November 16, 2020

The Martha’s Vineyard Commission and Oak Bluffs Planning Board,

I have been made aware of the Martha’s Vineyard Commission and Oak Bluffs Planning Board pending review for a synthetic turf project. Our organization has been conducting research on PFAS content in commercial and residential indoor carpet, as well as synthetic artificial turf, for the last two years. We have analyzed 100’s of residential carpet samples and dozens of synthetic artificial turf samples. This work, carried out with external contract labs and university-based scientists, includes testing carpet and synthetic turf fiber for individual PFAS chemicals, total oxidizable precursors and for total fluorine, an indicator of PFAS. My understanding is that the applicant, Martha’s Vineyard Regional High School, is objecting to the testing methods recommended by your hired third party consultant, Horsley Whitten.

The turf industry (or in your case, a third party hired to test the proposed products) should conduct elemental fluorine testing for all products. Total fluorine testing is now required for certification systems for PFAS-free firefighting foams and PFAS-free food packaging, and should be the standard for polymers like turf as well.

Of the nine synthetic turf fibers we tested last year, fluorine was detected in 100%. Fluorine levels ranged from 44 to 255 parts per million. Additional tests not detailed here on two of the samples found evidence of organic fluorine, supporting the likelihood that PFAS is present. These turf samples included both new and installed product. This sampling is limited and does not represent the entire market. However, we continue to conduct ongoing testing of samples and testing of additional samples had similar findings. And it highlights the need for companies to provide clear test results if they are claiming PFAS-free.

Total fluorine tests do not tell us exactly which PFAS chemicals are present, but based on industry literature, we believe a likely source of the detected fluorine is processing aids used in the production of synthetic turf fibers. PFAS-based processing aids are not included in commonly used test methods and thus can be missed.

For this reason, it is critical for companies to conduct testing of fibers using an appropriate method. Most manufacturer-provided test results we have reviewed used a method designed for water testing. While this method is not designed specifically for solid polymer samples, it has been widely, and appropriately used to look at PFAS in variety of matrices. However, these tests are limited due to the fact they can detect only a portion (typically 24 – 40 compounds, depending on the lab) of the hundreds of possible PFAS chemicals which may be present.

The testing method that has typically been used by companies attempting to demonstrate PFAS-free composition is EPA Method 537.1, "Determination of Selected Per- and Polyfluorinated Alkyl Substances in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry.” I see that is the method being recommended to you by Huntress Associates and Cooperstown Environmental LLC.

As your third party consultant Horsley Whitten correctly states, due to the limited number of chemicals it can detect, this US EPA method is likely not sufficient to demonstrate a carpet or turf fiber is PFAS-free. We routinely request contract labs run both EPA Method 537.1 and one of the total fluorine methods to document . We often see that the targeted analysis for inidviudual PFAS chemicals significantly underreport the actual PFAS content of products in which PFAS is used. In addition to the two methods that measure total fluorine, other techniques can measure total organic fluorine, thus ensuring results are not skewed by the possible presence of inorganic fluorine (which is distinct from PFAS).

A company claiming PFAS-free turf fiber should thus be able to produce testing results showing less than 1 part per million of total organic fluorine or total fluorine. In the case of Martha's Vineyard Regional High School, it seems they may not be aiming for a PFAS-free synthetic turf system. While they state they "should guarantee the safety of our groundwater," according to the project specifications, Section 38 13 23.29 Synthetic Field Sports Surfacing (July 28, 2020), the requirement only states that the synthetic turf should "not use any PFAS chemicals currently listed as part of California's Proposition 65 regulations or identified as part of US EPA's Method 537 to manufacture the components of its turf field products, including the fibers, backing and any coating materials."

