Chesapeake Quarterly

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Complicated Contaminants

Finding PFAS in the Chesapeake Bay

in this issue

Volume 23, Number 1

PFAS are found nearly everywhere, including in the Chesapeake Bay. What are these so-called "forever chemicals" and what do they mean for the people and wildlife that call the Bay watershed home?

This print edition of *Chesapeake Quarterly* includes the issue's feature story: "Diagnosing the PFAS Problem." Read four more articles in our complete online issue at chesapeakequarterly.net or scan code:

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Cover: *Osprey and menhaden in Whitehall Bay near the mouth of the Severn River.*

PHOTO, JAY FLEMING

Diagnosing *the* PFAS Problem

Scientists Investigate So-Called 'Forever Chemicals' in the Chesapeake Bay

by Ashley Goetz

"We kind of think of ourselves as the doctors of the environment," says Upal Ghosh, a professor of chemical and environmental engineering at the University of Maryland, Baltimore County. In order to make a diagnosis, a doctor might study your symptoms, order tests, and review your medical reports. Similarly, when there are signs of sickness in an ecosystem, scientists start with the symptoms.

They formulate ways to gather information—collecting field samples, analyzing them in a lab, running experiments, and using mathematical models. And, like doctors, only once they learn enough to diagnose the problem can they begin to offer remedies.

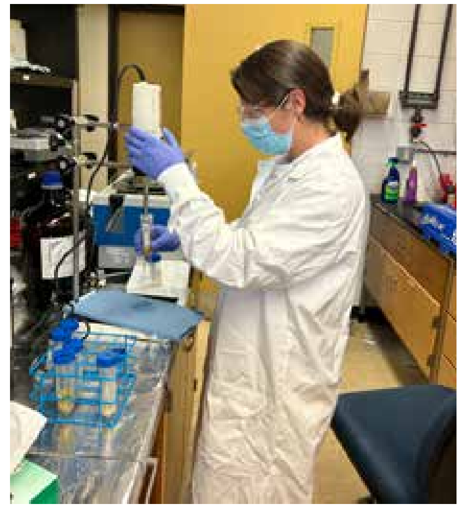
For per- and polyfluoroalkyl substances, or PFAS, science is still largely in the diagnosis stage.

PFAS, perhaps most commonly known by their nickname, "forever chemicals," are a vast group of human-made chemicals found in common household products, like nonstick pans, carpets, cosmetics, and fast-food packaging. They are widespread, long-lasting, and in some cases, toxic. Studies have shown that even at very low levels, certain PFAS can harm people and wildlife.

GRAPHIC, JILL GALLAGHER / MDSG

To correctly diagnose the PFAS problem, researchers need to understand how these chemicals behave once they get into the environment. "We often refer to that as fate and transport," says Chris Higgins, a professor of civil and environmental engineering at the Colorado School of Mines who has been studying PFAS since 2001. In short, fate and transport is the life cycle of a chemical in the environment—how a chemical changes as it moves through the environment and where it ends up.

Across the country, including throughout the Chesapeake Bay watershed, researchers are trying to piece together the fate and transport of PFAS. But PFAS behave differently than many legacy toxic chemicals like mercury and PCBs, and they are driving researchers to think about toxic contaminants in new ways.



Michella Salvitti, a PhD student at the University of Maryland Eastern Shore, is studying PFAS in the Chesapeake Bay.

