# FLUOROS 2015

## An International Symposium on Fluorinated Organics in the Environment

**July 12-14, 2015**
**Golden, Colorado**

COLORADO SCHOOL OF MINES
EARTH • ENERGY • ENVIRONMENT

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Greetings and Welcome to FLUOROS 2015!

I am very excited to be welcoming you to the *second* FLUOROS symposium, building off the tremendous success of the first FLUOROS organized by Prof. Scott Mabury at the University of Toronto in 2005. Like the first meeting, FLUOROS 2015 is dedicated to exploring progress and outstanding scientific, engineering, and policy questions related to "fluorinated organics" in the environment. With approximately 200 registrants, 150 poster presentations, and 17 invited speakers and session chairs from around the globe, I am excited to learn what questions have been answered in the last 10 years, but also about the new questions and challenges that have arisen.

This meeting arose out of a series of conversations I had with Prof. Mabury over the years, usually starting with me asking him as to when he was going to organize the next FLUOROS. At some point, Scott responded to my pestering by suggesting that I organize it. Whether he was serious or not, the idea grew on me, and I finally had the courage to take on the challenge. Though it will be hard to replicate the excitement and enthusiasm of that first FLUOROS, I truly hope that you'll approach this meeting with the same openness and dedication to thoughtful discussion that many of us experienced in 2005.

As with the original FLUOROS, this meeting has been organized with the tremendous support of a volunteer organizing committee and help from a variety of individuals here at the Colorado School of Mines. The generous support of our sponsors has also enabled us to offer registration fees at a very reasonable rate. I hope you'll take FLUOROS 2015 as an opportunity to examine and advance the state of knowledge of poly- and perfluoroalkyl substances in the environment through a meaningful exchange of ideas. Through our collective conversations, perhaps we'll start to solve many of the issues surrounding this important class of chemicals.

Christopher P. Higgins
**Chair, FLUOROS 2015**

# Meeting Schedule and Speaker Abstracts

**Sunday, July 12, 2015**

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| 6:00 – 8:00 PM | Registration and Welcome Reception, Green Center Lobby |

**Monday, July 13, 2015**

Analytical Chemistry, Monitoring, and Environmental Fate and Transport; Remediation, and Human Exposure

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|---|---|
| 7:00 – 8:00 AM | Continental Breakfast available in Friedhoff Hall (Green Center), Monday Poster set-up |
| 8:00 | Opening Remarks and Introduction, Christopher Higgins |
| 8:20 – 8:30 | Moderator, Andrew Lindstrom |
| 8:30 – 9:00 | Jonathan Benskin, *The Analytical Chemist's Toolbox for Measurement of Per- and Polyfluoroalkyl Substances* |
| 9:05 – 9:35 | Amila de Silva, *Per- and Polyfluoroalkyl Substances in the Biosphere: Spatio-Temporal Trends, New Directions, and Research Gaps* |
| 9:40 – 10:10 | Lutz Ahrens, *Transport and Fate of Per- and Polyfluoroalkyl Substances in the Abiotic Environment* |
| 10:15 – 10:30 | Open Discussion and Preview of Poster Session |
| 10:30 – 12:00 | Poster Session – *Coffee and Tea* |
| 12:00 – 1:30 | Lunch, Friedhoff Hall (Green Center) |
| 1:30 – 1:40 | Moderator, Andrew Hartten |
| 1:40 – 2:10 | Rainer Lohmann, *Sources, Distribution, and Fate of PFASs Across the Atmosphere and Oceans* |
| 2:15 – 2:45 | David Sedlak, *Remediation of Poly- and Perfluoroalkyl Substances by Chemical Oxidation: Cost-Effective Option or Fool's Errand?* |
| 2:50 – 3:10 | Jessica D'eon, *Using Concentrations in Human Sera to Understand Human Fluorochemical Exposure* |
| 3:15 – 3:35 | Robin Vestergen *Human Exposure Pathways of Legacy and Replacement PFASs and the Relative Importance of Dietary Intake* |
| 3:40 – 4:00 | Open Discussion and Preview of Poster Session |
| 4:00 – 6:00 | Poster Session – *Coffee, Tea & Other Beverages* |
| 6:00-8:00 | BBQ Dinner – Stratton Commons |

**Tuesday, July 14, 2015**
Toxicology, Epidemiology, and Human Health

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|---|---|
| 7:00 – 8:15 AM | Continental Breakfast available in Friedhoff Hall (Green Center), Tuesday Poster set-up |
| 8:15 – 8:20 | Housekeeping |
| 8:20 – 8:30 | Moderator, Jamie DeWitt |
| 8:30 – 9:00 | Sue Chang, *A Synopsis of the Toxicology of Per– and Polyfluoroalkyl Substances* |
| 9:05 – 9:35 | Jia-Yin Dai, *Progress in Ecotoxicology of Perfluoroalkyl Acids* |
| 9:40 – 10:10 | Tony Fletcher, *The Epidemiology of Perfluorinated Compounds –Where Are We Now?* |
| 10:15 – 10:30 | Open Discussion and Preview of Poster Session |
| 10:30 – 12:00 | Poster Session – *Coffee and Tea* |
| 12:00 – 1:30 | Lunch, Friedhoff Hall (Green Center) |

Risk Assessment and Regulatory Policy, and New Chemicals

| | |
|---|---|
| 1:30 – 1:40 | Moderator, Guibin Jiang |
| 1:40 – 2:10 | Christophe Schulte, *Assessment and Regulatory Approaches in Europe* |
| 2:15 – 2:45 | Tala Henry, *Risk Assessment & Risk Management of PFASs at US EPA* |
| 2:50 – 3:10 | Ian Cousins, *Fluorinated Alternatives to Long-Chain PFASs: What We Know About Them and Proposals on How They Should be Managed and Regulated* |
| 3:15 – 3:30 | Open Discussion and Preview of Poster Session |
| 3:30 – 5:00 | Poster Session – *Coffee, Tea & Other Beverages* |
| 5:00 – 5:30 | FLUOROS Summary and Wrap-up and Awards |

## Analytical Chemistry, Monitoring, and Environmental Fate and Transport

There have been a number of revolutionary developments during the past decade that have led to a much more comprehensive understanding of per- and polyfluoroalkyl substances (PFASs) in the environment. Improvements in analytical instrumentation have made liquid chromatography triple quadrupole mass spectrometry commonplace, making targeted analysis of historical PFASs routine. The availability of relatively inexpensive high resolution instrumentation and sophisticated software and databases has made it possible to accurately predict compound composition and structure, leading to a vast increase in the number and type of compounds now observable. With the growing awareness of the ubiquity and diversity of fluorinated compounds, there has been a great increase in the availability of analytical standards, enabling accurate measurements of previously undescribed or unverified materials. Additional advances have made it increasingly clear that we have only been able to characterize a small fraction of what remains to be discovered. Perhaps most importantly, with the application of these increasingly sophisticated approaches, we have developed a much greater understanding of the environmental distribution of PFASs, how they move and are transformed, and how their presence ultimately leads to exposure in the natural environment. The speakers in this session will summarize these key historical developments and the challenges that remain by giving us a description of the state of the science regarding analytical approaches, the occurrence and transformation of PFASs in nature, and summaries of some of the historical and geographical trends in key environmental matrices and species worldwide.

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### Session Chair

**ANDREW B. LINDSTROM** has a Ph.D. from the University of North Carolina's School of Public Health and has been working for the United States Environmental Protection Agency's National Exposure Research Laboratory for the past 24 years. He is currently conducting method development research for the Exposure Measurements and Analysis Branch, where his areas of expertise include measurement of trace level contaminants in environmental and biological matrices and human exposure assessment.



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## The Analytical Chemist's Toolbox for Measurement of Per- and Polyfluoroalkyl Substances

The analytical chemistry of per- and polyfluoroalkyl substances (PFASs) has grown considerably since the first detection of PFOS and PFOA in human blood in 2001. The analysis of perfluoroalkyl acids (PFAAs) is more accurate and precise than ever before. The scope of what we can measure has also expanded. In addition to perfluoroalkyl carboxylates and suflonates, a full suite of phosphorous-based fluorosurfactants, neutral and cationic organofluorines, cyclic fluorinated species and even fluorinated polymers can be measured in environmental samples. The availability of indirect analytical approaches has aided in the characterization of 'what's missing' in targeted analysis, while new discovery-based approaches using high resolution mass spectrometry and mass spectral libraries have aided in the identification of novel PFASs. However, despite these considerable achievements, challenges remain. Recent analysis suggests that only a fraction of organofluorine in environmental samples is captured by targeted analysis. This is exacerbated by the ongoing introduction of alternative organofluorine substances into the global marketplace with little accompanying information or authentic standards for method development and monitoring. This presentation will provide a broad overview of the analytical chemist's toolbox for measuring PFASs in environmental samples, including state-of-the-art analytical approaches, potential deficiencies, and future areas for development. The goal is to initiate discussion among analytical chemists and end-users on what tools are currently available and what still needs to be developed to address the most important knowledge gaps in our field.

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**JONATHAN BENSKIN** is an Associate Professor and Group Leader in the Department of Environmental Science and Analytical Chemistry (ACES) at Stockholm University (Stockholm, Sweden). He holds a B.Sc. (Chemistry) from the University of Victoria and a Ph.D. (Medical Sciences) from the University of Alberta. From 2011-2014, he held positions as an NSERC Industrial Fellow and then Principal Scientist with AXYS Analytical Services Ltd. and as a Visiting Scientist at the Institute of Ocean Sciences (Fisheries and Oceans Canada). Dr. Benskin's research focuses on the development of novel analytical tools for characterizing the occurrence, behavior, and sub-lethal effects of emerging organic contaminants.



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## Per- and Polyfluoroalkyl Substances in the Biosphere: Spatio-Temporal Trends, New Directions, and Research Gaps

The global inventory of per- and polyfluoroalkyl substances (PFASs) in biota continues to grow since Giesy and Kannan's seminal study on perfluorooctane sulfonate (PFOS) in 2001. Biomonitoring of PFASs provides insight into patterns of emission, transport, partitioning, and bioaccumulation. PFASs, particularly perfluorocarboxylates (PFCAs) and perfluorosulfonates (PFSAs), have been measured at all trophic levels in marine, freshwater, and terrestrial foodwebs. The geographical locations for PFASs biomonitoring are extensive in recent years including South America, Russia, Australia, and Antarctica. Temporal studies in biological samples show varying trends but recent publications have emerged in temperate regions, building on the numerous publications focusing on historical trends in Arctic regions. Very few biota measurements have been published on perfluorophosphonates, perfluorophosphinates, polyfluorinated phosphoric diesters, and fluorotelomer sulfonates. Indeed, several gaps in biomonitoring research remain. Many fluorinated alternatives to PFCAs and PFSAs detected in water or human samples have yet to be reported in other biological samples such as monochlorine-substituted PFCAs, monohydro substituted PFCAs, monochlorine-substituted PFSAs, polyfluorinated ether sulfonates, and polyfluorinated ketone sulfonates. Geographical trends are also lacking for some regions such as the African continent. Further, mechanisms and driving factors for bioaccumulation in various species for PFASs are still being studied and elucidated. Understanding bioaccumulation of PFCAs and PFSAs can further prediction of bioaccumulation propensity for fluorinated alternatives.

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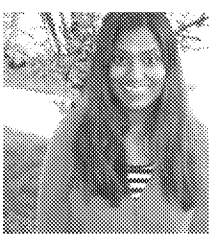

**Amila O. De Silva** is a research scientist at Environment Canada in the Water Science & Technology Directorate in Burlington, Ontario. Her research program focuses on the analysis of and environmental fate and disposition of emerging organic pollutants. Since obtaining a Ph.D. in environmental chemistry at the University of Toronto with Scott Mabury, she completed a postdoctoral fellowship with Derek Muir at Environment Canada. She conducts research on per- and polyfluorinated substances including their bioaccumulation and biomagnification as well as research on their presence in precipitation and sediment in regions such as the Arctic. She holds an adjunct professorship in the Department of Chemistry at Memorial University in Newfoundland, Canada.



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## Transport and Fate of Per- and Polyfluoroalkyl Substances in the Abiotic Environment

Poly- and perfluoroalky substances (PFASs) comprise a diverse group of chemicals that have been widely used for over 50 years in various industrial applications and consumer products. It has now been more than a decade since the first landmark publications identified the global contamination of the environment with long-chain PFASs. However, critical knowledge gaps remain regarding their sources, transport, and fate in the abiotic environment. This presentation aims to reassess the state-of-the-art knowledge of PFASs in the abiotic environment, so as to point out real progress understanding and fate of these chemicals in the environment. This presentation will include: i) identity and evidence of occurrence for PFASs in the abiotic environment (water, soil, sediment, air), including legacy categories that have been largely ignored (e.g., branched isomers, phosphonic acids), ii) physicochemical properties, including key differences between anions and acids, their partitioning and/or binding behavior in abiotic phases, and degradation pathways in the environment, iii) sources and emissions trends, including comparisons between developed and developing countries and understanding of urban sources (indoor vs. outdoor, wastewater), iv) environmental fate, including key processes and mechanisms that control the transport and removal of different PFAS classes, and v) promising remediation and engineered degradation technologies.

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**Lutz Ahrens** is an Associate Professor and Research Scientist at the Department of Aquatic Sciences and Assessment, Swedish University of Agricultural Sciences (SLU), Uppsala, Sweden. He is an expert in analytical and environmental chemistry for emerging contaminants such as per- and polyfluoroalky substances. His research is focused on the development of new analytical methods for quantification of emerging contaminants in water, soil, sediment, air and biota using advanced mass spectrometry methods, and application of these for transport



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## PFAS Environmental Fate, Transport and Remediation-Learnings from the Past 15 Years

Assessment of sources of PFAS to the environment have ranged from fluoropolymer manufacturing facilities, airports, fire training facilities, and waste management locations to the global environment such as the atmosphere and the oceans. Some assessments have included detailed studies to determine PFAS fate and transport pathways and presence in environmental media, to conduct exposure analysis (EA), and, where needed, to implement groundwater remediation. Others have examined human exposure on a much larger scale. Some assessments of legacy PFAS-use sites have discovered large dilute groundwater plumes that have migrated beyond site boundaries and have impacted nearby drinking water supplies, making source treatment non-value adding when the situation requires point-of-use or point-of-entry treatment. Remediation of PFAS can be very difficult based on their chemical properties and many conventional in-situ remedial technologies such as bioremediation, oxidation, or electrochemical treatment are ineffective or still unproven at scale. However, at a location in the Ohio River Valley, remediation of drinking water via treatment systems utilizing granular activated carbon at public water supply and residential (private well) locations that have been installed during the past eight to ten years continue to operate successfully. A two-phase EA involving the sampling of a wide variety of environmental media, including air, surface water, soil, groundwater, fish, beef and untreated drinking water, and treated drinking water was conducted for this location. The EA determined that treatment of drinking water was responsible for an approximately 15-to 5-fold reduction in total PFOA exposure.

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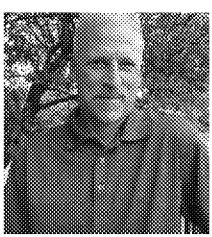
### Session Chair



**ANDREW HARTTEN** is a Principal Remediation Project Manager and Hydrogeologist with the Chemours (formally DuPont) Corporate Remediation Group. He has worked 27 years in the environmental remediation, site assessment, and risk/exposure management fields. His professional work related to PFASs began in the early 1990s and has included sites around the world. From 2003 to 2012, he managed DuPont's PFOA site assessment program, including a phased investigation/exposure assessment of a West Virginia facility. He managed implementation of drinking water treatment installation for PFOA at six public facilities and over 90 private residences. He has also completed three groundwater treatment facility projects which included PFOA.



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## Sources, Distribution, and Fate of PFASs Across the Atmosphere and Oceans

Per- and polyfluorinated alkyl substances (PFASs) have become truly global contaminants, with their widespread detection in air and water across the oceans, and from pole to pole. Major progress has been made in estimating inventories and emissions of perfluoroalkyl acids (PFAAs). Less clear is the relative importance of atmosphere versus rivers as sources of PFAAs on the global scale. Atmospheric measurements of the volatile PFASs are now routinely performed, but little is known about PFAAs in the atmosphere themselves. The oceans have been described as the main and final sink for PFAAs, yet we know surprisingly little about the sources, distributions and processes affecting PFAAs in the oceans. Most measurements have reported PFAA concentrations for the surface oceans only. Recent measurements imply that there are significant masses of PFAAs below the surface ocean, the reasons for which will be discussed. Potential pathways include physical transport (mixing), and the movement with organic particles to depth. Advanced ocean models can help us better understand where, why, and how PFASs are distributed across the oceans. Coupled models will also help assess sources of PFASs, and might be able to explain time-trends; first reports have been made of decreasing PFAS concentrations in the southern ocean.

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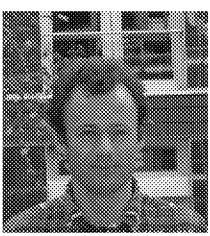

**Rainer Lohmann** is a Professor of Oceanography at the Graduate School of Oceanography at the University of Rhode Island. He obtained a Ph.D. in Environmental Science from Lancaster University (UK) in 1999, and was a postdoc at MIT under Phil Gschwend during 2000-2002. Dr. Lohmann was awarded fellowships by the Alexander-von-Humboldt Foundation in 2011, the Research Center for Ocean Margins (Bremen) in 2004, and the German Academic Exchange Service in 2000. Currently, his research focuses on environmental and marine chemistry and specifically the environmental processes (fate, transport, bioaccumulation) of organic contaminants and black carbon. He serves as Editor for Environmental Toxicology and Chemistry and CLEAN – Air, Soil, Water.



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## Remediation of Poly- and Perfluoroalkyl Substances by Chemical Oxidation: Cost-Effective Option or Fool's Errand?

Early reports suggesting that perfluorocarboxylic acids were amenable to oxidation by sulfate radical created considerable interest in using persulfate for the remediation of soil, sediments, and groundwater at sites that were contaminated from fire-fighting activities. However, recognition that aqueous film forming foam (AFFF) contains a suite of poly- and perfluoroalkyl substances (PFAS) and that perfluorocarboxylic acids only react with sulfate radical under specific conditions dampened enthusiasm for this approach. Through carefully controlled studies with pure substances, AFFF, and samples collected from contaminated sites, we have developed a better understanding of the ways in which in situ chemical oxidation (ISCO) can be used effectively for AFFF remediation. For certain polyfluorinated substances in AFFF, reaction with sulfate or hydroxyl radical results in formation of intermediates that are eventually converted into perfluorocarboxylic acids, some of which undergo partial breakdown (i.e., shortening) of the perfluorinated chain. Complete transformation of perfluorocarboxylic acids may be possible under acidic conditions with high doses of persulfate. Overall, ISCO has the potential to lower the concentrations of many PFASs, but complete remediation of contaminated sites will require an understanding of the composition of the contaminants and conditions occurring in the subsurface as well as the use of other, complimentary remediation methods.

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**DAVID SEDLAK** is the Malozemoff Professor in the Department of Civil & Environmental Engineering at UC Berkeley, Co-Director of the Berkeley Water Center and Deputy Director of the NSF engineering research center for Reinventing the Nation's Urban Water Infrastructure (ReNUWIt). He received his PhD from the University of Wisconsin in Madison and was a postdoctoral researcher at eawag in Zurich, Switzerland. Professor Sedlak's research addresses the use of natural and engineered systems to remove chemical contaminants from water prior to potable water reuse or use for habitat restoration and remediation of contaminated soil and groundwater. In addition to maintaining an active research program, Sedlak is the author of *Water 4.0* and editor of the ACS journal, *Environmental Science & Technology*.



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## Using Concentrations in Human Sera to Understand Human Fluorochemical Exposure

Human fluorochemical contamination is a very interesting puzzle as concentrations vary only a little across geography, age, sex, and income. Determining the source of this ubiquitous exposure is complicated as the compounds typically measured, the perfluorinated carboxylates (PFCAs) and sulfonates (PFSAs), are not the materials used commercially. It is of research and regulatory interest to understand whether legacy environmental contamination or current commercial materials dominate this exposure. The issue is also toxicologically relevant as certain biotransformation pathways produce reactive intermediates with a demonstrated ability to form protein adducts. One approach to this question is to scrutinize trends in human sera in the context of commercial activities. This tactic is possible because fluorochemicals have been produced via two distinct manufacturing processes, electrochemical fluorination and telomerization, with different production histories. Temporal trends in human sera, together with isomer and congener profiles, all indicate some exposure to precursor compounds (either commercial materials or their building blocks) followed by metabolism into fluorinated acids within the body. This conclusion is consistent with total organofluorine measurements that demonstrate PFCAs and PFSAs only account for a small percentage of the organofluorine compounds present in human sera. A concrete connection between commercial products and human exposure was made with the observation of polyfluoroalkyl phosphates in human sera. Looking comprehensively at human fluorochemical contamination we see a clear connection between the concentrations observed and current-use commercial materials.

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**JESSICA D'EON** is currently a teaching faculty member in environmental chemistry in the Department of Chemistry at the University of Toronto. She received her Ph.D. in environmental chemistry at the University of Toronto under the supervision of Prof. Scott Mabury, where she used a variety of techniques to understand the fate and disposition of commercial fluorochemicals in the body and the environment. She complemented her doctoral research experience with a postdoctoral position at the Ontario Ministry of the Environment that used ultra-high resolution mass spectral analysis and nuclear magnetic resonance (NMR) to understand sub-lethal effects of contaminants on aquatic invertebrates.



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## Human Exposure Pathways of Legacy and Replacement PFASs and the Relative Importance of Dietary Intake

Understanding the major human exposure pathway(s) of per- and polyfluoroalkyl substances (PFASs) is a crucial step in risk assessment and a prerequisite for the development of effective management strategies for these chemicals. Two diverging hypotheses have been presented to explain the ubiquitous presence of perfluoroalkyl acids (PFAAs) in human serum from the general population. One hypothesis, the indirect exposure hypothesis, emphasizes the importance of near-field exposure to precursor compounds which can be metabolized to form PFAAs. The second hypothesis stipulates that human exposure is primarily a consequence of integrated environmental emissions and direct exposure to PFAAs via dietary intake. Significant progress on this topic has been made over the last decade due to improvements in analytical techniques and comprehensive monitoring of humans and a wide range of exposure media. The development of different exposure modelling approaches has allowed the consistency of estimated external exposures to be quantitatively evaluated against biomonitoring data. The increasing data on molecular markers of exposure, including intermediate metabolites and isomer profiles, have provided independent evidence to differentiate between multiple exposure pathways. Despite these advances, the relative importance of various exposure pathways of legacy PFASs in humans remains debated. Furthermore, little is known about human exposure potential for replacement PFASs being produced in increasing quantities. This presentation will summarize the current state of science regarding human exposure pathways for legacy and replacement PFASs with a particular focus on dietary intake.

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**ROBIN VESTERGREN** is a junior researcher in the Department of Environmental Science and Analytical Chemistry (ACES) at Stockholm University, Sweden. He holds a M.Sc. in chemistry and chemical engineering from the Royal Institute of Technology and a Ph.D. in environmental science from Stockholm University. Dr. Vestergren's research focuses on the development and application of analytical techniques and modelling approaches to gain understanding of the environmental fate, transport and exposure of per- and polyfluoroalkyl substances. Over the past couple of years Robin has established a strong collaboration with scientists at the Research Center for Eco-Environmental Sciences (RCEES) in Beijing, China. Current research projects include mechanistic studies on human exposure to legacy and replacement PFASs in a highly exposed human cohort.



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## Toxicology, Epidemiology, and Human Health

Reports of cancers in rodent models exposed to per– and polyfluoroalkyl substances (PFASs) began appearing in the literature several decades ago and the number of publications related to PFAS toxicity and potential human health effects has increased dramatically in the ensuing decades. Based on this extensive body of research, PFASs are now regarded as multisystem toxicants, which has made it challenging to identify a single mode or mechanism of action for these compounds. While governments and organizations have assessed the potential human health risks of specific compounds and health advisories have been established, questions surrounding PFAS toxicity, the extent of the human exposome, and the toxicity of replacement PFAS compounds for those taken out of production remain. This session will address toxicological findings of PFASs, including epidemiological data from highly exposed human populations, and the potential implications of these findings for human health.

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### Session Chair

**JAMIE DEWITT** is an Assistant Professor in the Department of Pharmacology and Toxicology at the Brody School of Medicine at East Carolina University. She received Ph.D. degrees in Environmental Science and Neural Science from Indiana University-Bloomington, completed postdoctoral training in Developmental Cardiotoxicity at Indiana University-Bloomington and in Immunotoxicology at the U.S. Environmental Protection Agency. Dr. DeWitt's research focus is on how toxicants found in the environment can lead to neurodevelopmental and neurodegenerative disorders via disruption of the developing immune system.



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## A Synopsis of the Toxicology of Perfluoroalkyl Acids

Ever since the confirmation of the widespread presence of perfluoroalkyl acids (PFAAs) in the environmental biota in the late 1990s, significant advancements have been made in the understanding of the biological interactions of many of these related compounds. Even though perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) have been the anchor points for investigation, the number of other compounds that have come under study has continued to increase. This presentation will highlight significant areas of consensus in the toxicology of PFAAs as well as data gaps that require further research. In addition, the use of physiologically-based pharmacokinetic (PBPK) models in toxicological research is an exciting area of opportunity for further refinement of epidemiological research. As the scientific literature related to exposures to these compounds continues to expand, it is important to synthesize all the information available.

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SUE CHANG is a senior toxicology specialist within the Medical Department of 3M Company. She received her Ph.D. in Toxicology from the University of Minnesota and she is a member of the Society of Toxicology as well as Northland Chapter of SOT. Dr. Chang is responsible for the toxicology research and health risk assessment programs associated with perfluoroalkyl chemicals produced by 3M and she has contributed to over 30 peer-reviewed scientific papers and numerous presentations on the toxicology of perfluoroalkyl acids.



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## Progress in Ecotoxicology of Perfluoroalkyl Acids

Perfluoroalkyl acids (PFAAs) are a diverse group of chemicals that are not easily metabolized or excreted from the body, with longer carbon chain PFAAs ($n \geq 7$) exhibiting higher accumulation capability and being more physiologically persistent than shorter chain PFAAs. Adverse effects have been observed in laboratory animals following PFAA exposure. However, the precise details of the toxic effects and the mode of action of PFAA toxicity have yet to be elucidated. We hypothesized that captivity in industrialized areas increased PFAA levels in wildlife and presented a health risk to these animals. Therefore we analyzed PFAAs in the serum of highly endangered Chinese alligators held at the Anhui Research Center for Chinese Alligator Reproduction, far from point sources of PFAAs. Furthermore, we assessed exposure to PFAAs in occupational workers of a fluorochemical plant and nearby residents. Results showed perfluorooctanoic acid (PFOA) to be negatively associated with high-density lipoprotein cholesterol in plant workers. To identify the mode of action of PFAA toxicity, we applied a toxicogenomic approach to hepatic gene expression profile analysis in rare minnows. Our results demonstrated that PFAAs induced hepatic steatosis via perturbing fatty acid uptake, lipogenesis, and fatty acid oxidation. Moreover, we confirmed that liver fatty acid-binding protein (L-FABP) can bind PFAAs with moderate affinity. L-FABP may be a cytosolic transporter for these major pollutants, transporting PFAAs within the hepatocyte cytoplasm to the nucleus for peroxisome proliferator activated receptor (PPAR)-mediated transcriptional regulation.

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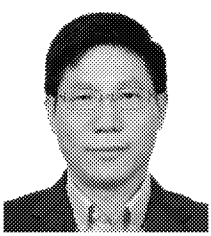

**JIAYIN DAI** is a Professor at the Key Laboratory of Animal Ecology and Conservation Biology, Institute of Zoology, Chinese Academy of Sciences and Director of the Key Laboratory of Animal Ecology and Conservation Biology. He earned his Ph.D. in Environmental Sciences from Nanjing University in 1999. Professor Dai was awarded funding from the National Science Foundation of China for Distinguished Young Scholars in 2010. He has been a member of The American Society of Toxicology (SOT) and he is also a council member of the Chinese Society for Environmental Sciences Division of Persistent Organic Pollutants. His research focuses on the toxicity of poly-and perfluoroalkyl substances as well as their distribution, fate, sources, and pharmacokinetics in the environment and wildlife.



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## The Epidemiology of Perfluorinated Compounds – Where Are We Now?

Most epidemiology research has focused on perfluorooctanoic acid (PFOA) and to a lesser degree on perfluorooctane sulfonate (PFOS). Endocrine disrupting and carcinogenic risks have been of particular interest and two reviews published last year brought together a lot of evidence. Multiple studies on birth weight have shown an association between fetal growth and indicators of PFOA exposure, and a recent major review concluded this association was causal. The International Agency for Research on Cancer recently classified PFOA as possibly carcinogenic to humans (Category Group 2B). Taking these two examples of potential risks of PFOA, methodological design issues in PFOA research which inform the assessment of causality will be presented. These include: the choice of cross-sectional studies where exposure is measured at the same time as health effects versus longitudinal studies where exposure demonstrably precedes effect; and the choice of biological measures of exposure such as serum concentration versus external measures of exposure. The C8 Science panel studies on a large population with substantial and well-characterized PFOA exposure have provided both important evidence on a range of health effects related to PFOA and insights into these methodological problems. Looking ahead, given the restrictions on manufacture and use of PFOA and PFOS, exposure is shifting to other perfluorinated compounds with different chain lengths. Epidemiology of these compounds is up to now sparse, but sporadic results are suggesting some associations. Future research trends will be addressed and lessons from PFOA research to improving designs in future studies will be presented.

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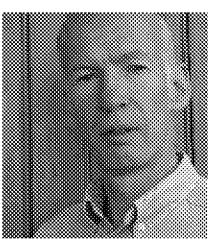

**Tony Fletcher** works as an Environmental Epidemiologist at the London University at London School of Hygiene and Tropical Medicine and for the UK Government in the Centre for Radiation Chemical and Environmental Hazards of Public Health England. He is an Adjunct Research Professor at the Boston University School of Public Health. He was President of the International Society for Environmental Epidemiology 2004 to 2005. During 2006 to 2013, he was part of the C8 Science Panel established to assess the links between PFOA contamination and disease in West Virginia and Ohio. He has over 30 years work in occupational and environmental epidemiology and risk assessment, with experience of studies of risk factors for cancer, respiratory disease, endocrine disruptors, and other adverse effects.



ED_002330_00143654-00022

## Risk Assessment, Regulatory Policy, and New Chemicals

Hazard assessment of per- and polyfluoroalkyl substances (PFASs) in the environment is never a conformist task, which is particularly hindered by limited toxicology data of various kinds of current PFASs as well as their ubiquitous properties compared with other persistent organic pollutants. Efforts from scientific communities and authority organizations have undertaken extensive studies evaluating emission sources, exposure pathways, and epidemiological evidence of effects of long chain PFASs, with successful experiences gained on reduction of public health risks. Nevertheless, continuous evaluation of existing PFASs and identification of novel PFASs in recent years suggests the challenges still remained. Environmental fates of some alternatives are quite similar to those of existing ones, while others might not be. The speakers in this session will present perspectives and research strategies on how to evaluate from a risk and regulatory perspective both existing PFASs and new fluorinated chemicals. They will discuss and suggest which actions should be made based on past actions and experiences as well as the filling of various knowledge gaps.