The California Proposition 65 and US EPA's Method 537 are not relevant standards for asserting a product is PFAS-free. California Proposition 65 only regulates few PFAS chemicals. US EPA's Method 537 is a test method not even a definitive list of chemicals. The list of chemicals that can be analyzed by US EPA's Method 537 is limited by the availability of laboratory reference standards for the many hundreds of PFAS chemicals that should be analyzed for. Labs routinely use US EPA's Method 537 (with modifications) to analyze 11 to 40 PFAS chemicals, depending on the lab. As I stated earlier, recent PFAS-free certification standards (*GreenScreen Certified*) for both firefighting foams and food packaging have specified total elemental fluorine testing.

Given the concerns around groundwater contamination (something Martha's Vineyard has already experienced due to the use of AFFF at the Martha's Vineyard Airport), as well as athlete health, your boards should require reliable third-party testing using both one of the total fluorine methods and one of the targeted methods:

To certify a product to be PFAS -free, we would recommend the following tests:

1. Combustion Ion Chromatography OR Oxygen Flask Combustion and Ion-Selective Electrode to identify elemental fluorine content;
2. It is also helpful to run EPA Method 537.1 modified for polymers with the ability to detect 40 PFAS compounds; AND a TOP Assay to identify the presence of some PFAS precursors.

In addition to our academic collaborators, we have found a range of third-party labs capable of conducting this type of analysis. These include, but are not limited to: Eurofins Australia or Test America (Sacramento); Galbraith Labs; ALS Environmental; and SGS.

I have also included a fact sheet from University of Massachusetts Toxics Use Reduction Institute; and the Cancer Free Economy Network (CFEN) guide entitled “A Short Guide to Common testing methods for Per- and Polyfluoroalkyl Substances (PFAS)” which discusses these issues. The CFEN guide discusses in more detail the range methods and references which test methods are commercially available

Please feel free to contact me directly if you have further questions.

Sincerely,

Jeff Gearhart
Research Director

Ecology Center
jeffg@ecocenter.org

FACT SHEET: AUGUST 2020

A SHORT GUIDE
TO COMMON TESTING METHODS
FOR PER- AND POLYFLUOROALKYL SUBSTANCES (PFAS)

A challenge to eliminating the use and exposure to per- and polyfluoroalkyl substances (PFAS) is knowing where these chemicals are used and found. Testing, be it of products, water, or food, is critical to ascertain whether PFAS are present and at what levels. But what test methods are appropriate in which application? This guide to PFAS test methods is to help manufacturers, researchers, government agencies, and NGOs understand the different types of PFAS testing techniques available to support their work in knowing where PFAS are found and at what level.

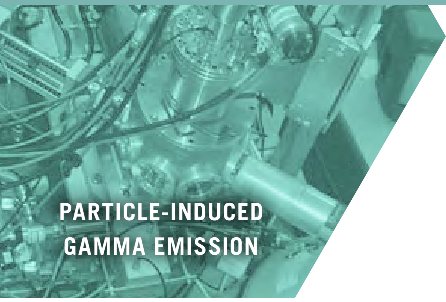
PFAS BACKGROUND

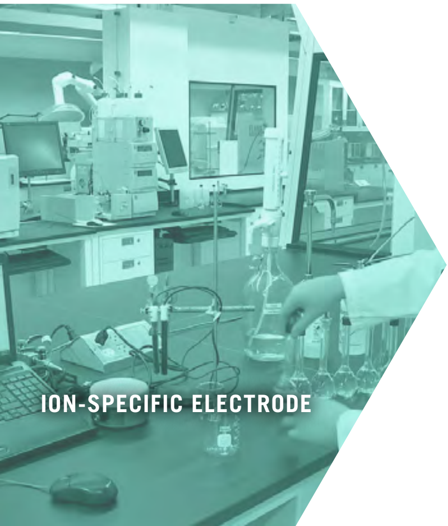
Per- and polyfluoroalkyl substances (PFAS) are a class of fluorinated organic chemicals that contain at least one fully fluorinated carbon atom, with over 5,000 chemicals identified in the class. PFAS are used in a wide variety of products, from non-stick cookware and textiles to firefighting foams and food packaging. One of the main concerns surrounding PFAS is their high potential to persist in the environment. Given their ubiquitous use and persistence, testing for PFAS is an important part of monitoring and limiting their continued use in supply chains.

