

YALE SYMPOSIUM

Per- and Polyfluoroalkyl Substances (PFAS): Challenges and Opportunities

DECEMBER 13, 2019

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Per- and polyfluoroalkyl substances (PFAS), a group of over 4,700 synthetic chemicals, have captured public attention in Connecticut and across the nation due to growing concerns about their impacts on public health and the environment. Since their introduction in the 1940s, PFAS have become widely used in consumer products and industrial processes because of their unique chemical composition, which makes them stable, heat-resistant, and oil- and water-repellent. However, these same properties make PFAS pervasive and persistent when released to the environment and enable some PFAS to build up in human bodies and biota. Scientific studies have so far focused on only a limited number of PFAS and have linked these compounds to human health effects ranging from developmental effects and immunotoxicity to certain forms of cancer.

In this daylong symposium hosted by the Yale School of Public Health, experts from **Yale** (*Vasilis Vasiliou, Gary Ginsberg, Zeyan Liew, Krystal Pollitt, Nicole Deziel, Shannon Whirledge, Paul Anastas, Yawei Zhang, John Fortner, Jaehong Kim*), **National Institute of Environmental Health Sciences** (*Suzanne Fenton, Alexandre Borrel, Nicole Kleinstreuer*), **University of Massachusetts Amherst** (*Youssef Oulhote*), **University of Connecticut** (*Yu Lei, Christopher Perkins*), **State and Federal Government Agencies** (*Raymond Frigon, Anna Hagstrom, Lori Mathieu, Cheryl Fields, Brian Toal, Andrea Boissevain, Sara Nason, Chelli Stanley, Nubia Zuverza-Mena*), and the **Public and Private Sectors** (*Kari Organtini, Nikolas Franceschi-Hofmann, Eric Weiner*) will review the current state of the science on these chemicals, highlighting the challenges unique to PFAS and exploring promising opportunities for addressing them.

Yale SCHOOL OF PUBLIC HEALTH
Environmental Health Sciences

- 8:00-8:30 **Coffee and Continental Breakfast**
- 8:30-8:45 **Vasilis Vasiliou**, Yale School of Public Health, “PFAS: Challenges and Opportunities”
- 8:45-9:10 **Gary Ginsberg**, Yale School of Public Health and NYS DOH: “Introduction to the World of PFAS”
- 9:10-9:30 **Zeyan Liew**, YSPH, “Epidemiological Evidence for Developmental Exposure to PFAS and Adverse health effects”
- 9:30-9:50 **Youssef Oulhote**, University of Massachusetts Amherst, “Advances in Studying PFAS-related Health Effects: Lessons from the Faroese Birth Cohorts and Local Communities in Western Massachusetts”
- 9:50-10:10 **Suzanne Fenton**, NIH/NIEHS, “Evidence for Developmental Exposure to PFAS and Adverse Health Effects in Rodent Models”
- 10:10-10:20 **Vasilis Vasiliou**, Yale School of Public Health, “Current Knowledge on PFAS and Cancer”
- 10:20-10:30 **Shannon Whirledge**, YSM and YSPH, “The Endocrine Disrupting Potential of PFAS: Past Lessons and Future Directions”
- 10:30-11:00 **Cheryl Fields** and **Brian Toal**, CT Department of Public Health, “PFAS Risk Assessment”
- 11:00-11:30 **Coffee Break**
- 11:30-11:50 **Alexandre Borrel**, NIH/NIEHS, “Exploration of PFAS chemical space using www.chemmaps.com”
- 11:50-12:10 **Raymond Frigon** and **Anna Hagstrom**, CT Department of Energy and Environmental Protection, “An Overview of Connecticut’s PFAS Action Plan”
- 12:10-12:30 **Lori Mathieu**, CT Department of Public Health, “PFAS and Public Health in Connecticut”
- 12:30-1:30 **Lunch**
- 1:30-1:50 **Eric J. Weiner** and **Andrea Boissevain**, Clean Water Task Force at Windsor Climate Action, Town of Stratford Health Director “PFAS in Your Town, State, Country and Throughout the World: Community Engagement Triggers Action”