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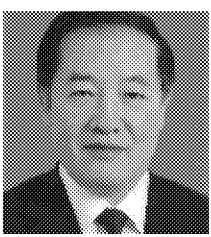
### Session Chair



**GUIBIN JIANG** received his Ph.D in environmental chemistry from the Research Center for Eco-Environmental Sciences of the Chinese Academy of Sciences in 1991. He was a visiting scholar in National Research Council of Canada during 1989-1991 and a postdoc fellow at the University of Antwerp, during 1994-1996. He is currently Director-General of the Research Center for Eco-Environmental Sciences and the Director of the State Key Laboratory of Environmental Chemistry and Ecotoxicology. His research mainly focuses on environmental analytical chemistry and toxicology. He received the Chang Jiang Scholars Achievement Award in 2007 and the National Natural Science Award in 2003 and 2011and the Outstanding Achievement Award on POPs of Chinese Academy of Sciences in 2013.



ED_002330_00143654-00023

## Assessment and Regulatory Approaches in Europe

Due to their high persistence, per- and polyfluoralkyl substances (PFASs) are distributed ubiquitous in humans and the environment. PFASs are monitored all around the world, in environmental samples and in human blood. These findings are of concern due to the combination environmental behavior and persistency, toxicological profile of certain PFASs, and the potential to accumulate in the body and in food chains. Many industrialized countries have started to undertake regulatory actions for PFASs. As a persistent organic pollutant (POP) perfluorooctane sulfonate (PFOS) was included into Annex B of the Stockholm Convention on POPs in 2010 aiming at a worldwide phase out. Recently, Germany and Norway proposed an EU-wide restriction of production, use, and import of perfluorooctanoic acid (PFOA) and precursors as such, and also in (imported) products. Additional activities to assess and to regulate PFASs are ongoing and in preparation under REACH. These activities also include short chain PFASs and PFOA substitutes. In 2006, OECD established an interest group to gather information on production, uses, and releases of long chain PFASs. Later the group was expanded to become the OECD/UNEP Global PFC Group also contributing to the objectives of the Strategic Approach on International Chemicals Management. The objectives of the Group are to provide scientific information to interested countries. Experts from industry, research, authorities, and NGOs work on an exchange of information on PFASs. This might be the basis for further international measures to reduce the emissions of PFASs and to support the transition to safer alternatives. This should also include the risk arising from the use of short chain PFASs.

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**Christoph Schulte** is with the Chemicals Safety Division of the German Umweltbundesamt - UBA (Federal Environment Agency). Since February 2008 he has led UBA's chemicals branch. He is an expert in risk assessment for chemicals and actively involved in the implementation of the European Chemical Regulation REACH. He is responsible for risk assessment for substances of very high environmental concern, e.g. chemicals with persistent, bioaccumulating and toxic properties (PBT-substances). His UBA career started in 1998 in the pesticides branch. After finalizing his PhD, he joined the Fraunhofer Gesellschaft and worked as a project manager. He is a biologist by teaching and started his research in aquatic ecotoxicology in the group of Roland Nagel at the Universities of Mainz and Dresden.



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## Risk Assessment & Risk Management of PFASs at US EPA

The US EPA is assessing and managing risks to per- and poly-fluorochemcials (PFASs) through several different statutory authorities and Program Offices. Legacy contamination of water and land by PFASs are being addressed through EPA's Office of Water and Office of Solid Waste & Emergency Response. EPA's Office of Chemical Safety and Pollution Prevention (OCSPP) has a number of regulatory and non-regulatory activities on-going to manage risks of existing PFASs. Action taken by the Office of Pesticide Programs and the Office of Pollution Prevention & Toxics (OPPT) within OCSPP will be presented. In OPPT's New Chemicals Program substitutes for perfluorinated substances are reviewed against toxicity, fate and bioaccumulation issues that have caused past concerns with PFASs, as well as any issues that may be raised by new chemistries. The wide range in properties and limited available data on the majority of PFASs notices received presents challenges in risk assessment process, requiring risk assessors to make use of limited analog information, professional judgement and often assumptions. These pchem, fate, exposure and hazard assessment assumptions will be presented. EPA's regulatory approach in the New Chemicals Program may include requirements for testing or restricted uses pending development of an adequate understanding of the chemical's fate and effects. The success of EPA's efforts are demonstrated by significant reductions in human blood concentrations of PFOS and PFOA, approximately 32% and 25% respectively, in samples collected 2003-2004 from levels found in samples collected 1999-2000. These reductions are most likely related to EPA efforts on these chemicals and other related efforts by government and industry.

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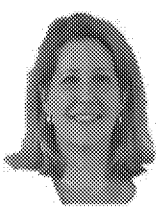

**TALA HENRY** has been with the US EPA for 20+ years. She is currently Director of the Risk Assessment Division in the Office of Pollution Prevention and Toxics where she leads EPA programs that assess the health and environmental hazards, exposures and risks of microorganisms and applications of biotechnology and new and existing chemicals, including perfluorochemicals. Dr. Henry has also served as the US representative and technical expert for a number of international chemical assessment and management activities. Dr. Tala Henry received a B.A. in Biology from the College of St. Scholastica, a Ph.D. in Pharmacology from the University of Minnesota and completed a Post-Doctoral Fellowship at the University of Wisconsin-Madison.



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## Fluorinated Alternatives to Long-Chain PFASs: What We Know About Them and Proposals on How They Should be Managed and Regulated

Long-chain poly-and perfluorinated substances (PFASs) are being substituted by alternative substances including many structurally similar fluorinated alternatives. In recent work, we have identified more than 20 fluorinated alternatives and reviewed the data available for conducting hazard and risk assessments. We found that fluorinated alternatives possess high environmental stability and mobility ensuring a high global contamination potential. In addition to their potential for causing global exposures, certain fluorinated alternatives were identified as toxic and are thus likely to pose risks to humans and the environment. In the Madrid Statement, a group of >200 scientists supported limiting the production and use of all PFASs despite the diverse physicochemical properties, environmental fate behavior, bioaccumulation potentials and toxicities. The high ultimate environmental persistence of all perfluoroalkyl acids (PFAAs) is a major motivation behind the Madrid Statement. Releasing large amounts of highly persistent chemicals will certainly lead to the occurrence of poorly reversible exposures in some parts of the environment and this is a major motivation for application of the precautionary principle in chemicals management. An example of PFAS contaminated groundwater used as a drinking water source will be used to illustrate the potential problems that are likely to arise from the use of short-chain PFASs in fire-fighting foams. I will demonstrate that the reversibility of human exposure arising from consuming this contaminated drinking water is not related to the magnitude of the bioaccumulation potential.

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**Ian Cousins** is a Professor in the Department of Environmental Science and Analytical Chemistry (ACES) at Stockholm University in Sweden. He received a Ph.D. in Environmental Chemistry at Lancaster University under Kevin Jones. He then undertook postdoctoral studies with Donald Mackay at Trent University in Canada. He is primarily an expert on modelling organic pollutants, although he has undertaken a number of experimental studies on PFASs and other chemicals and even recently ventured into the area of chemical management and policy. He made the first global source inventory for perfluorocarboxylates, has conducted several multimedia modelling studies on legacy PFASs, and has recently turned his attention to better understand the fluorinated alternatives to the long-chain PFASs.



ED_002330_00143654-00026

# Poster Abstracts:

# Analytical Chemistry and Monitoring

# Perfluoroalkyl Acids: An Assessment of a Coastal Population of the American Alligator

JACQUELINE T. BANGMA[1], JOHN BOWDEN[2], JESSICA REINER[2], RUSSELL LOWERS[3], MATTHEW P. GUILLETTE[1], LOUIS J. GUILLETTE JR.[1]

Limited literature exists on perfluorinated alkyl acids (PFAAs) in coastal regions of the United States, and few studies have published data on PFAAs in a crocodilian species. As a long-lived top predator, crocodilians have the potential to accumulate high levels of PFAAs. A recent initial study from our laboratory observed unusually high levels of PFAAs in the plasma of adult alligators caught at Kennedy Space Center (KSC) when compared to several other sampling sites throughout the southeast. Recently, a small percentage of alligators from KSC have been documented to exhibit a waste-like disease, yet the etiology for this disease remains unknown. Therefore, it is vital to characterize PFAAs in alligator plasma surrounding this facility and other coastal areas to understand whether the compromised health and disease susceptibility posed by PFAAs are a risk to the alligators, other wildlife, and humans living and working in this area. This study examines PFAAs in alligator plasma samples from animals identified as exhibiting the waste-like disease and healthy alligators.

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[2] *NIST, Organic Chemical Metrology, South Carolina*
[3] *InoMedic Health Applications (IHA), Kennedy Space Center, Florida*



ED_002330_00143654-00033

# PFOA Vs. Its Replacement Substance HFPO-DA: Their Current Environmental Releases and Fates in The Rivers and Coastal Environment of Germany and China

FRANZISKA HEYDEBRECK[1], ZHIYONG XIE[2], JIANHUI TANG[2], RALF EBINGHAUS[1]

Long-chain PFASs, such as PFOA, are of high concern because they are highly persistent, bioaccumulative, toxic, and ubiquitously present in the environment. Thus there is the attempt of the fluoropolymer industry to develop other fluorinated substances with more favourable toxicological and environmental properties. Information on structural properties, production volumes, uses, and environmental as well as biological effects of those alternatives is limited. One fluorinated alternative is the chemical 2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propanoic acid, shortly HFPO-DA. The ammonium salt of HFPO-DA, namely GenX, is known as an APFO or PFOA alternative which has been produced as a processing aid for the fluoropolymer resin manufacturing since 2010. The producer developed an exposure control strategy to keep the substance within the manufacturing site. However, it is uncertain whether HFPO-DA is truly not emitted during the manufacturing process. In this study we investigated whether there is an exposure of HFPO-DA to the rivers and coastal environment of Germany and China. The current environmental releases of HFPO-DA and its predecessor, PFOA, were compared trying to assess the environmental relevance of the fluorinated alternative HFPO-DA.

[1] *Helmholtz-Zentrum Geesthacht*
[2] *Key Laboratory of Coastal Zone Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research, China*



ED_002330_00143654-00034

# The CEEP Project: Understanding Children's Exposure to Per- and Polyfluoroalkyl Substances

KERSTIN WINKENS[1], JANI KOPONEN[2], ROBIN VESTERGREN[1], URS BERGER[3], IAN COUSINS[1]

Exposure to chemicals during sensitive childhood stages has been hypothesized to be a key factor in the development of several diseases. However, knowledge about early life exposure to many chemicals is limited. "Childhood Exposure to Environmental Pollutants (CEEP)" is a joint research project with focus on childhood exposure to perfluoroalkyl acids (PFAAs) and their precursors. The study participants comprise 55 randomly selected Finnish children subsampled from a larger study in Kuopio, Finland. Repeated blood samples were taken at the age of 1, 6 and 10 years (2004-2015) and external exposure media, including indoor dust, air and drinking water, were collected for the same individuals. Individual food frequency questionnaires will be utilized to estimate exposure to PFASs via food. Urine samples were taken to investigate excretion. The combination of longitudinal serum trends and concentrations in multiple exposure media will provide a unique dataset for quantifying the relative importance of different exposure pathways over time. The results will be valuable inputs for evaluation of pharmacokinetic models. Risk assessment and management strategies to reduce exposure to PFAAs will be facilitated. Additionally, interpretation of epidemiological studies linking exposure to diseases could be supported by our data.

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[2] *Department of Environmental Health, National Institute for Health and Welfare (THL), Kuopio, Finland*
[3] *Department Analytical Chemistry, Helmholtz Centre for Environmental Research (UFZ), Leipzig, Germany*



ED_002330_00143654-00035

# Development of a Method for the Simultaneous Determination of Polyfluorinated Phosphate Esters (PAPs) and Other Per- and Polyfluorinated Alkyl Substances (PFAS) in Sediments.

ANN-KRISTIN SIEGMUND[1], FRANZISKA HEYDEBRECK[1], RENATE STURM[1], RALF EBINGHAUS[1]

Fluorotelomer-based polyfluorinated phosphate mono-, di-, and tri-esters (mono-, di-, and triPAPs) are precursors of perfluoroalkyl carboxylic acids (PFCAs). They are widely-used to make food packaging materials made of paper and paperboard water- and grease-proof (Buck, 2011). The production of perfluorooctane sulfonate (PFOS) and perfluoro-n-octanoic acid (PFOA) is presently reduced or discontinued in Europe and North America, whereas the production of fluorotelomer chemicals is increasing (D'Eon 2011). Due to the variable chemical structure and varying pKa-values of the analytes, the simultaneous extraction of PAPs and other PFASs caused problems in former methods. Moreover, different pH-values in the sediments show problems in the extraction. In this study a method was developed to extract eight PAPs, eleven PFCAs, five perfluoroalkane sulfonic acids (PFSAs), three perfluorinated phosphinates (PFPiAs) and three perfluoroalkyl phosphonates (PFPAs) from sediments. Three different extraction-methods were compared, such as Accelerated Solvent Extraction (ASE), QuEChERS and ultrasonic supported liquid extraction followed by clean-up on Oasis'® WAX SPE cartridges. In all methods the purification was the critical step. Purification is necessary to lower matrix effect during the analysis. Simultaneously minor losses of the analytes have to be ensured. The extracts were analyzed by liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS).

[1] *Helmholtz-Zentrum Geesthacht*



ED_002330_00143654-00036

# Quantitative Determination of Per- and Polyfluoroalkyl Substances on Paper by LC-MS/MS & Total Oxidizable Precursor (TOP) Assay with Confirmation by Total Fluorine

ALIX E. ROBEL[1], MCKAY ALLRED[2], MARGARET DICKINSON[3], DAVID LUNDERBERG[3], GRAHAM PEASLEE[3], JOHNSIE LANG[4], MORTON BARLAZ[4], JENNIFER FIELD[5]

Per-and Polyfluoroalkyl substances (PFASs) are ubiquitous in the environment and in blood and organs of humans, partially from exposure to consumer products during their use and after disposal. Fifteen representative papers and 9 textiles samples were analyzed for PFASs using three techniques: liquid chromatography tandem mass spectrometry (LC-MS/MS), total oxidizable precursor (TOP) assay, and total fluorine by particle-induced gamma-ray emission (PIGE) spectroscopy. Seventy individual PFASs in commerce were determined by LC-MS/MS, and TOP assay was used to quantify the presence of PFAS precursors that dead-end to perfluoroalkyl carboxylates (PFCAs). The net production of PFCA that could not be accounted for by LC-MS/MS was used for the quantification of unknown precursors. Finally, the nanomolar quantities of PFASs determined by LC-MS/MS and TOP assay were compared to total fluorine content determined by PIGE. Total PFASs measured by LC-MS/MS were low compared to results from TOP assay. However, TOP Assay and PIGE showed agreement, highlighting the utility of these assays for obtaining mass balance on fluorinated substances in paper and textiles. Because PIGE is an inexpensive, high throughput technique, PIGE will be used as the total fluorine method of choice to guide future studies aimed at closing mass balance on PFASs in consumer products.

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[2] *Department of Chemistry, Oregon State University*
[3] *Chemistry Dept., Hope College, Michigan*
[4] *Department of Civil, Constructional, and Environmental Engineering, North Carolina State University*
[5] *Department of Environmental and Molecular Toxicology Oregon State University*



ED_002330_00143654-00037

# Comprehensive Characterization of Per- and Polyfluoroalkyl Substances (PFASs) in a Waste Water Treatment Plant Using Continuum Source-Molecular Absorption Spectrometry (CS-MAS), UHPLC-MS/MS and GC-MS

LARA R. SCHULTES[1], URS BERGER[2], JÖRG FELDMANN[3], MARCUS FRENZEL[4], JILL MATTSSON[4], JONATHAN P. BENSKIN[1].

Wastewater treatment plants (WWTPs) are known point sources of per- and polyfluoroalkyl substances (PFASs) to the aqueous, atmospheric, and terrestrial environment. Mass balance studies for evaluating containment and remediation strategies are hampered by the wide range of PFASs and degradation products occurring in these systems, which are not captured by routine, targeted analysis. In the present work, total organofluorine measurements were combined with mass spectrometry-based targeted analysis to comprehensively characterize PFAS occurrence at various stages of waste water treatment. Samples of influent, effluent, and upstream water along with primary, excess, thickened, digested and dewatered sludge were sampled from a WWTP over 2 weeks. A suite of 50 individual PFASs were quantified using UHPLC-MS/MS and GC-MS. Total organofluorine content was determined using fluorine-specific continuum source-molecular absorption spectrometry (CS-MAS). CS-MAS has the advantage of chromatographic separation prior to detection, which is not possible using traditional total organofluorine techniques (for example combustion ion chromatography). Organofluorines underlying the peaks observed in the HPLC-CS-MAS chromatogram can be structurally elucidated by matching retention times to peaks observed in LC-HRMS. Overall, this "fluoronomic" strategy facilitates quantification of both known PFASs and total organofluorine, while aiding in the identification of novel and hitherto unidentified organofluorine substances.

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[1] *Department of Environmental Science and Analytical Chemistry (ACES), Stockholm University, Stockholm, Sweden*
[2] *Department Analytical Chemistry, Helmholtz Centre for Environmental Research (UFZ), Leipzig, Germany*
[3] *Trace Element Speciation Laboratory (TESLA), University of Aberdeen, Aberdeen, Scotland UK*
[4] *Käppalaförbundet, Lidingö, Sweden*



ED_002330_00143654-00038

# Sorption of Anionic, Zwitterionic, and Cationic Per- and Polyfluorinated Alkyl Substances to Soil and Sediment

KRISTA BARZEN-HANSON[1], MARKUS KLEBER[2], JENNIFER FIELD[3]

Routine discharge of aqueous film-forming foam (AFFF) at U.S. military bases during fire-fighter training resulted in elevated concentrations of per- and polyfluorinated alkyl substances (PFASs) in groundwater. Newly-identified anionic, zwitterionic, and cationic PFASs plus the fluorotelomer sulfonic acids (FtSAs) present in AFFF formulations are not characterized with respect to their sorption (partitioning) behavior and subsurface transport. The sorption of anionic FtSAs, zwitterionic fluorotelomer sulfonamido betaines (FtSABs), and the cationic fluorotelomer sulfonamido amines (FtSaAms) were investigated using the National Foam AFFF and an analogous commerical reference material. Batch sorption experiments were conducted using solutions comprised of 0.5 mM calcium chloride and National Foam AFFF with initial concentrations ranging from 1,000 ng/L up to 138,000,000 ng/L. Analysis of the aqueous fraction by liquid chromatography tandem mass spectrometry after 24 h of shaking resulted in partial depletion of the anionic FtSAs and zwitterionic FtSaBs and complete depletion of the cationic FtSaAms from solution. Organic carbon-water partition coefficients (log Koc) ranged from 2.9 to 4.2 for the anionic 8:2 FtSA and zwitterionic 6:2 and 8:2 FtSaBs, respectively. The influence of organic carbon and cation exchange capacity on the sorption of the FtSAs, FtSaBs, and FtSaAms to various soils under a narrower concentration range (1,000-250,000 ng/L) using National Foam AFFF will be discussed. The determination of partition coefficients and their dependence on organic carbon and cation exchange capacity will aid in the development of models to predict the behavior of the anionic FtSAs, zwitterionic FtSaBs, and cationic FtSaAms in soil and subsurface environments.

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[2] *Department of Crop and Soil Science, Oregon State University*
[3] *Department of Environmental and Molecular Toxicology, Oregon State University*



ED_002330_00143654-00039

## Are Perfluoroalkyl Acids Leaching into Our Food?

LIESL KRONE[1], ANDRE SCHREIBER[2], JEFF MCDONALD[3]

The purpose of "Are Perfluoroalkyl Acids Leaching Into Our Food?" was to study the presence of PFAAs (Perfluoroalkyl Acids) in a variety of foods that are surrounded by materials that use these compounds for moisture wicking. PFAAs have been synthesized for more than 50 years and are used in numerous industrial and consumer products. They repel oil and water from clothing, carpeting, furniture, and are used in food packaging such as pizza boxes, fast-food containers, and microwave popcorn. They are also commonly used in cooking utensils as nonstick coatings. A triple quad mass spectrometer setup with a method to look for a number of PFAAs was used to analyze a variety of different food samples that come in contact with packaging thought to contain PFAAs. The mass spectrometer is a powerful analytical instrument used in many labs to detect targeted analytes such as PFAAs at really low levels. Samples were first weighed then extracted, analyzed by mass spectrometry and data reviewed using a quantitation software. We did not detect PFOA or PFOS (this is positive since they are banned and not produced anymore), but we detected some new replacement chemicals which are known to be used in packaging material. These new chemicals are less concerning for the environment since they degrade faster and are less persistent. However, it is not known yet if there is a negative effect on human health. Future studies are needed to investigate this.

[1] *Granbury High School*
[2] *SCIEX*
[3] *UT Southwestern Medical Center*



ED_002330_00143654-00040

# Development of a Novel Method to Measure Perfluorinated Compounds in Groundwater

DAVID M. LUNDERBERG[1], MARGARET DICKINSON[1], ALIX ROBEL[2], MCKAY ALLRED[2], JENNIFER FIELD[2], GRAHAM PEASLEE[1]

Because of the environmental persistence of per- and polyfluoroalkyl substances (PFASs), their ability to bioaccumulate, and their suspected human toxicity, new methods to identify these chemicals at trace levels in groundwater are needed. Particle induced gamma-ray emission (PIGE) spectroscopy is an established ion beam analysis technique that has been used to quantitatively measure light elements in diverse target materials. In this study, PIGE utilizes a beam of accelerated protons to excite $^{19}F$ nuclei in a target. As these nuclei return to their ground state, they emit characteristic gamma-rays that can be used to quantify the total fluorine concentration in a sample. An in-air PIGE methodology has been developed as an effective tool to determine the presence or absence of PFASs extracted from groundwater samples. Solutions of perfluoroakylsulfonate (PFOS) were extracted onto the surface of a weak anion exchange SPE column, and the total fluorine measured on this column by PIGE correlate well with the initial PFOS concentrations. Subsequent experiments with actual groundwater samples demonstrate PIGE to be an inexpensive, rapid, and non-destructive method for total fluorine analysis, which can be adapted to detect environmentally relevant PFASs concentrations in groundwater.

[1] *Hope College*
[2] *Oregon State University*



ED_002330_00143654-00041

# Development of a Novel Method to Measure Perfluorinated Compounds in Paper and Textiles

MARGARET E. DICKINSON[1], DAVID LUNDERBERG[1], ALIX ROBEL[2], MCKAY ALLRED[2], JENNIFER FIELD[2], JOHNSIE LANG[3], MORTON BARLAZ[3], GRAHAM PEASLEE[1]

Per- and Polyfluoroalkyl substances (PFASs) are chemical compounds used as powerful, long-lived surfactants in many consumer products. Because of the environmental persistence of PFASs, their ability to bioaccumulate, and their suspected human toxicity, new methods to identify these chemicals in consumer products are needed. Current techniques to measure PFASs involve liquid chromatography-tandem mass spectrometry (LC-MS/MS), which requires significant time and expense per sample for analysis. Particle Induced Gamma-ray Emission (PIGE) spectroscopy is an established ion beam analysis method used to measure total fluorine concentrations in various objects, typically sediments and minerals. PIGE utilizes a beam of accelerated protons to excite $^{19}F$ nuclei on the surface of a sample. As these nuclei return to their ground state, they emit characteristic gamma-rays that can be used to identify and quantify the total fluorine content in a sample. In this study, fifteen papers and nine textile samples were analyzed with LC-MS/MS, the total oxidizable (TOP) assay, and PIGE. A comparison of the results reveals that PIGE is an effective tool to determine the presence or absence of PFASs added to these consumer products. Limits of detection and the application of this method for rapid, non-destructive screening for certain consumer products were explored.

[1] *Hope College*
[2] *Oregon State University*
[3] *North Carolina State University*



ED_002330_00143654-00042

# Development of a Gas Phase Source For Perfluoroalkyl Acids to Examine Atmospheric Sampling Methods

JOHN J. MACINNIS[1], TREVOR C. VANDENBOER[2], CORA J. YOUNG[3]

Perfluoroalkyl acids (PFAAs) are ubiquitous compounds in the environment. Evidence suggests that the atmosphere contributes to long-range transport of PFAAs to remote locations, like the arctic. In recent years, it has been an analytical challenge to characterize the quantity of PFAAs in aerosol samples. This difficulty arises from sampling artifacts, such as sorption of gas phase PFAAs to filter substrates, which are persistent during sample measurements. As a result, this leads to inevitable inaccuracy. In the absence of a gas phase calibration source for PFAAs, it is difficult to quantify sampling artifacts. A common technique in atmospheric analytical chemistry is the use of acid displacement to produce calibration standards of gas phase acids. In this work, a gas phase source for PFAAs based on the acid displacement technique was constructed. This allows improvement in our certainty when atmospheric sampling of PFAAs is performed by selectively scrubbing PFAAs from the gas phase prior to particle collection. The effect of relative humidity on reaction efficiencies will be discussed, as well as the versatility of the source with respect to several PFAAs.

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[3] *Department of Chemistry, Memorial University*



ED_002330_00143654-00043

# Characterization of New Per- and Poly-Fluorinated Chemical Classes in a Chinese WWTP Sample by HPLC-Orbitrap-MS/MS

YANNA LIU[1]

The presence of unknown organofluorine compounds in environmental samples has prompted the development of non-targeted analytical methods capable of detecting new per-/polyfluoroalkyl substances (PFASs). By combining high volume injection with HPLC and ultrahigh resolution Orbitrap mass spectrometry, a sensitive untargeted workflow was developed for discovery and characterization of novel PFASs in water. First, up to 5 mL water is injected to in-line solid phase extraction, chromatographed by HPLC, and detected by electrospray ionization with mass spectral acquisition in parallel modes cycling back and forth: (i) full scan with ultrahigh resolution (R=120,000, mass accuracy of 3 ppm), and (ii) in-source fragmentation flagging scans designed to yield marker fragment ions (e.g. $[C_2F_5]$-). For flagged PFASs, plausible empirical formulae were generated from accurate masses, isotopic patterns and fragment ions. Secondly, another injection is made to collect high resolution MS/MS spectra of suspect PFAS ions, allowing further confirmation of empirical formulae while also enabling preliminary structural characterization. The method was validated by applying it to an industrial wastewater, and 36 new PFASs were discovered. Of these, 26 were confidently assigned to 3 new PFAS classes that have not previously been reported in the environment: polyfluoroalkylsulfates, chlorine substituted perfluorocarboxylates, and hydro-substituted perfluorocarboxylates.

[1] *University of Alberta*



ED_002330_00143654-00044

# Trifluoroacetic Acid Level in the Atmosphere of Beijing and Its Relationship with PM2.5

JUNYU GUO[1]

Atmospheric concentrations of trifluoroacetic acid (TFA), one of the main degradation products of HCFC-123, HCFC-124 and HFC-134a, were detected in Beijing, China between 2013 and 2014. By analyzing the 137 atmospheric samples, the results showed that the annual mean atmospheric concentration of TFA was 1459±223 pg/m$^3$. TFA was mainly distributed in gaseous phase, for the concentration was 1396±225 pg/m$^3$, while that in particle phase was 62±8 pg/m$^3$. Considering the frequent occurrence of hazy weather in Beijing, the relationship between TFA and PM2.5 in atmosphere was analyzed. The correlation analysis shows that the proportion of particle phase in atmosphere concentration of TFA and mass concentration of PM2.5 are positively correlated with each other ($P<0.001$), indicating the particles have an absorption effect on TFA. When mass concentration of PM2.5 in atmosphere is high, atmospheric concentration of TFA is relatively low. According to the correlation analysis, mass concentration of PM2.5 and atmospheric concentration of TFA are negatively correlated with each other ($P=0.005$). The main reason is very likely that the particle's extinction for light can be enhanced as particle level rises, which causes TFA precursors photolysis to weaken. The results indicate that PM2.5 has a significant impact on TFA.

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# Human Exposure to Per- and Polyfluoroalkyl substances Through Inhalation of Air- Results from Paired Samples of Household Indoor Air and Personal Air

JUAN A. PADILLA-SÁNCHEZ[1], SOMRUTAI POOTHONG[1], ELENI PAPADOPOULOU[1], LINE S. HAUG[1]

Indoor air samples from the living room of 61 households in Oslo, Norway were collected, and concentrations of volatile per- and polyfluoroalkyl substances (PFASs) were determined. Fluorotelomer alcohols (FTOHs) were detected in all samples with average concentrations of 8.6, 29, and 12 ng/m3 for 6:2, 8:2, and 10:2-FTOH, respectively. While average concentrations of N-methyl and N-ethyl perfluorooctane sulfonamidoethanols (MeFOSE and EtFOSE) were 3.0 and 1.6 ng/m3 with 70% and 49% detection frequency, respectively. N-methyl and N-ethyl perfluorooctane sulfonamides (MeFOSA and EtFOSA) showed detection frequencies below 15%. Personal air samples from participants living in fifteen of the 61 households were also collected and volatile PFASs determined. A 100% detection frequency of FTOHs was obtained in personal air with average concentrations at 4.9, 11 and 2.6 ng/m3 for 6:2, 8:2 and 10:2-FTOH, respectively. FTOH concentrations in personal air were lower than indoor air. 8:2-FTOH was the predominant FTOH in both types of air samples. Preliminary results showed no significant correlation between indoor and personal air samples. The intake of PFOA in adult through biotransformation of FTOHs from inhalation of in indoor air was estimated to be in the range 0.010-0.21 and 0.001–0.033 ng PFOA/kg bw/day for 8:2-FTOH and 10:2-FTOH, respectively.

[1] *Division of Environmental Medicine, Norwegian Institute of Public Health*



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# Investigation of Environmental PFAS Contamination: Sampling and Analysis

NICHOLAS BATTYE[1]

A series of experiments was conducted from 2011-2013 to address challenges encountered in the management of aqueous film-forming foam contaminated sites. The primary issue was the data itself; results appeared almost random with inter-laboratory results sometimes off by several orders of magnitude. The goal of the work was to determine possible causes of analytical variation, both laboratory- and field-derived, and resolve the issue of inter-laboratory disagreement. To identify potential laboratory-derived analytical variation, the Environmental Sciences Group (ESG) standardized the sample container sizes and eliminated the practice of subsampling on the hypothesis that the poor reproducibility was due to stratification. The significance of stratification was also assessed in relation to field equipment and field sampling practices. Examinations of two different field sampling protocols and three different groundwater sampling methods were carried out, and a limited study was conducted to assess the suitability of existing monitoring wells for per- and polyfluoroalkyl substance PFAS assessment. ESG's studies have shown that significant advances in analytical methodology since 2011 have enabled the acquisition of meaningful data and provided custodians with steps to assess data quality. Overly-conservative field protocols do not seem to be required and given the limited data so far, standard well designs and well sampling practices seem to be acceptable.