PHOTO, MICHELLA SALVITTI / UNIVERSITY OF MARYLAND EASTERN SHORE

Accidental Origins

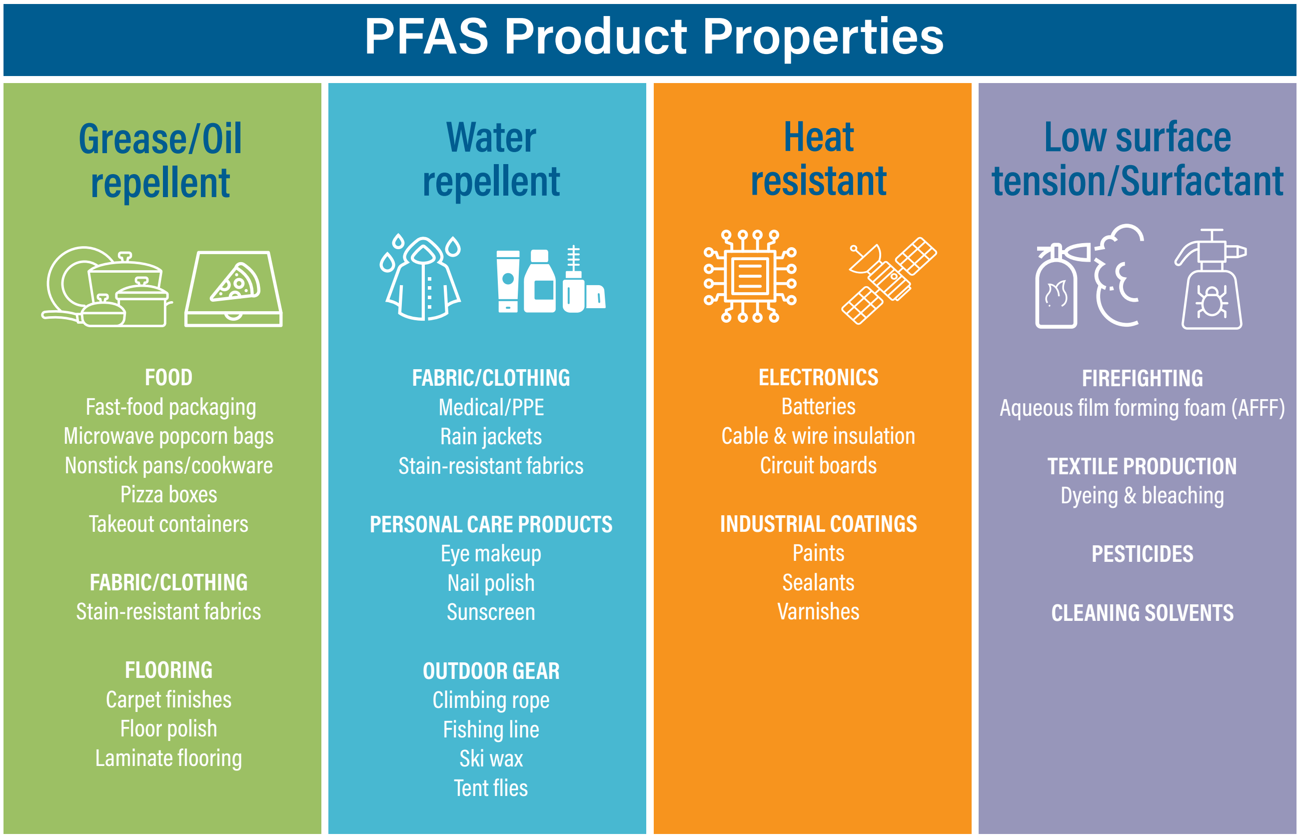
Like penicillin or the mess-free adhesive that makes Post-it notes stick, the first PFAS were discovered by chance. It was 1938 when a failed experiment led DuPont chemist Roy J. Plunkett to create PTFE resin, a waxy, slippery, white substance. It was heat-resistant with low surface friction. In 1945, this new PFAS was trademarked Teflon. Later, while trying to develop a rubber for use in jet fuel lines, scientists at the Minnesota Mining and Manufacturing Company, or 3M, discovered a substance that repelled water and oil. Their PFAS would come to be known as Scotchgard.

PFAS are typically characterized by a chain of carbon atoms bonded to fluorine atoms. Those chains are often joined with groups of atoms, called functional groups, that have distinct chemical properties. Those functional groups include carboxylic acids, sulfonic acids, and alcohols. The carbon-fluorine bond is incredibly strong and prevents PFAS from degrading. At the time, this was yet another advantage of this new class of chemicals. Their applications seemed endless.

In 1963, the US Navy patented the first firefighting foam containing fluorocarbon compounds as a main ingredient. The PFAS in the foam repelled water and hydrocarbons, the latter of which form the base for natural gas and crude oil. The foam was especially useful for putting out fuel fires—such as fires from kerosene, jet fuel, diesel oil, or gasoline—and controlling flammable vapors. The formula was refined, and a few years later, aqueous film forming foam, or AFFF, appeared on the market.

In 1967, after 134 sailors died in a fire involving jet fuel aboard the USS Forrestal aircraft carrier, the Navy began requiring its vessels to carry AFFF. "This was a quick way to extinguish those fires, save lives, ultimately save these billion-dollar assets—planes, people, and ships," says Lance McDaniel, environmental director at Naval Air Station (NAS) Patuxent River in Southern Maryland.

By the 1970s, military bases across the US were using AFFF to douse chemical and oil fires, including during training exercises. By 1979, they were in use at more than 90 airports across the country. AFFF quickly became an essential tool for firefighting facilities, shipyards, military bases, airports, chemical plants, and oil and gas refineries. Where fuel fires were common, AFFF was indispensable.



GRAPHIC, JILL GALLAGHER / MDSG

Miracle or Mishap?

As useful and ubiquitous as PFAS rapidly became, it was not long before the same companies manufacturing the chemicals began to document their potential harm.

As early as the 1950s, 3M studies showed PFAS building up in the blood of mice. By the 1960s and 70s, DuPont studies indicated that exposure to PFAS in food packaging could cause liver damage. In 1977, 3M concluded that perfluorooctane sulfonate (PFOS), the PFAS in Scotchgard, was "more toxic than anticipated." A year later, they determined that PFOS and perfluorooctanoic acid (PFOA), the chemical used in DuPont's Teflon, "should be regarded as toxic." By the 1980s and 90s, the companies were uncovering evidence of effects on reproduction and fertility, as well as elevated risks of cancer. The Centers for Disease Control and Prevention (CDC) detected PFAS in more than 98% of blood serum samples collected from the general population in 1999-2000.