- 1:50-2:10 **Kari Organtini**, Waters Corporation, “Determination of Legacy and Emerging Perfluoroalkyl Substances in Water Samples using LC-MS/MS”
- 2:10-2:30 **Yu Lei**, University of Connecticut, “PFAS Detection: Current Technologies and Future Trends”
- 2:30-2:50 **Krystal Pollitt**, Yale School of Public Health, “Analysis of PFAS in Dried Blood Spots: A promising exposure assessment tool for evaluating PFAS and health”
- 2:50-3:00 **Jeremy Koelmel**, YSPH, “The Plethora of Perfluoros: Screening Thousands of Compounds using LC and GC HRMS/MS and FluoroMatch Software”
- 3:00-3:10 **Nicole Deziel**, Yale School of Public Health, “Exposure to Perfluorinated Chemicals, Thyroid Hormone Disruption, and Pediatric Thyroid Cancer”
- 3:10-3:20 **Yawei Zhang**, Yale School of Public Health, “PFAS exposures in China”
- 3:20-3:30 **Nikolas Franceschi-Hofmann**, Geyser Remediation LLC, “Photocatalysis: A Promising Remediation Approach”
- 3:30-3:50 **John Fortner**, Department of Chemical and Environmental Engineering, “PFAS Remediation: Current Strategies and Future Possibilities”
- 3:50-4:00 **Sara Nason**, Connecticut Agricultural Experiment Station, “Phytoremediation of PFAS”
- 4:00-4:10 **Paul Anastas**, Yale School of Public Health, “PFAS, Green Chemistry and Alternatives to PFAS”
- 4:10-4:20 **Jim Saiers**, Yale School of Environmental Studies, “Vulnerability of Connecticut’s Private Water Wells to PFAS Contamination”
- 4:20-5:20 Round Table “Research Priorities” and the P30 from Yale (**Vasilis Vasiliou**)
- 5:20-6:20 **Wine and Cheese**



PFAS: Challenges and Opportunities

Vasilis Vasiliou, Yale School of Public Health

Introduction

Introduction to the World of PFAS

Gary Ginsberg, YSPH and NYS DOH, Director, Center for Environmental Health

The emerging contaminants known as per- and polyfluoroalkyl substances (PFAS) have received widespread use in consumer products, manufacturing and firefighting foam leading to numerous pathways of environmental contamination and human exposure. An overview of the toxicology, epidemiology and human exposure reveals health concerns stemming from contaminated water supplies, ingestion of fish and other foods, and occupational exposure with endpoints ranging from cancer, immunotoxicity, endocrine disruption, target organ (liver) toxicity and effects on development. Policy and regulatory approaches to track PFAS sources, limit PFAS releases and in particular protect drinking water supplies will be summarized. Challenges to effective regulation include the large number of PFAS compounds, their environmental transformation from precursor compounds, and their changing uses over time.

Epidemiological evidence of PFAS exposure on maternal and child health

Zeyan Liew, Department of Environmental Health Sciences, Yale School of Public Health

Human exposures to PFAS are ubiquitous globally, but studies that addressed the potential health effects of PFAS have only begun to accumulate in recent years. Animal studies suggest adverse effects resulting from developmental exposures to PFAS. In human, the developing fetus is exposed to PFAS via active or passive placenta transfer, while newborn might be exposed via breastfeeding or PFAS in the home environment. In this talk, I will present a series of studies conducted in the Danish National Birth Cohort (DNBC) that investigated the associations between PFAS exposure on multiple pregnancy complications and neurodevelopmental consequences in the offspring. The DNBC is the first cohort that showed placenta transfer of PFAS from mother to the developing fetus and the exposures affected fetal growth. Furthermore, our studies indicated a gestational-week specific interference of PFAS on maternal thyroid hormone function in early pregnancy and subsequently a sex-specific association of PFAS exposure and risk for cerebral palsy in the offspring. Our newer (unpublished) findings have also suggested prenatal PFAS exposure may increase risk for miscarriage, negatively impacted facial features of children indicative of fetal CNS development, and behavioral problems in childhood assessed at age 11 years. Overall, our research findings add to the growing literature supporting PFAS exposure could influence maternal and child health and public health strategies reducing PFAS exposures especially among the vulnerable population are needed.