[1] *Environmental Sciences Group , Royal Military College of Canada*



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# PFAS Analysis: Differences in Analytical Techniques and Effects in Sample Results

ANN BERNHARDT[1], SEAN GORMLEY[1]

Aqueous film forming foam (AFFF) has proven very effective in fighting fuel related fires. Per- and polyfluoroalkyl substances (PFASs) are present in AFFF and extensive sampling and analysis is underway to determine the presence of PFASs due to AFFF use. This compound class creates many challenges for generating reliable data to determine PFAS presence. Lack of commercially available performance evaluation samples, differing analytical method modifications, different extraction techniques, challenging matrices, and the very high potential for false positives have required additional quality control measures. The poster will present the dataset from a quality control perspective to understand effects of field controls to limit contamination, method modifications by multiple laboratories, differences in extraction procedures, and method sensitivity. The dataset includes several hundred datapoints and associated quality control data generated by multiple laboratories. This poster presentation will highlight the analytical challenges and impact of analytical differences of this emerging contaminant class.

[1] *Amec Foster Wheeler*



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# Analysis of Perfluorobutanesulfonamide (FBSA) in Serum, Urine, Liver, and Feces

ALAN EVELAND[1], RYAN KRISKO[1], JILL HART[1], DAVID EHRESMAN[1], SUE CHANG[1]

The purpose of this study was to develop and optimize the analytical method for the quantification of perfluorobutanesulfonamide ($C_4F_9SO_2NH_2$, FBSA) in various biological matrices using solid-phase extraction (SPE) and LC-MS/MS. In addition, prior to SPE, enzymatic deconjugation using beta-glucuronidase was also evaluated for all the samples because FBSA can potentially undergo glucuronidation due to the presence of amide group. Serum, liver, urine, and fecal samples obtained from male Sprague Dawley rats (N=3) were used for this study. Rats were given a single oral dose of 3 mg FBSA (in 0.5% Tween 20) per kg body weight and urine and fecal samples were collected overnight. At 24 hours post-dose, blood and liver samples were collected from all the rats after euthanasia. Subsequent to primary sample preparation (i.e., homogenization for liver and fecal samples), 100 uL of serum, liver homogenate, urine, or fecal extracts were processed through SPE followed by LC-MS/MS or incubated with 100 uL of beta-glucuronidase (5U/uL, 24 hours at 37°C) followed by SPE and LC-MS/MS. Our data demonstrated that pre-treatment with beta-glucuronidase improved the recoveries of FBSA in urine, liver, serum, and feces.

[1] *3M Company*



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# Per- and Polyfluoroalkyl Substances in Source and Treated Waters from 25 Drinking Water Treatment Plants and the Effect of Activated Carbon on Their Removal

J.S. BOONE[1], C. BYRNE[2], S.T. GLASSMEYER[3], E.T. FURLONG[4], D.W. KOLPIN[5], AND J.B. FERRARIO[2]

The USEPA and USGS conducted a national study of source and treated water from 25 drinking water treatment plants (DWTPs) in the U.S. for contaminants of emerging concern. Seventeen per- and polyfluoroalkyl substances (PFASs) were analyzed in both source and treated water. At least one PFAS was detected at all sampling locations. Based upon mean concentrations, the most abundant PFASs (with maximum concentrations in ng/L) in descending order were: PFPeA (510) > PFOA (110) > PFBA (100) > PFHpA (180) > PFHxA (60) > PFOS (50) > PFHxS (50) > PFNA (40)= PFDA (30)= PFBS > PFUnDA > PFDoDA; and upon detection frequency, the most prevalent PFASs were: PFHxA > PFBS > PFBA = PFPeA = PFHpA > PFNA > PFHxS > PFOS > PFOA > PFDA > PFUnDA > PFDoDA. Five PFASs were never detected: PFTrDA, PFTeDA, PFHxDA, PFOcDA, and PFDS. Concentrations of individual PFASs in treated waters were similar to their source waters at all sites tested with the exception of one DWTP that had the highest amount of graphitized active carbon (GAC), with the longest reportable empty bed contact time (EBCT), and the shortest time between GAC bed replacements. In most cases, PFASs were not well removed by conventional drinking water treatment processes.

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[2] *USEPA/OCSPP/OPP/BEAD/Environmental Chemistry Branch, Stennis Space Center, MS, USA (currently: retired).*
[3] *USEPA, ORD, National Exposure Research Laboratory, Cincinnati, OH.*
[4] *USGS, National Water Quality Laboratory, Denver, CO.*
[5] *USGS, Iowa City, IA.*



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# Occurrence of Perfluorinated Compounds (PFASs) in Northern Spain Municipal Solid Waste Landfill Leachates

SONIA GÓMEZ-LAVÍN[1], INMACULADA ORTIZ[1], ANE URTIAGA[2]

Per- and polyfluorinated compounds (PFASs) are recognized as chemicals of environmental concern due to their ubiquitous presence in the environment. PFASs are highly persistent and some are bioaccumulative. They are used as surfactants, coatings and fire-fighting agents, as well as chemical components of an extensive array of consumer products that are ultimately disposed of in waste and wastewater systems. Given the potential for landfills to act as important environmental point sources of PFASs, the characterization of the PFASs present in landfill leachates is of paramount importance to provide details on loadings and sources to the environment. The few available data on PFASs occurrence in leachates correspond to landfills from North America and Europe, and have reported concentrations of PFASs among the highest levels in environmental waters, second only to US military groundwater contaminated by aqueous film forming foam. Recent surveys have revealed that leachates can contain levels of PFASs as high as 59700 ng/L. This work aims to study for the first time the PFAS concentration in untreated leachate samples from municipal solid waste landfills in Northern Spain. The levels of eleven perfluoroalkylcarboxylic acids and five perfluoroalkylsulfonates will be assessed and compared with the levels in the treated leachates.

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[2] *University of Cantabria*



ED_002330_00143654-00051

# Relative Performance of Different Procedures for Extraction of Perfluoroalkyl Acids from Soil: A Limited Study

SEAN GORMLEY[1], ANN BERNHARDT[1], MARIE BEVIER[1], ALLISON CLARKE[2], BRYAN ROBERTS[2], EMILIE SCHNEIDER[2], ANDREW PATTERSON[2], MARTHA MAIER[2], NORM FARMER[3]

Perfluorinated surfactants related to Aqueous Film Forming Foams (AFFFs) have recently surfaced as an emerging class of environmental contaminants. Due to the relatively limited experience of the analytical community in analysis of this compound class, and the lack of reference methods that have been subjected to multi-lab testing, several different extraction methods have been employed by different labs including:

1) Extraction with methanol only;
2) Extraction with alkaline methanol (consistent with ASTM Method D7968-14); or,
3) Pretreatment with caustic followed by extraction with a 50:50 acetonitrile/methanol mixture (consistent with Draft Procedure for Analysis of Perfluorinated Carboxylic Acids and Sulfonic Acids in Sewage Sludge and Biosolids by HPLC/MS/MS, December 2011).

This poster will present the results of a study comparing perfluoroalkyl acid results obtained by extracting a limited number of samples using the three different methods.

[1] *Amec Foster Wheeler*
[2] *Vista Analytical Laboratory*
[3] *Accutest Laboratories Southeast*



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# Current PFAS Profiles in San Francisco Bay Municipal and Industrial Wastewater Effluent

ERIKA HOUTZ[1], JUNE-SOO PARK[1], REBECCA SUTTON[1], MEG SEDLAK[1]

PFOS has been measured at persistently high concentrations in San Francisco Bay wildlife. To assess potential sources of PFOS and other poly- and perfluoroalkyl substances (PFASs) to the region, wastewater effluent samples from eight local treatment plants were collected for PFAS analysis. The treatment plants receive different types of influent, including municipal and industrial waste, and they utilize a range of different treatment processes. Wastewater samples were analyzed directly for a suite of PFASs and were also subjected to an oxidation assay to indirectly estimate the total concentration of polyfluorinated compounds. In all but two samples, the concentrations of C4 and C6 perfluorocarboxylic acids (PFCAs) were equal to or higher than those of PFOA, PFOS, and PFHxS, reflecting the shift to shorter-chained chemicals that has occurred in PFAS manufacturing. The oxidation assay indicated 30% to 60% of total molar PFASs were polyfluorinated (median = 42%). Similar to perfluorinated acids, the oxidation assay showed a preponderance of C6 and shorter polyfluorinated chemicals in all wastewater samples. These results indicate that C8 PFASs are waning relative to their shorter chain counterparts in SF Bay effluent. The views expressed herein are those of the authors and do not necessarily reflect those of the California Department of Toxic Substances Control.

[1] *Environmental Chemistry Lab, California Dept. of Toxic Substances Control*



ED_002330_00143654-00053

# Identification of Highly Fluorinated Substances in Fire Fighting Foams

ANNA KARRMAN[1]

The objective of the study is to give an overview of the content of fluorinated substances in firefighting foams present on the Swedish market. Firefighting products commonly used (high volume products according to the Chemical Agency register) were provided from different sources, both users and suppliers, and were analyzed for known per- and polyfluorinated alkyl substances (PFAS) using LC-MSMS and GC-MS, and for unknowns (non-target) by MSE-QTOF. PFAS was found in the majority of products analyzed; most commonly detected were short chain perfluorinated carboxylates, from low ppb levels up to ppm levels. The presence of PFAS could in some cases be related to the fluorinated main ingredient, but in some cases contamination is suspected. PFOS was found in a product that was provided by three different users; however, only one sample contained PFOS. This means that tanks and other equipment probably still contains PFOS and possible other PFAS despite the product turnover. The structure of the main ingredients were tentatively elucidated and were found to contain perfluorinated parts in some cases. The environmental fate of the tentatively identified fluorinated substances is likely transformation into persistent perfluorinated acids.

[1] *MTM Research Centre*



ED_002330_00143654-00054

# Novel Microsampling Technique with Mitra™ in Analysis of Perfluoroalkyl Acids in Blood

JANI M. KOPONEN[1], JAMES RUDGE[2], STUART KUSHON[2], HANNU KIVIRANTA[1]

Microsampling is an attractive option for significantly reducing the volume of blood taken for analysis allowing for blood samples taken as a 'finger-prick' with a lancet. A novel, patent-pending microsampling device, Mitra(TM) reproducibly collects a small volume (10 µL) of whole blood in a haematocrit-independent manner and, as a result, overcomes the major challenge and limitation of conventional dried blood spot cards that have historically been used for microsampling. In this study the Mitra microsamplers have been evaluated in an environmental monitoring setting, and have been utilized for analysis of perfluoroalkyl acids (PFAA). PFAA have been associated with various adverse health effects, such as elevated total and LDL cholesterol, increased breast cancer risk and disruption of thyroid hormones. After the microsampling, the PFAA were extracted with methanol. The PFOS, PFOA and other sulfonates/carboxylates were separated and detected with LC-MS/MS. Based on the preliminary results, the limit of quantitations (LOQs) for individual PFAA in blood were from 0.3 to 1.0 ng/ml and coefficient of variation from 5 to 10%. The results show that the microsampling technique is applicable for PFAA analysis, the method has good repeatability and is sufficiently sensitive for samples from general populations. Furthermore, as well as allowing for a quick and efficient extraction flow path, Mitra microsampler is an easy to use device in a real-world sample collection scenario.

[1] *Finnish National Institute for Health and Welfare (THL)*
[2] *Neoteryx, CA*



ED_002330_00143654-00055

# Poly- and Perfluoroalkyl Substances in Antarctic Seabird Plasma: Optimization and Validation of an On-Line Solid Phase Extraction Ultra-High Performance Liquid Chromatography Tandem Mass Spectrometry Method

PIERRE LABADIE[1,2], GABRIEL MUNOZ[1], PATRICK PARDON[1], OLIVIER CHASTEL[3], SABRINA TARTU[3], HÉLÈNE BUDZINSKI[2]

The aim of this work was to develop a robust, sensitive and rapid analytical procedure to determine 23 legacy and emerging poly- and perfluoroalkyl substances (PFASs) in Antarctic seabird plasma. This method was based on minimal sample pretreatment along with on-line solid phase extraction (SPE) coupled to liquid chromatography and tandem mass spectrometry (LC-MS/MS), using a small amount of plasma (25 µL). Sample preparation consisted in protein precipitation, followed by centrifugation, filtration and dilution of extracts with water; quantification was performed by isotope dilution. Method optimization was conducted using experimental designs and it focused on factors such as protein precipitation solvent, sample pH, on-line SPE sorbent, sample volume and loading flow rate. Detection limits, linearity range, recovery, accuracy and matrix effects were assessed on fortified plasma. Method accuracy was further evaluated by analyzing reference material NIST SRM 1957. Environmentally relevant detection limits were reported (0.0001-0.13 $ng.g^{-1}$) and 17 out of 23 target analytes showed excellent accuracy. The optimized method was applied to Antarctic seabird species, 11 analytes being detected (ΣPFASs: 0.4-19.1 $ng.g^{-1}$). The low plasma volume required for analysis (25 µL) implies that this method could also be applied to the analysis of PFASs in smaller target species.

[1] *University of Bordeaux, France*
[2] *CNRS, France*
[3] *CNRS, Université de La Rochelle, Villiers-en-bois, France*



ED_002330_00143654-00056

# Assessing the Optimal Spiking Ratio of Native to Isotopically-Labeled Standard During Quantitative Analysis of Perfluoroalkyl Acids in Biota

HOLLY LEE[1], XIAOMING ZHAO[1], SATYENDRA P. BHAVSAR[1], ERIC J. REINER[1]

Challenges associated with the analysis of perfluoroalkyl acids (PFAAs) in biota, such as matrix effects, may be countered by matrix-matched calibration, standard addition, and isotopically-labeled internal standards, the last of which are generally regarded to provide the highest accuracy and precision. However, PFAA concentrations may vary among samples and among congeners within the same sample, sometimes by orders of magnitude. This complicates the choice of how much of the isotopically-labeled surrogates should be added relative to their corresponding native analogues. In this study, native-to-label ratios were determined for Alaskan Pollock spiked with a suite of PFAAs by varying the amount of isotopically-labeled internal standards added over four orders of magnitude. Recoveries of 100 ± 20% were obtained when the native-to-label ratios ranged between 0.1 and 10, but deviated beyond these ratios. An additional ten samples of different fish species with varying perfluorooctane sulfonate (PFOS) concentrations (~0.1-1000 ng/g) were quantified using different $^{13}$C-PFOS concentrations to correlate the errors with different native-to-label ratios. Similar error propagation studies have been performed for isotope dilution-based metal analyses but, to our knowledge, this work is the first to focus on organic compounds and has important implications for data quality during biological monitoring of PFAAs.

[1] *Ontario Ministry of the Environment and Climate Change*



ED_002330_00143654-00057

# Dos and Don'ts in Perfluoroalkyl Substance (PFAS) Analysis: From Sampling, Analysis to Results Reporting

LAM LEUNG[1], ROBIN VESTERGREN[2]

Over the past 10+ years, the determination of perfluoroalkyl substances (PFASs) in various media has been widely studied and has been extensively published. While the advances in analytical methods allow us to quantify PFASs in virtually any environmental sample, the accuracy and precision may vary greatly between different analytes, matrices and the contamination level. As PFAS analysis is becoming common practice, there are some precautions and subtle procedures which require continuous attention, but are not always explicitly mentioned. This poster will address the dos and don'ts in PFAS analysis which will include sampling, sample storage and preparations, the analytical procedures and data analysis. In addition, we will address procedures to confirm the final results as well as ways to establish Limit of Detection (LOD) and Limit of Quantitation (LOQ).

[1] *The Chemours Company LLC*
[2] *Stockholm University, Stockholm, Sweden*



ED_002330_00143654-00058

# Analytical Methods Used to Detect PFOA and Related Substances in Various Matrices: Is There a Standard Analytical Method?

ANGELA LYNCH[1], ANTHONY BONNET[2], ANDREW KAHN[2], SHIN-YA SEIJI[3], STEPHEN KORZENIOWSKI[4], TAKAYUKI NAKAMURA[5], MARCO MALVASI[6], CAROLE MISLIN[7], MARISSA MAIER[8], RANJIT MACHADO[8]

The European Chemical Agency (ECHA) recently proposed to restrict the use, manufacture and sale of products containing PFOA and PFOA-related substances exceeding 2 ppb (ECHA, 2014). We questioned whether a standard analytical method exists to evaluate such levels in fluoropolymer and fluorotelomers products. To answer the question, analytical methods used to evaluate these substances in various matrices were reviewed from the published literature as well as collected from FluoroCouncil members. The results indicate that high performance liquid chromatography coupled to tandem mass spectrometry (LS/MS/MS) is consistently used for PFOA analysis; however, for 8:2 FTOH and 8:2 monomers, methods vary. Also, results indicate that analytical sensitivity is highly dependent on the extraction of the substance from the matrix and the control of analytical interference. PFOA in textiles is the only category of fluorotelomer products identified with a limit of quantification (LOQ) less than 5 ppb (Larson, 2006; Mawn, 2006; Stadalius, 2006; Liu, 2009; Guo, 2009; Shao, 2012). PFOA- related substances have also been analyzed in consumer products (Knepper et al., 2014; Liu et al., 2014). Therefore, it is not feasible to apply a 2 ppb threshold concentration of PFOA and PFOA-related substances to all fluoropolymer and fluorotelomer products.

[1] *FluoroCouncil*
[2] *Arkema France*
[3] *Asahi Glass Co, Ltd.*
[4] *The Chemours Company, LLC*
[5] *Daikin Industries, Ltd.*
[6] *Solvay Specialty Polymers*
[7] *Archroma Management, LLC*
[8] *Environ International Ltd.*



ED_002330_00143654-00059

# The Implementation of Ion Mobility Quadruopole Time-of-Flight Mass Spectrometric Analysis of PFOS Isomers

LAUREN G. MULLIN[1]

Perfluoroalkyl substances (PFASs) are formed by either electrochemical fluorination or telomerization, the former process resulting in a mixture of branched, linear and short chain perfluoroalkyl compound forms. In the case of PFOS and PFOA, numerous branched structures have been determined. This presents an analytical challenge as chromatographic co-elutions of the branched isomers 3-, 4-, and 5-PFOS, among other branched isomers, result in uncertainty in identifications in samples. Here, we propose the use of ion mobility quadrupole time-of-flight mass spectrometry (IM-qTOF-MS) to address these challenges in PFOS analysis. Ion mobility is an orthogonal separation technique which separates ions based on their size, shape and charge. Ions traverse through a gas filled drift cell, and are assigned a drift time based on their travel time. Drift time can be used as a unique experimental characteristic of an ion, and in many cases can differentiate between isobaric compounds that co-elute chromatographically. In this work, we show the utility of ion mobility separations for PFOS branched isomers characterized first in commercially available analytical standards, and then in complex biological samples.

[1] *Waters Corporation and MTM Research Centre Örebro University*



ED_002330_00143654-00060

# Analysis of Perfluoroalkyl Acids Specified Under the UCMR3 Using the QTRAP® 6500 LC/MS/MS System

MATTHEW NOESTHEDEN[1], LILY SANCHEZ[2], LEE YOO[2], MIKE WEHNER[2]

This poster highlights the sensitivity and precision of the QTRAP® 6500 LC/MS/MS system for the analysis of perfluoroalkyl acids (PFAAs) in drinking water. The PFAAs analyzed are outlined in the Unregulated Contaminant Monitoring Rule 3 Assessment Monitoring list (UCMR3) and comprise a subset of EPA Method 537. A complete method validation package in support of a successful UCMR3 accreditation is presented. The sensitivity of the QTRAP® 6500 LC/MS/MS system resulted in signal-to-noise values up to 1700:1 at ½ the UCMR3 reporting limits. Method detection limits ranged from 1.4 – 35.9 ng/L. Additional work is shown demonstrating proof-of-concept for the resolution of PFAAs using SelexION™.

[1] *SCIEX*
[2] *Orange County Water District, Fountain Valley, CA*



ED_002330_00143654-00061

# Trace-level Analysis of Perfluorinated Organic Compounds in Water by ASPE-LC/MS-MS

OSCAR QUINONES[1], ERIC R.V. DICKENSON[1], BRETT J. VANDERFORS[1]

The environmental prevalence and persistence of perfluorinated organic compounds along with reports suggesting links between exposure and adverse health effects in mammals have fueled a growing interest in understanding their behavior and fate. As traditional water sources are increasingly impacted by waste discharge and the demand for planned potable reuse grows, there is particular interest in determining their occurrence and behavior in water systems at environmentally-relevant levels. Here we report on methods developed in the course of our work for the analysis of thirteen perfluorocarboxylic and perfluorosulfonic acids in water and wastewater, and also for select fluorotelomer carboxylates, flourotelomer sulfonates and other suspected precursors or degradation products. Sample volumes were fortified with isotopically- labeled versions of the target compounds and then processed by automated solid phase extraction (ASPE) for cleanup/concentration. Analysis was conducted using liquid chromatography/tandem mass spectrometry (LC/MS-MS), and target values determined against calibrators using isotope-dilution correction. A secondary MS-MS transition was monitored for confirmation of target values. To eliminate background levels of perfluorinated compounds, mitigation strategies were adopted for ASPE and LC/MS-MS analysis and are discussed. Conservative reporting limits for target compounds in drinking, surface and wastewater samples were established at or below 5.0 ng/L in each case, suitable for environmental analysis.

[1] *Southern Nevada Water Authority*



ED_002330_00143654-00062

# Perfluorinated Alkyl Acids (PFAAs) in Hawaiian Monk Seal Plasma and Serum Samples

JESSICA L. REINER[1], COLLEEN BRYAN[1]

Since Hawaiian monk seals were listed as an endangered species under US Federal law in 1976 their overall population has continued to decline prompting the need to better understand their overall state of health and environmental factors that may be contributing to population decline. Organochlorine contaminants have previously been measured in Hawaiian monk seals in the Northwestern Hawaiian Islands (NWHI) and in the Main Hawaiian Islands (MHI). However, perfluorinated alkyl acids (PFAAs) have not been studied to date in this species. PFAAs, mostly perfluorinated carboxylic and sulfonic acids, have been identified in wildlife worldwide, with some of the highest levels of PFAAs being measured in marine mammals. While there have been studies focusing on PFAAs in marine mammals from the Arctic and temperate coastal areas, no studies have documented PFAAs in the wildlife from the Pacific Islands region. Using archived samples from the NOAA Pacific Islands Fisheries Science Center Hawaiian Monk Seal Research Program, we measured baseline levels of fifteen PFAAs in serum and plasma samples to help understand the level of exposure along with gender, age class, spatial, and temporal patterns for these analytes in Hawaiian monk seals and these results will be discussed.

[1] *NIST*



ED_002330_00143654-00063

# Identification of Novel Poly- and Perfluorinated Compounds in AFFF-Impacted Groundwater

SIMON ROBERTS[1], KRISTA BARZEN-HANSON[2], JENNIFER FIELD[2], CHRISTOPHER HIGGINS[1]

Contamination of soil and groundwater with poly- and perfluorinated substances (PFASs) is an issue of global concern at military and civilian sites where aqueous film-forming foam (AFFF) has been used. However, the identity of approximately 50% of the fluorinated substances at these sites is unknown. While numerous PFASs have been identified in AFFF commercial products, little is known regarding their environmental fate and potential degradation products. Liquid chromatography (LC) with quadrupole time-of-flight mass spectrometry (qTOF-MS) was used to identify polyfluorinated PFCA and PFSA precursors in groundwater from AFFF-impacted sites. Samples were screened in positive and negative ionization electrospray mode, and compound identification was performed using AB Sciex Masterview software to analyze the accurate mass (within 5 ppm error), isotope ratio (within 10%), and fragmentation spectra. At least six novel classes of polyfluorinated compounds were identified in groundwater, as well as several classes of PFASs that have not yet been reported in AFFF-impacted groundwater. Each compound class that was identified exhibited multiple chain lengths, with the highest relative response corresponding to compounds containing $C_6F_{13}$ and shorter perfluorinated chains. Several of the novel compounds were identified as components of an AFFF commercial mixture used in the 1980s.

[1] *Colorado School of Mines*
[2] *Oregon State University*



ED_002330_00143654-00064

# Spatial and Temporal Patterns in Concentrations of Per- and Polyfluoroalkyl Substaces in Bald Eagle Nestlings in the Upper Midwestern United States

WILLIAM T. ROUTE[1], ROBIN E. RUSSELL[2], ANDREW B. LINDSTROM[3], MARK J. STRYNAR[3], REBECCA L. KEY[1]

Between 2006 and 2011 we collected blood plasma from 261 bald eagle nestlings in six study areas from the upper Midwestern United States to measure levels of per- and polyfluoroalkyl substances (PFASs). Samples were measured for up to 16 different PFASs by three independent laboratories. We used regression analysis in a Bayesian framework to evaluate spatial and temporal trends for 12 analytes that were quantifiable. We found concentrations as high as 7370 ng/mL for the sum of all 16 PFASs (ΣPFASs). Perfluorooctane sulfonate (PFOS) and perfluorodecane sulfonate (PFDS) made up 67% and 23% of the PFAS burden, respectively. For ΣPFAS, PFOS, and PFDS, nestlings in urban and industrial areas had the highest levels, while Lake Superior nestlings had moderate levels, and nestlings on the remote upper St. Croix River had the lowest levels. We suggest that PFDS should be considered more often in wildlife and human studies because it is longer-chained and therefore prone to bioaccumulation and toxicity. We found evidence that ΣPFASs, PFOS, PFDS, perfluorooctanoic acid (PFOA), and four other analytes declined; three analytes showed no trend; and two analytes increased.

[1] *U.S. National Park Service Great Lakes Inventory and Monitoring Network*
[2] *U.S. Geological Survey, National Wildlife Health Center*
[3] *National Exposure Research Laboratory, U.S. Environmental Protection Agency*



ED_002330_00143654-00065

# Distribution of PFOS Alternatives in Municipal Sewage Sludge in China: Identification of Novel Polyfluorinated Ether Sulfonates

TING RUAN[1], GUIBIN JIANG[1]

6:2 Chlorinated polyfluorinated ether sulfonate (6:2 Cl-PFAES) with the trade name F-53B, is an alternative to perfluorooctane sulfonate (PFOS) in electroplating industry that is uniquely used as a mist suppressant in China since the 1970s. In this work, the occurrence and distribution of perfluoroalkyl sulfonate (PFSA), fluorotelomer sulfonate (FTS) and PFAES analogues were investigated in fifty-six municipal sewage sludge samples. Four PFSAs (C4, 6, 8, 10), 6:2 and 8:2 FTSs as well as the emerging 6:2 Cl-PFAES were detected. Moreover, novel polyfluorinated contaminants, i.e. 8:2 and 10:2 Cl-PFAESs, were identified for the first time by using high resolution mass spectrometry. These fluorinated analytes were further quantified with the aid of authorized and laboratory-purified standards. PFOS was the predominant contaminant with a geometric mean (GM) value of 3.19 ng/g dry weight (d.w.), which was subsequently followed by 6:2 Cl-PFAES and 8:2 Cl-PFAES (GM: 2.15 and 0.50 ng/g d.w., respectively). More empirical studies on the fate and potential adverse effects of the newly identified Cl-PFAES analogues are warranted in order to better elucidate their behaviors in the environment.

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# Dramatic Decline in Perfluorooctane Sulfonate (PFOS), but Not Perfluoroalkyl Carboxylic Acids (PFCAs) in San Francisco Bay Wildlife Suggest Shifting Sources in the Bay Area

MEG SEDLAK[1], JONATHAN BENSKIN[2], ADAM WONG[3], RICHARD GRACE[4], DENISE GRIEG[5]

Samples of San Francisco Bay cormorant egg (n=45) and seal blood (n=105) from 2004-2014 were analyzed for 9 perfluoroalkyl carboxylic acids, 3 perfluoroalkyl sulfonic acids and perfluorooctane sulfonamide. Perfluorooctane sulfonate (PFOS) was the dominant perfluoroalkyl acid (PFAA) in both seals (9.9-1,960 ng/mL) and eggs (36.1-1,760 ng/mL) over all time points and locations. A decline in PFOS was observed by 2012 in bird eggs and by 2014 in seal blood. To shed light on exposure source(s), PFAAs were measured in prey-fish (n=26 composites; 2010-2013) and both PFAAs and PFAA-precursors (3 fluorotelomer sulfonates, 6 fluorotelomer acids, 10 phosphorous-based surfactants, and 3 perfluorooctane sulfonamides) were measured in sediments (3 sites, n=3/site) and wastewater treatment plant (WWTP) effluents (3 sites, n=3/site) around the Bay Area (2012-2013). PFOS followed by perfluorooctane sulfonamide were the major organofluorines in small fish. In sediments, PFOS was also the dominant PFAA; however, at one site, PFOS-precursor concentrations were similar to PFOS. Polyfluoroalkyl phosphate diesters were also observed at concentrations >10-fold higher than PFAAs in sediment. Remarkably, only low levels of PFAAs and PFOS-precursors were observed in WWTP effluents, and each site had a unique PFAS profile. These results point to shifting manufacturing and use patterns within the Bay Area.

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# Nationwide Investigation of Perfluorinated Alkyl Substances in Japan by Using Bivalve and Dragonfly as Bioindicators

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The pollution situation of perfluorooctane sulfonate and perfluoroalkyl carboxylates were widely investigated by using bivalves and dragonflies as biomonitoring tools in Japan. As a result of the bivalve monitoring, localized pollution of per- and polyfluorinated alkyl substances (PFASs) was also found at coasts near the Hokuriku Area and the Northern Kanto Area. Particularly, most PFASs were detected with relatively high concentration at the Hokuriku Area. The result of the terrestrial monitoring by dragonflies exhibited a similar tendency on the Hokuriku Area. To understand an annual trend, we compared the results of the bivalve monitoring during 2006 to 2013. So far, we have seen that the Hokuriku Area showed 26.9 ng/g as total PFAS concentration in 2006, whereas the total concentration decreased to approximately 6 ng/g in 2013. The same observation applied to the Northern Kanto Area. In addition to the area along the coast affected by industrial effluent including PFASs, the situation that PFAS pollution from the mountainous area where final treatment sites for industrial waste are located was also clarified by the biomonitoring. In this study, the sample collection was supported by cooperation with other domestic research institutes, the biotope network on dragonfly, and ordinary citizens.

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# Perfluorinated Alkyl Acids in Northern California Cats: Temporal Trends and Comparison with Humans

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The environment and dietary intake are considered to be major human exposure pathways of perfluoroalkyl acids (PFAAs). Cats have similar exposures with humans in their residential environments, while they have different diet, body sizes and outdoor activities. Here we report serum PFAAs levels of northern California cats collected during two time periods: 2009-10 (n=26) and 2012-13 (n=23). While measured ∑PFAAs of the latter time period (11.9 ng/mL, mean) was lower than that of the first time period, they showed similar PFAAs profiles. We also found that the cat serum ∑PFAAs level was significantly higher than that of humans from similar time period and location (2008-10, 21.8 vs. 16.8 ng/mL, mean) but with different PFAAs profiles. Cats have higher percent fractions of PFHxS and other long chain PFCAs such as PFNA and PFUA compared to those in humans. Further investigations are underway to explore the relationships between PFAA levels and profiles, and age, exposure pathways, and any possible links to thyroid diseases in cats.