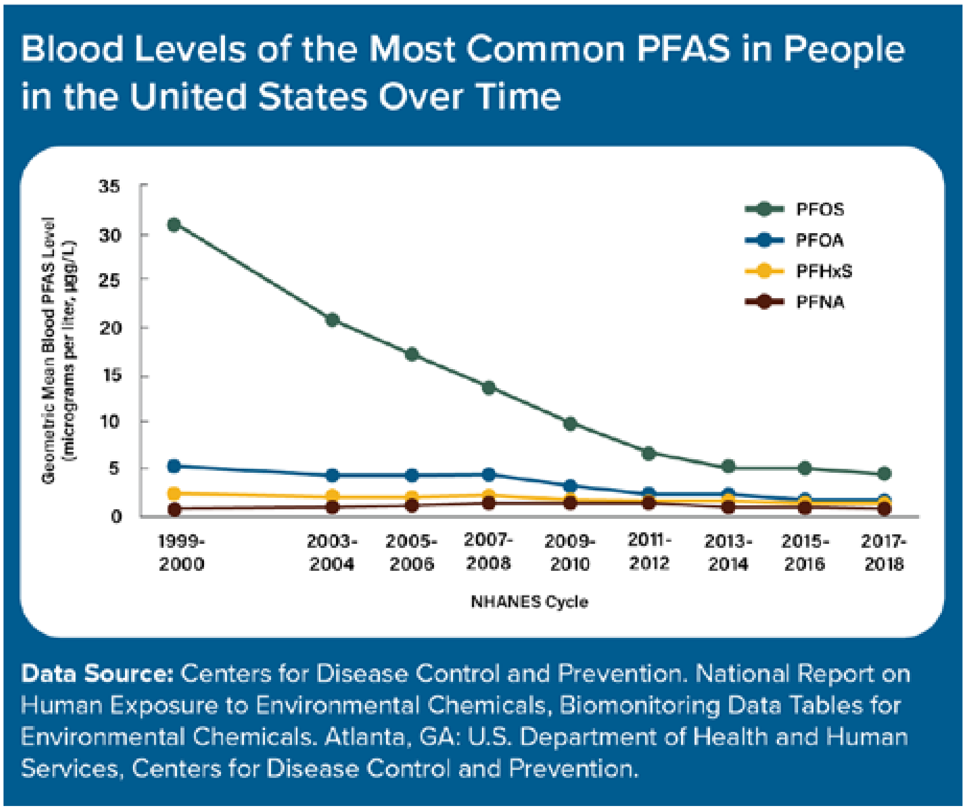
The US Environmental Protection Agency (EPA) estimates there are more than 14,700 known chemicals within the PFAS family. Not all PFAS are toxic, but only a fraction of the compounds are well-studied and understood. Today, it's widely accepted that many PFAS pose a health risk to humans, animals, and the environment. In 2000, the EPA and 3M began the voluntary phase-out of PFOS. Shortly after, 3M also began the phaseout of PFOA. By 2017-2018, CDC reports indicated that blood PFOS levels in the US population had declined by more than 85% and blood PFOA levels had declined by more than 70%.

Although PFOA and PFOS are no longer made in the United States, they are still regularly detected in water and soil samples. That's because PFAS don't get recycled in the environment. The carbon-fluorine bond in PFAS is one of the strongest in chemistry, making PFAS super-stable. "People have called the perfluorochemicals molecular rebars," says Ghosh. "They don't break down." Over time, PFAS have escaped from the places they were made, used, and thrown away into the soil, air, and water that support life on Earth. And once introduced, PFAS tend to stick around.

On the Move

PFAS take many routes into the environment, starting in the facilities where the chemicals, or the products containing them, are made. They reach local streams and rivers in the form of wastewater or enter the air through smokestack emissions in the manufacturing process. PFAS have even been found in rain as a result of transport into the atmosphere. Through wear and tear, washing, and aging, PFAS coatings can flake off products and run down drains as wastewater. Carried by stormwater, the chemicals slip into streams or seep into soil and groundwater.

Disposable products are another common source of PFAS. "When you're done with your carpet or your clothing, what do you do with it? You throw it away. It goes into a landfill," says Higgins. Pollutants that leach out



Blood PFAS levels have gone down as the production and use of some PFAS compounds have declined. According to the CDC, finding a measurable amount of PFAS in blood serum does not imply that the levels of PFAS cause an adverse health effect. However, biomonitoring studies on PFAS levels can give doctors and public health officials reference values to determine if a person has been exposed to higher levels of PFAS than the general population. The data can also help scientists conduct research on PFAS exposure and health effects.

GRAPHIC, CENTERS FOR DISEASE CONTROL AND PREVENTION

of landfills can contaminate the local environment. In some cases, landfill leachate is sent to wastewater treatment plants. The treated sludge, called biosolids, is often later used on farms as fertilizer.