This fact sheet focuses on testing techniques and methods that can be used to identify PFAS in food packaging, firefighting foams, and drinking water. While some test methods apply to multiple products and drinking water, there are few standardized PFAS test methods, which makes comparing results between different laboratories and studies difficult.

TESTING TECHNIQUES

PFAS analytical testing techniques can be divided into two categories: (1) targeted testing, and (2) total fluorine test methods. Targeted testing techniques measure a subset of PFAS (e.g., 30 of the 5,000 PFAS chemicals), while total fluorine tests are indirect methods designed to measure a representative element indicative of PFAS.





TOTAL FLUORINE METHODS

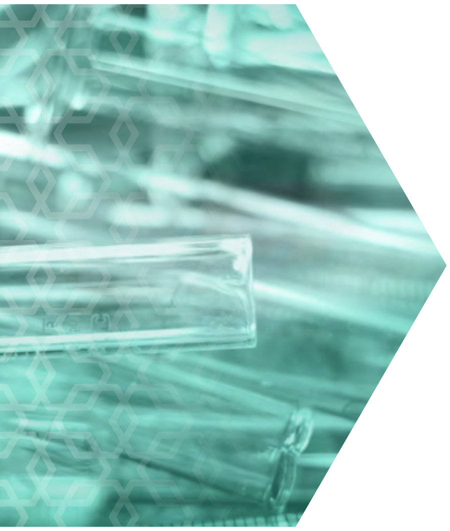
Total fluorine techniques measure either total organic fluorine or total fluorine. These techniques are efficient ways to identify whether PFAS are likely present. They can be used for screening as well as in a tiered approach to quantify PFAS in a product.

Total fluorine methods include: (1) particle-induced gamma emission (PIGE), (2) combustion ion chromatography (CIC), (3) instrumental neutron activation analysis (INAA), (4) ion-specific electrode (ISE), and (5) x-ray photoelectron spectroscopy (XPS). CIC can be used to quantify total organic fluorine or total fluorine. PIGE can be used to quantify total fluorine. PIGE, XPS, and INAA are non-destructive, meaning a single sample can be analyzed multiple times, which is beneficial when using more than one technique. PIGE and XPS are surface measurements, providing information on fluorine present on the surface rather than the concentration in the entire sample. CIC and ISE are both destructive, requiring combustion of the product sample, and measure fluorine in the entire sample. Table A includes more specific information on these methods.

TARGETED TESTING

Targeted testing techniques identify and quantify the presence of a specific set of PFAS. The chemicals of interest being identified and quantified are called analytes. The majority of targeted test methods use chromatography, with most relying on a combination of gas or liquid chromatography (GC or LC) and mass spectrometry (MS) analysis. GC/MS and LC/MS methods are used to both identify and quantify different types of specific chemical analytes.

Standards are required to identify and quantify an analyte and, to date, less than 100 of the 5,000 PFAS can be identified and quantified using targeted testing. Targeted testing techniques have the advantage of positively identifying the specific chemical as well as the concentration of that chemical in the sample. In addition, there are standardized and validated test methods in this category, such as those for drinking water. The primary disadvantage is that in most cases these methods measure only a small fraction of the PFAS that may be present in the



sample, missing those present in polymers and others not on the list of target analytes. The table includes more specific information on these techniques.

Two other methods incorporate LC/MS, namely quadrupole time-of-flight mass spec (QTOF-MS) and total oxidizable precursors (TOP) assay. QTOF-MS can determine a wide range of compounds in the PFAS family. TOP assay is used to convert precursors to PFAS that can be quantified using standard methods.