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# Analysis of Perfluoroalkyl Acids in Environmental Samples using a QTRAP® to Acquire Full Scan MS/MS Spectra for Improved Compound Identification

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Liquid Chromatography with Tandem Mass Spectrometry (LC-MS/MS) has become the preferred method of analysis for perfluoroalkyl acids (PFAA) in environmental samples because it provides superior selectivity and the sensitivity required to meet required data quality objectives. In common use, however, situations arise where the identification of a compound is compromised due to interferences from the matrix even with the specificity of MS/MS. The identification uncertainty is caused by interferences in either the primary or secondary transition and results in an error in the measurement of the acceptable ion ratio. When these situations occur, more spectral data may be needed for absolute compound identification. We investigated the use of a QTRAP® instrument to provide full scan MS/MS spectra for peaks that were observed in environmental samples. There are several important parameters that must be evaluated to successfully obtain data dependent mass spectra in practical applications. The acquisition conditions and data dependent spectral coverage are discussed and results that demonstrate the applicability of full scan data to compound identification are presented.

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# Quantification for Perfluoroalkyl and Polyfluoroalkyl Substances in Human Blood

SHERRY (XIAOYUN) YE[1]

Perfluoroalkyl and polyfluoroalkyl substances (PFASs) are chemicals that persist in humans and the environment. Electrochemical fluorination yields branched and linear PFAS isomers, and telomerization produces almost exclusively linear compounds. The structural isomeric patterns of perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS) in humans may be useful for understanding pathways of exposure. Serum is the main biomoniotoring matrix for PFASs; however, other blood-related matrices may be also useful. We have modified our analytical method in serum to allow for the concurrent quantification of 19 PFASs, including both linear and branched isomers of PFOS and PFOA, in other blood-related matrices. The method uses on-line solid phase extraction (SPE) coupled with high-performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS). After dilution with formic acid, the target PFASs present in 50 µL of matrix (plasma or whole blood) are retained and concentrated on the SPE column, separated from each other and from other matrix components by HPLC, and detected by isotope-dilution MS/MS. Sensitivity, accuracy (spike recovery), and precision (repeated measurements of quality control materials) were similar in whole blood (or plasma) and serum. These results confirm the suitability of the analytical approach for the concurrent quantification at trace levels of 19 PFASs in alternative matrices.

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# Are humans exposed to increasing amounts of unidentified organofluorine?

LEO YEUNG[1], SCOTT MABURY[2]

Measuring PFOS and PFOA in environmental or human samples may reflect how well industries are fulfilling their commitments towards national and international regulations. Declining trends in PFOS and PFOA concentrations in human blood following the phase-out of perfluorooctanesulfonyl fluoride (POSF)-based products in 2000 were reported; however, data remain sparse with respect to their precursors and some newly identified PFASs as well as unrecognized fluorinated contaminants. In the present investigation, human plasma samples (n=122) from two German cities (Münster and Halle, collected in 1982-2009, excluding 1994) were analyzed for 49 PFASs using LC-MS/MS and extractable organofluorine (EOF) using total organofluorine combustion ion chromatography (TOF-CIC). The PFASs included some newly identified and commercially-available chemicals (PFPAs, PFPiAs, FTSAs, PAPs, di-SAmPAP), metabolites of fluorotelomer-based products (FTCAs/FTUCAs), PFCAs, PFSAs, FASAs, and FOSAAs. Our results showed that the reductions of PFOA and other related precursor compounds observed in human sera were less than the targets by the PFOA Stewardship Program. After year 2000, increasing amounts of unidentified organofluorine were observed in Münster samples; this increasing trend of unidentified organofluorine in plasma samples suggested humans are being exposed to new and unidentified fluorinated products.

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# An Ultra-Sensitive Method for the Analysis of Perfluorinated Alkyl Acids (PFAAs) in Drinking Water Using a Column Switching HPLC-MS/MS

MITSUHA YOSHIKANE[1], SHOJI F. NAKAYAMA, MD, PH.D.[2], KAVITHA DASU, PH.D.[3], SHELLEY EHRLICH, MD, SCD, MPH[4], MARC A. MILLS, PH.D.[5], J. MICHAEL WRIGHT, SCD[6]

In epidemiological research, it has become more and more important to assess subjects' exposure to multiple chemicals in multiple environmental media. It is a common practice to aliquot limited volumes of samples into smaller quantities for such chemical analyses. Sometimes only a few mL of samples may be available for each trace level measurement. In general, a hundred to a thousand mL of samples have been used for the analysis of perfluorinated alkyl acids (PFAAs) in drinking water. In this study, we developed a method for the determination of 14 PFAAs in drinking water using a column-switching high performance liquid chromatography tandem mass spectrometer (HPLC-MS/MS) with solid phase extraction (SPE) pretreatment. This method requires approximately 10 mL of samples. Ten mL of drinking water was concentrated with an SPE cartridge and eluted by methanol. The extract was introduced to a column-switching HPLC-MS/MS using a mix-mode SPE column. The lowest concentration minimum reporting levels (LCMRL) for the 14 PFAAs were ranged from 0.43 to 3.4 ng/L.

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ED_002330_00143654-00073

# Comparison of Liver Homogenization Techniques for Perfluorooctanoate (PFOA) and Perfluorooctanesulfonate (PFOS)

JEREMY ZITZOW[1], ALAN EVELAND[1], JILL HART[1], TRINA JOHN[2], RYAN KRISKO[1], SUE CHANG[1]

Perfluorooctanoate (PFOA) and perfluorooctanesulfonate (PFOS) are environmentally persistent compounds. Because PFOA and PFOS are primarily distributed to blood and liver, these two matrices from laboratory studies are routinely analyzed for their concentrations. Homogenization techniques are important in preparing liver samples for the quantifications of PFOA and PFOS present in the livers. In this study, tissue homogenization techniques using an automatic tissue homogenizer (bead-based tissue lysis instrument, Precellys, Bertin Technologies) vs. a hand-held tissue homogenizer (probe-based grinding disperser, IKA® Turrax, IKA Works) were compared. In addition, ceramic beads and stainless steel beads were also compared for the automatic tissue homogenizer. Liver samples were obtained from rats given a single oral dose of either ammonium PFOA (in distilled water) or potassium PFOS (in 0.5% Tween 20) and both homogenization techniques were used to prepare the livers prior to solidphase extraction followed by LC-MS/MS. Concentrations of PFOS and PFOA were compared for each technique. The results and conclusions will be presented in detail for these comparisons.

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ED_002330_00143654-00074

# Temporal Trends of Perfluoroalkyl Substances in Plasma of Bottlenose Dolphins Residing in Sarasota Bay, FL.

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The long-term monitoring of free-ranging populations is a useful tool to evaluate the presence and fate of environmental contaminants and help assess and manage their risks to wildlife. A suite of perfluoroalkyl substances (PFASs) were analyzed in plasma bottlenose dolphins (*Tursiops truncatus*) collected during capture-release health assessment of the resident population of Sarasota Bay, FL over an 11 year period (sampling years 2002-2005, 2011, 2012, and 2013). Results of the temporal analyses of individual congeners indicated an increase in concentrations of PFOA, PFNA, PFDoA, PFTA, and PFTriA in plasma of dolphins while levels of PFUA, PFOS, PFHxS, and PFOSA decreased over time. Perfluoroethylcyclohexane sulfonate (PFECHS), which was not determined in previous studies, was detected in all plasma samples. PFECHS declined in concentration from means of 20 ng/g w.w. in 2004 to 6.2 ng/g w.w. in 2013. Overall, the data indicate a decrease in the concentrations of sum of perfluoroalkyl sulfonates and constant levels for the sum of perfluoroalkyl carboxylic acids (PFCAs) over the 12-year span of sampling. The results suggest continued inputs of PFCAs, and their precursors in commercial products, to the Western Florida coastal region and underline the need for continuous monitoring of PFASs in wildlife populations.

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# Poster Abstracts:

# Environmental Fate and Transport

# Substitution of Prioritized Poly- and Perfluorinated Chemicals to Eliminate Diffuse Sources (SUPFES)

STEFFEN SCHELLENBERGER[1], HANNA MARIA ANDERSSON[2], URS BERGER[3], IAN COUSINS[1], PHILIP GILLGARD[4], PIM LEONARDS[5], GREGORY PETERS[2], STEFAN POSNER[4], IKE VAN DER VEEN[5], JANA WEISS[5], CHRISTINA JÖNSSON[4]

Fabric's repellency against liquids while maintaining breathability is a key functionality in modern textiles. Durable water repellents (DWR) based polymers with perfluorinated (PF) side chains can provide these properties and are therefore produced in high ton-nages. Textiles treated with these polymers however might be a source of persistent organic pollutants (POPs). The phase-out of persistent, bioaccumulative and toxic long chain PF raw materials that were used for very effective DWRs in the past resulted in the development of alternatives based on short chain fluorocarbons (C6 and C4). Although these this side chain fluorinated polymers can be considered less toxic and less bioaccumulative, their potential to form POPs is not fully understood. Other 'ecofriendly' DWR technologies based on silicones or novel star-shaped hydrocarbons (dendrimers) have unclear enviromental fate as well. This lack of reliable data makes a corresponding risk assessment impossible. The aim of the interdisciplinary collaboration SUPFES is to help industry in finding alternatives that can replace long-chain flurocarbons in textiles with environmentally more benign alternatives. Within the project a unique consortium of scientific and industrial partners collaborate to make sure that functionality and environmental impact can be balanced in the design of future DWR products.

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# Can Washout of Known Precursors Account for the PFAA Concentrations Measured in Precipitation?

JANA H. JOHANSSON[1], IAN COUSINS[1], ULLA SELLSTRÖM[1]

Atmospheric deposition has been pointed out as an important input pathway of perfluoroalkyl acids (PFAAs) to remote environments as well as to highly populated areas essential for food production, such as the Baltic Sea. Our knowledge of the relative importance of possible sources of PFAAs to the atmosphere and how PFAAs are transported in the atmosphere is limited. Modeling work has shown that degradation of volatile precursor compounds can account for only a few percent of the PFAAs present in background precipitation. We will measure perfluoroalkyl substance concentrations in air and precipitation sampled simultaneously. The target analytes are PFAAs, fluorotelomer alcohols and perfluoroalkane sulfonamide substances. The data will show whether PFAA concentrations in the precipitation samples can be accounted for by the air concentrations of PFAAs only, the sum of PFAAs and their precursors, or whether they cannot be accounted for. This will answer questions about the relative importance of direct and indirect emissions to air. Furthermore, it will resolve whether there is justification for the concern that additional unknown precursor compounds contribute to the levels of PFAAs in precipitation. Total washout ratios and their variation with chain length will be reported, to enable a physical-chemical description of the wet deposition process.

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# Biodegradation Potential of Two Quaternary Ammonium Polyfluoroalkyl Surfactants

SANDRA MEJIA-AVENDANO[1], JINXIA LIU[1]

Significant levels of polyfluoroalkyl surfactants with various hydrocarbon functionalities have been detected in sites impacted by the use of Aqueous Film Forming Foams (AFFFs). The study of environmental fate and impact of AFFFs is greatly complicated by this coexistence of numerous substances in a foam mixture. The evaluation of the fate of major single components provides valuable information for assessment and management of AFFF-impacted sites. The biodegradation in soil of two components patented for their use in AFFFs was studied: N,N,N-Trimethyl[(perfluorooctanesulfonamido)propyl] ammonium iodide and N,N,N-Trimethyl[(perfluorooctaneamido)propyl] ammonium iodide. The experiment setup consisted of closed-bottle soil microcosms spiked with a single component, and exhaustive solvent extraction was performed. The headspace and soil extracts were analyzed qualitatively and quantitatively for the test compounds and possible metabolites. Generation of perfluorooctane sulfonic (PFOS) and carboxylic acids (PFOA) was observed, proving the biodegradability of the surfactants despite the presence of perfluoroalkyl chain and their strong sorption to soil. The degradation rates, metabolite tends, and implications of the discovery are discussed.

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# Indoor Exposure to PFOS and PFOS Related Compounds in Norwegian Population

ANA MIRALLES-MARCO[1]

Perfluoroalkyl substances (PFASs) are a well known family of environmental pollutants because of their physicochemical carachteristics, persistence, bioaccumulation and widespreading. Among them, perfluorooctanesulfonate (PFOS) is one of the most frequently detected compounds in both environmental and biological samples. These causes led to its incorporation in the Stockholm Convention on Persistent Organic Pollutants (POPs) in 2009. Notwithstanding absolute levels of FPOS in biomonitoring studies tend to decline, recent published studies with environmental, dietary exposure data and biomonitoring levels highlight that uncertainties in terms of exposure and metabolism still remain. So, indirect exposure to PFOS-precursor compounds followed by in vivo metabolism to PFOS as end-product has been suggested as an important source of current levels of PFOS present in biological samples. Modelling studies also suggest PFOS-precursors exposure from 10% to 40% of total PFOS body burdens. Such PFOS-precursor compounds include perfluorooctane sulfonamides (FOSAs) and sulfonamidoethanols (FOSEs). In the current work, results on the analysis of PFOS and PFOS related compounds levels in indoor environment from Norwegian population are shown. Also an overview of sampling and analysis strategies for a better understanding of the present exposure pathways will be presented.

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# Re-investigation of Aerobic Biodegradation of 6:2 and 8:2 Polyfluroalkyl Phosphate Diesters (6:2 diPAP and 8:2 diPAP) in Soil

CHEN LIU[1], JINXIA LIU[1]

Polyfluoroalkyl phosphate esters (PAPs) have been widely detected in soil, indoor dust, food packaging, and human serum. They have been determined or proposed as potential precursors of persistent perfluoroalkyl carboxylic acids (PFCAs). During an investigation of environmental fate of 6:2 diPAP and 8:2 diPAP in soils, it was found that soil extraction methods have great impact in study outcome and estimation of their environmental half-lives. Some commonly used extraction methods either cannot efficiently recover the PAPs, or caused substantial solvent-enhanced hydrolysis. Extraction using MTBE/acetic acid or ACN/acetic acid were found satisfactory for quantitative recovery of the diPAPs, while methanol/ammonium hydroxide, acetonitrile (ACN)/sodium hydroxide, ethyl acetate, or methyl tert-butyl ether (MTBE) were unsuitable. 6:2 and 8:2 monoPAPs exhibited rapid solvent-enhanced hydrolysis in all of the solvents, and therefore quantitative recoveries were not possible. With the improved extraction methods, aerobic soil biotransformation of 6:2 diPAP and 8:2 diPAP were re-investigated in semi-dynamic soil microcosms over 100 days. The study will discuss degradation rates, metabolites trends, yields of PFCAs, as well as the implications of solvent-induced hydrolysis in estimating environmental half-lives.

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ED_002330_00143654-00083

# Subsurface PFAS Transport Resulting from Multiple Source Locations at a Site in Northern Canada

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Aqueous film forming foam (AFFF) is used at Canadian airports for the suppression of hydrocarbon-based fires. Historical use of AFFF containing per- and polyfluoroalkyl substances (PFASs) for training or fire suppression has led to PFAS impacted soil and groundwater. The site of interest is located in Northern Canada and has two identified source locations containing multiple contaminants including PFASs, Volatile Organic Compounds (VOCs) and hydrocarbons. Since the late 1980s, many hydrological and contaminant studies have been conducted. Information from these studies has been used to show the interaction of the contaminant plumes from the individual sources. Local stratigraphy and a storm water pipe have been shown to be the primary factors influencing groundwater (and contaminant) movement. For PFASs, recent work has been done to measure contaminant concentrations in many new and pre-existing wells. These measured values correspond to groundwater flow. Laboratory based one dimensional column transport studies using soil procured from the site of interest will be used to better understand site specific (PFAS) retardation dynamics. Preliminary results for groundwater hydrology and a PFAS transport model will be presented.

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ED_002330_00143654-00084

# Fluorochemical Leaching in Laboratory-Scale Anaerobic Bioreactors Filled with Carpet and Textiles

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Carpets are known to be treated with stain protection coatings containing per- and polyfluoroalkyl substances (PFASs) and are typically landfilled at the end of their useful life. Data on the release of PFASs from specific materials (e.g., carpets) during the anaerobic decomposition of municipal waste is needed to fully understand the contribution of landfills to global PFAS cycling. The objective of this work was to quantify the concentrations of PFASs in biologically-active and abiotic (killed control) laboratory-scale reactors containing carpet. The reactors were designed and operated to simulate decomposition of municipal waste under methanogenic conditions in a landfill. Leachate concentrations of fluorotelomer carboxylic acids (∑FTCAs) increased from 32 to 10,296 pmol/L in one of the biologically-active reactors during the 552 days of operation. No significant production of FTCAs occurred in the abiotic reactors, indicating that their accumulation was due to biological processes. The production of FTCAs were likely the result of precursor degradation since there were no significant reductions in any of the other precursor PFASs measured for the study. Using final leachate concentrations, although concentrations were still increasing at the time the reactor operation was termination, the ∑FTCAs released from the carpet was 8.8 ng PFOA equivalents per gram of carpet.

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ED_002330_00143654-00085

# Is Ongoing Sulfluramid Use in South America a Source of Perfluoroalkyl Acids in the Southern Atlantic? A Pilot Study in Baia de Todos os Santos (BTS)

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The pesticide Sulfluramid (N-ethyl perfluorooctane sulfonamide; EtFOSA) is a known precursor to perfluorooctane sulfonate (PFOS) which has been used extensively in Brazil (30 tons/year in 2007) for control of fire ants. While the extent of exposure to PFOS arising from Sulfluramid use in this region remains unclear, recent surveys of Atlantic surface water reported elevated perfluoroalkyl acid (PFAA) concentrations along coastal South America. Regional use of Sulfluramid was speculated as a possible source of these elevated PFAA concentrations; however, Sulfluramid has never been measured directly in Latin America. In the present work, a method for simultaneous determination of EtFOSA, its intermediate degradation products, and perfluoroalkyl sulfonic (C4, C6, C8, C10) and carboxylic (C6-12) acids was developed and applied to water samples collected around Baia de Todos os Santos (BTS), Salvador, Brazil. The method utilizes isotope dilution and WAX-SPE extraction followed by UHPLC-MS/MS. Spike/recovery experiments demonstrated excellent accuracy (average 99%; range 63-114%) and precision (average 18% RSD; range 3-43%) of the method for all targets. These data shed light on sources of PFAAs to the southern Atlantic Ocean.

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ED_002330_00143654-00086

# Mass Balance of Perfluorinated Alkyl Acids in a Pristine Boreal Catchment

MARKO FILIPOVIC[1]

Currently an increasing number of studies have reported the occurrence of perfluorinated alkyl acids (PFAAs) in seemingly pristine groundwater and rivers worldwide. However, there are no studies which have evaluated how PFAAs enter surface water from pristine terrestrial ecosystems even though the fate and transport need to be understood. The aim of this study was to investigate the transport of PFAAs from atmospheric deposition and snowmelt to river water in a pristine terrestrial environment. The study was conducted within a low populated, uniquely instrumented research catchment in Northern Sweden. 14 target PFAAs (9 PFCAs, 4 PFSAs and FOSA) were analyzed. Qualitative and quantitative analysis of PFAA concentrations in atmospheric deposition (rain and snow) as well as two rivers was performed using SPE UPLC/MS/MS. A PFAA mass balance of the two catchments was assembled to study their fate. The mass balance calculations show that atmospheric deposition is the most relevant pathway for PFAAs to the remote rivers. Furthermore, the results suggest that both physical-chemical property differences between the PFAAs as well as the water transit time between atmospheric deposition and riverine outflow in combination with emission changes over time alter the PFAA pattern within the catchments.

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# Monitoring of Long-Range Transport of Perfluoroalkyl Acids in Precipitation from the Newfoundland and Labrador Boreal Ecosystem Latitudinal Transect

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Perfluoroalkyl acids (PFAAs) are persistent and bioaccumulative compounds found ubiquitously in the environment. It has been proposed that PFAAs can be transported to remote locations, such as the arctic, through long-range atmospheric transport. Rain droplets can scavenge both gas phase and particulate PFAAs during rainfall events. The measurement of PFAAs in atmospheric precipitation will help to understand long-range transport processes. In this work, precipitation was collected along the four Newfoundland and Labrador Boreal Ecosystem Latitudinal Transect sites ranging from rural to remote areas. Precipitation samples were collected passively into a polyvinylchloride tube, and actively using custom-built automated high-density polyethylene precipitation samplers. In order to accurately quantify PFAAs in rainwater, liquid chromatography-tandem mass spectrometry (LC-MS/MS) was used as the method of detection. Spatial and temporal trends will be discussed, as well as the implications for mechanisms of long-range transport.

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ED_002330_00143654-00088

# Volatile Poly/Perfluoroalkyl Substances in Influents, Effluents and Air from Wastewater Treatment Plants

PIM DE VOOGT[1], IAN K. DIMZON[2], THOMAS P. KNEPPER[3]

Volatile poly/perfluoroalkyl substances (PFASs) can be released from sewage water into air through wastewater treatment plants (WWTP). Volatile PFASs have very low solubilities in water. As a consequence these substances have very high Henry's Law constants and partition easily into the air. In this research work, the influents, effluents and air in three different WWTP were analyzed for representative volatile PFAS that include perfluoroalkyl iodides (PFAI), fluorotelomer iodides (FTI), fluorotelomer olefins (FTO), fluorotelomer acrylates (FTAC) and fluorotelomer methacrylates (FTMAC). Results showed that the industrial WWTP influents and air showed relatively high levels of perfluorooctyl iodide; 6:2, 8:2 and 10:2 FTO; 6:2 FTI and 6:2 FTMAC. This result can be due to the presence of a manufacturing facility in the surrounding area. The effluent samples had very low to non detectable concentrations (0.01 µg/L) of the volatile PFASs indicating volatilization, and efficient removal or transformation of these compounds in water. The influent, effluent and air samples coming from residential WWTP do not contain the volatile PFASs at concentrations above LOD (0.01 µg/L in water and 0.0005 µg/L in air). The volatile PFASs could be lost during the transport of the sewage water from the residential sources to the WWTP site.

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# Comprehensive Monitoring of PFAS Precursors in Industrial and Municipal Wastewater Treatment Plants

CHRISTOPH GREMMEL[1], IAN K. DIMZON[1], TOBIAS FRÖMEL[1], THOMAS P. KNEPPER[2], PIM DE VOOGT[2]

Although precursors of perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFSAs) have been identified in laboratory experiments for more than a decade, the significance of these precursors in the environment is still largely unknown. Therefore, a comprehensive study was carried out in the framework of a project funded by the German Environmental Agency, sampling six municipal and industrial wastewater treatment plants. A total of 66 PFASs were monitored using HPLC-ESI-MS/MS and GC-EI-MS methods. For wastewater treatment plants, eight influent samples and four effluent samples were taken over a period of four weeks. Additionally, eight corresponding air samples above the influent were taken in order to verify the presence of volatile PFASs as well as four grab sludge samples to account for adsorbable PFASs. Various findings of precursors, biotransformation intermediates, and stable PFASs will be presented and discussed.

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# Reversible and Irreversible Sorption of Perfluoroalkyl Acids (PFAAs) by Sediments of an Urban Reservoir

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Sorption isotherms and distribution coefficients (KD) developed in laboratory experiments are typically reported without consideration of exposure history and hysteretic and aging effects. The influence of these factors on KD are poorly understood. They are hypothesized to be reasons why field-based KDs are consistently larger than those determined laboratory experiments. This study investigated the sorption of several PFAAs (C4, C6, C8 to C10 perfluoroalkanoate homologues (PFBA, PFHxA, PFOA, PFNA and PFDA, respectively) and perfluorooctane and hexane sulfonate (PFOS and PFHxS, respectively) by sediments of an urban reservoir. The absorption isotherms of PFOS, PFNA and PFDA were nearly linear. Desorption experiments indicated that a fraction of the sorbed PFAAs were entrapped and resistant to desorption. The fraction that was reversibly sorbed desorbed along a linear isotherm. Irreversibility increased with chain lengths and was highest for PFDA (thermodynamic irreversibility index (TII) 0.98). The weakly sorbing PFOA and PFHxS were entrapped to a much smaller extent. For the strongly sorbing PFAAs, sediments act predominantly as irreversible sinks. Concentration of the moderately and largely reversibly sorbing PFAAs are buffered by suspended sediments. While not sorbing PFAAs (PFBA and PFHxA) have a higher potential for long-range transport via aqueous phase. Results suggest that for modeling contaminant behavior in surface waters, field-based KD data should be complemented with desorption studies.

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# Surface Modification of Activated Carbon for Enhanced Adsorption of Perfluorooctane Sulfonic (PFOS) and Carboxylic Acids

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The objective of the research was to examine the effect of increasing surface basicity of activated carbon on adsorption of perfluorooctane sulfonic (PFOS) and carboxylic acids (PFOA) from aqueous solutions. Four granular activated carbon made of different raw materials (coal, coconut shell, and wood) and one type of activated carbon fiber were modified by high-temperature and ammonia gas treatments, respectively, to facilitate systematical evaluation of the impact of basicity of different origins. Comparison of adsorption isotherms and adsorption distribution coefficients (Kd) showed that the ammonia treatment was generally more effective than the high-temperature treatment in enhancing surface basicity expressed as point of zero charge or total HCl update, and in greatly improving adsorption affinity for PFOS and PFOA. The effectiveness of surface modification to enhance adsorption also varied with carbon raw material. Wood-based carbons and activated carbon fibers showed most enhancements with Kd values increased by one to three orders of magnitude, while other materials could experience adsorption reduction towards either PFOS or PFOA. Finally, it was proposed that as the surface modification processes used in the study could increase PFOS and PFOA removal efficiency, competitive sorption by natural organic matter could be potentially mitigated.

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# Wastewater Treatment Plant Sludge Biodegradation of Two Fluorotelomer Surfactants Found In Aqueous Film Forming Foams

LISA D'AGOSTINO[1], SCOTT A. MABURY[1]

The 6:2 fluorotelomer sulfonamide alkylbetaine (FTAB) and 6:2 fluorotelomer sulfonamide alkylamine (FTAA) are used in fluorotelomer alternatives to perfluorooctanesulfonate (PFOS)-based aqueous film forming foams (AFFFs). 6:2 FTAB and 6:2 FTAA were detected in 4 of 10 fluorinated AFFFs collected in Ontario, Canada. Biodegradation of these two fluorotelomer surfactants in the presence of aerobic wastewater treatment plant (WWTP) sludge was investigated using in-house synthesized material. 6:2 FTAB and 6:2 FTAA were found to be more recalcitrant to biodegradation than the fluorotelomer phosphate esters (PAPs) and 6:2 fluorotelomermercaptoalkylamido sulfonate previously investigated in similar studies. Over the course of 109 days, production of perfluorohexanoate (PFHxA), perfluoropentanoate (PFPeA), 5:3 fluorotelomer carboxylic acid (FTCA), and 6:2 fluorotelomer alcohol (FTOH) occurred with both 6:2 FTAB and 6:2 FTAA in the presence of active WWTP sludge. Production of 6:2 fluorotelomer unsaturated carboxylic acid (FTUCA) was also confirmed in bottles containing 6:2 FTAA. This shows that biodegradation of 6:2 FTAB and 6:2 FTAA can produce persistent perfluoroalkyl carboxylates (PFCAs). Additional intermediates in the degradation of 6:2 FTAB and 6:2 FTAA were also identified, which may assist in elucidating the contributions of previously unknown degradation products to perfluoroalkyl and polyfluoroalkyl substance (PFAS) contamination at AFFF impacted sites.

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# Subsurface Transport of Perfluoroalkyl Acids in Active Microbiological Settings

TESS WEATHERS[1], CHRISTOPHER HIGGINS[1], JONATHAN SHARP[1]

The fate and transport of perfluoroalkyl acids (PFAAs) in the presence of active microbial communities has not been widely investigated. This study explores the transport of a suite of perfluorocarboxylic acids and perfluoroalkylsulfonates, including perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), in microbiologically active settings. Organic carbon normalized sorption coefficients derived by exposing inactive cellular material to PFAAs result in more than an order of magnitude increase in sorption compared to soil organic carbon sorption coefficients found in literature (e.g. sorption coefficients for PFOS are 4.05±0.07 L/kg for cellular organic carbon and 2.80±0.08 L/kg for soil organic carbon). This increase in sorption, coupled with enhanced extracellular polymeric substance produced as a biological response to PFAA exposure at source-level concentrations may result in PFAA retardation in situ and/or changes in subsurface flow parameters. To address the upscaling of this phenomenon, fourteen flow-through columns packed with low-organic carbon sediment were biostimulated with glucose and exposed to PFAA concentrations of 11, 55, or 110 mg/L total of 11 distinct analytes for approximately 200 pore volumes at 6 $cm^3$/hr. Each concentration of PFAAs were assigned to columns in triplicate, including a control without PFAAs. Two columns inactivated with sodium azide were also employed. Breakthrough and tailing of each analyte was measured and modeled with Hydrus-1D to explore sorption coefficients over time for microbially active columns.

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# Occurrence and Point Source Characterization of Perfluoroalkyl Acids in Sewage Sludge

ALFREDO C. ALDER[1], JUERGEN VAN DER VOET

The occurrence and levels of perfluoroalkyl acids (PFAAs) emitted from specific pollution sources into the aquatic environment in Switzerland were studied using digested sewage sludges from 45 WWTPs in catchments containing potential industrial emitters. Concentrations of individual PFAAs show a high spatial and temporal variability, which infers different contributions from industrial technologies and activities. Perfluorooctane sulfonic acid (PFOS) was generally the predominant PFAA with concentrations varying between 4 and 2440 µg/kg (median 75 µg/kg). Elevated emissions were observed in catchments capturing discharges from metal plating industries (median 88 µg/kg), aqueous firefighting foams (median 211 µg/kg) and landfill leachates (median 107 µg/kg). Some elevated perfluoroalkyl carboxylic acids (PFCAs) levels could be attributed to emissions from textile finishing industries with concentrations up to 233 µg/kg in sewage sludge. Assuming sorption to sludge for PFOS and PFCAs of 15 and 2%, respectively, concentrations in wastewater effluents up to the low µg/L level were estimated. Even if wastewater may be expected to be diluted between 10 and 100 times by the receiving waters, elevated concentrations may be reached at specific locations. Although sewage sludge is a minor compartment for PFAAs, these investigations are helpful for the identification of hot-spots from industrial emitters.

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# Occurrence of Select Perfluoroalkyl Substances at U.S. Air Force Aqueous Film-Forming Foam Release Sites Other than Fire-Training Areas: Field-Validation of Critical Fate and Transport Properties

RICHARD ANDERSON[1], CORNELL LONG[1], RON PORTER[2], JANET ANDERSON[1]

The use of aqueous film-forming foam (AFFF) to extinguish hydrocarbon-based fires is recognized as a significant environmental source of poly- and perfluoroalkyl substances (PFASs). Although the occurrence of select PFASs in soil and groundwater at former fire-training areas (FTAs) at military installations operable since 1970 has been consistently confirmed, studies reporting the occurrence of PFASs at other AFFF-impacted sites are largely missing from the literature. Further, studies have mostly focused on a single site (i.e., FTAs at military installations) and, thus, lack a comparison of sites with diverse AFFF release history. Therefore, the purpose of this investigation was to evaluate select PFAS occurrence at non-FTA sites on active U.S. Air Force installations with historic AFFF use of varying capacity. Concentrations of fifteen perfluoroalkyl acids (PFAAs) and perfluorooctane sulfonamide (PFOSA), an important precursor, were measured from several hundred samples among multiple media (i.e., surface soil, subsurface soil, sediment, surface water, and groundwater) collected from forty AFFF-impacted sites across ten installations between March and September 2014, representing one of the most comprehensive datasets on environmental PFAS occurrence to date. This dataset was also used to empirically test critical fate and transport assumptions. Detection frequencies and environmentally-relevant concentrations are presented along with rigorous data analyses that demonstrate phase-dependent (i.e., solid-phase vs aqueous-phase) differences in the chemical signature as a function of carbon chain-length and in situ PFOS (and to a lesser extent PFHxS) formation, presumably due to precursor oxidation.