Advances in studying PFAS-related health effects: lessons from the Faroese birth cohorts and local communities in Western Massachusetts

Youssef Oulhote, Department of Biostatistics and Epidemiology, School of Public Health and Health Sciences, University of Massachusetts Amherst

Per- and polyfluoroalkyl substances (PFASs) are a growing public health concern. Some longer chain PFASs bioaccumulate and many compounds persist in the environment for long time periods, and very little is known about short chain PFAS. In this talk, we will summarize the main findings pertaining to metabolic, neurodevelopmental, and immune functions from birth cohorts conducted in the Faroe Islands where populations are exposed through a consumption of seafood, especially whale. We will also present recent findings regarding transplacental transfer of short chain PFAS, microbiome disruption, and effects on thyroid hormones. Finally, we will discuss issues related to contamination from aqueous foam films in Westfield, MA and ongoing project in partnership with the local communities.

Evidence for Developmental Exposure to PFAS and Adverse Health Effects in Rodent Models

Suzanne E Fenton, Division of the National Toxicology Program, NTP Laboratory, NIEHS, RTP, NC USA

Poly- and Perfluoroalkyl Substances (PFAS) are man-made surfactants that are abundant in our environment. Due to their wide variety of structures/chemistries, they have variable half-lives, unpredictable bioaccumulation rates, and may or may not be metabolized when ingested. They also share some similarities; they cause adverse health effects in laboratory models and exposures have been associated with similar health effects in epidemiologic studies in many cases. When compared, developmental exposures result in lower effective doses and potentially different modes of action than effects in adult tissues. Perfluorooctanoic acid (PFOA) is an example PFAS for which there is substantial evidence of developmental exposure effects, and most non-cancer reference doses selected for state and federal minimal risk levels have included increased liver weight and developmental effects such as delayed ossification, accelerated male puberty, skeletal changes in adulthood, neurobehavioral effects, as well as mammary development and immune response. This presentation will highlight species concordance of health effects following PFOA exposure, gaps in knowledge for mode of action, and those tissues that may be sensitive targets for other PFAS currently being evaluated.



Current Knowledge on PFAS and Cancer

Vasilis Vasiliou, Department of Environmental Health, Yale School of Public Health

Today there are concerns for the potential cancer risk for the PFAS chemicals that stems from animal and some epidemiological studies. These indicate that PFAS play a possible role in breast, kidney, liver and testis carcinogenesis. The International Agency for Research on Cancer (IARC) classified PFOA as a possibly carcinogenic to humans (Group 2B) and no IARC evaluation is available for PFOS. This presentation will overview the link between the PFAS and cancer and recommend future studies.

The Endocrine Disrupting Potential of PFAS: Past Lessons and Future Directions

Shannon Whirlledge, Yale school of Medicine and Yale School of Public Health

PFAS (per- and poly-fluorinated alkyl substances) comprise a group of over 5,000 man-made chemicals, highly persistent in the environment and human body. PFAS are used in many consumer and household products, where they can be released into the environment. Thus, exposure to PFAS is nearly ubiquitous, and an estimated 98% of the U.S. population has detectable levels of PFAS in their serum. In addition to toxic and carcinogenic activities, PFAS have the potential to critically disrupt the endocrine system. Most notably, PFAS can compete with thyroxine (T₄) for binding to the thyroid hormone transport protein transthyretin, leading to disrupted thyroid hormone signaling. Moreover, PFAS levels have been positively associated with thyroid stimulating hormone levels and altered thyroid function. PFAS can also disrupt endocrine regulation of the hypothalamic-pituitary-gonadal axis, as demonstrated by alterations in reproductive development, reproductive hormone production, and gonadal failure. In women, serum PFOS concentrations were reported to be inversely correlated with salivary progesterone levels. A prospective birth cohort also reported an inverse correlation between serum PFOS and progesterone levels in mothers and female infants, suggesting a multi-generational effect. A case-control study found that high exposures to perfluorooctanate (PFOA), perfluorooctane sulfonate (PFOS), and perfluorohexanesulfonate (PFHxS) were negatively associated with estradiol levels and positively associated with premature ovarian insufficiency. Despite numerous studies linking PFAS levels and endocrine disrupting effects, studies determining the mechanism of action in humans are lacking; thus, it is not clear whether the effects of PFAS on the endocrine system are direct or indirect. Future studies should take a systematic approach to determining the mechanisms by which PFAS can alter endocrine physiology.



