility Mass Spectrometry.

E. Ahmed, K.M.M. Kabir, H. Wang...; Analytica Chimica Acta. 2019

A new method that can rapidly separate branched and linear PFAS isomers for analytical identification was developed. Differential mobility spectrometry (DMS) was used to rapidly separate isomers (in milliseconds), and then isomers were

identified using coupled mass spectrometry. PFAS isomers with differing positions of a single perfluoromethyl group could be accurately identified. With further validation, this method would significantly reduce the time required to separate and identify PFAS isomers.

Monitoring – Environment

Characterization of PFAS in Sediment Cores from High and Low Arctic Lakes in Canada. J.J. MacInnis, I. Lehnherr, D.C.G. Muir...; <u>Sci.</u> <u>Tot. Environ.</u> 2019

Levels of 23 PFAS were determined in intact sediment core samples from 2 arctic lakes in Canada. Levels of PFOA, PFDA, PFBS, and PFOS increased in Lake Hazen between 1963-2011, while levels of PFHpA, PFOA, PFNA, and PFUnDA increased in Lake B35 between 1952-2009. Temporal trends of PFAS in the sediment cores followed historic changes in manufacturing processes, demonstrating continuous artic transport.

Monitoring — Biomonitoring

PFAAs in Paired Serum, Urine, and Hair Samples: Correlations with Demographic Factors and Dietary Habits.

D.H. Kim, J.H. Lee, J.E. Oh; *Environ. Pollut.* 2019

Levels of 11 PFAAs in paired hair, urine, and serum samples were determined for 94 Korean children and adults. Levels of short-chain PFCAs PFPeA and PFHxA were 1.5-5 times higher in hair or urine than in serum. Most PFAAs had serum (but not hair or urine) sexspecific differences, with higher levels detected in males. Fish and water consumption rates were positively correlated with serum and negatively correlated with hair concentrations, respectively. The authors suggest hair and/or urine may be more suitable for assessing exposure to some shortchain PFAAs.

Relationship Between PFOA and PFOS Blood Concentrations in the General Population and Routine Drinking Water Exposure.

S. Zhang, Q. Kang, H. Peng...; Environ. Int. 2019

PFOA and PFOS levels were measured in drinking water and human blood from several cities across China. The correlation between concentration in drinking water and in human blood was significant for PFOA. Relative source contributions of drinking water PFOA and PFOS were estimated to be 23% and 13% for PFOA and PFOS, respectively.

Toxicology — Mechanism of Action

Antioxidant Defense System is Responsible for the Toxicological Interactions of Mixtures: A Case Study on PFOS and PFOA in *Daphnia magna*.

<u>Y. Hong-Bo, Z. Ya-Zhou, Y. Tang...; Sci. Tot.</u> Environ. 2019

The acute and chronic toxicity of PFOA and PFOS to Daphnia was tested individually and as mixtures. Mixtures of PFOA and PFOS showed synergistic effects in acute (2-day) lethality and chronic (21-day) reproduction tests. Molecular docking simulations showed that PFOA and PFOS bound to catalase in a similar fashion, while had different binding modes to superoxide dismutase, which led the authors to postulate that binding of PFOA and PFOS to certain components of the antioxidant defense system contributes to the observed synergism.

Effects of PFAS on a Multigenerational Scale: A Case Study with *Chironomus riparius*. L. Marziali, F. Rosignoli, S. Valsecchi...; <u>Environ. Toxicol. Chem.</u> 2019

Larval C. riparius were exposed to 10 parts per billion (ppb) PFOS, PFOA, or PFBS for 10 generations. No effects on survival, reproduction, or population growth rate were observed across the exposure period. The authors concluded that PFOA, PFOS, and PFBS do not appear to pose a risk to this type of ecological receptor.

Low Concentrations of PFOS Repress Osteogenic and Enhance Adipogenic Differentiation of Human Mesenchymal Stem Cells (MSCs).