STANDARDIZED AND VALIDATED TEST METHODS

Most of the standardized and validated test methods are written for drinking water, groundwater, and open waterways. They are all chromatography-based methods, with differences mainly appearing in the sample preparation step. The complex nature of samples containing multiple materials, such as packaging, require significantly more sample preparation and clean-up when compared to drinking water. The number of analytes that can be determined varies depending on which method is employed and ranges from 11 to 40. The US Environmental Protection Agency (EPA) test method 537.1 is commonly referenced as it is a multi-laboratory validated test method.

PFAS testing is an evolving science that will benefit from standardized test methods for a wider variety of matrices and analytical techniques. Standardization allows for better reproducibility and comparison of PFAS determination, which will become more important as governments, agencies, and supply chains aim to reduce and eliminate the use of PFAS.

ANALYTICAL TECHNIQUES	APPLICATIONS	TARGET SUBSTANCE(S)	ADDITIONAL INFORMATION
COMBUSTION ION CHROMATOGRAPHY (CIC)	Food packaging Firefighting foams Water samples	Total fluorine or total organic fluorine	• Offers possibility of fast, accurate analysis • Destructive to sample • Direct combustion of the sample measures the total fluorine of the entire sample, independent of thickness. Direct combustion can be combined with a separate measurement of total inorganic fluorine through water extraction of the sample followed by combustion to determine total, inorganic, and organic fluorine. • Instead of directly combusting the sample, the organic fluorine can be either extracted or adsorbed and then combusted to measure total organic fluorine (either extractable or adsorbable). These techniques result in lower limits of reporting than direct combustion. These techniques are known as Extractable Organic Fluorine (EOF) and Adsorbable Organic Fluorine (used for waters/ wastewater) methods. • Technique referenced in Clean Production Action's firefighting foam standard - 1 ppm total organic fluorine threshold requirement for certification • Commercially available
INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS (INAA)	Food packaging Textiles Other organic materials	Total fluorine	• Measures total of entire sample, independent of thickness • Non-destructive and rapid • Since technique relies on nuclear, rather than chemical reaction, samples may be analyzed without dissolution or decomposition • No chemical prep needed • Samples are irradiated followed by a decay period, emitting gamma rays, and target nuclide identified via gamma ray spectroscopy. Quantification accomplished by comparison with standards. • Not commercially available
ION-SPECIFIC ELECTRODE (ISE)	Food packaging	Total fluorine	• Combustion with known amount of buffer solution, then analyzed with fluoride-specific electrode • Destructive method, low-cost • Commercially available
PARTICLE-INDUCED GAMMA EMISSION (PIGE)	Food packaging Firefighting foam	Total fluorine	• Surface measurement, so results dependent on sample thickness • Good result accuracy, well-used, cost-effective • Not commercially available
QUADRUPOLE TIME-OF-FLIGHT-MASS SPEC (QTOF-MS)	Water samples Materials	Full range of potential compounds in the PFAS family	• QTOF-MS combines TOF and quadrupole instruments, a pairing that results in high mass accuracy; speed and sensitivity are benefits of the QTOF • Coupled with LC or GC for analyte determination • Expensive and time consuming
TOTAL OXIDIZABLE PRECURSORS (TOP) ASSAY	Foam products Textiles Water samples	Quantifies total amount of chemical precursors to perfluoroalkyl acids (PFAAs)	• Selective PFAS method (only those that can be oxidized to form targeted PFAAs) • Destructive, relatively rapid, low cost • Sample treated so precursor substances contained within the sample are oxidized, then PFAS determination done using methods like LC-MS/MS