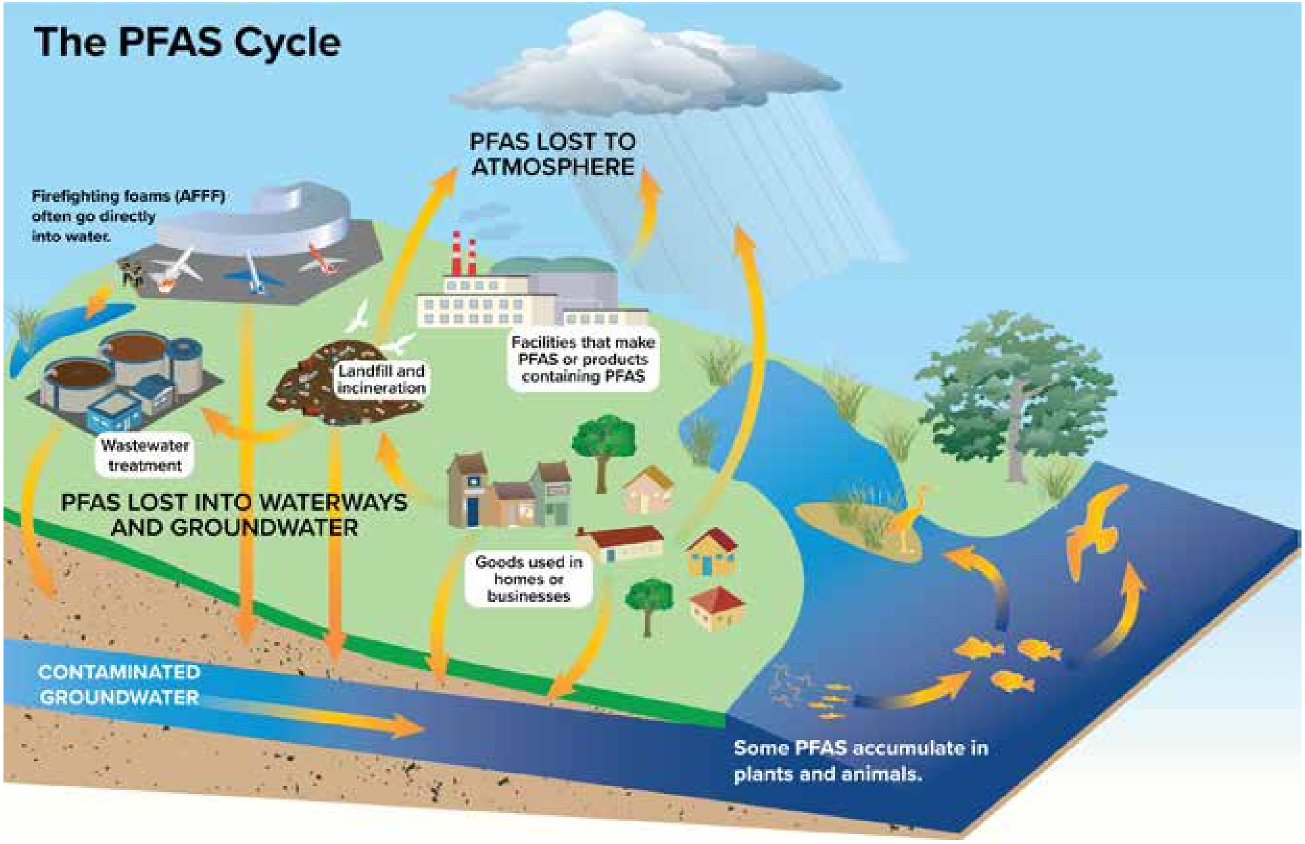
Some products, like the firefighting foam AFFF, introduce PFAS directly into the environment as they are used. PFOS, one of the most well-studied compounds and a main ingredient in AFFF, is often detected in waters near facilities where the foam was deployed.

"In years past, people didn't understand that firefighting foams had these contaminants in them, so there was no thought of containing them," says David Steckler, hydrogeologist and remedial project manager for naval facilities in the Washington, DC, region. Steckler is leading efforts to study and remediate PFAS at Naval Air Station (NAS) Patuxent River, which sits on a peninsula at the confluence of the Patuxent River and the Chesapeake Bay.

The Department of Defense has invested billions of dollars in research and development to find substitutes for AFFF and to clean up PFAS in the

US Coast Guard Academy cadets and a US Navy sailor rinse aqueous film forming foam (AFFF) from the flight deck aboard the Spearhead-class expeditionary fast transport ship USNS Carson City on August 4, 2019.

PHOTO, MASS COMMUNICATION SPECIALIST 2ND CLASS SARA ESHLEMAN / US NAVY, RELEASED



Today, PFAS can be found in densely populated areas as well as remote regions far from their manufactured origins. They have been detected nearly everywhere researchers look, from the Arctic Ocean to snow at the base camps of Mt. Everest to the tributaries of the Chesapeake Bay. GRAPHIC, JILL GALLAGHER / MDSG

environment. At NAS Patuxent River, remedial investigations are focused on 16 sites where PFAS were found. In the coming months, researchers will install monitoring wells, collect groundwater and soil samples, measure PFAS concentrations, and look at the flow of groundwater and surface water. "The remedial investigation looks at both the nature and extent of contamination, as well as the fate and transport of the contaminant, and then ultimately includes ecological and human health risk assessments," Steckler explains.