PFAS Risk Assessment

Brian Toal and Cheryl Fields, State of Connecticut Department of Public Health, Environmental Health Section

Risk assessment is a standardized process that involves multiple steps and requires the use of science-based professional judgement. After providing a general overview of the Risk Assessment process, we review the various approaches used by states and federal agencies to derive public health-protective drinking water guidelines for PFAS.

Exploration of PFAS chemical space using www.chemmaps.com

Alexandre Borrel¹ and Nicole Kleinstreuer^{1,2}, ¹NIH/NIEHS/DIR/BCBB, RTP, NC, United States; ²NIH/NIEHS/DNTP/NICEATM, RTP, NC, United States.

The first version of ChemMaps.com was developed to browse and visualize the space of >8,000 FDA-approved drugs and drug candidates from the DrugBank database, and was subsequently extended to include the full Tox21 10k chemical library and the EPA's Distributed Structure-Searchable Toxicity (DSSTox) Database (>700,000 chemicals). In addition, a Per- and Polyfluoroalkyl Substances (PFAS) map has been developed to allow navigation of all 7,866 PFAS chemicals in the EPA DSSTox DB. Users can search for specific compounds, overlay regulatory classification and labeling based on acute oral systemic toxicity data, explore and export nearest neighbor space, refine the projections based on physicochemical properties, and link out to the EPA's CompTox Dashboard (<https://comptox.epa.gov/dashboard>) for detailed information on a chemical to provide real-time chemical space visualization specific to the compound of interest. User can also now upload their own set of chemicals and visualize them on the available maps or/and define a new map from them, where all the data computed, e.g. coordinates, chemical descriptors, can now be downloaded. To improve the user experience, the search function was improved to be able to consider SMILES strings and other IDs such as the EPA's DTXSID. Different navigation options have been also developed, including computing on the fly a distance metric for two selected chemicals and a faster and more responsive environment. Specific examples of navigation and options will be exemplified in this presentation.

An Overview of the Connecticut Interagency PFAS Action Plan

Raymond Frigon¹ and Anna Hagstrom^{1,2}. ¹Connecticut Department of Energy and Environmental Protection. ²Connecticut Academy of Science and Engineering

To protect the health of Connecticut residents and the environment from the harmful effects of per- and polyfluoroalkyl substances (PFAS), Governor Ned Lamont established the Connecticut Interagency PFAS Task Force on July 8, 2019. He charged this group with producing, by November 1, 2019, an action plan laying out a comprehensive State strategy for addressing PFAS. The Task Force was led by the Connecticut Department of Public Health (DPH) and Department of Energy and Environmental Protection (DEEP) and comprised representatives of nearly twenty State agencies and entities. To



ensure broad stakeholder input, the Task Force established three subcommittees, all open to public participation, focused on human health, pollution prevention, and remediation. The joint efforts of the Task Force and its subcommittees culminated in a draft PFAS Action Plan released on October 1, 2019 for public comment. After review and revision to reflect public feedback, the Task Force submitted the finalized PFAS Action Plan to Governor Lamont. In this presentation, DEEP representatives will provide an overview of the initiatives recommended in the PFAS Action Plan to (1) minimize residents' exposure to PFAS, (2) minimize future releases of PFAS to the environment, (3) identify, assess, and clean up historical PFAS releases, and (4) enhance education, outreach, and communication on PFAS.

PFAS and Public Health in Connecticut

Mathiew Lori, CT Department of Public Health

This presentation will provide a brief background on PFAS from perspective of the CT Department of Public Health with an emphasis on public drinking water, the drinking water advisory level for the "Connecticut Five," and an overview of the recommended actions in the CT PFAS Action Plan's Human Health Strategic Focus Area.

PFAS in Your Town, State, Country and Throughout the World: Community Engagement Triggers Action

Eric J. Weiner¹ and Andrea Boissevain², ¹Clean Water Task Force at Windsor Climate Action, ²Stratford Health Department