STANDARDIZED TEST METHODS	APPLICATIONS	TARGET SUBSTANCE(S)	ADDITIONAL INFORMATION
DIN EN ISO 10304-1	Water samples	Total organic fluorine	• Validated standardized test method is for water samples
ASTM D7979	Water samples	Individual PFAS (39 analytes)	• Direct injection method, LC-MS/MS analysis • Performance-based method (i.e., can adjust measurement sensitivity), wider range of analytes
ISO METHOD 25101	Unfiltered drinking water	Determination of linear isomers of PFOS and PFOA	• Solid phase extraction (SPE), high performance mass spec (HPLC-MS/MS) technique
USEPA METHOD 533	Drinking water	Individual PFAS (25 analytes)	• Isotope dilution anion exchange, solid phase extraction (SPE), and liquid chromatography/ mass spectrometry (LCMS/MS) techniques
USEPA METHOD 537	Drinking water	Selected PFAAs	• Solid phase extraction (SPE) liquid chromatography/tandem mass spectrometry (LCMS/MS) techniques utilized
USEPA METHOD 537.1	Drinking water	Individual PFAS (18 analytes)	• Multi-laboratory validated • Solid phase extraction (SPE), liquid chromatography/tandem mass spectrometry (LCMS/MS) techniques utilized

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Per- and Poly-fluoroalkyl Substances (PFAS) in Artificial Turf Carpet

Introduction

The Massachusetts Toxics Use Reduction Institute (TURI) has received inquiries from municipalities and community members regarding the presence of per- and poly-fluoroalkyl substances (PFAS) in artificial turf carpet. This brief fact sheet provides some basic background information on PFAS and on recent testing for these chemicals in artificial turf as reported by nonprofit organizations. This information is provided under TURI's mandate to provide information on toxic chemicals and safer alternatives to businesses, municipalities, community members and others.

TURI has conducted background research on health and environmental effects of PFAS in its work with the Toxics Use Reduction Act (TURA) program's Science Advisory Board. TURI has neither conducted nor sponsored any laboratory testing of PFAS in turf or other products.

What are PFAS?

PFAS are a category of chemicals that contain multiple fluorine atoms bonded to a chain of carbon atoms. Thousands of such chemicals exist. A study by the Organization for Economic Cooperation and Development (OECD) identified over 4,700 PFAS-related Chemical Abstract Service (CAS) numbers.[1] PFAS chemicals have properties that can be useful in a variety of settings, such as water and stain resistance. They also pose concerns, including persistence, bioaccumulation, and adverse health effects, as summarized below.

PFAS Nomenclature and Vocabulary

PFAS are sometimes described as "long-chain" or "short-chain" based on the length of the fluorinated carbon chain. They can also be categorized and described based on the number of carbons; for example, a PFAS chemical with an 8-carbon chain may be referred to as "C8." For more information, see the ITRC fact sheet "Naming Conventions and Physical and Chemical Properties of Per- and Polyfluoroalkyl Substances (PFAS)."[2]

PFAS "precursors" are complex chemicals that break down into other simpler PFAS compounds ("degradation products"). In addition, some PFAS are fluoropolymers (longer chains of molecules containing carbon and fluorine).

TURI
TOXICS USE REDUCTION INSTITUTE
UMASS LOWELL

February 2020

Persistence

Although there are thousands of PFAS, most of them break down into a common set of degradation products. These degradation products are characterized by very high persistence in the environment.[3] Persistent chemicals do not break down under normal environmental conditions, and some can last in the environment for hundreds of years or longer. As a result, introducing these chemicals into the environment has lasting consequences.

Bioaccumulation

All PFAS pose some degree of bioaccumulation concern, especially in air-breathing organisms.[3] In other words, they can accumulate in plants, animals, and humans.

Health Effects

Due to widespread contamination of drinking water in some areas of the US, the human health effects of certain PFAS have been studied in depth. Other PFAS have been studied in laboratory animals. Because the class of PFAS is so large, many individual PFAS have not been studied in depth. Researchers have emphasized the need to address PFAS as a group rather than one by one. Health effects documented for some PFAS include effects on the endocrine system, including liver and thyroid, as well as metabolic effects, developmental effects, neurotoxicity, and immunotoxicity.[3]

PFAS have been studied by a number of government entities. For example, OECD has done the most comprehensive work on PFAS as a class; the US Environmental Protection Agency (US EPA) has done extensive research on several PFAS compounds; and certain states have researched individual PFAS chemicals in depth.