In addition to remediation, NAS Patuxent River also considers where firefighting foam is no longer needed. "We no longer train with it like we used to," says Public Affairs Officer Patrick Gordon. Fire training with crash trucks that used to be done with AFFF now uses water, for example. The NAS Patuxent River PFAS project team works with an advisory board that includes academic, government, Tribal, and community representatives. "We've really tried to bring in people that represent a community, so they can take the information we give them and share it out to their larger community," says Steckler.

Notably, NAS Patuxent River has not detected PFAS in its drinking water. Elsewhere in Maryland, the story is different.

What's in the Water?

In 2016, the EPA released national drinking water health advisories for PFOA and PFOS at 70 parts per trillion (ppt). Though not mandatory, many states chose to follow these advisories for public drinking water sources. The advisory levels were lowered considerably in 2022, based on new science. That same year, the EPA issued advisories for GenX and PFBS—two PFAS that were manufactured as replacements for PFOA and PFOS.

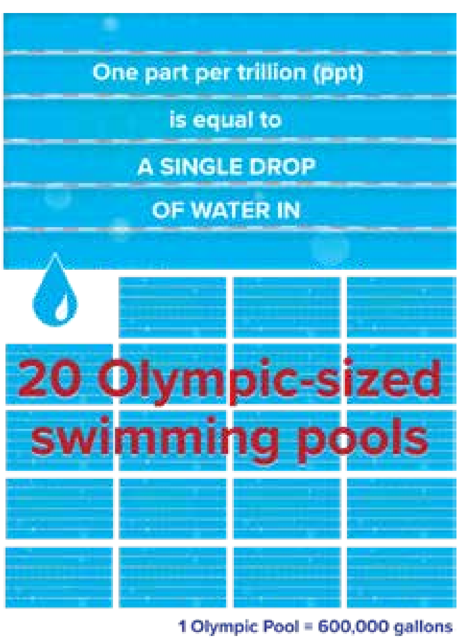
On April 10, 2024, the EPA announced its first-ever national drinking water regulations for PFAS , setting maximum contaminant levels of 4 ppt for PFOA and PFOS and 10 ppt for PFNA, PFHxS, and GenX. These new rules are legally enforceable. The agency also set a nonenforceable health-based goal of 0 ppt for PFOA and PFAS, reflecting the latest science that shows there is no level of exposure without possible health risks.

From 2020 through 2022, the Maryland Department of the Environment sampled more than 450 of the state's community water systems for PFAS. Those systems serve nearly 90% of Maryland's population. They found that 16% of the systems have higher levels of PFAS than the EPA's proposed limit of 4 ppt. The agency works with communities to find alternate water sources, install treatment processes, and obtain funding and technical assistance.

Of more than 450 fish consumption advisories in Maryland, only 71 are for PFAS (as of May 2024). Though limited in scope, they signify PFAS joining the ranks of contaminants like PCBs, mercury, and pesticides.

"Due to the human health effects, monitoring in the [Chesapeake Bay] region for PFAS has been largely focused on drinking water, and rightfully so," says Emily Majcher, a hydrologist with the US Geological Survey and co-chair of the Chesapeake Bay Program's Toxic Contaminants Workgroup.

Now, that focus is shifting. Researchers from a range of disciplines are investigating how PFAS move through the Chesapeake Bay watershed. Chris Salice, director of Towson University's Environmental Science and Studies Program, has been studying PFAS since 2010. His early work focused on PFAS in bayous in Louisiana near former firefighting training sites. Since then, he's continued to study the ecological impacts of PFAS, including ecotoxicity—the effects of toxic chemicals on nonhuman organisms and ecosystems—in fish, invertebrates, birds, and lizards.



GRAPHIC, JILL GALLAGHER / MDSG

"It's certainly an interesting challenge from a purely academic standpoint," Salice says. "Unfortunately, it's tied to all these potential negative consequences on the environment that puts a sharp edge to it." One of his latest studies looks at how PFAS bioaccumulate, or build up, in sunfish, bass, and other fish species in a Maryland creek.

The Maryland Department of the Environment began monitoring fish for PFAS in 2020, and a year later the agency released its first fish consumption advisories for PFAS. A consumption advisory is a recommendation to limit or avoid eating certain fish caught in specific waters due to environmental factors like contamination. In December 2023, the department announced additional PFAS advisories for 15 species found in Maryland waters.

Of more than 450 fish consumption advisories in Maryland, only 71 are for PFAS (as of May 2024). Though limited in scope, they signify PFAS joining the ranks of contaminants like PCBs, mercury, and pesticides.