[1] *AFCEC*
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# Edible Crop Uptake of Perfluoroalkyl Acids from Land-Applied Biosolids and Reclaimed Water

ANDREA BLAINE[1]

Perfluoroalkyl acids (PFAAs) are persistent, bioaccumulative, and toxic anthropogenic compounds with a myriad of applications (e.g., non-stick packaging, stain-resistant textiles). Due to their widespread use, municipal wastewaters are a collection vehicle for these compounds; however, most conventional wastewater treatment plants (WWTPs) are ineffective at removal of PFAAs resulting in the persistence of these compounds in both the aqueous effluent and the treated sludge (i.e., biosolids) of WWTPs. Sustainability movements coupled with growing water scarcity encourage the land application of both biosolids and reclaimed water from WWTPs. However, concerns around these practices have recently arisen regarding the potential uptake and subsequent bioaccumulation of PFAAs into food crops. In this study, various types of fresh food crops including lettuce, tomato, snap pea, radish, celery, and strawberry were grown either in biosolids-amended soils or using reclaimed water. Significant uptake factors and bioaccumulation trends of PFAAs were explored. If the current use of land-applied biosolids and reclaimed water for food crops is to be sustained or increase in future years, these concerns about the potential contamination of food products must be fully addressed through careful scientific study, evaluation, and communication with the public.

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# Short-Chain Fluorotelomer-Based Substances: Common Biodegradation Pathways

ROBERT C. BUCK[1], NING WANG[2]

Short-chain fluorotelomer-based products are surfactants or polymers derived from 6:2 fluorotelomer alcohol or iodide raw materials. To develop an understanding of the environmental fate of this family of products and raw materials, aerobic and anaerobic biodegradation studies have been conducted in a variety of environmental matrices such as soil, sludge, sediment, etc. In general, when the 6:2 fluorotelomer-based products degrade aerobically, they converge to common biodegradation pathways first identified for 6:2 fluorotelomer alcohol which lead to per- and poly-fluoro carboxylic acids. In anaerobic settings, the formation of perfluorocarboxylic acids is minimal. The amount of each biodegradation product has been seen to vary significantly by test matrix and study setting. This poster will present an overview of this body of work.

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# Perfluorophosphinates and Other Perfluorinated Acids in Northern Pike and Double-Crested Cormorants

AMILA DE SILVA[1], M. HOUDE[1], S. R. DE SOLLA[1], C. SPENCER[1], D. HO[1], M. AL TARHUNI[1], L.E. KING[1]

Perfluorophosphinates (PFPIA), perfluorophosphonates (PFPA), and polyfluorophosphoric acid diesters (diPAP) were measured in plasma of northern pike (*Esox lucius*) and double-crested cormorants (*Phalacrocorax auritus*). Pike were sampled at two locations upstream and downstream of Montréal in the St. Lawrence River, Canada. Cormorants were sampled from six colonies throughout the lower Great Lakes in Ontario. The PFPAs and diPAPs were all below detection limits but PFPIA had a 100% detection frequency. To our knowledge, this is the first report of PFPIA in fish and bird plasma. Concentrations were statistically higher in fish downstream of the island of Montréal and its wastewater treatment plant outfall compared to the upstream reference site. The dominant congeners were 6:8 PFPIA (0.27 ± 0.097 ng/g upstream and 0.56 ± 0.36 ng/g downstream) followed by 6:6 PFPIA (0.058 ± 0.031 ng/g u/s and 0.20 ± 0.14 ng/g d/s). The PFPIA levels in cormorants were greater than in pike. In cormorants from the Hamilton Harbour colony, total PFPIA was 5.9 ± 0.88 ng/g. The lowest cormorant concentrations were from Bergin Island, 0.51 ± 0.083 ng/g sum PFPIA. Lab studies have suggested that PFPIAs are not bioaccumulative and can be readily metabolized and excreted by organisms. Therefore short-term dietary habits and point sources may be factors and less so, trophic position. For example, PFPIA concentrations were significantly correlated with carbon stable isotope ratio $^{13}C/^{12}C$ for pike, suggesting elevated PFPIA with benthic feeding strategies. This research indicates that PFPIAs are widely present in fish and birds albeit at concentrations lower than perfluorocarboxylates and perfluorosulfonates.

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# A Case Study and Data Gap Analysis at Former Wurtsmith Air Force Base (WFAB)

ROBERT DELANEY[1], DORIN BOGDAN, PH.D., E.I.T.[2], DALE J. CORSI, P.E.[3]

At the Former Wurtsmith Air Force Base (WAFB) over 10,000 people either worked or lived on the base. B-52 bombers and KC-135 support airplanes operated at the base until its closure in 1993. In 2010, groundwater from the entire base was randomly sampled for perfluoroalkyl and polyfluoroalkyl (PFASs) substances. Soil, sediment, and biological samples have also been collected for 9 different fish species and Tree Swallows. The analysis of the fish resulted in a "Do Not Eat" fish advisory. By April 2015, the first treatment system for PFASs on a former Air Force base will begin to operate at WFAB. Out of 67 groundwater wells sampled on base or down gradient of the base, only 3 did not show any PFASs contamination. Many samples at WAFB from groundwater, soil, sediments, fish, and birds showed some of the highest concentrations reported in literature. The extent, contaminant fate, transport, and bioaccumulation and magnification of PFASs from WAFB will be presented as a case study. The WAFB can be used as a reference site providing insight into the types of studies required, data gap analysis, and potential for future scientific enquiry on the fate, transport, and risks of exposure from such sites.

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# Fate of Commercial Fluorinated Polymers in Waste Incineration at End of Life

ROBERT GIRAUD[1], P. H. TAYLOR[2], T. YAMADA[2], R. C. STRIEBICH[3], R. C. BUCK[1]

In light of the widespread presence of perfluorooctanoic acid (PFOA) in the environment, two comprehensive laboratory-scale studies have developed data requested by U.S. EPA to determine whether municipal and/or medical waste incineration of either commercial fluorotelomer-based polymers or commercial fluoropolymers at end of life is a potential source of PFOA that may contribute to environmental and human exposures. Each study was divided into two phases (I and II) and conducted in accordance with U.S. EPA Good Laboratory Practices (GLPs) as described in the quality assurance project plan (QAPP) for each phase. Phase I testing (in common between the two studies) met its Data Quality Objective (DQO); the resulting PFOA transport efficiency across the thermal reactor system to be used in Phase II was greater than 90%. Phase II combustion testing of the test substance composites for both studies in this thermal reactor system met their respective DQOs and yielded results demonstrating that waste incineration of neither fluorotelomer-based polymers nor fluoropolymers emit detectable levels of PFOA under conditions representative of typical municipal waste combustor operations in the U.S. Therefore, waste incineration of these polymers is not expected to be a source of PFOA in the environment.

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# Effects of AFFF on TCE Dechlorination by a Dehalococcoides Enrichment Culture

KATIE C. MARJANOVIC[1], SHAN YI[2], TESS S. WEATHERS[3], JONATHAN O. SHARPE[3], DAVID L. SEDLAK[2], LISA ALVAREZ-COHEN[2]

The application of aqueous film-forming foams (AFFF) to extinguish chlorinated solvent-fueled fires has led to the co-contamination of poly- and perfluorinated alkyl substances (PFASs) and trichloroethene (TCE) in groundwater and soil. Reductive dechlorination of TCE by Dehalococcoides (Dhc) is a frequently used in situ remediation strategy at many contaminated sites; however, the effects of AFFF and PFASs on TCE dechlorination have not been well described. In this study three different AFFF formulations and various PFASs were amended to the growth medium of a Dhc-containing microbial community to determine their impacts on TCE dechlorination. TCE was dechlorinated in the presence of one AFFF formulation, while no dechlorination occurred in the presence of two other formulations after 60 days. In PFAS-amended experiments, 16 and 32 mg/L FtSaB inhibited dechlorination, suggesting dechlorination did not occur in one AFFF-amended experiment due to the presence of its most abundant PFAS. In cultures amended with perfluoroalkyl acids (PFAAs), 110 mg/L total perfluorosulfonic acids (PFSAs) did not inhibit TCE dechlorination, while 110 mg/L total PFAAs (PFSAs + perfluorocarboxylic acids, PFCAs) did, suggesting that inhibition may be dependent on PFAS structure as well as concentration. This study reveals a dynamic interplay between AFFF and TCE bioremediation communities that may be dependent on the AFFF formulation and composition.

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# Conceptual Site Models for the Investigation and Delineation of Per- and Polyfluoroalkyl Substances Derived From Aqueous Film-Forming Foam Agents (AFFF)

JIM HATTON[1], BILL DIGUISEPPI[1]

As awareness of the environmental impact of releases of AFFF increases, users are beginning to assess the potential impact of PFAs in AFFF on the environment, including groundwater. A Conceptual Site Model (CSM) approach will be used to identify and organize the current thinking on PFAs behavior in groundwater systems to help investigators better understand issues related to PFAS storage and migration. A series of CSMs will depict how AFFF released from fire-fighting related activities can impact groundwater and how the PFAS compounds in the AFFF can be stored and migrate in a groundwater system. The focus will be on modes of release and potential chemical and geochemical transformations of the compounds. Data will be provided from the literature and testing of oxidation processes on AFFF. The 14-compartment model (Sale and Newell 2011), developed as a remediation decision tool for chlorinated compounds, will be used to allow comparison of expected PFAS behavior to that of better-understood compounds. The models are intended as an aid in the investigation and delineation of contaminants at PFAS-contaminated sites, and to help identify potential data gaps in defining PFAS fate in groundwater systems.

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ED_002330_00143654-00103

# Presence of Per- and Polyfluoroalkyl Substances (PFASs) in Surface and Deep Waters of the Western South Atlantic Ocean, and Implications for Global Budgets

ERIN MARKHAM[1,2], PAVLÍNA KARÁSKOVÁ[2], JITKA BEČANOVÁ[2], JANA KLÁNOVÁ[2], RAINER LOHMANN[1]

Vertical seawater profiles were collected at 12 stations throughout the Western Atlantic Ocean in the spring of 2013 to better understand the presence of PFASs in the deep ocean. Particular care was taken to sample specific deep ocean water masses that might hold clues to the penetration efficiency and circulation of PFASs in the Atlantic Ocean, including Antarctic Bottom Water (AABW), Antarctic Intermediate Water (AAIW), and North Atlantic Deep Water (NADW). Our results suggest that PFASs are widespread below the surface, being regularly detected at 100s pg/L in the South Atlantic down to bottom waters. Lower concentrations and less penetration of PFASs to depth was observed in samples collected in the North Atlantic. The South Equatorial Current emerged as a major source of PFASs to the tropical Atlantic Ocean, probably from African sources. At most sites, PFASs show basically flat vertical profiles down to at least 1000 m depth, often even deeper than that. These results imply that the Atlantic Ocean is a much greater sink of PFASs than currently thought. The presence of PFASs at depth was not consistent with the current movement; their transport to depth is likely a combination of particle settling and convective mixing to depth.

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# Understanding Organofluorine Binding to Natural Organic Matter Using NMR

JAMES LONGSTAFFE[1]

This poster will describe research into the use of Nuclear Magnetic Resonance (NMR) spectroscopy to probe the interactions between organofluorine compounds and natural organic matter (NOM) in both aquatic and soil samples. $^{1}H$ NMR spectroscopy is a powerful analytical tool to study the composition of NOM, while $^{19}F$ NMR spectroscopy is a selective tool to measure organofluorine compounds. When organofluorine compounds interact with NOM, the nuclear dipole interaction between $^{1}H$ and $^{19}F$ can be exploited using double resonance $^{1}H/^{19}F$ NMR experiments to reveal a detailed molecular-level picture of the nature of this interaction, including the orientation of the organofluorine compound, the components of NOM where the interaction occur, and the relative strengths of these interactions. Pulsed-field gradient (PFG) NMR methods can be used to study the role the supramolecular structure of NOM plays in the binding of organofluorine compounds as well as a tool to study the dynamics of these interactions. Together, these NMR methods provide a unique opportunity to probe the molecular-level mechanisms that govern the binding of organofluorine compounds to NOM, interactions that may ultimately play a role in governing the fate and transport of these compounds in the environment in general.

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ED_002330_00143654-00105

# Aerobic Degradation of Fluorotelomer-Based Acrylic Polymers

MARK H. RUSSELL[1]

This poster compares the results of multiple studies that have been performed for fluorotelomer-based acrylate polymers (FTACP) and fluorotelomer acrylate monomer (FTAC). The biodegradation of a high molecular weight, long polymer chain commercial FTACP (MW 40,000, 25-30 FT side chains, 100-300μ particles) has been studied in four aerobic soils over a period of two years. Based on PFOA formation rate, the half-life of the parent polymer was 1200-1700 years. A similar biodegradation study with a more coarsely grained FTACP (~1700-5000μ) resulted in estimated half-lives of 870-1400 years in aerobic soil. More recently, a biodegradation study with a custom synthesized short polymer chain FTACP (MW ~3400, six or fewer monomeric units, aka oligomer) resulted in estimated half-lives of 8-111 years. A final study examined the biodegradation rate of the 8:2 FTAC monomer in soil in three aerobic soils. The half-lives of the FTAC monomer ranged between 3 and 5 days. The results of these studies indicate that the FTAC monomer is readily degradable in soil (half-lives of days) while fluorotelomer-based acrylate polymers degrade much more slowly with half-lives ranging between tens of years for short polymer chain test substance up to thousands of years for high molecular weight, long polymer chain commercial products.

[1] *The Chemours Company, LLC*



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# Septic Systems as Sources of Perfluoroalkyl Acids in Drinking Water Wells on Cape Cod, Massachusetts

LAUREL A. SCHAIDER[1], JANET M. ACKERMAN[1], KATHRYN M. RODGERS[1], RUTHANN A. RUDEL[1]

Perfluoroalkyl acids (PFAAs) in household products may end up in domestic wastewater and ultimately in drinking water sources following discharge from septic systems and wastewater treatment plants. We tested for 14 PFAAs and 100 other trace organic compounds in 20 domestic drinking water wells on Cape Cod, Massachusetts (USA), a region where septic systems are prevalent and all residents rely on groundwater for their drinking water. We selected wells that encompassed a range of likely septic system impacts, as indicated by nitrate and boron concentrations, with an emphasis on the most impacted wells. Six PFAAs were detected at least once (LODs 0.16-1.3 ng/L), and four PFAAs (PFHxS, PFBS, PFOS, and PFHxA) were detected in 50% of wells tested, at concentrations up to 41 ng/L (PFHxS). The sum of detected PFAA concentrations was significantly correlated with concentrations of nitrate, boron, and acesulfame (artificial sweetener), indicative of septic systems as the primary source. We will compare these results with preliminary analyses of PFAAs in septic tanks and published studies of PFAAs in wastewater treatment plants to evaluate domestic wastewater as a source of PFAAs to these wells and other drinking water sources.

[1] *Silent Spring Institute*



ED_002330_00143654-00107

# Combining Riverine Discharge Calculations and Isomer Profiles to Characterize Emissions of PFCAs from Fluoropolymer Production Facilities: A Case Study of Xiaoqing River, China

ROBIN VESTERGREN[1], YALI SHI[2], LIN XU[2], XIAOWEI SONG[2], XIAMENG NIU[2], CHUNHUI ZHANG[3], YAQI CAI[2]

The initiatives to phase out perfluorooctyl compounds have partly resulted in an industrial transition of production and use from Europe and North America to emerging economies including China. Recent emission inventories estimate that direct emissions from fluoropolymer production in China, is the major ongoing source of perfluoroalkyl carboxylic acids (PFCAs) on a global scale. Yet, there is a paucity of empirical data to evaluate the key assumptions of emission inventories. Here, we present the results from a spatial trend study of Xiaoqing River which receives discharges from one of the major fluoropolymer manufacturers in China. Highly elevated PFCA concentrations (median = PFCAs 31500 ng/L) in water downstream of the fluoropolymer manufacturer demonstrated that the emissions from this FP production facility dominated total riverine discharges. Isomer profiles of perfluorooctanoic acid (PFOA) in water displayed a marked increase in percentage branched PFOA downstream of the fluoropolymer manufacturer reflecting the use of ECF based PFOA. Riverine discharges of PFOA (23-67 t/yr) were in agreement with theoretical emission calculations from FP production (68 t/yr) whereas large discrepancies between the two methodologies were observed for perfluorobutanoic acid and perfluoropentanoic acid. The implications for understanding global sources of PFASs will be discussed in the poster.

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# Avinor AS: Results From Monitoring PFOS at Norwegian Airports

BENTE WEJDEN[1], TRINE REISTAD[1], JARL ØVSTEDAL[1]

Avinor is a state limited company under the Norwegian Ministry of Transport and Communications and is responsible for 46 Airports. Through history, there have been strict regulations for the frequency of fire drills and equipment testing. Different foams have been used since the 1970s, some of it containing PFOS or other PFASs. In 2011/2012 Avinor systematically surveyed soil and water at and downstream active and abandoned firefighting drill grounds. The results showed that even on drill grounds abandoned in the mid-eighties, PFOS was found in concentrations up to 1200 µg/kg. On drill grounds used more recently, single samples of soil contains up to 20 000 µg PFOS/kg. Soil characteristics seem to influence the results, and the highest concentrations are often found in peaty layers. Water samples are analysed for 12 different PFAS, and monitoring is ongoing. PFOS is the dominating PFAS in water samples. Monitoring results show that PFAS are still found in discharge water from firefighting drill grounds, even though Avinor has used PFAS-free foam since 2012. Results also indicate that mechanical influence on soil mobilizes PFOS. In 2013 biota was sampled in the surroundings of 18 airports. Risk assessments for human health and environment are currently carried out.

[1] *Avinor AS*



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# Fate and Transport of Per- and Polyfluoroalkyl Substances (PFASs): Results from Characterizing Several Dozen Sites Around the Globe

DAVID WOODWARD[1], DORA CHIANG[2], RACHAEL CASSON[3]

This evaluation presents the results from characterizing several dozen PFAS impacted sites and highlights a number of unique concerns and protocols that must be followed due to the characteristics of PFCs and significant potential for sample contamination. Data and experiences were gathered via AECOM's PFAS Technical Practices Group (TPG), which collaborates on technical issues to improve our overall understanding of PFASs. The data were then evaluated to identify both common and unique results. Special sampling protocols were also captured from the experience of the PFAS TPG, available literature on the topic, and recommendations provided by analytical laboratories. The experience was then combined to develop a detailed list of sampling protocols and procedures. The site data were also evaluated to identify any trends and outliers or unique situations. The results of this evaluation and associated lessons learned provide valuable insight into: sources of background and non-point sources of PFASs, common fate and transport characteristics of PFAS soil, groundwater, surface water, and sediment impacts, and reinforce that PFAS characterization activities must be very rigorous and involve new protocols and procedures.

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# Vertical Profiles of Perfluoroalkyl Acids (PFAAs) in Seawater Samples from the Arctic Region

LEO YEUNG[1], SCOTT MABURY[2], CAOXIN SUN[3], RAINER LOHMANN[3]

PFAAs such as PFOS and PFOA are global contaminants. Atmospheric transport of volatile fluorotelomer alcohols or other precursor compounds, and subsequent oxidative reactions of these compounds are believed to be the sources of PFAAs in remote areas like the Arctic. Examining the vertical profiles of PFAA levels along the water depth as well as their relationship with other physical parameters allow better understanding on their fate and transport. Seawater samples were collected at North Barent Sea, Nansen Basin—West Gakkel Ridge, Amundsen Basin—East Gakkel Ridge, and near the North Pole from surface to bottom (4220m) with the research vessel Polarstern in September 2012. Another seven CTD profiles surface to bottom (~350m) along the Arctic shelf were also collected with the research vessel Healy in October 2012. The 1L water samples were extracted in duplicate (400mL) using a solid-phase extraction method; the 40 PFAAs, including C5-C14 PFCAs/PFSAs, FOSAs, some newly identified and commercially available chemicals, were analyzed using a Acquity UPLC coupled with a Xevo TQS MS/MS. Nine PFAAs showed detectable concentrations (<1-80 pg/L); C8 PFSA and PFCAs (C8 and C9) were frequently detected. In the present investigation, higher PFAA concentrations were found in samples collected along the Arctic shelf.

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# Identification of Anaerobic Biotransformation Products of 6:2 Fluorotelomer Thioamidosulfonate in Aqueous Film-Forming Foams Through Computer-Aided Target Screening and Mass Spectrometry Analyses

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Aqueous film-forming foams (AFFFs) that have been used to extinguish solvent based fires contain complex chemical mixtures including poly- or per-fluoroalkyl substances (PFASs). Although the use of perfluoroalkyl acids (PFAAs), such as perfluorooctane sulfonate and perfluorooctanoic acid in AFFFs is being phased out due to their environmental impact, the PFASs that contain perfluoroalkyl chains and various ionic alkyl functional heads in AFFFs have been identified. Currently, knowledge of the environmental fate and specifically the anaerobic biotransformation products (TPs) of these PFASs are still lacking. The objective of this study was to investigate the microbial TPs of 6:2 fluorotelomer thioamidosulfonate (6:2FtTAoS) in a widely used AFFF formulation. Microcosms, representing the nitrate- and sulfate-reducing conditions were constructed with this AFFF using either pristine sediment or AFFF impacted soil. A high-throughput target screening method was developed to identify plausible TPs in live and control microcosms using both liquid-chromatography-tandem mass spectrometry (MS) and high resolution MS analyses. Our results indicate that 6:2FtTAoS was transformed to a list of TPs including a fluorotelomer thiol carboxylic acid intermediate. This study expands the understanding of the fate of PFASs in the environment, which will help determine appropriate monitoring and remedial strategies applied to AFFF-impacted sites.

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# Minnesota Megaplume Illustrates the Extreme Persistence and Mobility of Perfluoroalkyl Acids (PFAAs) in the Environment

VIRGINIA YINGLING[1]

Perfluoralkyl acid (PFAA)-bearing wastes were disposed in unlined landfills in southern Washington County, Minnesota in the 1940s to 1970s. The resulting groundwater plumes coalesced to cover an area of over 100 square miles, affecting four major aquifers and impacting the municipal water supplies of eight communities and thousands of private drinking water wells. Modeling predicted a much smaller area of contamination. Groundwater and surface water sampling revealed a complex transport history that explains the genesis of this megaplume. The extreme persistence and mobility of PFAAs, particularly perfluorobutanoic acid (PFBA), allowed multiple transfers of PFAAs between groundwater and surface water, permitting them even to cross a groundwater divide. Bedrock features (karst, buried valleys, faults, and joints) and stormwater management features further facilitated the unusual growth of the plumes. The unique PFAA chemical signatures in each disposal site have also helped to elucidate partitioning of the PFAAs between various environmental media.

[1] *MN Dept. of Health*



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# Deposition of Perfluoroalkyl Acids to the Devon Ice Cap from 1995 to 2007

CORA YOUNG[1], CHRISTINE SPENCER[2], KATHERINE FRENCH[2], MARTIN SHARP[3], AMILA O. DE SILVA[2], DEREK C.G. MUIR[2]

Perfluoroalkyl acids (PFAAs) are present ubiquitously in the environment, including in remote regions such as the Arctic, where local contamination is insignificant. Previous work demonstrated the presence of five PFAAs on the remote Devon Ice Cap in 2007, which could only have been deposited through atmospheric transport. Further samples were collected from the Devon Ice Cap in the spring of 2008. These samples were analyzed for a full suite of PFAAs, including C4, C14, C16, C18 perfluorocarboxylic acids (PFCAs), C4, C6, C8, C10 perfluorosulfonic acids (PFSAs), perfluoroethanecyclohexane sulfonic acid, and perfluorooctanesulfonamide. Samples were collected horizontally from the side of the snow pit, allowing detection of yearly deposition from 1995 to 2007. Time trends for PFAAs will be presented, along with correlations between congeners and comparisons to low-latitude precipitation and fresh water. Implications for long-range transport mechanisms will be discussed.

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ED_002330_00143654-00114

# Poster Abstracts:

# Remediation

# Transformation of Poly- And Perfluoroalkyl Substances by Chemical Oxidants in AFFF-Impacted Groundwater

THOMAS BRUTON[1], FIONA DOYLE[2], DAVID SEDLAK[1]

Application of aqueous film-forming foams (AFFFs) at fire-training facilities has led to contamination of groundwater with poly- and perfluoroalkyl substances (PFAS). In situ chemical oxidation has received attention as a potential remedy for PFAS contamination. The purpose of this research is to assess the fate of poly- and perfluoroalkyl substances in AFFF during oxidative chemical treatment. PFAS-containing solutions were amended with Fenton's reagent, persulfate, or permanganate. Of these three treatments, only persulfate effectively transformed PFOA, and its efficacy was related to solution pH. In experiments using Ansul AFFF, all treatments resulted in full removal of the primary PFAS component, 6:2 fluorotelomer thioamido sulfonate (6:2 FtTAoS). Recovery of known transformation products relative to 6:2 FtTAoS loss ranged from 3 to 46% for the different treatments, with permanganate resulting in the lowest concentration of known transformation products. Future efforts will attempt to improve the 6:2 FtTAoS materials balance by identifying additional transformation products.

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ED_002330_00143654-00117

# Removal of Polyfluoroalkyl Substances from Impacted Water Following the Lac Mégantic Catastrophe

GUOWEI ZHONG[1], JEAN PAQUIN[2], JINXIA LIU[3]

Following the Lac Mégantic (QC, Canada) derailment accident, aqueous film-forming foams (AFFFs) containing polyfluoroalkyl and perfluoroalkyl substances (PFAS) were used to control fires caused by spilled crude oil. During the cleanup efforts, water contaminated by crude oil and AFFFs was treated through various physical treatment processes intended for hydrocarbon removal, but significant PFAS removal was also achieved. This study will present results of PFAS removal in lab-scale and full-scale treatment systems, evaluation methods used and their limitations. For a small and large modular treatment systems employed at Lac Mégantic, PFAS removal efficiencies were 87.3% and 99.9%, respectively, when assessed using a total oxidizable precursors (TOP) assay. Sand filtration removed little PFAS, while Ultrasorption® and activated carbon adsorption each contributed to approximately half of the total removal. A lab-scale system, which was operated to elucidate PFAS removal mechanisms, achieved comparable total PFAS removal to the full-scale systems, but most of the removal was attributed to activated carbon adsorption. Thus, the role PFAS-colloids association and the impact of hydraulic retention time was further investigated. Strong linear correlation between levels of TOP with surface tension of water samples suggests that surface tension can approximate PFAS levels for AFFF-impacted waters.

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[2] *Sanexen Environmental Services, Inc., Brossard, QC, Canada*
[3] *McGill University, Department of Civil Engineering, Montreal, QC, Canada*



ED_002330_00143654-00118

# In Situ Treatment Train for Remediation of Perfluoroalkyl Contaminated Groundwater: In Situ Chemical Oxidation of Sorbed Contaminants (ISCO-SC)

DINUSHA SIRIWARDENA[1], NAGESHRAO KUNTE[1], MICHELLE CRIMI[1], THOMAS HOLSEN[1], CHRISTOPHER BELLONA[1]

Perfluoroalkyl and polyfluoroalkyl substances (PFASs) are a stable synthetic class of chemicals ubiquitously spread in environmental media. The substances' strong polar carbon-fluorine bonds and their high thermal and chemical stability make them resistant to biological, chemical, and physical degradation. The purpose of this research is to develop a predictable and low cost in situ treatment train for remediating perfluoroalkyl contaminated groundwater. The treatment train involves first the sorption of PFASs onto granular activated carbon (GAC), followed by treatment and regeneration of the GAC using activated persulfate. The research is being conducted in two parallel phases. First, sorption isotherm and kinetic data are being collected for four types of PFASs, perfluorooctanoic acids, perfluorooctanesulfonate, perfluorohexanesulfonate and perfluorobutanesulfonate, and five types of Calgon Corporation GAC. Results to date indicate that all tested sources of GAC have large sorption capacities for PFOA, and F300 and F400 have the highest sorption capacity of the carbons tested. This presentation will focus on these results, as well as results of pending studies on the impact of common co-contaminants and varied groundwater conditions on PFAS sorption. In the second phase of this research the oxidative treatment effectiveness of several processes for PFASs will be evaluated. Research to date has focused on treatment of PFASs by alkaline pH activated persulfate, heat activated persulfate, and dual oxidation (combined $H_2O_2$ and persulfate). The presentation will focus on early experimental results, which indicate that, of those evaluated techniques thus far, heat activated persulfate shows the highest oxidation efficiency for both PFOA and PFOS.

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[1] *Institute for a Sustainable Environment, Environmental Science and Engineering,Clarkson University, Potsdam, NY*



ED_002330_00143654-00119

# Persulfate Oxidation for Effective Removal of Perfluoroalkyl Contaminants Sorbed onto Granular Activated Carbon

NAGESHRAO KUNTE PANDURANGARAO[1], MICHELLE CRIMI[1], THOMAS M. HOLSEN[1], CHRISTOPHER BELLONA[1], DINUSHA SIRIWARDENA[1]

Perfluoroalkyl and polyfluoroalkyl substances (PFASs) are characterized as contaminants of concern. Their ubiquitous presence in environmental media including groundwater has initiated awareness for the need of remediation techniques. In situ chemical oxidation of sorbed PFASs is a treatment approach to remediate contaminated groundwater which incorporates the sorption of PFASs onto granular activated carbon (GAC) in situ followed by effective contaminant treatment and regeneration of the carbon using chemical oxidation. Amongst oxidation methods, heat activated persulfate is indicated as a promising approach for effective degradation of PFASs. The purpose of this study was to evaluate the effectiveness of in situ persulfate oxidation and to establish dose standards considering by-products and varied groundwater conditions. The laboratory study focuses on more commonly detected long chain PFASs, perfluorooctanoic acids (PFOA) and perfluorooctane sufonic acid (PFOS). Two different types of Filtrasorb brand of GAC manufactured by Calgon Corporation, which have shown efficient adsorption capacity according to previous experimental results, are first employed to develop adsorption isotherm and sorption kinetic data. The carbon containing sorbed PFOA and PFOS are then exposed to persulfate heat activated at 80°C. The presentation focuses on experimental results that represent the impacts of varied groundwater conditions such as persulfate loading rate, sulfate concentration, pH, and co-contaminant concentration during PFASs degradation. The prospective features of per-sulfate oxidation in ISCO application will also be described.