Drinking Water Contamination

PFAS have been found as drinking water contaminants in many states. For example, the Massachusetts Department of Environmental Protection (MassDEP) has worked with municipalities to gather data on levels of six PFAS in groundwater and drinking water. According to MassDEP, "since 2013, the sum of the concentrations of the six PFAS compounds above 20 ppt [parts per trillion] have been detected at over 20 PWSs [public water systems] in Massachusetts." MassDEP has issued a proposed regulation that would set a Maximum Contaminant Level (MCL) in drinking water of 20 ppt for the sum of the concentrations of these six PFAS. MassDEP has also finalized and adopted standards for groundwater cleanup.[4]

PFAS Testing

PFAS testing is difficult due to the large number of individual chemicals in the class, as well as the very low concentrations at which adverse effects may occur. Additional difficulties result from the fact that while methods have been developed for testing drinking water and wastewater, there are no consistent guidelines for testing solid materials. Some of these difficulties have been addressed through the development of methods for testing the total presence of fluorine-containing organic (carbon-containing) compounds.

In many cases, testing may be conducted for a small group of PFAS that have been a particular focus of regulatory activity. The absence of these chemicals does not indicate that all PFAS are absent. For example, US EPA has published methods for testing just 29 PFAS in water.[5]

Difficulty of Testing Products

Difficulties may be encountered in choosing appropriate test methods for a given material. For example, guidance that has been developed for drinking water is not necessarily applicable to a solid material. In addition, some laboratories use a modified version of a US EPA method; US EPA has not validated these approaches.[5]

In any testing effort, it is important to adopt an appropriate study design. For example, US EPA has provided guidance on approaches to understanding potential leaching of chemicals from liquids, soils and wastes into rainwater. This includes consideration of the acidity of rainwater in certain areas of the US. US EPA recommends choosing an appropriate extraction fluid depending on the relevant environmental conditions in the region.[6]

Total Fluorine Analysis

In addition to testing for individual compounds, it can also be useful to conduct a Total Fluorine Analysis. This can be carried out using Particle-Induced Gamma Ray Emission (PIGE) spectroscopy, and other techniques such as Combustion Ion Chromatography (CIC).

These tests do not look for specific PFAS chemicals. Rather, they look for fluorine atoms as an indicator of the presence of PFAS chemicals. This kind of test can be useful because testing standards have not been developed for all the types of PFAS that are available on the market. These measurements can also be performed on solid samples.

TOP Assay

Another test used to gather information about PFAS present in a sample is a Total Oxidizable Precursor (TOP) assay. This test creates the conditions in which precursors are broken down into degradation products. These degradation products are among the PFAS that can be measured by EPA methods in water. TOP assay enables researchers to detect the presence of precursors, even if they do not know which specific precursors are present.[7]

Understanding Test Results

When interpreting results of testing conducted on products, including turf carpet samples, it is important to understand what test was conducted and what that test has the ability to detect. For example, if a fluoropolymer is present in the product, an appropriate test must be selected to detect its presence.

In summary, lack of detection of one or more specific PFAS does not mean that a material is free of PFAS. To determine whether PFAS are likely to be present, a total fluorine test and/or a TOP assay may be helpful.

Another factor to consider is that in some cases, a test may be carried out only for long-chain chemicals that were used more frequently in the past, or that appear primarily as degradation products in the environment. Knowing the presence of these chemicals is important, but they are not the most likely chemicals to appear in a new product.

PFAS Testing in Artificial Turf Carpet

Determining what chemicals are present in a product can be challenging because chemical contents are frequently not disclosed by the manufacturer. Two nonprofit organizations recently tested artificial turf carpet and found evidence of the presence of PFAS in the material.[8] The nonprofit organizations tested backing of both new turf and older, discarded turf. They also tested a number of samples of artificial grass blades (carpet fibers).