Fishing for Answers

As Maryland's fish consumption advisories indicate, PFAS can move from the environment into wildlife—and ultimately onto our plates. But which species accumulate PFAS? And how do the chemicals affect them? Investigating these questions could help inform public health and wildlife management. US Geological Survey researchers Vicki Blazer and Heather Walsh are looking for answers in the Chesapeake Bay's smallmouth bass (*Micropterus dolomieu*). Blazer and Walsh's team had amassed a number of smallmouth bass blood and tissue samples from a previous study. They decided to look back at these archived samples, collected from two sites in Pennsylvania's Susquehanna River and two sites in the Potomac River in Maryland and West Virginia, to see if they could detect PFAS.

"And, indeed, we did find them," says Blazer. "That initial study made it clear that we did need to continue to look at PFAS as a potential contaminant of concern for smallmouth bass health," she adds.

Now, they are collecting more smallmouth bass samples from additional sites to see how PFAS levels in plasma change over time. State agencies like the Pennsylvania Department of Environmental Protection and Maryland Department of Natural Resources help Blazer and Walsh collect fish for their studies. When the boats arrive back on shore with bass, the researchers swing into action.

They set up their gear right on the boat ramp or riverbank and form an assembly line to humanely euthanize the fish and collect blood, kidney, and tissue samples. They weigh and measure the liver, gonads, and other organs, and they document any abnormalities they see.

Their samples are sent to a lab where analysts test them for about 40 different PFAS. Blazer, Walsh, and graduate student Cheyenne Smith are also looking at how PFAS may affect immune function in fish. "To us, that's one of the important things. If these fish are not mounting a good immune response or don't have good disease resistance, then they're going to get sick and die," says Blazer. Wild fish encounter many disease-causing bacteria and viruses in the water throughout their lives. If PFAS change how their immune systems respond to threats, Bay fish could face more frequent die-offs and other health impacts.

Pictured, from top: Vicki Blazer draws blood from a smallmouth bass (Micropterus dolomieu) in an earlier study; researchers set up a table to collect smallmouth bass samples from the Shenandoah River in an earlier study; Heather Walsh collects samples from a smallmouth bass for the PFAS study.

PHOTOS, WILL PARSON / CHESAPEAKE BAY PROGRAM

The researchers see four PFAS in nearly every fish they look at—PFOS, PFUnA, PFDA, and PFDoA. They also tend to see higher concentrations of the chemicals in males. "Most of our collections are in the spring, and that's the time that the males are down in the sediment building nests and trying to attract females," says Blazer. She wonders if the muddy sediments at the bottom of the Bay might contain higher concentrations of PFAS.

"Sediments are a reservoir for a lot of different contaminants, including PFAS," explains Carrie McDonough, an assistant professor of chemistry at Carnegie Mellon University. McDonough is looking at PFAS in coastal and marine environments. One of her new studies focuses on creatures that live in the sediment, like shellfish and marine worms. She's investigating how these benthic organisms accumulate PFAS from the sediment, and whether they are a source of PFAS for animals higher up the food chain.

Understanding how PFAS bioaccumulate, or build up in organisms, is an important piece of the fate and transport puzzle. But the structure and behavior of PFAS complicate the picture.

Building Up

In general, when a chemical bioaccumulates, that means it's "sticking around in the body of organisms at an elevated level, compared to either the food they're eating or the air they're breathing or the water they're drinking," says Chris Higgins. Well-known

A smallmouth bass (Micropterus dolomieu).

PHOTO, BRETT BILLINGS / USFWS, PUBLIC DOMAIN contaminants like PCBs and the insecticide DDT tend to bioaccumulate because they are lipophilic, meaning they accumulate in lipids, or fat, Higgins explains. Those contaminants get absorbed by the body and stored in fatty tissues.

But PFAS defy the scientific community's traditional understanding of bioaccumulation. "For a lot of legacy pollutants, you can model the exchange between sediment and water or sediment and organisms pretty easily by assuming that [the pollutants] are hydrophobic and they like lipids and organic carbon," explains McDonough. "But PFAS are a lot more complicated."

PFAS often have hydrophilic heads and hydrophobic tails—meaning portions that like to interact with water and portions that do not, all in the same compound. They often attach to proteins, especially transporter proteins like serum albumin. Produced by the liver, serum albumin is the most abundant protein in our blood plasma. PFAS don't tend to accumulate in fatty tissues, but they do associate with the phospholipids that are key components of cell membranes. For these reasons, PFAS tend to accumulate in the blood and liver, rather than in fat. Their mechanisms of fate and transport differ from other contaminants.