[1] *Department of Environmental Science and Engineering, Clarkson University*



ED_002330_00143654-00120

# Abiotic Reductive Transformation of PFOS by Various Electron Donors with Vitamin $B_{12}$

SAEROM PARK[1], JENNY ZENOBIO[1], LINDA S. LEE[1]

Vitamin $B_{12}$, a well-known an electron mediator produced by anaerobic bacteria, in combination with varied electron donors or catalysts to reductively transform PFOS was evaluated as a function of temperature and time in aqueous batch systems. Headspace was collected and the aqueous phase subsampled followed by 4 sequential ethyl acetate extractions. Loss of linear and branched PFOS isomers were quantified using HPLC/MS/MS and time of flight (TOF)/SelexION™ detection and generation of fluoride and sulfate/sulfite using ion chromatography. Identification of polyfluoroalkyl intermediates from partial transformation using TOF/MS is underway. At 70 °C and pH 9.54, $B_{12}$ with Ti-citrate (electron donor) showed PFOS removal 32.5%. Addition of Cu° or Fe° to the $B_{12}$-Ti-citrate system enhanced PFOS removal to 50.4% and 56.7%, respectively. $B_{12}$ with Fe° (solid electron donor) showed PFOS transformation up to 71.7% at 70 °C and pH 10.41 with 8 moles of $F^-$ and 0.6 moles of $SO_4^{2-}$ produced per mole of PFOS lost. Adding Pd° to the $B_{12}$-Fe° system resulted in similar PFOS loss, but somewhat different moles of $F^-$ (6.2) and $SO_4^{2-}$ (1.0) generated per mole of PFOS lost. Generation of $F^-$ and $SO_4^{2-}$ confirmed reductive transformation of PFOS. Mechanisms involved and further optimization are being explored.

[1] *Purdue University*



ED_002330_00143654-00121

# Laccase Catalyzed Degradation of Perfluorooctanoic Acid

QI LUO[1], DORA CHIANG[2], DAVE WOODWARD[2], QINGGUO HUANG[1]

Perfluorooctanoic acid (PFOA) causes a great concern due to its widespread presence, persistence, bioaccumulation, and toxicity to animals. However, the remediation of PFOA remains a significant challenge. A novel scheme involving enzyme-catalyzed oxidative humification reaction (ECOHR) sheds a light on the remediation of PFOA. We have conducted systematic experiments in both aqueous and soil phase that verified the efficiency of PFOA removal by ECOHR. The experiments were performed with laccase, a stable oxidase that is ubiquitous in the environment, as a model enzyme in combination with different mediators that are able to induce ECOHR along with laccase. Additional experiments were also conducted in soil with natural organic matter serving as the mediators. Significant degradation of PFOA was observed in systems with ECOHR treatment. The reaction products were determined through high resolution mass spectrometry, and were identified as more environmentally benign than PFOA. The result in this study provides valuable information for incorporating ECOHR in in-situ remediation of PFOA.

[1] *University of Georgia*
[2] *AECOM*



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# Coagulant-Enhanced Sorption of Perfluoroalkyl Substances

YOUSOF ALY[1], DANIEL MCINNIS[1], CHEN LIU[2], BONNIE LYON[2], BILL ARNOLD[1], KURT PENNELL[2], MATT SIMCIK[1]

Sorption to mineral surfaces is an important process in controlling the fate, mobility, and bioavailability of perfluoroalkyl substances (PFASs) in aquatic systems. Unlike other persistent organic pollutants, PFASs are highly water-soluble due to their hydrophilic head group and thus their solid-phase partitioning is limited under natural conditions. However, recent research has shown that sorption of PFASs to suspended solids in surface water can be enhanced by addition of cationic coagulants, through a combination of electrostatic and hydrophobic effects. Whether coagulant-enhanced sorption can be adapted for in situ remediation of PFAS-contaminated groundwater remains an open question. We investigated sorption of six PFASs at environmentally relevant concentrations in the presence of four cationic coagulants: polyaluminum chloride, polyamine, polydiallyldimethyl ammonium chloride (polyDADMAC), and a tannin-based cationic polymer. PFAS adsorption isotherms were determined on Ottawa sand and on aquifer material from a known PFAS-contaminated site. Preliminary results suggest that this method shows promise for in situ remediation of PFAS-contaminated groundwater.

[1] *University of Minnesota*
[2] *Tufts University*



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# Remediation of Per- and Polyfluoroalkyl Substances (PFASs) with OxyZone®, a Multi-Oxidant Blend

RAYMOND BALL[1], THOMAS BOVING[2]

This poster will present field and laboratory results of PFAS remediation with a blend of ozone, hydrogen peroxide, and buffered persulfate commercially available as OxyZone® from EnChem Engineering, Inc. The Fire Fighting Area at Joint Base Langley- Eustis Site is contaminated with aromatic and chlorinated VOCs and PFASs from releases of fire-fighting foams. Following OxyZone® treatment of the VOCs, EnChem observed decreases in the concentration of the PFASs in the groundwater, suggesting in situ PFAS degradation had occurred rather than dilution. Laboratory treatability studies were then performed to investigate to what extent OxyZone® could degrade and destroy PFASs, specifically PFOS and PFOA. These experiments exposed spiked DI water and Site groundwater to continuously ozonated OxyZone® for a 6-7 hour period. The results showed that concentrations of PFOS and PFOA in spiked DI water decreased by 98-99% to a concentration of ~ 1 ppb in one hour. In spiked Site groundwater, PFOS and PFOA destruction was slower and less complete, requiring about 6 hours to destroy 93-96% of the PFASs to concentrations of 2-4 ppb. This is presumably due to other competing contaminants exerting an oxidant demand. The analytical results also showed that transformations of many other PFASs also took place during treatment.

[1] *EnChem Engineering, Inc.*
[2] *Department of Civil and Environmental Engineering, University of Rhode Island*



ED_002330_00143654-00124

# Treatment of PFOS and PFOA in Groundwater Using Sequential Electrocoagulation and Electro-oxidation Technologies

DORA CHIANG[1], HUI LIN[1], JACK HUANG[2], JUNFENG NIU[3], DAVE WOODWARD[1]

PFOA and PFOS can be effectively mineralized during electro-oxidation (EO). EO is a proven process that is operated at room temperature and atmospheric pressure without added reagents and with half-lives typically below ten minutes. EO is most applicable for PFASs treatment at high concentrations in small volumes. This prevents its application on groundwater plumes because the energy consumption of the direct EO process is prohibitively high. EO is most applicable if a low-energy technology is used to concentrate PFASs prior to EO. Our studies showed that PFOA/PFOS at ppb to ppm levels can be effectively separated (80-100 %) within 30 minutes using electrocoagulation (EC) which is more efficient than conventional chemical coagulation (20-40%). EC removes PFASs by coagulation, adsorption, precipitation and flotation and leads to high concentration metal hydroxide flocs (sludge). These flocs have high BET surface areas that adsorb PFASs. We have also found that the PFASs on flocs can be released back to water at elevated concentrations via centrifugation, through which PFASs can be concentrated for further destruction (such as EO). Therefore EC separates PFASs from groundwater and is also a pre-enrichment step to concentrate PFASs for subsequent EO degradation. As PFASs-laden flocs are released back to water via centrifugation, PFASs can be subsequently destructed with EO using a modified $PbO_2$ film electrode.

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[3] *School of Environment, Beijing Normal University, China*



ED_002330_00143654-00125

# Occurrence and Treatment of Poly- and Perfluoroalkyl Substances in North American Drinking Waters

ERIC DICKENSON[1]

The near ubiquitous presence of poly- and perfluoroalkyl substances (PFASs) in humans has raised concerns about potential human health effects from these chemicals, some of which are both extremely persistent and bioaccumulative. Because some of these chemicals are highly water soluble, one major pathway for human exposure is the consumption of contaminated drinking water. This study measured concentrations of PFASs in 18 raw drinking water sources and 2 treated wastewater effluents and evaluated 15 full-scale treatment systems for the attenuation of PFASs in water treatment utilities throughout the U.S. Despite the differences in reporting levels (23 PFASs monitored), PFASs that were detected in >70% of the source water samples (n = 39) included, perfluorobutane sulfonic acid (74%), perfluorohexane sulfonic acid (79%), and perfluorooctane sulfonic acid (84%), perfluoropentanoic acid (74%), perfluorohexanoic acid (79%), perfluoroheptanoic acid (74%), and perfluorooctanoic acid (74%). More importantly, water treatment techniques such as ferric or alum coagulation, granular/micro-/ultrafiltration, aeration, oxidation (i.e., permanganate, ultraviolet/hydrogen peroxide), and disinfection (i.e., ozonation, chlorine dioxide, chlorination, and chloramination) were mostly ineffective in removing PFASs. However, anion exchange and granular activated carbon treatment preferably removed longer-chain PFASs, and reverse osmosis demonstrated significant removal for all the PFASs, including the smallest PFAS, perfluorobutanoic acid.

[1] *Southern Nevada Water Authority*



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# Sustainable Removal of Poly- and Perfluorinated Alkyl Substances (PFASs) from Groundwater Using Synthetic Media

NATHAN HAGELIN[1], STEVEN WOODARD[2], MICHAEL NICKELSON[2]

Polyfluorinated and perfluorinated alkyl substances have proven difficult to treat. They are recalcitrant to chemical oxidation and biological treatment. Granular Activated Carbon is effective, but requires frequent regeneration and is inefficient at low concentrations. Synthetic media (resin) was tested at bench scale and shows significant promise at treating PFASs. PFAS isotherm screening of seven polymeric, carbonaceous and ion exchange resins was performed on a synthetic water for PFAS removal capability. Subsequent bench-scale column testing of the top three resins was then conducted on groundwater collected from a site with known impacts to municipal water supply. The objectives of the testing were to demonstrate treatment performance and regenerability of the technology and then scale up the technology for an on-site pilot demonstration. Column testing utilized three identically-sized columns containing three different ion exchange resins plus an empty control column. All columns used an empty bed contact time of 15 minutes. Two of the three resin columns performed well. All eleven of the PFASs analyzed were removed to levels below the EPA Provisional Health Advisory Level. Regeneration proved effective for one of the resins. A pilot scale system will be designed on the basis of the bench scale results.

[1] *Amec Foster Wheeler Environment and Infrastructure, Inc.*
[2] *Emerging Contaminants Treatment Technology, LLC*



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# Granular Activated Carbon Treatment of Drinking Water and Groundwater for Removal of PFOA: 8 Years of Successful Operation

ANDREW S. HARTTEN[1], MARK RUSSELL[2]

Perfluorooctanoic acid (PFOA) is an environmentally persistent surfactant that has been detected in a wide range of media including surface water and groundwater supplies that serve as sources of drinking water. At public water utility locations in the Ohio River Valley, treatment systems using granular activated carbon (GAC) have successfully operated since 2006 to remove PFOA. In some instances, the GAC treatment was integrated into public drinking water systems with existing treatment systems. Smaller scale GAC treatment systems were used for residential drinking water treatment and for point source groundwater treatment at a closed solid waste landfill. Other viable water treatment technologies are available for PFOA, but none are presently available that can be practically applied and address the high flow conditions at public utilities.

[1] *Chemours Corporate Remediation Group*
[2] *Chemours & Bjorn Cuento, AECOM*



ED_002330_00143654-00128

# Granular Activated Carbon Treatment of Groundwater

GARY HOHENSTEIN[1], BRIAN BACHMEIER[2]

In October 2006, a granular activated carbon treatment system commenced operation in the City of Oakdale, MN to treat perfluoroalkyl substances present in two municipal wells. The system was designed and installed to ensure that drinking water criteria established by the Minnesota Department of Health were consistently and reliably met by the municipality's water supply. While these criteria have changed over time, the system has operated continuously since startup and met all performance expectations. Five Calgon Carbon Corporation Model 10 systems, each consisting of a lead and lag vessel, were installed to treat a maximum design flow of 2400 gpm. Each vessel has contained 20,000 lbs of 12x40 mesh bituminous coal-based GAC (Filtrasorb® 600 from Calgon Carbon). The empty bed contact time for each vessel at maximum flow conditions is 8 minutes. Routine monitoring at the inlet, mid-system and outlet has occurred for PFBA (7 ug/L), PFPeA, PFHxA, PFOA (0.3 ug/L), PFBS (7 ug/L), PFHS and PFOS (0.3 ug/L) (MDH Health Risk Limit values). Constituents with highest inlet concentrations are PFBA, PFOS and PFOA with long-term averages of 1.7, 0.71 and 0.64 ug/L, respectively. Little removal of PFBA occurs while very good removals are consistently observed for PFOS and PFOA.

[1] *3M Company*
[2] *Public Works Director, City of Oakdale, MN*



ED_002330_00143654-00129

# Using Carbon Adsorbents to Remove Perfluoroalkyl Acids in Potable Reuse Systems

MANDU INYANG[1], MARCO VELARDE[2], ERIC DICKENSON[2]

In this work, bench-scale testing of biochar, a low-cost carbon adsorbent derived from the pyrolysis of waste biomass was conducted to determine its sorption ability for two perfluoroalkyl acids (PFAAs), perfluorooctanoic acid (PFOA), and perfluorobutanoic acid (PFBA). Sorption kinetics of PFOA and PFBA on two biochars, pine wood and hardwood biochar was determined by spiking 1000 ng/L PFOA or PFBA into sample bottles containing tertiary treated wastewater effluent from a full-scale water treatment facility, mixed with 50 mg of each biochar on an orbital shaker for 30 days. Sorption kinetics results showed that PFOA was better sorbed on pinewood and hardwood biochars than PFBA. PFOA sorption capacity of pinewood and hardwood biochars in different water matrices was also evaluated in batch sorption isotherm experiments. Pilot-scale tests were performed to compare PFAA removal efficiency on hardwood biochar to two other carbon media; anthracite, and granular activated carbon. Three pilot filters containing the three carbon media were each fed the same tertiary-filtered wastewater used for the batch tests, and operated at the same target flow rate of 1.77 GPM (gallons per minute). Ambient PFAA levels in the aqueous phase across the filters were monitored by collecting monthly samples from the filter influent and effluents over a six month period. Break-through data from the pilot tests suggest that the fate of PFAAs during sorption on granular carbons is dependent on the carbon media type and the structural properties of PFAAs.

[1] *Las Vegas Valley Water District*
[2] *Southern Nevada Water Authority*



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# Full-Scale, Pilot-Scale, and Rapid Small-Scale: A Comparison of PFAS Adsorption

DAVID KEMPISTY[1], R. SCOTT SUMMERS[2], DETLEF KNAPPE[3], ERIC DICKENSON[4]

This effort evaluated the merit of using activated carbon as a viable treatment technology for the removal of 10 different perfluoroalkyl substances (PFASs). To accomplish this, bench top (batch experiments and rapid small-scale column tests (RSSCT), pilot-scale, and full-scale granular activated carbon (GAC) adsorbers were employed to treat two natural waters (1 surface, 1 groundwater). Three different carbon types at three empty bed contact times (EBCTs) (7, 7.5, and 13 minutes) were used in this study. The 7 minute RSSCT data was compared to a pilot scale adsorber while the 13 minute RSSCT was compared with the performance of a full-scale adsorber that operated for 4.8 years. Scale-up between the RSSCT and the larger scale adsorbers was also investigated. Significant differences in the carbon use rate were observed due to carbon chain length for the PFAS compounds. The background matrix of the source water, to include both the character and concentration of dissolved organic matter, substantially affected the GAC capacity for PFASs. The RSSCT performance using a groundwater matrix resulted in less overprediction than expected and previously observed with micropollutant removal. Finally, thermally activated powdered activated carbon performed as well or better than the bituminous GACs for every PFAS tested.

[1] *Air Force Institute of Technology*
[2] *University of Colorado - Boulder*
[3] *North Carolina State University*
[4] *Southern Nevada Water Authority*



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# Remediation of Sites Contaminated with Per- and Polyfluoroalkyl Substances: Challenges and Opportunities

SRIRAM MADABHUSHI[1], VINCE BONIFERA[1], BRAD JUNEAU[2]

Remediation of contaminated sites with per- and polyfluoroalkyl substances (PFASs) is still in its infancy. Several potential technologies are being tested and show promise in addressing complex issues related to cleanup of sites contaminated with these chemicals. Due to the ubiquitous nature of these chemicals, and their persistent behavior in subsurface, they are often difficult to detect, characterize and clean up in the environment. Traditional technologies are not very effective in removing these chemicals from the vadose as well as saturated zones. In this presentation, we discuss several traditional and innovative approaches to remediate sites contaminated with PFASs in different media, highlighting some of challenges to be aware of during remedy selection and implementation process. We also highlight some of the opportunities to use innovative techniques and ways to avoid potential pitfalls.

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# Destruction of PFOS in Groundwater: A New in Situ Remediation Technology for Per / Polyfluorinated Alkyl Substances

IAN ROSS[1], TESSA PANCRAS[2], JEFF BURDICK[3]

Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are emerging as contaminants of concern in many countries and authorities around the world have recently established regulatory limits for groundwater. However, there are many other perfluorinated or polyfluorinated alkyl substances compounds (PFAS) found in aqueous film forming foam (AFFF). These perfluorinated or polyfluorinated compound are sometimes termed "precursors" as they can biodegrade to form of more simple perfluorooctanoic acids such as PFOA. Therefore, there are analytical challenges to overcome when considering how to assess soil and groundwater contaminated with PFAS as there are multiple analytes to consider, not just PFOS and PFOA. Methods to overcome these analytical challenges will be discussed and cost effective comprehensive approaches presented using both the TOP (total oxidiseable precursors) assay and Proton Induced Gamma-Ray Emission (PIGE) Spectroscopy. Per/ polyfluorinated compounds are difficult to remediate in soil and groundwater systems due to their recalcitrant nature (i.e. are not amenable to microbial biodegradation) and lack of volatility, therefore in situ remedial options are limited. Activated persulfate chemistry has been used effectively to treat soil and groundwater contaminated by a wide range of pollutants of concern. Recent laboratory work has demonstrated that activated persulfate is capable of oxidizing and reducing perfluorinated compounds in soil and groundwater but only when a specific activation method is employed, as with the smart combined oxidation and reduction (ScisoR®) technology. Laboratory data will be presented to demonstrate how this technology defluorinates and hence mineralise PFOS. A mass balance will be presented demonstrating stoichiometric conversion of PFOS to $CO_2$ and fluoride. However, using other methods of oxidation, such as Fenton's reagent, alternative persulfate activators, to oxidise PFAS from a site soil, an increased mass of perfluorooctanoic acids is observed as the precursors are simply transformed to simpler PFAS as a result of this oxidation reaction.

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# Electrochemical Treatment of Perfluorooctanoic Acid (PFOA) and Perfluorooctane Sulfonic Acid (PFOS) in Groundwater

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Laboratory experiments were performed to evaluate the use of electrochemical treatment for the decomposition of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), as well as other perfluoroalkyl acids (PFAAs), in aqueous film forming foam (AFFF)-impacted groundwater collected from a former firefighter training area and PFAA-spiked synthetic groundwater. Using a commercially-produced Ti/RuO2 anode in a divided electrochemical cell, PFOA and PFOS decomposition was evaluated as a function of current density (0 to 20 mA/cm2). Decomposition of both PFOA and PFOS increased with increasing current density, although the decomposition of PFOS did not increase as the current density was increased above 2.5 mA/cm2. At a current density of 10 mA/cm2, the first-order rate constant, normalized for current density and treatment volume, for electrochemical treatment of both PFOA and PFOS was 120 x $10^{-5}$ [($min^{-1}$) ($mA/cm^2$)$^{-1}$ (L)]. Defluorination was confirmed for both PFOS and PFOA, with 98% and 58% recovery as fluoride, respectively (based upon the mass of PFOA and PFOS degraded). Treatment of other PFAAs present in the groundwater also was observed, with shorter chain PFAAs generally being more recalcitrant. Results highlight the potential for electrochemical treatment of PFAAs, particularly PFOA and PFOS, in AFFF-impacted groundwater.

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# Immobilization of PFASs in Soil Using Activated Carbon and Aluminium Hydroxide

RICHARD J. STEWART[1], CHRIS LAWRENCE[1], JODY ELSWORTH[1], JOEL KIRK[1]

Per- and polyfluorinated alkyl substance (PFAS) contaminated soil from two airport fire training grounds in Australia were used as part of an independent validation of the commercial immobilization product RemBind, which contains predominantly activated carbon and aluminium hydroxide and clay materials. The trials were independently supervised by an external party to ensure a high level of scrutiny. Soils were mixed with 5% to 20% RemBind (standard grade) or RemBind Plus (high grade), fixed for 48 hours, and then analysed for 20 PFAS compounds at a commercial laboratory using the Toxicity Characterization Leaching Procedure (TCLP). Selected samples were further analysed using the Multiple Extraction Procedure (US EPA Method 1320) as an indication of long term binding stability. Results showed that RemBind treatment reduced the soil leachability of PFOS from 37 µg/L (soil 1) and 341 µg/L (Site 2) to below the Minnesota drinking water guideline value of 0.3 µg/L. Furthermore, selected samples passed the MEP test which simulates 1,000 years of acid rain in an improperly designed sanitary landfill. This work paves the way for the in situ treatment of PFAS contaminated soils and retention of the soil on site to provide immediate response to spills and to prevent further source contamination of groundwater in the longer term.

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# Adsorption of Perfluoroalkyl Substances, Including a Fluorinated Alternative, by Powdered Activated Carbon

MEI SUN[1], ELISA AREVALO[1], LEIGH-ANN DUDLEY[1], DETLEF KNAPPE[1], ANDREW LINDSTROM[2], MARK STRYNAR[2]

Because of their persistence, bioaccumulation potential, and (eco)toxicity, long-chain perfluoroalkyl substances (PFASs) such as perfluorooctanoic acid and perfluorooctane sulfonate are being replaced with short-chain PFASs and fluorinated alternatives. Almost no information exists about the behaviors of fluorinated alternatives during water treatment. The objective of this research is to identify parameters that control the adsorption of one fluorinated alternative, GenX [$CF_3CF_2CF_2OCF(CF_3)COO^-$] by powdered activated carbon (PAC). GenX adsorbability was compared to that of seven perfluoroalkyl carboxylic acids and three perfluorosulfonic acids at environmentally relevant concentrations (~500 ng/L). The PFAS adsorption capacity increased with increasing carbon chain length, and for a given carbon chain length, sulfonates were more adsorbable than carboxylates. The adsorbability of GenX fell between perfluoropentanoic acid and perfluorohexanoic acid. The latter has the same number of perfluorinated carbons as GenX but lacks the ether bond present in GenX. PFAS adsorption on superfine PACs was faster than on as-received PACs. Decreasing pH and ionic strength increased PFAS adsorbability in ultrapure water but had no measurable impact in natural water containing dissolved organic matter (DOM). The presence of DOM greatly decreased the PFAS adsorption capacity of PAC, and PFAS removal increased when DOM was removed by coagulation.

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# Radiolytic Decomposition of PFOA with the Use of Gamma and Electron Beam Irradiation

MAREK TROJANOWICZ[1,2], ANNA BOJANOWSKA-CZAJKA[2], GABRIEL KCIUK[2], MONIKA ŁYCZKO[2] AND KRZYSZTOF KULISA[2]

Perfluorinated organic compounds belong to the class of especially persistent anthropogenic pollutants of the natural environment, which are practically not biodegraded; and among different examined Advanced Oxidation/Reduction Processes (AO/RP) as the most efficient was reported sonolysis. In this work the radiolytic decomposition of perfluorooctanoic acid (PFOA) was examined as a result of treatment with gamma and electron beam irradiation. The radiolytic decomposition in dilute aqueous solutions is based on radical reactions of PFOA with products of radiolysis of water (OH• and H• radicals, hydrated electron). The employing of particular chemical conditions of irradiation allows the increasing of efficiency of the formation of particular radicals, which exhibit the fastest reaction. It was found that among radicals produced from the radiolysis of water, the fastest reaction takes place with hydrogen radicals, for which reaction rate-constant with PFOA was determined using the pulse radiolysis with spectrophotometric detection as 9.0 x 107 $M^{-1}s^{-1}$. The decomposition reaction yield is strongly affected by the dose-rate of irradiation, which significantly differs between gamma and EB irradiation. The observed reaction times for decomposition of PFOA at initial ppm level are essentially shorter than reported for many other AO/RP methods.

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# Estimating the Breadth of Potential PFAS Contamination from AFFF in Canada

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A Canada wide screening study was performed to partially estimate the number of per- and polyfluoroalkyl substance (PFAS) impacted sites in Canada. This study focused on identifying PFAS impacted airport locations where current or historical use of aqueous film-forming foam (AFFF) was likely. Over 2000 Canadian airports were identified as either currently or historically operational through the years of 1950 to current day. A decision tree was developed to help identify airport locations where AFFF use was likely, or screen out those that would not have seen AFFF use. At sites where AFFF use was identified it was then assumed that PFAS contamination in the soil or groundwater was probable. The screening process was completed using publicly available resources including airport websites, the Canadian Owners and Pilots Association (COPA) website, Skyvector, Transport Safety Board of Canada aviation investigation reports, the aviation safety network website, and Google Maps. 156 airport locations (approximately 8% of the total) were identified as potential PFAS contaminated sites. These sites were then overlaid onto surficial geology maps to identify the most likely soil remediation scenarios to be encountered in Canada. The methodology presented could be used to identify additional PFAS impacted sites in Canada or other jurisdictions.

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# Preliminary Mechanistic Investigations into the Degradation of Perfluorinated Compounds using Density Functional Theory

DANIEL VAN HOOMISSEN[1], ZACHARY R. SMIALEK[1], SHUBHAM VYAS[1]

Anthropogenic perfluorinated molecules are some of the most environmentally persistent organic compounds known to date. Strong C-F bonds (~116 kcal/mol) contribute toward the insusceptibility of these molecules to degradation in orthodox environmental conditions. Increasing concerns over the environmental and health impacts of these molecules have warranted the exploration of their degradation mechanisms. Several experimental methods have been developed to oxidize and activate perfluorooctanoic acid (PFOA) species, however, a consensus on the mechanistic pathways following the generation of the PFOA radical has yet to be reached. To this end, we investigated various pathways involved in the breakdown of model PFOA using Density Functional Theory (DFT) computations. The polarizable continuum model of water was utilized to mimic the effect of solvation on the reaction energetics. Our preliminary computational work suggests a thermodynamically favorable cascading reaction mechanism resulting in the mineralization of PFOA. Elucidation of natural PFOA degradation pathways provide insight not only to the crucial reaction steps involved but also as to what chemical processes or materials could facilitate faster degradation kinetics.

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# Poster Abstracts:

# Toxicology, Epidemiology, and Human Health

# Dynamic Toxicokinetic Modeling of Direct and Indirect (Precursor) Exposure to Perfluorooctanoic Acid in the General Population.

MELISSA I. GOMIS[1], ROBIN VESTERGREN[1], IAN T. COUSINS[1], HELENA NILSSON[2]

8:2 Fluorotelomer alcohol (8:2 FTOH) has been found to be metabolized into Perfluorooctanoic acid (PFOA) by various species including humans. As a consequence, the ubiquitous presence of PFOA in human blood samples from the general population is thought to be a combination of exposure to PFOA (i.e. direct exposure) and 8:2 FTOH (i.e. indirect exposure). The relative contribution of direct and indirect exposure is, however, widely debated. In this study, a one-compartment, dynamic toxicokinetic model considering both direct and indirect exposure was developed and evaluated for a data set of occupationally exposed ski wax technician. The model, including the metabolism yield estimated from the ski wax technician data set, was subsequently applied to office workers, who were exposed to 8:2 FTOH in their office as a consequence of recent building renovations. Based on these model simulations we will discuss the relative importance of direct and indirect exposure under different exposure scenarios.

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# An Impairment in the Vesicular Trafficking and Fusion System Leading to Hepatic Autophagy Blockage After Perfluorooctanoic Acid Exposure

SHENGMIN YAN[1], JIAYIN DAI[1]

Perfluorooctanoic acid (PFOA) has been shown to cause hepatotoxicity and other toxicological effects, but the mechanism of PFOA-induced hepatotoxicity still remains unclear. In this study, we firstly analyzed the effects of PFOA on livers of mice exposed to PFOA at doses of 0, 0.08, 0.31, 1.25, 5 and 20 mg/kg/d for 28 days. We observed autophagosome accumulation in mouse livers without the occurrence of significant apoptosis. Using isobaric tags for relative and absolute quantification (iTRAQ), proteomic analysis of crude lysosomal fractions (CLFs) from HepG2 cells treated with PFOA revealed that 63 differentially expressed proteins were related to autophagy or vesicular trafficking and fusion. Among these proteins, the expression levels of N-ethylmaleimide-sensitive factor attachment protein α (NAPA) and V-ATPase $V_0$ *a3* (TCIRG1), both suggested to play critical roles in autophagy and vesicular trafficking, were reduced. This was further validated in the CLFs of cells *in vitro* and of livers *in vivo* after PFOA exposure, which revealed an impairment at the late stage of autophagy. These findings demonstrate that PFOA blocked hepatic autophagy at the late stage of autophagosome-lysosome fusion and digestion.

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# Cancer Incidence in Ammonium Perfluorooctanoate Production Workers

BRUCE ALEXANDER[1], KATHERINE K. RALEIGH[1], GEARY W. OLSEN[2], GURUMURTHY RAMACHANDRAN[1], SANDY S. MOREY[3], TIMOTHY R. CHURCH[1], PERRY W. LOGAN[2]

Objective: To evaluate cancer risk in a cohort of ammonium perfluorooctanoate (APFO) exposed workers.

Methods: We linked a combined cohort (N=8,018) of employees from APFO and non-APFO production facilities in east-central Minnesota to Minnesota and Wisconsin cancer registries to identify selected incident cancers diagnosed from 1988-2008. Industrial hygiene data and expert evaluation were used to create a job task-based exposure matrix to estimate APFO exposure. Hazard ratios (HR) and 95% confidence intervals (CI) for time dependent cumulative APFO exposure were estimated with an extended Cox model. A priori outcomes of interest included cancers of the liver, pancreas, testes, kidney, prostate, thyroid, and breast.

Results: We identified 441 prostate, 35 kidney, 25 pancreatic, 83 bladder, 9 liver, 62 breast, 5 testicular, and 5 thyroid cancers. There was limited evidence of association between these cancers and APFO exposure. Compared to the non-exposed population, slightly elevated, but imprecise HRs were observed in the higher exposure quartiles for bladder cancer (HR=1.66, 95% CI=0.86-3.18) and pancreatic cancer (HR =1.36, 95% CI=0.59-3.11). No association was observed between APFO exposure and kidney, breast, or prostate cancer.

Conclusion: This analysis provided little evidence that occupational APFO exposure was associated with mortality or cancer outcomes.

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[3] *More Consulting, Inc. St. Paul, MN*

# Half-life and Heightened Risk Following Long-Term Exposure to Drinking Water Contaminated with Perfluoroalkyl Substances

KRISTIN ANDERSSON[1], PIA TALLVING[1], BO A.G. JÖNSSON[1], KRISTINA JAKOBSSON[1]

From early 1980s through 2013 the drinking water in parts of Ronneby kommun, a rural municipality of about 28,000 inhabitants in southern Sweden, was contaminated with very high levels of PFAS from firefighting foam. About 1/3 of the population was exposed. Blood sampling of the population showed high levels of three compounds. Perfluorooctanoic acid (PFOA) had a median level of 20 ng/ml and the highest value 100 ng/ml, perfluorooctane sulfonate (PFOS) had a median level of 300 ng/ml and the highest value 1700 ng/ml, and perfluorohexane sulfonic acid (PFHxS) had a median level of 300 ng/ml and the highest value 1800 ng/ml. In the Swedish general population, levels of these compounds fall in the range of 2-20 ng/ml. We follow one-hundred individuals donating blood samples every third month to investigate the half-life of the compounds after exposure cessation. We evaluate increased disease prevalence in the exposed population using Swedish population and healthcare registries, such as the cancer, in- and out-patient, and drug prescription registries. Through linkage to the municipality registry of water distribution based on the real-estate codes, the exposure can be estimated on a yearly basis and verified by results from blood sampling.