W. Liu, H. Qin, Y. Pan...; *Toxicol. Appl. Pharmacol.* 2019

Exposure to PFOS affected MSC osteogenic and adipogenic differentiation in a non-monotonic dose-response. In differentiating osteocytes, PFOS repressed calcium deposition, and decreased expression of several key molecular markers of osteocyte differentiation. PFOS Alternatively, exposure increased differentiation, adipocyte resulting in increased lipid droplet formation, and increased expression of biomarkers associated with adipogenesis. These results demonstrate exposure to PFOS can disrupt adult stem cell differentiation in vitro: however, results need to be confirmed in vivo.

Screening of Potential PFOS Alternatives to Decrease Liver Bioaccumulation: Experimental and Computational Approaches.

H. Cao, Z. Zhou, L. Wang...; *Environ. Sci. Technol*. 2019

The binding affinity of several PFOS alternatives, including perfluorodecalin-2-sulfonic acid (PFDecS), N-diperfluorobutanoic acid (N-diPFBS), and 6:2 FTS, to liver fatty acid binding protein (FABPL) was estimated

using a quantitative structure activity relationship (QSAR) model. FABPL binding free energy for PFDecS was higher than that of PFOS indicating higher binding affinity, while 6:2 FTS and N-diPFBS had lower estimates of binding free energy, suggesting lower binding affinity. Modelled FABPL binding data correlated well with the relative degree of liver accumulation for PFDecS, N-diPFBS in *in vivo* experiments.

Blood Transcriptomics Analysis of Fish Exposed to PFAS: Assessment of Nonlethal Sampling Technique for Advancing Aquatic Toxicology Research.

I.A. Rodriguez-Jorquera, R.C. Colli-Dula, K. Kroll...; Environ. Sci. Technol. 2019

The transcriptomic response following exposure to PFOS or a mixture of 7 PFAS was assessed in the blood and liver of fathead minnows. The transcriptomic response in blood was more sensitive than the response in the liver. The transcriptomic responses indicated that PFAS were altering cellular pathways mediated by estrogen receptor alpha and PPAR beta and gamma receptors.

The Effects of PFOA on High Fat Diet Induced Non-alcoholic Fatty Liver Disease (NAFLD) in Mice.

X. Li, Z. Wang, J.E. Klaunig; *Toxicology*. 2019

Mice were fed a low-fat control diet or highfat diet (HFD) for 16 weeks and then administered 1 mg/kg/day PFOA for an additional 16 weeks. Regardless of diet, PFOA activated peroxisome proliferator-activated receptor alpha (PPARa), pregnane X receptor and constitutive androstane receptor. PFOA exacerbated hepatocyte growth rates and PPAR α activation in the context of a HFD. Alternatively, PFOA alleviated steatosis, reduced liver triglyceride levels, and attenuated hepatic fibrosis. These results demonstrate complex interactions between PFOA and NAFLD, and unexpectedly suggest PFOA can attenuate certain disease states.

Epidemiology

Liver Function Biomarkers Disorder is Associated with Exposure to PFAAs in Adults: Isomers of C8 Health Project in China.

M. Nian, Q.Q. Li, M. Bloom...; Environ. Res. 2019

Relationships between liver function and levels of 18 PFAAs were measured in the serum of 1605 adults enrolled in the C8 Health Project in China. Serum levels of total (branched and linear) PFOA, PFNA, and branched PFOS were all positively associated with higher serum alanine aminotransferase (ALT) levels.

Prenatal Exposure to PFAS is Associated with Lower Hand, Foot and Mouth Disease (HFMD) Viruses Antibody Response in Infancy.

X.W. Zeng, M.S. Bloom, S.C. Dharmage; *Sci. Tot. Environ.* 2019

The relationship between total sum PFAS serum levels and antibody response to HFMD was assessed in 201 mother-infant pairs from the Guangzhou Birth Cohort Study. Cord blood sum PFAS levels were found to be inversely related to levels of antibodies against HFMD viruses enterovirus 71 and coxsackie virus A 16. These results suggest exposure to PFAS may increase risk of HFMD in infants; however, these results need to be replicated in additional study populations.

Serum PFAS and Lung Function in Adolescents Exposed to the World Trade Center Disaster.