There are unintended consequences to the chemical industry's tagline "Better Living through Chemistry". The specter of emerging contaminants in drinking water is fraught with uncertainty about risk and appropriate courses of action, creating an atmosphere of confusion, blame, anxiety and, most importantly, mistrust. For PFAS, it is especially true. The class of chemicals that provides us non-stick cookware, fabric softeners, and life-saving firefighting foam also has been associated with adverse health effects like endocrine disruption, thyroid problems and even cancer. Communities whose sources of drinking water have been contaminated with PFAS are at a loss as to what to do or who to believe, especially in the absence of federal drinking water standards. States like Connecticut and New York are left to grapple with determining what is an acceptable level, how do water systems remediate and what do you do in the interim. The solution will not happen overnight and is projected to cost billions of dollars to achieve cleanup levels. Briefly we will describe global and national PFAS incidents, and then focus on two recent incidents at Bradley Airport and the impact the use of firefighting foam had on the Farmington River. These real-life examples will highlight how important it is to engage the community whose "backyards" have been impacted. Creating bidirectional partnerships with target communities enhances their ability to understand the health risks posed by emergent water contaminants (like PFAS) and is key to effective engagement and communication. It requires knowledge of the communities'



demographics, education level, language, level of civic participation, preferred avenues of communication, etc.; it also requires intentional listening and encouraging participation in decisions that impact their lives, such as interventional strategies—all with the intent to improve public health and inform health policy.

Determination of Legacy and Emerging Perfluoroalkyl Substances in Water Samples using LC-MS/MS

Kari Organtini, Jenifer Lewis and Naren Meruva, Waters Corporation, Milford MA, USA

Perfluoroalkyl substances (PFAS) are common persistent environmental contaminants used in the production of many consumer products. They are used as surfactants and for nonstick, stain, and water resistance coatings and in firefighting foams. Global use of these compounds over decades has led to their release into the environment. PFAS are classified as persistent organic pollutants. Currently, PFOS and PFOA are included in many drinking water health advisories in the United States (e.g. 70 ppt [ng/L]). In Europe, the Water Framework Directive and Drinking Water Directive have set minimum quality standards of PFOS and PFOA, which range from the ppb to sub-ppt levels. Such regulations have driven the need for highly sensitive analytical measurements to detect PFAS. Sample preparation, such as described in the ISO 25101 method, is typically applied for enrichment of PFAS in water samples. The scope of the ISO 25101 procedure has been expanded to cover approximately 40 legacy and emerging PFAS compounds, including GenX, using a weak anion exchange SPE cartridge. The method was assessed using surface, ground, influent and effluent water. The modified method was found to be robust in all types of matrices tested, with detection limits in the low to sub ppt range, making this method suitable for testing compliance with the guidelines/limits set in both the USA and EU. Recoveries were within the prescribed range of 70 - 130 % and method repeatability was assessed with RSDs < 15%.

PFAS detection: Current Technologies and Future Trends

Yu Lei, Department of Chemical and Biomolecular Engineering, University of Connecticut

As emerging contaminants, per- and polyfluoroalkyl substances (PFASs) make up a large group of persistent anthropogenic chemicals that are persistent and not easily degradable in the environment. Recent studies in humans have shown that certain PFASs (e.g., perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS)) may negatively affect fetus development, child learning and behavior, adult fertility, hormonal balance, and liver function. Due to the long-term impact of these PFASs on human health, the lifetime exposure health advisory of PFOA and PFOS in drinking water recommended by the Environmental Protection Agency (EPA) is 70 parts per trillion (70 pg/mL or ppt), which make their detection extremely challenge. In this presentation, we will start with introduction of current standard detection methods for PFOA



and PFOS relying on chromatographic techniques coupled with mass spectrometry (e.g., GC-MS, LC-MS, and LC-MS-MS), followed by presenting a number of new approaches recently developed with potential portability and field applicability. Finally, we will discuss the challenges and future trends in the development of field-deployable PFASs sensors.

Analysis of PFAS in Dried Blood Spots: A promising exposure assessment tool for evaluating PFAS and health

Krystal Pollitt¹, Sara Nason², Elizabeth Lin¹, Jeremy Koelmel¹, Nicole Deziel¹, John Fortner³; ¹Yale School of Public Health, Department of Environmental Health Sciences; ²Connecticut Agricultural Experiment Station, Departments of Environmental Science and Analytical Chemistry, ³Yale University, Department of Chemical and Environmental Engineering