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# Oral Dosing of Perfluorooctanesufloante in Cynomolgus Monkeys with 1-Year Follow-up

KARA L. ANDRES[1], SUE CHANG[1], DAVID EHRESMAN[1], RIA FALVO[2], GEARY OLSEN[1], JOHN BUTENHOFF[1]

Perfluorooctanesulfonate (PFOS) is a stable perfluoroalkyl found in the general population where it is highly bound to serum albumin. To identify potential causal associations of serum PFOS with serum clinical chemistry parameters, an intermittent oral dose study was undertaken in purpose-bred cynomolgus monkeys (*Macaca fascicularis*). Young adult monkeys (N = 18/sex) were randomly assigned to one of three treatment groups: Group 1: untreated (sham-dosed); Group 2: treated; Group 3: treated. Males and females were housed separately, two from the same group to each enrichment cage with periodic checkups and daily observations for health conditions. Certified primate chow and water were given ad libitum with additional dietary enrichment and treats. Vehicle (0.5% Tween®20 and 5% ethanol in DI water) was administered by flexible intragastric catheter to all groups on study day 1. Potassium PFOS in vehicle was administered to Group 2 on study days 43, 288, and 358; and to Group 3 on study days 106. Monkeys not receiving PFOS were sham-dosed with vehicle. Blood was drawn from all monkeys for PFOS analysis, standard clinical chemistry and coagulation parameters, and thyroid-related hormones on the same day prior to delivering vehicle or PFOS dose and at one, three, and six weeks post-treatment. There were no abnormal clinical observations (e.g., body weight) noted during the study and all monkeys were released back to colony on Day 422. The highest serum PFOS achieved was approximately 175,000 and 70,000 ng/mL in Group 2 and 3 monkeys, respectively. More data will be presented.

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# Toxicology of 6:2 Fluorotelomer Alcohol Raw Material

ROBERT C. BUCK[1], WILLIAM J. FASANO[1]

The global fluorochemical industry is moving to short-chain perfluoroalkyl based products which have a move favorable toxicological and environmental profile. A key attribute of the short-chain substances is their rapid elimination in living systems. The change is driven by an industry commitment to cease manufacture of long-chain perfluoroalkyl acids (PFAAs) such as perfluorooctane sulfonate, perfluorohexane sulfonate and perfluorooctanoic acid and precursor products which may degrade to form them. These and other long-chain substances have been shown to have long elimination half lives in living systems. A comprehensive, robust mammalian toxicology database has been developed for 6:2 fluorotelomer alcohol (6:2 FTOH), a key raw material used for manufacturing short-chain fluorotelomer-based products. First tier studies included acute oral and dermal toxicity, single- and repeated-dose uptake and elimination, genotoxicity and sensitization studies. Higher tier in-vivo studies followed and included repeated-dose toxicity and toxicokinetic assessments. This poster will present the results of these studies.

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# Toxicology of Short-Chain Fluorotelomer-Based Products

ROBERT C. BUCK[1], WILLIAM J. FASANO[1]

The global fluorochemical industry is moving to short-chain perfluoroalkyl based products. The change is driven by an industry commitment to cease manufacture of long-chain perfluoroalkyl acids (PFAAs) such as perfluorooctane sulfonate, perfluorohexane sulfonate and perfluorooctanoic acid and precursor products which may degrade to form them. A comprehensive approach was undertaken to develop robust mammalian and aquatic toxicology data for short-chain 6:2 fluorotelomer-based commercial products. These products include polymers (e.g., acrylates and urethanes) and surfactant (e.g., phosphates, ethoxylates, sulfonates and betaines) products. Initial studies included physical-chemical property determinations, acute oral and dermal toxicity, genotoxicity and sensitization studies. Higher tier studies on substance classes followed and included repeated-dose toxicity assessments. This poster will describe the substances evaluated and the study results.

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# Toxicology of 6:2 Fluorotelomer Sulfonate (6:2 FTSA)

ROBERT C. BUCK[1], WILLIAM J. FASANO[1]

6:2 fluorotelomer sulfonate (6:2 FTSA) is a fluorinated surfactant that has been reported in the environment. It may originate from its direct use or from degradation of precursor substances. The acute aquatic toxicity to fish, invertebrates and algae have been determined. In a 90-day early life-stage rainbow trout study, the NOEC was 2.62 mg/L based on mean, measured concentrations and first day of hatching. The LOEC (lowest observed effect concentration) and MATC (maximum acceptable toxicant concentration) for the same endpoint were 4.85 and 3.56 mg/L, respectively. A guideline study (OECD TG 305) that included the addition of a dietary exposure conducted under GLP was conducted to evaluate the bioconcentration and bioaccumulation potential of 6:2 FTSA. Exposure conditions included a dilution water control, 1 ug/L and 10 ug/L aqueous exposures, and a 10 ug/kg dietary exposure with a 56 day uptake phase followed by a 28 day depuration phase. Tissue residues of the test substance in whole fish were evaluated at multiple time points during both study phases. The test results indicated that 6:2 FTSA is not bioaccumulative in aquatic ecosystems according to regulatory criteria. Similarly, the acute oral, dermal and inhalation toxicity, genotoxicity and repeated dose toxicity in rats have been studied. This poster will present the results of these studies.

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# Determination of the Toxicological Profile of a New Polymerization Processing Aid

L. WILLIAM BUXTON[1], S. RANDY FRAME[2], ROBERT A. HOKE[2]

Ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)-propanoate has been developed as a polymerization processing aid to be used in the synthesis of fluoropolymers. The kinetic behavior of the test substance was shown to be rapidly and extensively absorbed following oral and intravenous exposure in multiple species, not metabolized, and eliminated completely and rapidly. In a chronic toxicity and carcinogenicity study in rats, liver and kidney changes and the PPARα agonist tumor triad (liver, pancreas, testes) were observed at the highest dose level tested. The no-observed-adverse-effect-level (NOAEL) in this study lies between 1 and 50 mg/kg for males and between 50 and 500 mg/kg for females. In both aquatic and avian studies, the substance has low bioaccumulation potential. The relatively high dose necessary to elicit test substance-related effects, combined with the rapid elimination, makes this compound appropriate for use as a polymerization processing aid.

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# Effects of Dietary PFOA on Serum Cholesterol In ApoE*3.Leiden Mice

SUE CHANG[1], GEARY W. OLSEN[1]

The study reported herein investigated the effects of PFOA on cholesterol and triglyceride in male ApoE*3.Leiden transgenic mice, a mouse model with a human-like lipoprotein profile. Ammonium PFOA (APFO) was incorporated into rodent diet at 0.0001% or 0.0003% and they were administered to mice (N=8/dose group) for 6 weeks. Plasma concentrations of PFOA, total cholesterol, triglyceride, and high density lipoprotein were measured prior to, after 3 and 6 weeks of dietary APFO administration. For mice receiving 0.0001% dietary APFO, mean plasma PFOA concentration reached 2,500 and 3,900 ng/mL (ppb) after 3 an 6 weeks, respectively. For mice receiving 0.0003% dietary APFO, mean plasma PFOA concentration reached 9,110 and 12,860 ng/mL (ppb) after 3 an 6 weeks, respectively. In both groups, treatment of male ApoE*3.Leiden mice with PFOA resulted in significant reduction in plasma cholesterol and triglycerides.

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# Pharmacodynamic Modeling of PFOA Exposure Based on Data from a Phase I Chemotherapy Trial

TIMOTHY CHURCH[1], MATTEO CONVERTINO[1], GEARY OLSEN[1]

Epidemiologic results have shown mixed and inconsistent results for human health effects of PFOA exposure. Some studies have found lipid metabolism effects. To address such issues, we analyzed a phase I dose-escalation trial that administered a range of weekly PFOA doses to 50 solid-tumor cancer patients who had failed standard therapy. Weekly doses ranged from 50 mg to 1200 mg and were administered weekly doses. Clinical chemistries and PFOA concentrations were measured pre-dose and 2, 3, 4, 24, 48, and 72 hours after each administration. The time-dependent relationships between chemistries (including total cholesterol, low- and high-density lipoproteins, insulin, glucose, triiodothyronine, and thyroxine) were examined graphically and distributions of response were estimated using smoothing splines. Preliminary results indicate that increasing PFOA, especially at higher levels, leads to modest decreases in lipids and modest increases in thyroid hormones. These results suggest that even high levels of exposure are likely to have only small effects on these aspects of metabolism and that reported effects at the many times lower exposures seen in the general population are unlikely to be due to PFOA exposure.

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# Development of Historic Similar PFOS-Related Exposure Teams at the 3M Decatur Plant

DAVID COURINGTON[1], PERRY LOGAN[1], SANDY MOREY[1], STEPHANIE BATTISTA[1], KARA ANDRES[1], GEARY OLSEN[1]

The 3M Decatur (Alabama) plant began manufacturing PFOS related materials in the early 1960s and ended shortly after the company's phase-out announcement in 2000. We are currently updating the 3M Decatur cohort mortality study with an advanced job department exposure matrix, utilizing extensive production and equipment knowledge, led by a (now retired) production manager with 38 years' workplace experience. To assess exposure rather than rely on job title, an alternative method was used to develop "teams" based on Similar Exposure Groups (SEGs). The SEGs were defined by production area, equipment used, exposure controls, product mix, production volume, and equipment changes. Approximately 70 teams were identified depending on the SEG and associated timeline. For each time-dependent team, an estimated daily time weighted average was calculated for PFOS, POSF, and 5 other PFOS-related perfluorochemicals based on historic personal and environmental monitoring data, the amount of time spent in tasks related to production, and professional judgment. A key was to identify individuals who were in each team and then record the team identifying number into the individuals' computerized work history records to be ultimately used in the epidemiologic cohort mortality analyses.

[1] *3M Company*



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# Environmental Monitoring, Site Conceptual Model Development and Exposure Assessment for PFOA at a Fluoropolymer Manufacturing Facility

ANDREW S. HARTTEN[1], KATHERINE L. DAVIS[2]

Two phases of environmental monitoring and exposure analysis (EA) for perfluorooctanoic acid (PFOA) were conducted at a fluoropolymer manufacturing facility. Environmental media sampled initially included air, surface water, soil, groundwater, fish and untreated drinking water. Other media such as plants, beef, milk, poultry and eggs were modeled. A site conceptual model describing transport pathways from the sources to environmental media was developed. The second EA phase took place after abatement technologies were installed at the facility and treatment was installed at the drinking water sources. In this second phase, many of the modeled environmental media and treated drinking water sources were sampled. The results from the second EA phase show that total PFOA intakes substantially decreased on an absolute basis, while relative contributions of some pathways have increased compared to the first EA phase. This shift is due to the relatively larger decrease in PFOA in treated drinking water compared to the changes in PFOA concentrations in other environmental media. Overall, total PFOA intakes calculated for the most conservative scenario in the second EA phase are approximately 15- to 5-fold lower compared to the first EA phase.

[1] *Chemours Corporate Remediation Group*
[2] *AECOM*



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# Perfluoroalkyl Acid Concentrations and WHO Incidence Time Series Data for Diphtheria and Tetanus: A Descriptive Analysis of Western Europe, North America, and China, 1980 – 2013

RYAN KRISKO[1], SUE CHANG[1], GEARY W. OLSKEN[1]

Grandjean et al. reported perfluoroalkyl acid (PFAA) serum concentrations in children of the Faroe Islands were negatively correlated with their antibody titers for diphtheria and tetanus. Specifically, a 2-fold increase in PFOS and PFOA concentrations at age 5 years were associated with odds ratios of 4.2 (95% CI 1.5-11.4) and 2.4 (95% CI 0.9-6.4) for falling below a clinically protective level (0.1 IU/mL) for diphtheria and tetanus antibodies at age 7 years, respectfully. Grandjean et al. suggested that, if these associations were causal, then exposure to PFAAs may increase a child's risk for not being protected, despite a full schedule of vaccinations. To examine their hypothesis, the World Health Organization (WHO) incidence time series data were examined for diphtheria and tetanus (1980-2013) in 25 developed countries with high percentages of the population immunized with DTaP. Several countries have reported declining trends of PFOS since the early 2000s. For most countries the highest number of annual cases occurred in the early 1980s when lower percentages were vaccinated. The few reported cases reported suggests these populations are protected via immunization.

[1] *3M Company*



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# Human Nail and Hair Analysis as Bioindicator of Exposure to Perfluoroalkyl Compounds

WEI LIU[1]

Extensive human exposure to perfluoroalkyl compounds (PFAAs) together with their persistence and various toxicities have arisen public, scientific, and governmental concern. A noninvasive method would improve exposure assessment for large population, especially the children susceptible to persistent organic compounds. The aim of the study was to assess the use of PFAAs measurements in human nail and hair as bioindicator of exposure to PFAAs. Significant correlations were observed between PFAAs concentrations in human nails, hair, and serum. Moreover, significant positive correlations as well as similar PFAA profiles were observed between hair, serum, liver and other tissues in rats. Besides, hair PFAAs were negatively correlated with the urinary excretion rate. Nail PFAAs concentrations in subjects from different cities in China suggested the relatively high accumulation of PFAAs with long carbon chain. The nail PFAAs concentrations exhibited some correlation with the geographical distribution of fluorine chemical production and usage. However, PFAAs were unexpectedly detected in human nail samples collected from the underdeveloped area.

[1] *Dalian University of Technology*



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# Effects of Developmental Exposure to PFOS on the Cognitive Ability and the Synaptic Mechanisms

WEI LIU[1]

The present study aims to explore the effects of perfluorooctanesulfonate (PFOS) on cognitive function in developing rats and the underlying mechanism associated with synaptic plasticity. A cross-fostering model was employed to expose Wistar rats offspring on prenatal and/or postnatal days. Results of the Morris water maze revealed that PFOS exposure reduced the spatial learning and memory abilities of the offspring, particularly of those with prenatal exposure. The internal exposure measurement indicated a substantial PFOS accumulation in the hippocampus. On postnatal day 1, the hippocampus PFOS concentration was even higher than the serum levels in the newborn rats. Then the electrophysiological activity was tested and the results showed that PFOS and alternatives inhibited long term potentiation (LTP) in a dose-dependent manner, without significant effects on the normal synaptic transmission. The expression pattern of the synaptic plasticity-related genes and proteins found that protein levels of growth-associated protein-43 (GAP-43), neural cell adhesion molecule 1 (NCAM1), nerve growth factor (NGF), and brain-derived neurotrophic factor (BDNF) decreased. In contrast, significant increase at the mRNA level was observed, possibly due to the post-transcriptional mechanism. Results of both behavioral effects and molecular endpoints suggested the relatively higher risk of prenatal PFOS exposure. The decline of spatial learning and memory abilities induced by developmental PFOS exposure was closely related to synaptic plasticity.

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# Perfluoroalkyl Acids Biomonitoring in Minnesota Communities with Past Drinking Water Exposures

CHRISTINA ROSEBUSH[1], JESSICA NELSON[2], CARIN HUSET[2], PAUL SWEDENBORG[3], JEAN JOHNSON[2], ADRIENNE LANDSTEINER[2]

Background: The Minnesota Department of Health has conducted longitudinal biomonitoring to measure perfluoroalkyl acids (PFAAs) in residents of Washington County, Minnesota. In 2004, state agencies discovered PFAA contamination in area groundwater and private drinking water wells. In response, public health interventions were initiated including construction of a granular activated carbon treatment facility. The purpose of the biomonitoring projects is to check effectiveness of the interventions at reducing drinking water exposures to PFAAs in Washington County communities.

Methods: Biomonitoring projects conducted in 2008 (n=196) and 2010 (n=164) measured PFAAs serum concentrations in a group of residents with known drinking water exposures prior to the interventions. A 2014/15 project will obtain follow-up data on this cohort. The MDH Pubic Health Laboratory analyzed serum samples for up to eight PFAAs using liquid chromatography tandem mass spectrometry (LC/MS/MS).

Results and Conclusions: Serum concentrations of the three most frequently detected PFAAs (PFOS, PFOA, and PFHxS) declined by 13-26% between 2008 and 2010. Because these declines are similar to those seen in other exposed populations, results indicate that interventions to reduce drinking water exposures to PFAAs were effective. The 2014/15 project will check whether serum concentrations have continued to decline as expected consistent with published human half-lives.

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# Determining the Intrinsic Elimination Half-Life of PFOA from Blood

MARK H. RUSSELL[1], ROBERT L. WATERLAND[2]

Determination of the clearance rate of xenobiotic chemicals from human blood is a critical component of toxicokinetic exposure assessment. Analysis of longitudinal biomonitoring data without consideration of ongoing exposure results in calculation of apparent elimination half-life values that are longer than the inherent or intrinsic value. Confusion between intrinsic and apparent half-life values can lead to misinterpretation of biomonitoring data and can result in exaggerated predictions is subsequent modeling efforts. This poster summarizes the published human biomonitoring data of perfluorooctanoic acid (PFOA) and provides examples of low, medium and high bias in determination of the intrinsic elimination half-life of this substance. Once the intrinsic elimination half-life is known, declining longitudinal biomonitoring data can be used to estimate the extent of exposure reduction. Based on analysis of the available data, the intrinsic elimination half-life of PFOA in humans is 2.4 years and the declining concentration of PFOA in blood of the general USA adult population corresponds to an exposure reduction of 20-30% over the period 1999-2008.

[1] *The Chemours Company LLC, USA*
[2] *E. I. du Pont de Nemours and Company, Inc., USA*



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# Can the Association Between Serum Perfluoroalkyl Substances and Delayed Menarche be Explained on the Basis of Pharmacokinetics?

GINA SONG[1], HUALI WU[1], MIYOUNG YOON[1], MARC-ANDRÉ VERNER[2], JIANPING XUE[3], MAN LUO[1], MELVIN E. ANDERSEN[1], MATTHEW P. LONGNECKER[4], HARVEY J. CLEWELL III[1]

An association between two serum perfluoroalkyl substances (PFASs) and delayed age at menarche was reported in an epidemiologic study. Because PFASs have half-lives of years, growth dilution and the development of a new route of excretion could confound this association. This study aimed to estimate the influence of the correlation of growth and maturation with PFAS body burden on the association between PFASs and delayed menarche. A Monte-Carlo physiologically-based pharmacokinetic model of PFAS was developed to simulate plasma PFAS levels in female population aged 2 to 20 years old. Realistic distributions of physiological parameters as well as timing of growth spurts and menarche were incorporated in the model. The prevalence of menarche, distributions of age-dependent physiological parameters, and quartiles of serum PFAS concentrations in the simulated subjects were comparable to those reported in the epidemiologic study. The delay of menarche in days per natural log increase in PFAS concentrations in the simulated subjects were about one third as large as the observed values. Our findings suggest that the reported association between PFASs and age at menarche appears to be partly explained by PK rather than a toxic effect of these substances.

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# Uptake, Elimination and Toxicokinetic Modeling of $^{13}$C4-8:2 diPAPs Given with Food to Twelve Males

XENIA TRIER[1], JORGE NUMATA-JIMENEZ[2]

In a human intervention study, twelve healthy Danish men were given $^{13}$C4-8:2 diPAPs (a chemical used in food-contact materials) together with their food, and their serum levels of $^{13}$C4-8:2 diPAPs and its intermediate metabolite $^{13}$C2-8:2 monoPAPs and expected end-metabolites (PFOA and $^{13}$C-PFNA) were measured over 28 days, while other $^{13}$C labelled intermediate metabolites were subsequently extracted. The given dose was below the EFSA TDI-value over a two week period, during which volunteers were given food and advice to minimize their background exposure to per- and polyfluorinated alkyl substances (PFASs). An in-house developed method had LODs of typically 0.03 ng/mL in 350 µL serum (0.02-0.56 ng/mL) by online-SPE-UHPLC-ESI-HRMS. Before dosing, levels of 29 PFASs (PFCA, PFSA, FOSA/alkylated FOSE/ FOSAA/ mono- and diPAPs, FTS) in the volunteers blood were measured and found that PFOS>PFOA> PFNA>PFHxS. The uptake was minimum 0.5-3.7%, given that we most likely did not measure the Cmax. Formation of PFOA and $^{13}$C-PFNA was observed. This shows that diPAPs is uptaken from food and is a precursor of perfluoroaklyl acids (PFAAs) in humans. The elimination rate of diPAPs displayed unusual non-linear kinetics and a power-law type relation, being a signature of two competing saturable mechanisms, including saturable transport into another compartment releasing diPAPs from the blood. Implications are that there might be sinks of PFASs in compartments other than the blood, and that the half-life depends on the concentration in the bloodstream and distribution compartment. Half-lives of PFASs at high blood concentration (e.g. production workers) might therefore not be the same as at lower concentrations (general population).

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ED_002330_00143654-00162

# Effects of PFOA and PFOS on Cholesterol Efflux and Gene Expression in THP-1, Huh-7, and Caco-2 Cells

JACK VANDEN HEUVEL[1], JOSEPHINE A. GARBAN[1], DANIEL B. HANNON[1], KOJI TOYOKAWA[1]

Some epidemiological studies suggest that perfluorooctanoic acid (PFOA) and perfluorooctane sulphonic acid (PFOS) exposure is associated with increased cholesterol levels, although this is inconsistent with studies performed with laboratory animals. Reverse cholesterol transport (RCT) is a coordinated process involving multiple tissues that is involved in maintaining cholesterol homeostasis. Previous studies show that cholesterol efflux from macrophage-derived foam cells (MDFC), an important step in RCT, is increased by treatment with PFOA and PFOS. The purpose of the present studies was to examine the effects of PFOA and PFOS on cholesterol flux by examining its role on cholesterol transport in MDFC (THP-1), liver (Huh-7) and intestinal (Caco-2) model systems. Specifically, following treatment with various doses of these perflourinated compounds, cholesterol uptake and efflux as well as expression of key lipid metabolism and transport genes were determined in THP-1, Huh-7 and Caco-2 cells. By understanding the effects of PFOA and PFOS on these in vitro model systems, we will be better able to address if there is indeed a mechanistic link between exposure to these compounds and cholesterol concentrations.

[1] *Penn State University, University Park, PA and INDIGO Biosciences, Inc., State College, PA.*



ED_002330_00143654-00163

# The Association Between Prenatal Exposure to Perfluoroalkyl Substances (PFAS) and Reduced Birth Weight: Is Glomerular Filtration Rate the Underlying Cause?

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Prenatal exposure to PFAS has been associated with lower birth weight in epidemiologic studies. However, glomerular filtration rate (GFR) during pregnancy could confound the association because GFR is associated with PFAS excretion and birth weight. An existing physiologically-based pharmacokinetic (PBPK) model of human pregnancy was modified to reflect the association of birth weight with GFR and simulate PFAS levels in maternal and cord blood. The Monte-Carlo simulations estimated reductions of 2.61 g and 6.23 g in birth weight for each 1 ng/ml increase in cord PFOS and PFOA, respectively. Each 1 ng/ml increase in simulated maternal blood PFOS and PFOA levels at delivery was associated with reductions of 1.84 g and 6.99 g in birth weight. A meta-analysis of epidemiologic studies suggested each 1 ng/ml increase in prenatal PFOS and PFOA levels is associated with 5.00 g and 14.72 g reductions in birth weight. Our results revealed that a substantial portion of the reported association between prenatal PFAS and birth weight might be attributable to GFR. This study shows that PBPK models can be used to assess how much of an epidemiologic association can be explained on the basis of pharmacokinetics.

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# Perfluorooctanoic Acid Exposure for 28 Days Affects Glucose Homeostasis in Mice

HONGXIA ZHANG[1]

Perfluoroalkyl acids (PFAAs) are widely used in a number of applications due to their unique physical and chemical characteristics. Due to the increasing prevalence of metabolic syndromes such as obesity, dyslipidemia, and insulin resistance, concern has risen about the roles environmental pollutants may play in this trend. Earlier epidemiologic studies have shown a potential association between perfluorooctanoic acid (PFOA) and glucose metabolism, but how PFOA influences glucose homeostasis still unknown. In this study, male mice were exposed to 0, 0.08, 0.31, 1.25, 5, and 20 mg/kg/day of PFOA for 28 days. We analyzed the modulation of PI3K-AKT pathway in livers of mice after exposure, and compared with normal mice, PFOA exposure induced AKT activation along with decreased expression of the PTEN protein. Tolerance tests implied PFOA exposure increases insulin sensitivity in mice; and higher levels of phosphorylated AKT in livers and muscles from PFOA exposed mice after insulin injection further supported this hypothesis. Biochemical analysis revealed PFOA exposure reduced hepatic glycogen synthesis and this may be caused by gluconeogenesis impairment. After serum proteomic analysis using iTRAQ labeling combined with two-dimensional liquid chromatography and tandem mass spectrometry (2DLC-MS/MS), several circulating proteins levels were found to be altered after PFOA exposure, including proteins that have been reported to be potentially related to diabetes or liver diseases. Our results suggest that PFOA affects glucose metabolism and induces insulin hypersensitivity in mice.

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# Poster Abstracts:

# Risk Assessment and Policy

# What is the Effect of Phasing Out Long-Chain Per- and Polyfluoroalkyl Substances on the Concentrations of Perfluoroalkyl Acids and Their Precursors in the Environment?

JANA H. JOHANSSON[1], MAGNUS LAND[2], CYNTHIA A. DE WIT[1], IAN T. COUSINS[1], DORTE HERZKE[3], JONATHAN W MARTIN[4]

During the last 15 years the production and use of some per- and polyfluoroalkyl substances (PFASs) has been phased-out in some parts of the world. A number of monitoring studies, recording the developments during and after the phase-outs, have been published. However, a complete picture of what effect these actions have had on PFAS concentrations in the environment has not been put forward. We are currently undertaking a systematic review in order to determine whether the concentrations of these substances are changing in any particular direction with time, and whether the phase-outs have had any effects on the trends. A published protocol is followed to identify, appraise, select and synthesize all evidence relevant to the research question. Searches for primary research studies reporting on temporal variations of PFAS concentrations in the environment have been performed in the scientific literature as well as in other reports. Relevant samples include both abiotic and biological samples including humans. No particular time, document type, language or geographical constraints are applied. Relevant articles are critically appraised by four authors. Quality assessment is focused on selection bias, dating of samples, sample integrity and analytical procedures. Data synthesis will be based on statistical analysis of temporal concentration trends.

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# The Chinese Emission Inventory of HCFC-22 and HFC-410A from Residential Air-Conditioner Industry and Their Future Projection

ZIYUAN WANG[1]

China is the world's largest country of residential air-conditioner (RAC) production and consumption, which accounts 75% of global production. Now with the implementation of Montreal Protocol, China has gradually turned HCFC-22 into HFC-410A as RAC refrigerant. This paper applied bottom-up method to comprise a historic emission inventory of HCFC-22 and HFC-410A during 1995 to 2014, and make a projection till 2050. In the past 20 years, the HCFC-22 emissions from RAC industry in China increased from 0.9 kiloton/yr (1.5 $CO_2$-eq megaton/yr) in 1995 to 54.4 kiloton/yr (96.9 $CO_2$-eq megaton/yr) in 2014, with an accelerated growth rate. The consumption of HFC-410A started from 2006, and its emission increased to 11.3 kiloton/yr (23.5 $CO_2$-eq megaton/yr) in 2014. For the future projection, it's predicted that HFC-410A would replace HCFC-22 in 2022, and its accumulative emission would reach 5.4 megaton (11 $CO_2$-eq gigaton) until 2050 under Montreal Protocol Scenario (MPS). Under the HFC Regulation Scenario (HRS), HFC-410A would be replaced by HC-290 since 2024 gradually. This can bring an accumulative emission reduction of HFC-410A nearly 1.8 megaton (about 3.7 $CO_2$-eq gigaton) until 2050 compared to MPS. This study reviewed RAC refrigerants emissions and predicted for their future phase-out.

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# Forthcoming Increase of Total PFAS Emissions in China

LI LI[1], JIANGUO LIU[1], XUEWEN HAO[1], JIE WANG[1], JIANXIN HU[1]

This study provides an early warning on a forthcoming increase of total per- and polyfluoroalkyl substance (PFAS) emissions in China, with emphasis on the increase as a result of increasing uses of fluorinated alternatives to traditional long-chain species. First, we developed an inventory of major PFASs in use in China. The usage data were assembled from our comprehensive industry survey and literature review; gaps between top-down and bottom-up estimates and uncertainties therein were treated using a linear interval programming. Next, using a dynamic substance flow model coupled with a scenario analysis, we characterized in-use stocks and emissions of the major PFASs in China from 1995 to 2030. With the phase-out of long-chain PFASs and the switch towards their short-chain and other alternatives, there will come discontinued increases in emissions of perfluorooctane sulfonates (PFOS) and perfluorooctanoates (PFOA), but obvious rises in emissions of perfluorobutane sulfonates (PFBS), perfluorohexanoates (PFHxA), perfluorohexane sulfonates (PFHxS) and perfluoropolyethers (PFPEs, e.g., F-53B). In the future, environmental load of total PFASs is anticipated to increase due to: (i) the flow of PFASs from the in-use stock to waste in the wake of expiration of lifetime of PFAS-containing consumer products, and (ii) the ongoing shift from long-chain PFASs to their short-chain alternatives which warrants a heavier use of the short-chain compounds to compensate for their less effective performance. The increase of total PFAS emissions implies an increasing exposure to PFASs, and the associated environmental risks are needed to be evaluated with caution.

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# Poly- and Perfluoroalkyl Substances and the Role of Consumer Education and Involvement in Driving Market Change

DAVID ANDREWS[1]

The phase-out and transition to alternative fluorinated substances has primarily been driven by voluntary manufacturer actions in agreement and in consultation with EPA. The limited authority of the EPA to regulate and restrict the usage of chemicals under the Toxic Substances Control Act section 6, which provides EPA the authority to take action on chemicals that present an unreasonable risk, has forced the EPA to rely on voluntary phase-outs and significant new use rules to restrict future uses. Here we examine the transition to the current generation of fluorinated substances and their alternatives in consumer products. While reform of the TSCA remains a possibility, it may not necessarily provide an avenue to prompt action on chemicals of concern. Consumer and retailer driven changes that manifest through company initiatives such as the Zero Discharge of Hazardous Components is driving market change without regulations. Will consumer and retailer pressure effectively regulate the marketplace in the absence of strong federal regulations? What role can scientists play in providing consumer and public education in a fluid marketplace?