A. Gaylord, K.I. Berger, M. Naidu...; *Environ. <u>Res.</u> 2019*

The relationship between lung function and serum PFAS levels was measured in a cohort of

children from the World Trade Center Health Registry. Serum PFAS levels were not associated with any changes in lung function, asthma diagnosis, or eosinophil count.

Prenatal and Childhood Exposure to PFAS and Cognitive Development in Children at Age 8 Years.

A.M. Vuong, K. Yolton, C. Xie...; *Environ. Res.* 2019

The relationship between PFAS and cognitive function in children was investigated in 223 mother-child pairs from the Health Outcomes and Measures of the Environment Study. PFOS and PFHxS were not associated with Wechsler Intelligence Scale (WISC) measures. A 4.1point and 5.7-point increase in working memory for each 1-In unit increase in prenatal PFOA and PFNA, respectively, was measured. PFNA was also associated with enhanced WISC scores in male children at 3 years of age. These results suggest that prenatal and earlylife exposure to PFAS do not adversely affect cognitive function.

Cross-sectional Study of the Association between Serum PFAS and Dental Caries among US Adolescents (NHANES 1999-2012). <u>N. Ramest, M. Arora, J.M. Braun; *BMJ Open.* 2019</u>

The relationship between oral health and serum levels of PFOA, PFNA, PFHxS, and PFOS was investigated in 2,869 adolescents. PFOA, PFOS, and PFHxS were not associated with any indicator of declining dental health. PFNA was positively associated with reduced dental caries.

PFAS are Inversely Associated with Coronary Heart Disease (CHD) in Adults with Diabetes. K. Honda-Kohmo, R. Hutcheson, K.E. Innes...; J. Diabetes Complications. 2019

The relationship between PFOA, PFNA, PFOS, and PFHxS serum levels and CHD was

investigated in 5,270 adults with diabetes from the C8 Health Project. PFOA, PFOS, PFNA, and PFHxS were all found to be inversely associated with CHD and chronic kidney disease. The author's suggest these results may provide insight into CHD prevention strategies, if confirmed in additional studies.

Using 2003-2014 U.S. NHANES Data to Determine the Associations between PFAS and Cholesterol: Trend and Implications. <u>Z. Dong, H. Wang, Y.Y. Yu...; *Ecotoxicol. Environ. Safe.* 2019</u>

The relationship between serum PFAS levels and high cholesterol was investigated in 2003-14 NHANES participants. A 1.5 and 0.4 mg/dL increase in total cholesterol was observed for each unit increase in serum PFOA and PFOS, respectively. Reference doses (RfDs) were estimated to be 2.0 ng/kg-day PFOS and 0.8 ng/kg-day PFOA. However, the study author's urge caution when using the derived RfDs, as they are based on cross-sectional datasets.

Exposure Pathways -Household

PFAS in Saleswomen's Urine Linked to Indoor Dust in Clothing Shops.

N. Wu, D. Cai, M. Guo...; Sci Tot. Environ. 2019

PFAS levels were determined in 58 indoor dust and 73 paired saleswomen urine samples. PFDoDA and PFHxS were the predominant PFAS detected in dust, while PFOA was the predominant PFAS in urine. Levels of longchain PFAS were positively correlated with PFAS levels in urine. Daily intake values for PFAS from dust were determined, and even under high-end exposure scenarios exposure to PFOA and PFOS were well under tolerable daily intake values. The authors conclude that dust ingestion is only a minor pathway for human exposure to PFAS.

Exposure Pathways - Dietary

Comparing Levels of PFAS in Processed Marine Products.

<u>J. Yu-Jin, B. Sunah, K. Jihyun...; *Fd. Chem.* <u>Toxicol.</u> 2019</u>

Levels of 19 PFAS were determined in 302 processed seafood samples collected in South Korea. PFOA, PFTrDA, PFOS, and PFPeA were detected at the highest levels in dried seafood, canned seafood, processed fish food, and laver, respectively. Levels of PFOA and PFOS were found to be higher in demersal fish than in pelagic fish. Human intake of PFOA/PFOS from seafood products was found to be lower than the tolerable daily intake, suggesting these types of food products pose minimal risk to human health.