Poly- and Perfluoroalkyl Substances (PFAS) are a family of more than 4,000 highly fluorinated compounds. The carbon-fluorine bond of PFAS gives these chemicals desirable hydrophobic and oleophobic properties that have led to wide spread use in consumer products and industrial application since the 1940s. The strength of this bond also prevents appreciable degradation once released in the environment and has resulted in persistent contamination of drinking water, soil, and indoor surfaces. Despite a phase out of two compounds (PFOS and PFOA) between 2000-2002, elevated levels are still detected in a range of environmental samples as well as in blood collected from individuals across the US. PFAS exposure has been associated with tumours of the liver, pancreas, testis in animal studies. Early human occupational studies have also reported potential increased risks of prostate, bladder, and kidney cancer. The ability for PFAS to cross the placenta further highlights the utero period as an important window of vulnerability in the development of cancers at a young age. Understanding the relationship between PFAS and cancer risk in the general population requires sufficiently power epidemiology studies. Such studies would be enhanced by the development of sensitive exposure assessment techniques that could leverage archived repositories of biological samples, such as dried blood spots. We have developed an analytical method that enables detection of 24 PFAS in dried blood spots with detection limits in the ppt range. In this presentation, I will highlight application of our validated analysis technique to dried blood punches taken from California Newborn Screening dried blood samples collected between 1980 and 2019. PFOS and PFOA was detected in all samples. Quantifiable levels of other PFAS, including those measured under UCMR3 requirements in drinking water, were also detected. Overall, we have developed an analytical method to quantify PFAS in dried blood spots which support their use as a minimally invasive approach for quantifying exposure and offers promise as an exposure assessment tool in population-based studies exploring the link between PFAS and health.



The Plethora of Perfluoros: Screening Thousands of Compounds using LC and GC HRMS/MS and FluoroMatch Software

Jeremy P. Koelme¹, John A. Bowden², Mathew Paige¹, Paul Stelben¹, Sara Nason³, Elizabeth Lin¹, Vasilis Vasiliou¹, Krystal Pollitt¹, ¹Yale University, New Haven, CT 06520, USA; ²University of Florida, Gainesville, FL, 32601, USA, ³The Connecticut Agricultural Experiment Station, New Haven, CT 06504

There are a growing number of replacement per- and poly- fluorinated alkane substances (PFAS), which number in the thousands, with limited understanding of these compounds environmental and health impacts. In addition, a diverse array of legacy PFAS continue to persist in the environment. Over 5000 PFAS chemicals are compiled in the US EPA's CompTox Chemistry Dashboard ("The PFAS Master List"), and yet most analyses only cover a few to tens of PFAS species. One major bottleneck is in characterizing unknown and less common PFAS. Both gas chromatography (GC) and liquid chromatography (LC) high-resolution tandem mass spectrometry (HRMS/MS) are common approaches for untargeted PFAS analysis, and yet no software exists to mine the wealth of information provided by these techniques. Therefore we introduce software for the automated library generation and annotation of PFAS compounds. FluoroMatch consists of FluoroGenerator, a software which generates perfluorinated and polyfluorinated chemical structures given a SMILES string and the possible number of repetitions for repeating unit(s). FluoroGenerator also can be used to predict different types of fragmentation given a simple set of fragmentation rules (fixed neutral losses and fragment ions with m/z ratios that scale with the number of repeating units). Therefore FluoroGenerator provides the community a method to rapidly expand the coverage of perfluorinated species with repeating units by mass spectrometry. For a single point user-friendly solution, FluoroMatch will consist of preset libraries (over 3000 in-silico spectra). These libraries are being generated using both LC (HCD) and GC (EI and PCI) orbitrap mass spectrometers on over 150 standards across various compound classes collected from SynQuest Labs (Alachua, FL), Oakwood Chemicals (Columbia, SC), and Wellington Laboratories (Guelph, ON, Canada). The libraries are integrated with a simple to use user interface where files from multiple vendor formats can be dragged onto the software, and the software performs file conversion (utilizing MS-Convert), peak picking (utilizing MZMine 2), blank feature filtering, rule-based annotation, and combining results from negative and positive polarity. Preliminary results on automated non-targeted annotation of PFAS in AFFF contaminated soil, human blood, and leachate will be presented.