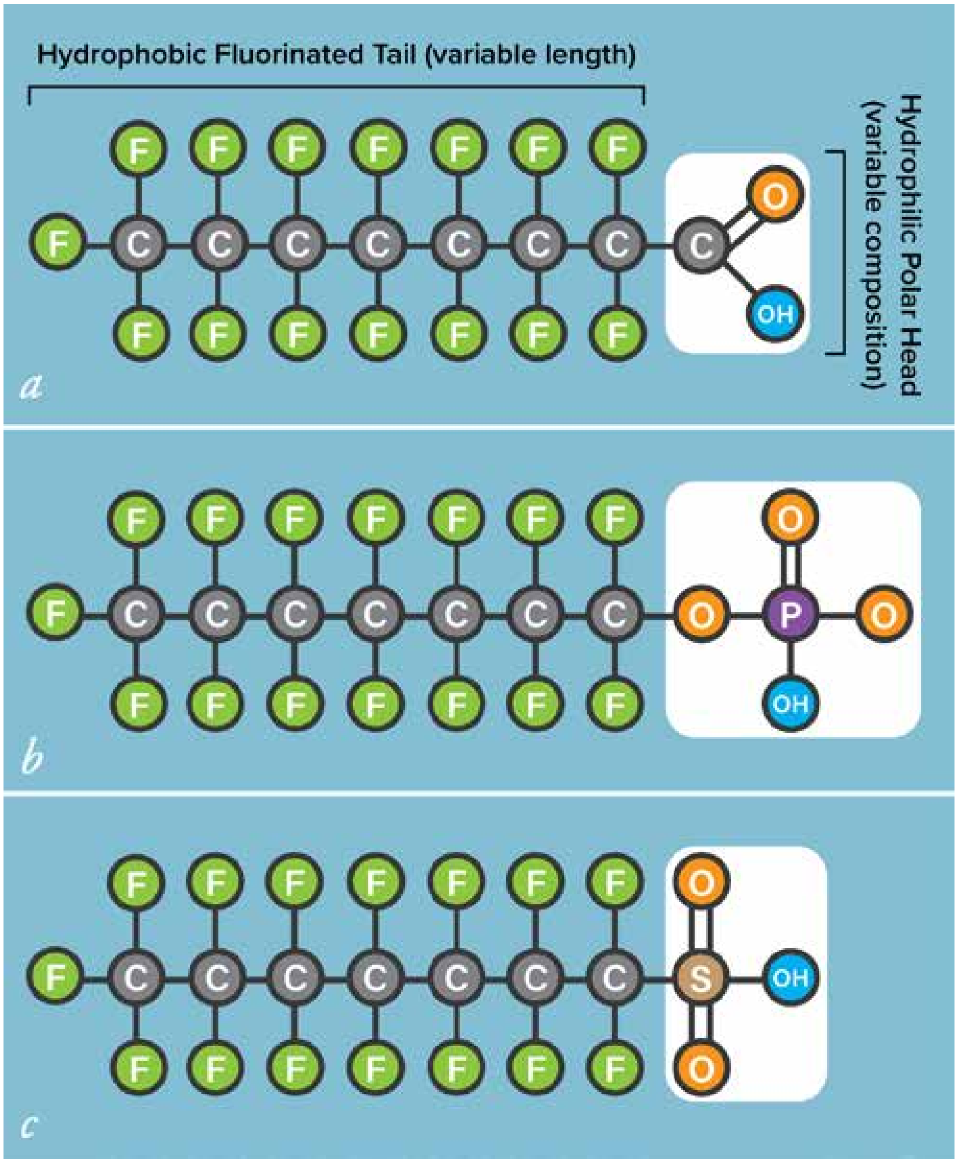
"It really changes how we think about PFAS in the aquatic food web," says Lee Blaney, a professor of chemical, biochemical, and environmental engineering at the University of Maryland, Baltimore County (UMBC). Blaney spent many years studying other contaminants in the Bay, like pharmaceuticals and chemicals used in personal care products. But he says PFAS just kept knocking on his door. Now, PFAS comprise about 90% of his lab's work.

"We can't treat them the same way that we've treated pollutants like PAHs and PCBs in the past, because PFAS have much more specific binding to particular targets in the bodies and organs of aquatic organisms," he says.

Bioaccumulation can also be species-specific. An organism's size and growth rate, its fat content, how and what it eats, where it lives, and how it spends its time can all influence how much of a contaminant it will be exposed to and accumulate. For example, a predator like the smallmouth bass that eats insects, crayfish, and other fish will amass chemicals differently than a menhaden that sits lower down the food chain and feeds on tiny plankton.

"Things that bioaccumulate have raised concerns because that prolongs

People fishing on the Chesapeake Bay near the mouth of the Choptank River. PHOTO, ALICIA PIMENTAL / CHESAPEAKE BAY PROGRAM



PFAS are typically characterized by a chain of carbon (C) atoms bonded to fluorine (F) atoms. Those chains are often joined with groups of atoms, called functional groups. The carbon-fluorine bond is incredibly strong and prevents PFAS from degrading. This diagram shows the PFAS molecules: PFOA (molecule a), PFAS (molecule b), and perfluorohexanesulfonic acid (molecule c). PFAS often have hydrophilic heads and hydrophobic tails—meaning portions that like to interact with water and portions that do not, all in the same compound.
GRAPHIC, JILL GALLAGHER / MDSG

the amount of time an organism is exposed to that chemical internally," says Higgins. Data shows that certain PFAS are highly bioaccumulative. Long-chain PFAS, or PFAS with eight or more carbons, tend to accumulate more readily in humans and fish. Although not all PFAS are known to be harmful, certain PFAS—including the long-chain compounds PFOA and PFOS—can be toxic to people or wildlife when they accumulate past certain thresholds.