Occurrence and Health Risk of PFAAs in Seafood from Yellow Sea, China.

<u>A. Zhang, P. Wang, Y. Lu...; Sci. Tot. Environ.</u> 2019

Levels of 17 PFAAs were determined in 42 pooled seafood samples comprising 14 difference species from the Yellow Sea in China. Sum PFAS levels ranged from

1-1067 ng/g (dry weight) in different species. Crabs were found to have the highest concentrations of PFAAs. Spatial distributions in PFAS levels were observed, and were attributed to PFAS contamination emanating from industrial areas. Contrary to other studies that have found PFOS to be the predominant PFAS in seafood, the authors report that the short-chain PFCA PFBA was the most abundant PFAA detected.

Miscellaneous

Phospholipid Levels Predict the Tissue Distribution of PFAS in a Marine Mammal. <u>C Dassuncao, H Pickard, M Pfohl...; Environ. Sci.</u> <u>Technol.</u> 2019

The relationship between phospholipids, total protein, total lipids, and accumulation of 24 PFAS was investigated in the heart, muscle, brain, kidney, liver, blubber, placenta, and spleen of pilot whales. The abundance of PFAS in the brain was associated with increasing chain length. Phospholipid levels were found be a good predictor of PFDS, PFDoDA, PFTrDA, and PFTA. Except in the brain, a 1 mg/g increase in phospholipids led to a 12-25% increase in PFAS. These results suggest shorter chain PFAS do not efficiently cross the blood-brain barrier, and that long chain PFAS may partition to phospholipids in whales.

Notes: PFAS Alerts is based on reviews of literature identified from Google Scholar and PubMed searches, and the following publications: Inside EPA, LAW360, Bloomberg BNA, CCNJ, and ChemInfo. This issue includes a subset of articles selected by Integral. Abbreviated abstracts are based on information presented by the authors. More detailed reviews in the Special Highlights are prepared by Integral based on the information available online. Integral has not verified the accuracy of information posted online.

Acronyms and Abbreviations

AFFF = aqueous film-forming foam DWQI = Drinking Water Quality Institute (NJ) F/C = fluorine/carbon FT = fluorotelomer FTAA = fluorotelomer sulfonamide alkylamine FTAB = fluorotelomer sulfonamide alkylbetaine FTAC = fluorotelemer acrylate FTCA = fluorotelomer carboxylic acid FTI = fluorotelemer iodide FTMAC = fluorotelemer methacrylate FTO = fluorotelemer olefin FTOH = fluorotelomer alcohol FTS = fluorotelomer sulfonate FTSA = fluorotelemer sulfonamide FTUCA = fluorotelomer unsaturated carboxylic acid NHANES = National Health and Nutrition Examination Survey NJDEP = New Jersey Department of Environmental Protection PFAA = perfluoroalkyl acid PFAI = perfluoroalkyl iodide PFAS = per- and poly-fluorinated alkyl substance PFBA = perfluorobutanoic acid (C4) PFBS = perfluorobutane sulfonate (C4) PFC = perfluorinated compound PFCA = perfluoroalkyl carboxylate PFDA and PFDeA = perfluorodecanoic acid (C10) PFDoDA = perfluorododecanoic acid PFDS = perfluorodecane sulfonic acid PFHpA = perfluoroheptanoic acid PFHxA = perfluorohexanoic acide (C6) PFHxS = perfluorohexane sulfonate (C6) PFNA = perfluorononanoic acid (C9) PFOA = perfluorooctanoic acid (C8) PFOS = perfluorooctane sulfonate (C8) PFPeA = pefluroopentanoic acid (C5) PFSA = perfluorinated sulfonate PFTA = perfluorotetradecanoic acid PFTrDA = PFTrDA and PFTriDA = perfluorotridecanoic acid PFUA and PFUnDA = perfluoroundecanoic acid (C11) RSC = relative source contribution T4 = thyroxine TSH = thyroid stimulating hormone USEPA = U.S. Environmental Protection Agency WWTP = wastewater treatment plant