Thyroid Hormone Disrupting Chemicals and Pediatric Thyroid Cancer

Nicole C. Deziel¹, Krystal Pollitt¹, Zeyan Liew¹, Joshua L. Warren², Yawei Zhang¹, Xiaomei Ma³, ¹ Yale School of Public Health Department of Environmental Health Sciences, ² Yale School of Public Health Department of Biostatistics, ³ Yale School of Public Health Department of Chronic Disease Epidemiology

Incidence rates of pediatric thyroid cancer (ages 0-19 yo) have doubled over a recent two-decade period. Children with thyroid cancer face a lifetime of therapy and surveillance and are at greater risk for second primary malignancies. Although the rise is likely partially attributable to changes in diagnostic procedures, environmental exposures have been postulated to be an important factor. We will evaluate our hypothesis that increasing exposures to thyroid disrupting chemicals (TDCs), including perfluorinated compounds, are contributing to the increasing incidence of pediatric thyroid cancer. We are planning a case-control study to evaluate the relationship between exposure to mixtures of TDCs and pediatric thyroid cancer including: legacy environmental contaminants (polybrominated diphenyl ethers and polychlorinated biphenyls) and emerging contaminants (perfluorinated compounds). We will measure TDCs in newborn blood spots, providing a unique assessment of prenatal and early-life exposures. We will apply cutting-edge statistical techniques to evaluate the joint exposure to multiple TDCs and pediatric thyroid cancer risk. Considering the ubiquitous exposure to TDCs, the recent rapid increase in pediatric thyroid cancer incidence, and the largely unknown etiology of this carcinoma, there is an urgent need to investigate whether legacy and emerging environmental chemicals are associated with thyroid cancer risk.

Health effects of perfluoroalkyl substances in China

Lan Jin and Yawei Zhang

Department of Environmental Health Sciences, Yale School of Public Health

Perfluoroalkyl substances (PFAS) are environmentally persistent and bioaccumulative chemicals. Recent studies have linked PFAS to a wide range of adverse health outcomes. This presentation will focus on epidemiologic studies of PFAS and human health in China. While a wide variety of outcomes have been studied in relation to PFAS globally, including cardiovascular diseases, liver disease, kidney disease, pregnancy or birth outcomes, thyroid toxicity, immunotoxicity, steroid hormones, neurodevelopment, and cancer, a majority of the Chinese studies focused on birth or pregnancy-related outcomes with few evidence existing for neurodevelopment, carcinogenicity, and liver disease. The cord-serum concentrations of PFAS tend to be lower in mainland China than western countries. The increases in PFAS concentrations in cord serum or vein blood were reported to be associated with reduced birth weight, increased risk of small for gestational age, increased gestational age, elevated postpartum blood glucose in



mothers, elevated fasting insulin or insulin resistance, or increased risks of preeclampsia or hypertensive disorder. The branched PFAS tend to have stronger effects than the linear PFAS isomers, regarding to the adverse effects on blood glucose or birth weight. The relationships between PFAS and birth length were conflicting. Effect modifications by gender were reported in some studies. None of the reviewed studies used ultrasound measurements to evaluate the impact of PFAS on gestational growth. More studies are needed to fill in the gaps for some adverse outcomes, confirm the reported associations, and explore the impacts of the mixtures of multiple PFAS chemicals.

Photocatalysis: A Promising Remediation Approach

Nikolas Franceschi Hofmann, CEO Geysler Remediation LLC

Geysler Remediation is a small, early-stage tech startup focused on finding a better solution for water utilities than exist currently to remove PFAS from drinking water. We are working on creating a scalable reactor design, using photocatalysis to destroy PFAS. Our goals include eliminating liabilities to utilities, and the environment by eliminating the need to concentrate and dispose of media that concentrate PFAS by breaking them down to non-toxic substances, and to do so for less cost overall and lower impact on the consumer.

PFAS Remediation: Current Strategies and Future Possibilities

John Fortner, Chemical and Environmental Engineering, Yale University

Perfluoroalkyl and polyfluoroalkyl substances (PFASs) are emerging contaminants of concern as they are found to be wide spread and recalcitrant to traditional degradation treatment due to strong carbon-fluorine (C-F) bonds. Advances in nanoscale engineering and material science allow for unique, novel remediation approaches for both sorption/separation and ultimate destruction. In addition to a brief state-of the art overview, I will describe ongoing research within CEE at Yale regarding both strategies. In particular, I will discuss high capacity, tailored sorbent strategies, which utilize not only high surface area nanoparticles designed for targeted adsorption, but also for subsequent (magnetic) recovery. For these we precisely prepared metal oxide nanoparticles via thermal decomposition of iron oleate (Fe-oleate) and manganese oleate (Mn-oleate) with specific ratios to achieve precise particle size and composition(s) and then functionalized with a series of organic surfactants. Additionally, I will present Prof. Jaehong Kim's work on developing various single atom catalysts anchored to substrates such as silicon carbide for hydrodefluorination of PFAS in a concentrated stream (such as RO concentrate). These inexpensive materials are designed to abstract fluorine atoms from PFAS (i.e. breaking C-F bond) onto their surface and immobilizing fluorine via covalent bonding so that they are ultimately discharged for land-fill.