In his lab at Towson University, Chris Salice and his students are exploring that relationship between exposure and toxicity. "In a given system, a key goal is to characterize the PFAS exposure, and then to compare the PFAS exposure to the relevant toxicity thresholds," says Salice. While some of their studies take place in the field and in the lab, Salice and his students also employ mathematical models to help bridge the gap between the knowns and unknowns.

The goal of a model is to provide a predictive tool, but models can also help researchers validate the data and results they see in the lab and in the field. "If we can mathematically 'predict it,' that's some validation that we understand it," Salice explains. Mathematical models can also be a form of "cheap experimentation" for researchers studying PFAS. They can offer clues as to whether food or water intake is key to bioaccumulation, for example, or how variations in PFAS concentrations affect bioaccumulation and toxicity. "Models are not a substitute for experimentation and field studies, but I think the approach is a very good partner or informative part of the process," says Salice. "All these pieces can really help solidify our understanding of what's happening or lead to the next, better question."

Fate and Forecast

When it comes to PFAS, nearly every researcher will tell you, "It's complicated." And they're right. Thousands of chemicals are classified as PFAS. They are seemingly everywhere, and they behave unlike many of the contaminants researchers and regulators have dealt with before.

Yet, buoyed by increasing public interest and concern, researchers continue to seek answers about PFAS. "How do you design a remedy? It really starts with defining the problem correctly," says Upal Ghosh. Only then, he says, can we turn our attention toward the interventions and engineering needed to treat the issue.

Designing a remedy for the PFAS problem in the Chesapeake Bay will require teamwork across scientific fields. The Chesapeake Bay Program, a regional partnership managed by the EPA, guides joint restoration and protection efforts in the watershed. The program's Toxic Contaminants Workgroup, which helps manage environmental risks like PFAS, is already working to pool resources and share findings across the region. "There's this big explosion of studies and investigations that have been going on, and no one had really been thinking about that collectively as a whole across the watershed," says Majcher. The workgroup has stepped in to fill that gap.

When considering the possible impacts of PFAS on an estuary as intricately connected as the Chesapeake Bay, scientists will have no shortage of research questions in the coming years.

How long do PFAS remain in sediment and water? What is the nature of their fate and transport in the Bay? What are the major sources? How do PFAS concentrations change over time? What wildlife species are impacted, and in what ways? How are PFAS changing the Bay ecosystem? How do we treat and remove them? And, perhaps most importantly, what are we missing? What haven't we asked yet?

"Well, it's unfortunate, but sometimes I call them 'career chemicals,'" says Salice. "There are a lot of questions to address, and there's a lot of research still to be done. And it's a critically important problem. We want to generate good science so that we can generate good policy and protect natural systems and human health."

—By Ashley Goetz,
goetza@mdsg.umd.edu

Baltimore's Inner Harbor sits at the end of the northwest branch of the Patapsco River, a 39-mile-long river in central Maryland that flows into the Chesapeake Bay. PHOTO, WILL PARSON / CHESAPEAKE BAY PROGRAM WITH AERIAL SUPPORT BY LIGHTHAWK

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Visit chesapeakequarterly.net or scan the QR code below to read the full issue, which includes four more stories about PFAS and their impact on the people and wildlife that call the Chesapeake Bay home.

Dinner on the Line

Their favorite fish, locations, and gear may vary, but all subsistence fishers have something in common: they eat what they catch. As a result, they may be at higher risk of consuming contaminants like PFAS. Maryland's fish consumption advisories are one tool used to communicate this risk.

PHOTO, WILL PARSON / CHESAPEAKE BAY PROGRAM

Strong, Sticky, and Tricky to Measure

Detecting PFAS in the Chesapeake Bay is tricky. Compared to freshwater, Bay water is a chemistry soup, and varying salinity adds an extra layer of complexity. In the lab and in the field, researchers are developing methods to detect and measure what's in the water.

PHOTO, UPAL GHOSH / UNIVERSITY OF MARYLAND BALTIMORE COUNTY

Flying Higher Up the Food Web

PFAS have circulated in coastal environments for decades, including in the Chesapeake Bay, where millions of migrating birds rest and nest each year. Through fieldwork, lab studies, and models, researchers are starting to unravel how these chemicals affect birds.

PHOTO, WILL PARSON / CHESAPEAKE BAY PROGRAM

Meet the Extension Specialist: Andy Lazur

PFAS are just the latest challenge Andy Lazur is tackling as a University of Maryland Extension specialist. From podcasts to pond visits, Lazur prioritizes getting information to the people who need it.

PHOTO, LOGAN BILBROUGH / UNIVERSITY OF MARYLAND EXTENSION AND MDSG

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