They detected one PFAS chemical in the backing of the new turf sample. Specifically, they detected 6:2-fluorotelomer sulfonic acid (known by the abbreviation 6:2 FTSA). 6:2 FTSA has a 6-carbon chain, and is considered a short-chain PFAS because of the way in which it breaks down. In many cases, short-chain PFAS have been adopted as substitutes for longer-chain PFAS.

They detected perfluorooctane sulfonate (PFOS) in the backing of the discarded, older turf sample. PFOS is a long-chain PFAS that is no longer manufactured in the US due to concerns about health and environmental effects.

They also tested a number of synthetic turf fiber samples and found that all of them contained quantities of fluorine that suggest the presence of PFAS.[8] These quantities were in the parts per million range, but given the large surface areas of a typical turf carpet, researchers note these may represent a source of PFAS in the environment.[9] Research on this topic is still in process and it will be important to review new scientific publications as the work continues.

One possible reason for the use of PFAS in the artificial turf grass blades is to serve as an extrusion aid.[10] That is, PFAS is added to the polymer mixture (which is a non-fluorinated plastic) before it is passed through an extruder. An extruder is manufacturing equipment that melts and forms the polymer mixture into its desired shape. The PFAS helps to prevent the polymer from sticking to the extruder. According to a researcher, artificial turf grass blades were previously made from low-density polyethylene, but the material had poor durability. Newer polymer mixtures have greater durability, but were not compatible with existing extrusion equipment. Therefore, PFAS were added in order to facilitate use of the new polymer mixture with existing equipment.[8,9]

The researchers who conducted this work do not know exactly what types of PFAS may be used as processing aids in this application. They are not present in US EPA's Method 537.1 ("Determination of Selected Per- and Polyfluorinated Alkyl Substances in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry"). Thus, using this US EPA method would not be informative in this application. However, the TOP assay allows researchers to confirm the presence of some type of PFAS. According to researchers, preliminary results on two samples indicated the presence of PFBA, PFBS, FPHxA, PFHpA, PFOA and PFOS in turf carpet fibers that had undergone TOP assay.[9]

Questions about Athletes' Exposure to PFAS

TURI has received questions about the possibility of PFAS exposure associated with playing on artificial turf. PFAS exposure has not been assessed specifically in relation to playing on artificial turf, and studying children's exposures often presents methodological and ethical challenges. More generally, the approach of the Toxics Use Reduction Institute is to identify opportunities to reduce or eliminate the use of toxic chemicals as a means to protect human health and the environment. Eliminating the use of a toxic chemical also makes it unnecessary to assess exposure.

The vast majority of PFAS research to date has focused on the results of ingestion exposure. There is also some emerging information on health effects of dermal exposure to PFAS. Some researchers have suggested that dermal exposure to consumer products treated with PFAS may contribute to over-all PFAS exposure.[11,12] In the absence of more specific information, it may be helpful to follow general guidelines provided by the Icahn School of Medicine at Mt. Sinai and others for helping to minimize exposure to chemicals that may be present in artificial turf.[13]

Learn more about PFAS

Technical fact sheets from the Interstate Technology Regulatory Council (ITRC) are available at: https://pfas-1.itrcweb.org/

Acknowledgements

Dr. Graham Peaslee (University of Notre Dame) provided comments on a draft of this fact sheet. Support for TURI's background research on this topic was provided by The Heinz Endowments.

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Note: For several points covered in this overview, we have provided the TURA Science Advisory Board's summaries of scientific information as a reference. These summaries draw upon a large set of authoritative government documents and peer reviewed studies.

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The Toxics Use Reduction Institute is a multi-disciplinary research, education, and policy center established by the Massachusetts Toxics Use Reduction Act of 1989. The Institute sponsors and conducts research, organizes education and training programs, and provides technical support to help Massachusetts companies and communities reduce the use of toxic chemicals.

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