Assessment of PFAS Phytoremediation at the Former Loring Air Force Base

Sara L. Nason^{1,2}, Chelli Stanley³, Nubia Zuverza-Mena¹. ¹Connecticut Agricultural Experiment Station Departments of Analytical Chemistry and ²Environmental Science, ³Upland Grassroots

The use of Aqueous Film-Forming Foams (AFFFs) has caused widespread contamination with per- and polyfluoroalkyl substances (PFAS) in areas that have been used for fire-fighter training. Such is the case at the Burn House site of the former Loring Air Force Base in northern Maine, USA, where the land now belongs to the Aroostook band of the Micmac nation. Upland Grassroots, a community group, grew industrial hemp on the land during Summer 2019 in an attempt to reduce the contamination levels, and scientists at the Connecticut Agricultural Experiment Station (CAES) are assisting them with assessing the effectiveness of their efforts. At CAES, we have developed methods to evaluate levels of AFFF related PFAS in soil and hemp tissue using liquid chromatography coupled with quadrupole-orbitrap mass spectrometry. These tandem, high resolution mass spectrometry methods have the advantage that we can both screen for a wide range of compounds and develop sensitive quantification methods for a more limited number of contaminants. We quantified 24 PFAS compounds and found 15 in soil and 8 in hemp tissue. Bioaccumulation factors were consistent with findings in the literature. We are continuing to work on screening for additional compounds. This community-based science project has been beneficial to all participants, and the methods developed at CAES will be helpful in the future for conducting testing for the state of Connecticut and developing collaborations with other researchers.

Green Chemistry and Alternatives to PFAS

Paul T. Anastas, Yale School of Public Health

When reviewing the wide range of problems associated with PFAS chemicals, it is reasonable to ask, “Why does this class of chemicals exist?”. These substances are not naturally occurring so what functionality are these providing that is desirable and can it be achieved through other means? Green chemistry is the design of chemical products and process that reduce or eliminate the use and generation of hazardous chemicals. This talk reviews the various hazards that are posed by PFAS chemicals throughout their life-cycle and looks at alternatives to PFAS through the lens of green chemistry.



Vulnerability of Connecticut's Private Water Wells to PFAS Contamination

James Saiers, Yale School of Environmental Studies

PFAS has been detected in groundwaters in Greenwich, Willamantic, and in the vicinity of the Hartford and Ellington landfills. Other landfills throughout Connecticut are considered potential sources of PFAS contamination, although few of these sites have been tested for possible PFAS pollution to groundwater. An increasing number of our state's residents have expressed concern that their household drinking-water wells may be contaminated by PFAS from known or suspected sources. The vulnerability of drinking-water supplies to PFAS contamination reflects the locations of the PFAS sources (e.g., landfills) and receptors (water wells) relative to the direction of groundwater flow and a variety of physicochemical factors that govern the migration of PFAS away from its source. We can quantify this vulnerability through application of hydrologic models that simulate groundwater flow patterns and PFAS transport behavior. This knowledge of which water-supply wells are more (or less) likely to be impaired by PFAS can, in turn, be used to target interventions or to design drinking-water monitoring programs. In collaboration with CT DEEP, we propose to conduct this hydrologically based vulnerability assessment focusing on sites prioritized by DEEP. Based on the results of these assessments, we will identify households with vulnerable drinking-water supplies and collect water samples from these homes for analysis of PFAS compounds and other water-quality indicators. Our analysis will leverage newly developed laboratory techniques suitable for resolving a large suite of PFAS compounds. Findings from this work will provide sorely needed data on the frequency of occurrence of PFAS in private wells and a means for evaluating the likelihood of exposure to PFAS via the groundwater track.



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