[1] *Environmental Working Group*



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# Science Informing Policy: The Madrid Statement on Poly- and Perfluoroalkyl Substances (PFASs)

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Scientific consensus statements and shared research results on persistent organic pollutants (POPs) and other harmful chemicals can inform policy and purchasing decisions to reduce the use of such substances in everyday products, and decrease the incidence of cancers and chronic health problems associated with chemical exposures. The Madrid Statement on Poly- and Perfluoroalkyl Substances (PFASs) documents the scientific consensus about the extreme persistence, bioaccumulation, and potential toxicity of the class of PFASs used in manufacturing and in consumer products such as cosmetics, food contact paper, carpeting, and water and stain repellant clothing. This consensus statement provides a road map for scientists, governments, product manufacturers, purchasing organizations, and consumers to cooperate in limiting the production and use of PFASs and in developing safer alternatives. By encouraging retailers, manufacturers and government decision-makers to address all PFASs as a class, the Madrid Statement has the potential to minimize the risk of regrettable substitutions and drive the development of safe and healthy green chemistry solutions. Due to concerns about the hazardous properties of PFASs, 206 scientists from 38 countries have signed the Madrid Statement to date.

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# Societal Benefits of FluoroTechnology

MIGUEL CARDONA[1], JESSICA BOWMAN[1], EVAN LAGANIS[2], STEVE KORZENIOWSKI[3]

FluoroTechnology provides important societal benefits for consumers and industry by enabling the safe and reliable function of numerous products and applications we rely on every day. Fluorine chemistries have unique properties and attributes that make them substantially different from other chemistries. The stability of the carbon-fluorine bond makes FluoroTechnology a powerful tool for providing strength, resilience, and durability to a variety of products for the manufacturing and consumer industries. FluoroTechnology provides a wide-range of societal benefits, including improved safety, reliability, and fuel-efficiency in applications like cars and airplanes, buildings, and electronics. Tubing, piping, and fuel-delivery systems, used in the manufacturing of pharmaceuticals and semiconductors, as well as in automobiles, industrial machinery, and commercial, space, and military aircraft are made with FluoroTechnology. FluoroTechnology also makes important contributions to consumer goods and even has a role in first response and emergency services. Products that rely on FluoroTechnology are beneficial to a wide range of industries that are major job creators. Globally, the FluoroTechnology industry was a $19.7 billion business in 2013. More than $1.2 trillion of global manufacturing output included FluoroTechnology in either the end product itself, or in its processing, supporting more than 625,000 jobs in the U.S. and Western Europe.

[1] *FluoroCouncil*
[2] *Asahi Glass Co., Ltd.*
[3] *The Chemours Company, LLC*



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# Comparison of Avian PFOS Exposures in Areas Affected by Aqueous Film Forming Foam Releases

JASON CONDER[1], DONGXU ZHOU[1]

Detectable levels of perfluorooctane sulfonate (PFOS) are present in environmental media at many sites as a result of Aqueous Film Forming Foam (AFFF) releases. Birds may have relatively high exposure potential due to consumption of fish, invertebrates, and sediment in aquatic habitats affected by AFFF releases. We evaluated avian PFOS exposures using measurements of PFOS from several different AFFF sites. Exposure modeling was conducted for a benthivorous species (lesser scaup, *Aythya affinis*), a piscivorous species (osprey, *Pandion haliaetus*), and a species with a mixed diet (great blue heron, *Ardea herodias*). Predicted exposures to all species were below levels associated with reproductive and lethal effects. In most cases, PFOS exposures to osprey were a factor of 1 to 2 higher than that of the other species. At one site, predicted exposure to lesser scaup was a factor of 3 to 4 times higher due to elevated concentrations of PFOS in sediment and subsequent bioaccumulation of PFOS in benthic invertebrates, the primary diet item of lesser scaup. Because of the variety of environmental compartments containing PFOS at sites affected by AFFF releases, site-specific ecological risk assessments should include multiple representative species with different dietary habits.

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# Decision Process for Assessing Potential Site Impacts from Per- and Poly-fluorinated Alkyl Substances

BILL DIGUISEPPI[1]

The identification of chemicals of emerging concern (CECs) at established remediation sites can have a significant effect on real or perceived liabilities associated with these sites. Early characterization phases at newly identified hazardous waste sites often have little available information, necessitating a broad (e.g., 'shotgun') approach to sampling for environmental contaminants. On the other hand, established remediation programs typically have a wealth of knowledge about hazardous materials used, housekeeping practices, circumstances of release, and distribution of known site co-contaminants. Within this framework of knowledge, valuable information can be gleaned regarding the likelihood of a given CEC being present and even at what levels it might occur. Additionally, key chemical characteristics of the specific CEC, such as solubility, vapor pressure, and sorption coefficient, govern the media likely to be impacted, and therefore can help focus a given sampling effort and avoid sampling of media less likely to be impacted. The application of a well-founded approach to CEC sampling can streamline the assessment process and avoid unnecessary sampling activities. A decision process will be presented which allows a rational and well-considered approach to be followed in determining when sampling is warranted and when it is unlikely to lead to useful information. This process will be demonstrated using 1,4-dioxane and perfluorinated compounds, two CECs of particular interest at present.

[1] *CH2M HILL*



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# Perfluoroalkyl Acids (PFAAs) in Drinking Water: Risk Assessment and Management in Sweden

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PFAA ground water (GW) contamination has been discovered in Sweden. In 5 counties with more than 300,000 consumers, drinking water (DW) production has been changed due to high levels of PFAAs (>100 ng/L) in GW. In one case, municipal DW with perfluorohexane and perfluorooctane sulfonate (PFHxS and PFOS) levels >1000 ng/L has been supplied to over 5,000 consumers. In scenario calculations of PFAA intake from DW it was conservatively assumed that the 7 PFAAs (PFAA7) mainly found in Swedish GWs all are as toxic as PFOS. In calculations of PFAA7 concentrations, resulting in intakes at the PFOS tolerable daily intake (TDI, 150 ng/kg/d), 10% of TDI was allocated to DW. For 3 week old infants (contaminated water in formula) the intake at 10% of TDI was estimated to 90 ng PFAA7/L, for 4-12 year old children 170-300 ng/L and for adults 500 ng/L. With DW levels >90 ng PFAA7/L, DW producers are recommended to promptly decrease PFAA levels as much as possible. With levels >900 ng PFAA7/L, women who are planning to become pregnant, are pregnant, or are nursing, are advised not to drink or use DW for cooking. This water should not be used for infant formula preparation.

[1] *Swedish National Food Agency*



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# Research Needs to Put the "Informed" into Informed Substitution. An Example of the Assessment of a Polyfluorinated Substance New to Canada

GREG HAMMOND[1], J. PRINDIVILLE[1], J. TIGNER[1]

Certain polyfluorinated substances, such as perfluorooctane sulfonate, perfluorooctanoic acid and long chain perfluorocarboxylic acids, including their salts and precursors, have been added to the List of Toxic Substances under the Canadian Environmental Protection Act, 1999. Regulatory efforts to minimize exposure have led some companies to propose alternative substances. Where an alternative is considered new to Canada, it is subject to the New Substances Notification Regulations (NSNR). Prescribed information on the substance is submitted by the notifer, including a base set of phys/chem and toxicity data, and an assessment is conducted by Environment Canada and Health Canada. Some substitutes can be described as structural variants of those substances found to be of concern. This raises questions as to whether they possess similar characteristics related to ecological fate and effects, and the availability of relevant test information to inform an assessment. For instance, toxicity data beyond those required by the regulations, such as results from multigenerational studies and microcosm studies, would facilitate a comprehensive assessment of effects. Also, data from the monitoring of environmental media and wildlife for substances and their metabolites would inform fate, transport and bioaccumulation assessment. Such critical information contributes to discerning substances which are viable alternatives from an ecological perspective, and those which may replicate problems of previous generations of poly and perfluorinated substances. Regulators and industry should work together to better understand these alternative chemistries to build the information needed to inform the decisions on substitutes for toxic substances.

[1] *New Chemicals Evaluation Section, Science and Technology Branch, Environment Canada*



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# Leveraging Historical Monitoring and Environmental Infrastructure to Develop Tactical PFAS Monitoring Approaches

MELISSA HELTON[1], ROB SINGER[1], DONNA SHARP[1], BETHANY FLYNN[1], GARY KIHN[1]

Many military facilities have gone through extensive periods of active environmental remediation and long term monitoring. As these remediation sites matured, wells were abandoned and groundwater assessments became locally focused; no longer using the larger chemical and hydrogeological knowledge bases developed though basewide investigations. This is especially true of military facilities that were closed under BRAC and redeveloped. With the increasing awareness of per- and polyfluoroalkyl substances (PFASs), a component of Aqueous Film Forming Foams (AFFF), the Air Force is making efforts to understand where AFFF was released at former and active military facilities and conduct investigations to determine where PFASs have impacted environmental media. Though site investigators typically are drawn towards recent reports as core information sources, developing an accurate PFAS conceptual site model (CSM), requires that investigators become intimately familiar with original source documents to develop a thorough understanding of basewide hydrogeologic conditions and migration pathways, while leveraging remaining investigation and remediation infrastructure to the maximum extent practical. The poster presentation will summarize how these elements are being used to develop strategic and tactical investigation approaches that will result in reliable data, complete PFAS CSMs, accelerated project schedules, and ultimately cost savings to the client.

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# Risk Assessments under EU REACH: The 6:2 Fluoromethacrylate (6:2 FTMAC) Monomer Experience

DEBBIE R. LANDER[1]

In 2013, the monomer 6:2 fluoromethacrylate (6:2 FTMAC) was registered under REACH. At the time of submission, this substance was not classified for human health so no risk assessment was required. The toxicity testing requirements were fulfilled by a read-across to 6:2 fluorotelomer alcohol (6:2 FTOH) which is the primary degradation product of 6:2 FTMAC. 6:2 FTMAC is used as a monomer which requires a risk assessment over the entire lifecycle even if it is used in strictly controlled conditions. Risk assessment requires developing exposure scenarios for each use and estimating derived no effect levels (DNELs) for all exposure routes. Addressing the entire lifecycle includes consideration of manufacturing, polymerization, downstream uses, consumer uses and disposal. There are several consumer uses of the polymerized product and gathering all the downstream use information is an extensive effort. This poster will show how the life cycle assessment of a monomer can be limited to manufacturing and polymerization if certain requirements are met which greatly reduces the effort of generating exposure estimates and subsequent risk assessment.

[1] *Chemours Company*



ED_002330_00143654-00180

# Toxicokinetic Modeling of PFAAs in Foodstuffs of Animal Origin for Consumer Risk Assessment

JORGE NUMATA[1], JANINE KOWALCZYK[1]

We have performed transfer experiments from perfluoroalkyl acid (PFAA)-contaminated feed using fattening pigs, laying hens, dairy cows and a rumen in-vitro technique. Transfer of PFAAs from feed into 24 fattening pigs was investigated (Numata et al., 2014). Four perfluoroalkyl sulfonates (PFSAs) and three perfluoroalkyl carboxylates (PFCAs) were quantifiable in feed, plasma, edible tissues and urine. Toxicokinetic modeling using the data revealed half-lives spanning 4.1 days (PFHxA) to 2 years (PFHxS). Using the model, an app with a user-friendly interface for surveillance authorities was developed. Twelve laying hens were fed PFAA-contaminated feed. Preliminary results show egg-yolk elimination half-lives of seven PFAAs to span a compact range between 1.7 days (PFBS) and 5.2 days (PFHxS). PFAAs partitioned preferentially to egg yolk (Numata et al., 2015 in preparation). Six Holstein cows were fed PFAA-contaminated feed for 28 days. Cumulative secretion was 14% (PFOS) and 2.5% (PFHxS), while PFBS and PFOA were barely secreted (Kowalczk et al., 2013). Toxicokinetic modeling showed a milk secretion half-life of 56 days for PFOS (Asselt et al., 2013). Separately, the behavior of PFAAs in the rumen was investigated with the in-vitro simulation technique RUSITEC. The rumen might biodegrade PFOS, as shown by a statistically significant loss of 6% PFOS (Kowalczyk et al., 2015 submitted).

[1] *BfR - Federal Institute for Risk Assessment*



ED_002330_00143654-00181

# Risk Assessment of Chronic Drinking Water Exposure to Perfluorononanoic Acid (PFNA)

GLORIA POST[1], JESSIE A. GLEASON[2]

Perfluorononanoic acid (PFNA) is detected in New Jersey drinking water more frequently and at higher concentrations than elsewhere in the U.S. Available information suggests that PFNA is excreted more slowly and causes toxicity at lower doses than the closely related compound, perfluorooctanoic acid (PFOA). A draft drinking water concentration protective for chronic exposure to PFNA was developed. Review of 44 epidemiology studies found the strongest evidence for associations with PFNA for serum cholesterol and the liver enzyme ALT. Effects seen in rodent studies include developmental effects, and liver, kidney, immune system, and male reproductive system toxicity. A serum level BMDL10 of 4900 ng/mL was developed for increased liver weight in pregnant mice. Uncertainty factors were applied, based on USEPA guidance, to develop a target human serum level, analogous to a Reference Dose, of 4.9 ng/mL. A chemical-specific Relative Source Contribution factor of 0.5 was derived from NHANES data on 95th percentile exposures in the U.S. general population. Based on the previously established serum:drinking water ratio of 100:1 for PFOA and relative half-lives of PFOA and PFNA in humans and animals, a serum:drinking water ratio of 200:1 was estimated for PFNA. The resulting draft chronic drinking water concentration is 0.013 µg/L (13 ng/L).

[1] *New Jersey Department of Environmental Protection*
[2] *New Jersey Department of Health*



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# Best Environmental Practices (BEP) Guidance for the Textile Industry

KAI-VOLKER SCHUBERT[1], STEVE KORZENIOWSKI[2], SEIJI SHIN-YA[3], TAKAYUKI NAKAMURA[4], MIKE CHEEK[5]

This poster presentation provides an overview of Best Environmental Practices (BEP) for the textile industry that can be utilized by stakeholders to reduce the environmental footprint when processing fluorinated durable water repellent (DWR) products. With focus on wet processing textile mills and finishers the BEP principles are mapped in 11 steps identifying practices to minimize exposure and environmental releases. In addition, the poster provides a tool for brands and retailers to ensure goods received are finished using Best Available Technology (BAT) and BEP principles. The goal of this guide is to encourage the utilization of BEP and BAT principles, therefore minimizing waste and environmental releases of fluorinated repellent products to help achieve good business and stewardship goals.

[1] *FluoroCouncil*
[2] *The Chemours Company, LLC*
[3] *Asahi Glass Co, Ltd*
[4] *Daikin Industries, Ltd.*
[5] *Huntsman*



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# 3M Fluorinated Material Stewardship

JAY SCHULZ[1], MICHAEL FALCO[1], JASON BONK[1]

3M recognizes fluorinated materials as one of the important technologies to developing high performance and valuable products. 3Ms philosophy and approach to developing fluorochemical products includes early hazard assessment, modeling, targeted application and exposure management. This poster illustrates the influence of these approaches on product development.

[1] *3M*



ED_002330_00143654-00184

# PFASs at Former Air Force Bases: Managing and Controlling Human Exposure to Emerging Contaminants

ROB SINGER[1], MELISSA HELTON[1], DONNA SHARP[1], BETHANY FLYNN[1], GARY KIHN[1]

Since 1991, the Air Force (AF) has transferred over 79,000 acres of the property at 39 bases to communities for redevelopment with the understanding that human exposure to known environmental contaminants has been managed and controlled. With the increasing awareness of per- and polyfluorinated substances (PFASs) as a chemical class of emerging concern, and the AF's widespread use of PFOS-containing AFFF for training and emergency response, the AF must now evaluate the potential for human exposure to PFAS at many formerly transferred AF properties. AMEC is assisting the AF with a nationwide, multi-media due diligence program to inventory historical AFFF use, screen locations for potential releases, and confirm PFAS presence/absence in environmental media. This program will provide the AF with an exposure point concentration data set enabling them to understand where potential human exposures exist, proactively address validated human exposures, and react rapidly as PFAS toxicology science and the resultant regulatory framework matures. The poster presentation will summarize methods used to proactively address this issue for the AF, present case studies detailing the AF response to validated human exposures, and highlight the efforts being deployed by the AF to meet its obligation to manage and control human exposure to these contaminants at transferred properties.

[1] *Amec Foster Wheeler*



ED_002330_00143654-00185

# Poster Abstracts:

# Replacement Chemistries

# Toxicokinetics of 6:2 FTOH and its metabolites in mammals

MARK H. RUSSELL[1], ROBERT C. BUCK[1], MATTHEW C. HIMMELSTEIN[1]

The toxicokinetics of 6:2 fluorotelomer alcohol (6:2 FTOH) and its terminal metabolites (PFBA, PFHxA, PFHpA and 5:3 acid) have been calculated from laboratory studies of rats and from a biomonitoring study of humans. Qualitatively similar pathways for the metabolism of 6:2 FTOH have been observed in vitro in studies with mouse, rat and human hepatocytes. In a one-day inhalation study of 6:2 FTOH in rats, the elimination half-lives of PFBA, PFHxA, PFHpA and 5:3 acid ranged between 1.3-15.4 hours with metabolic yields up to 2.7 mol%. In repeated dose studies, the plasma or serum concentration profile of 5:3 Acid was several-fold higher than concentrations observed in a single dose study, resulting in an estimated elimination half-life of 20-30 days. In contrast, PFBA, PFHxA and PFHpA showed little or no concentration increase with repeated exposure. Elimination half-lives of PFHxA, PFHpA and 5:3 acid in humans were estimated from a study of occupationally exposed ski wax technicians with elimination half-life values of PFHxA, PFHpA and 5:3 acid were 32, 70 and 43 days, respectively.

[1] *The Chemours Company, LLC*



ED_002330_00143654-00189

# Myths and Facts about Per- and Polyfluorinated Substances

KAI SCHUBERT[1], ROBERT BUCK[1], STEPHEN KORZENIOWSKI[1], MARK RUSSELL[1], WILLIAM BUXTON[1]

Over the last fifteen years many publications have reported the occurrence of per- and polyfluorinated substances in air, water, biota, soil, sediment, wastewater treatment plant effluent, and commercial and consumer products. Speculation has often accompanied these reports on their transport (from point or nonpoint sources), bioaccumulation, and ultimate fate in the environment. To understand these phenomena, it is necessary to know which commercial products and intermediates are being produced, their composition (especially raw materials and major impurities), and modes of emissions and exposure. Often this information is not available since manufacturers are unwilling to disclose this information for proprietary reasons. In this presentation we shall discuss product composition obtained from product analyses and from manufacturers' information from both peer-reviewed publications and governmental depositories. We shall also discuss how to differentiate point sources from nonpoint sources, and the importance of knowing the relevant physical properties of these materials.

[1] *The Chemours Company, LLC, Wilmington, DE, USA*



ED_002330_00143654-00190

# Levels of PFASs in Outdoor Clothing

IKE VAN DER VEEN[1], JANA WEISS[1], PIM LEONARDS[1]

Per- and polyfluoroalkyl substances (PFASs) have important technical properties in consumer products due to their hydrophilic and lipophilic character. In textiles they are used for their oil and water repellent properties. PFASs with long perfluorinated chains have been shown to be persistent in the environment, bioaccumulative and (eco)toxic. Certain PFASs have been restricted under the Stockholm convention and are added to the candidate list under the REACH. As a result, the industry is replacing the long-chain PFASs in textiles with alternatives, like short-chain PFASs, and non-fluorinated alternatives to deliver the desired durable water and soil repellent (DWR) effect. The aim of the SUPFES (Substitution in Practice of Prioritized Fluorinated Chemicals to Eliminate Diffuse Sources) project is to search for alternatives that can replace long-chain PFASs in textile applications which are environmentally more benign alternatives. Within the SUPFES project 44 samples of different types of outdoor clothes with different types of F-chemistry used (C4, C6, C8) were analysed for the concentration of PFASs. Concentration and profiles have been compared between sample types and the link between chemistry and PFASs has been studied.

[1] *Institute of Environmental Studies (IVM) VU University*



ED_002330_00143654-00191

# From Chemistry to the Environment: A Prospective Analysis of the Research into Environmental Exposure to PFASs in the Next Decade

ZHANYUN WANG[1], IAN T. COUSINS[2], KONRAD HUNGERBUEHLER[3], MARTIN SCHERINGER[3,4]

Poly- and perfluoroalkyl substances (PFASs) are a large family of anthropogenic chemicals that have been used in various industrial and consumer applications since the 1950s. Since 2001, when multiple PFASs were detected ubiquitously in the global environment and wildlife, there has been an exponential increase in research on these substances, from physicochemical and hazardous properties, exposure and occurrence, to adverse effects. Built on these efforts by the scientific community, several PFASs have been recognized as contaminants of high concern and control actions are thus in place to reduce the exposure to them on the national, regional or global scale. However, our recent analyses of emerging and novel PFASs show that despite years of research using extensive resources, knowledge on PFASs is still limited with a focus on a small selection of PFASs. In order to accelerate research into the environmental exposure to PFASs in the next decade, here we conduct a prospective analysis based on production and use information of emerging and novel PFASs with the aim to [i] draw an overall picture and identify critical knowledge gaps and [ii] recommend guiding hypotheses (e.g., a map of industrial and domestic hot spots, etc.) for future studies.

[1] *Institute for Chemical and Bioengineering, ETH Zurich*
[2] *Department of Applied Environmental Science (ITM), Stockholm University*
[3] *Institute for Chemical and Bioengineering, ETH Zurich*
[4] *Institute of Sustainable and Environmental Chemistry, Leuphana University Lüneburg*



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# General Information

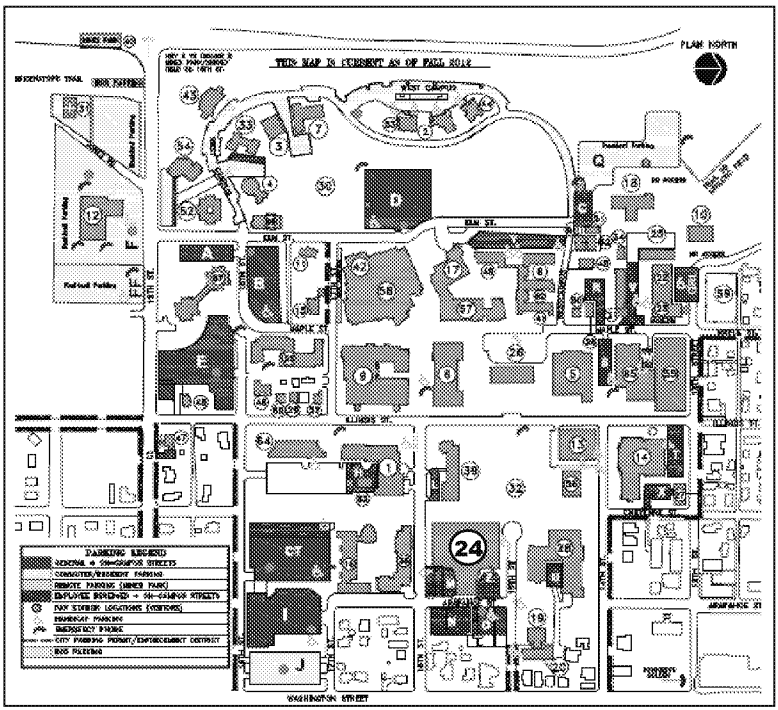
## About Colorado School of Mines

Colorado School of Mines is a public research university devoted to engineering and applied science. It has the highest admissions standards of any public university in Colorado and among the highest of any public university in the U.S.

Mines has distinguished itself by developing a curriculum and research program geared towards responsible stewardship of the earth and its resources. In addition to strong education and research programs in traditional fields of science and engineering, Mines is one of a very few institutions in the world having broad expertise in resource exploration, extraction, production and utilization. As such, Mines occupies a unique position among the world's institutions of higher education.

Since its founding in 1874, the translation of the school's mission into educational programs has been influenced by the needs of society. Those needs are now focused more clearly than ever before. The world faces a crisis in balancing resource availability with environmental protection and Mines and its programs are central to the solution.

## Parking




You must pay for parking using parking meters to get a meter receipt. You may use METER CODE **6042015** to reduce the cost of parking to $2.00 per day (full price is $4.00 per day).

The attached campus map shows blue and yellow parking lots where you may park. The Green Center is building 24 on the map. We recommend you park in blue lots CT or I, or yellow lot J. The orange dots represent the meters where you may purchase a meter receipt. Those parking in red lots, those parking without a permit, and those parking in the city permit district risk receiving a parking ticket. IF YOU PARK IN THE CITY PERMIT DISTRICT, YOU WILL BE TICKETED BY THE CITY OF GOLDEN.

Instructions for using a meter code:

Go to the meter and press any button on the right side of the screen.

1. Select the amount of time needed.
2. Press the # symbol on the keypad below the screen.
3. This displays a box where you enter the coupon (meter) code.
4. Enter the Coupon (meter) code number, then press "**D**" or the lowest button on the right side of the display screen.
5. Lift the handle and collect your meter receipt (near the bottom of the machine).
6. Display the receipt face up on the dash of your vehicle.

**CSM Guest Wireless Connection**

In order to use a wireless connection on campus, the guest wireless account will be available. When you arrive on campus, you will need to connect to the "CSMguest" network. The first time you bring up a web browser, you will be prompted to enter your email address into the Guest User Email field. Once you have been authenticated, you will be able to browse the web, check e-mail, etc. Please note this type of guest account provides Internet access only. Also, if you are using Internet Explorer, and having trouble accessing the login page, please disable SSL version 2. This can be done by going to the "Tools" menu in Internet Explorer, choosing "Internet Options" and then clicking on the "Advanced" tab. The "Use SSL 2.0" check box can be found near the bottom of the list.

**About Golden**

Golden is conveniently located just 15 miles from downtown Denver at the foot of the Rocky Mountains nestled between two mesas and under the watchful eye of Lookout Mountain. Whether you are traveling from the north, south, west or east, Golden is easily accessible as an intersection of five major highways, light rail and bus service as well as an extensive trail system for both bikes and pedestrians. With an elevation of 5,675 feet, Golden provides a mountain town experience without the drive. Golden was founded in 1859 and was the territorial capital of Colorado from 1862 until 1867. It was originally called "Golden City," not only because it was the supply center for miners of the region during the Pikes Peak Gold Rush, but also after Thomas L. Golden, one of the first prospectors to pan for gold in the area. Golden is an idyllic former gold rush town nestled between two mesas and against the foothills of the Colorado Rocky Mountains.

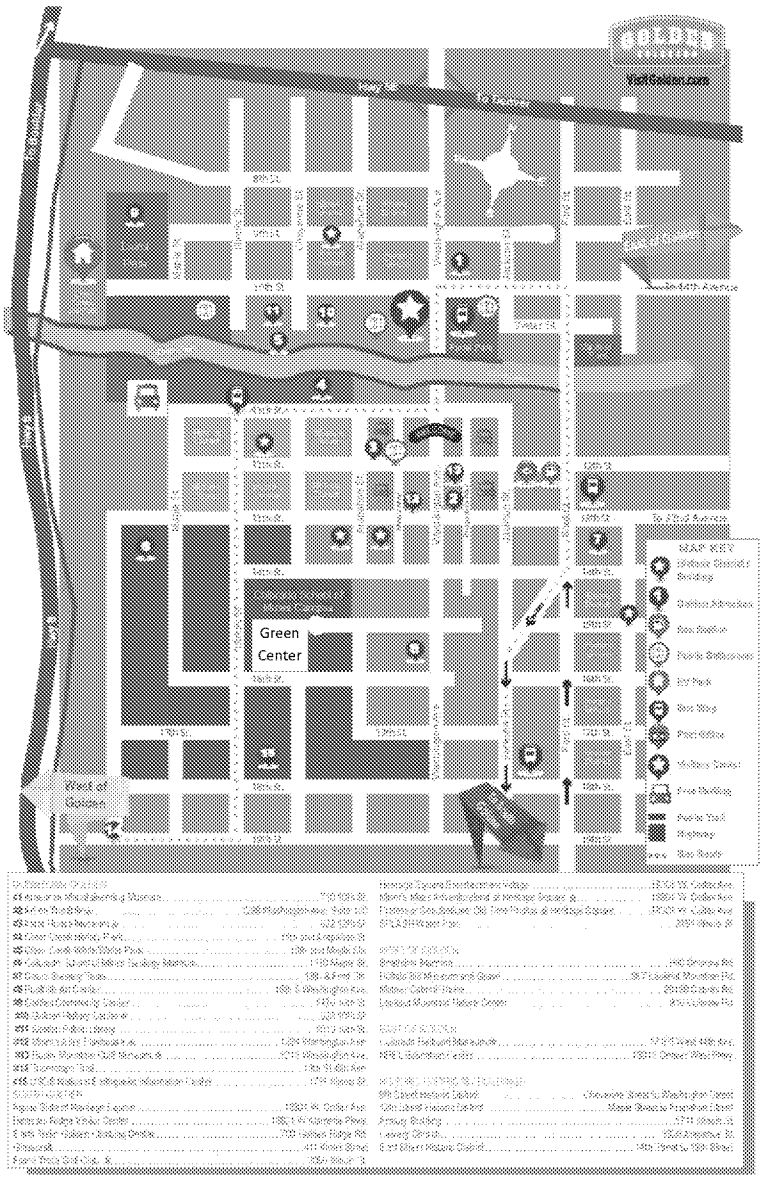
**Entertainment**

Golden offers a splendid array of culture, shopping, history and recreation. Visitors can browse for artwork, explore historic landmarks and buildings, hike or bike the trails of Golden Gate Canyon State Park and the Table Mountains, sip a cappuccino or cocktail in one of the eclectic shops lining Washington Avenue, and tour a variety of interesting museums for a look back in time to life on the Colorado frontier. Golden is proud to be home to a dozen museums. The extensive collection of museums and attractions Golden has to offer is a source of cultural pride for this modest-sized city. Highlights include:

- Three centrally located Golden History Museums, owned by the city, offer visitors the chance to learn about the life and culture of Golden pioneers and the city's distinctive past through insightful exhibits, old settlements and historic collections.
- For a great view of the entire city and beyond, visitors can head up Lookout Mountain to visit the gravesite of famed showman, Buffalo Bill Cody, as well as tour a museum honoring his life and work at the Buffalo Bill Museum and Grave.
- The world's largest single site brewery, the Coors Brewery, is a must see and offers free samples of its many brews.

*FLUOROS 2015*

# Map of Golden



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## Breweries and Microbreweries

Coors Brewery Tour

Two blocks east of the downtown shopping district is the starting point for touring the world's largest brewery. Tour vans collect visitors at the parking lot, take them on a brief drive through downtown, then over to the Brewery. The tour includes a brief history of the business, an explanation of the brewing process, a chance to see the beer being made, and a trip to the Coors hospitality room, where visitors of legal drinking age can sample Coors products for free!

**Monday-Saturday 10-4; Sunday 12-4**
**Address:** 13th and Ford Streets
**Phone:** 303-277-2337
**Website:** http://www.coors.com/agegate/

Golden City Brewery
**Address**: 920 12th Street
**Phone:** 303-279-8092
**Website:** http://www.gcbrewery.com/

Cannonball Creek Brewery
**Address**: 393 Washington Ave
**Phone:** 303-278-0111
**Website:** http://www.cannonballcreekbrewing.com/

Mountain Toad Brewing Company
**Address**: 900 Washington Ave
**Phone:** 720-638-3244
**Website:** http://www.mountaintoadbrewing.com/

Barrels and Bottles Brewery
**Address**: 600 12th Street
**Phone:** 720-328-3643
**Website:** http://www.barrelsbottles.com/

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