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How to take ‘forever’ out of forever chemicals

Stubborn compounds called PFAS in drinking water put health at risk. Technologies based on plasmas, pressure, sound or fungus could finally degrade these chemicals.

By Neil Savage

Water-treatment firm Aquagga's 'forever' chemical destruction unit in Fairbanks, Alaska, uses a technique called hydrothermal alkaline treatment. Credit: Gus Millevolte

Selma Thagard watched in astonishment as the indestructible chemicals did the one thing that they shouldn't do — fall apart.

A chemical engineer at Clarkson University in Potsdam, New York, Thagard was developing a plasma reactor for water treatment in 2016 when an environmental-engineer colleague suggested she add chemicals known as PFAS to the water she was testing. These per- and polyfluoroalkyl substances, also commonly referred to as forever chemicals, are made up of chains of carbon and fluorine atoms held together by some of the strongest chemical bonds in nature. They don't break down naturally, and many decontamination techniques can't touch them either. The PFAS wouldn't be destroyed by Thagard's plasma reactor, her colleague told her, but might act as a useful reference sample.

But it didn't play out that way. In just a few minutes, the chemicals were no more. "When plasma degraded PFAS so rapidly, within minutes, he told me: 'That's not right. Nothing can degrade PFAS,'" Thagard says. She ran the test seven or eight more times, and each time the chemicals disappeared.

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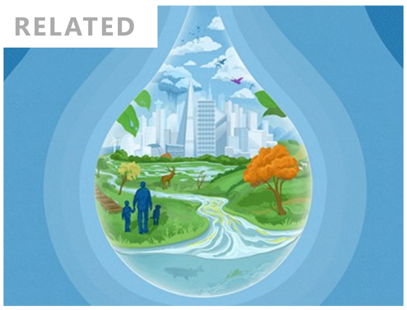


Nature Outlook: Water

Thousands of variations of PFAS chemicals have been used for decades in a wide variety of products, including food packaging, stain-resistant textiles and firefighting foam. Their widespread use, combined with their inability to break down naturally, means that they have spread to water, soil and wildlife. Thagard's colleague was studying the accumulation of the chemicals in fish in North America's Great Lakes, but they are present all around the globe.

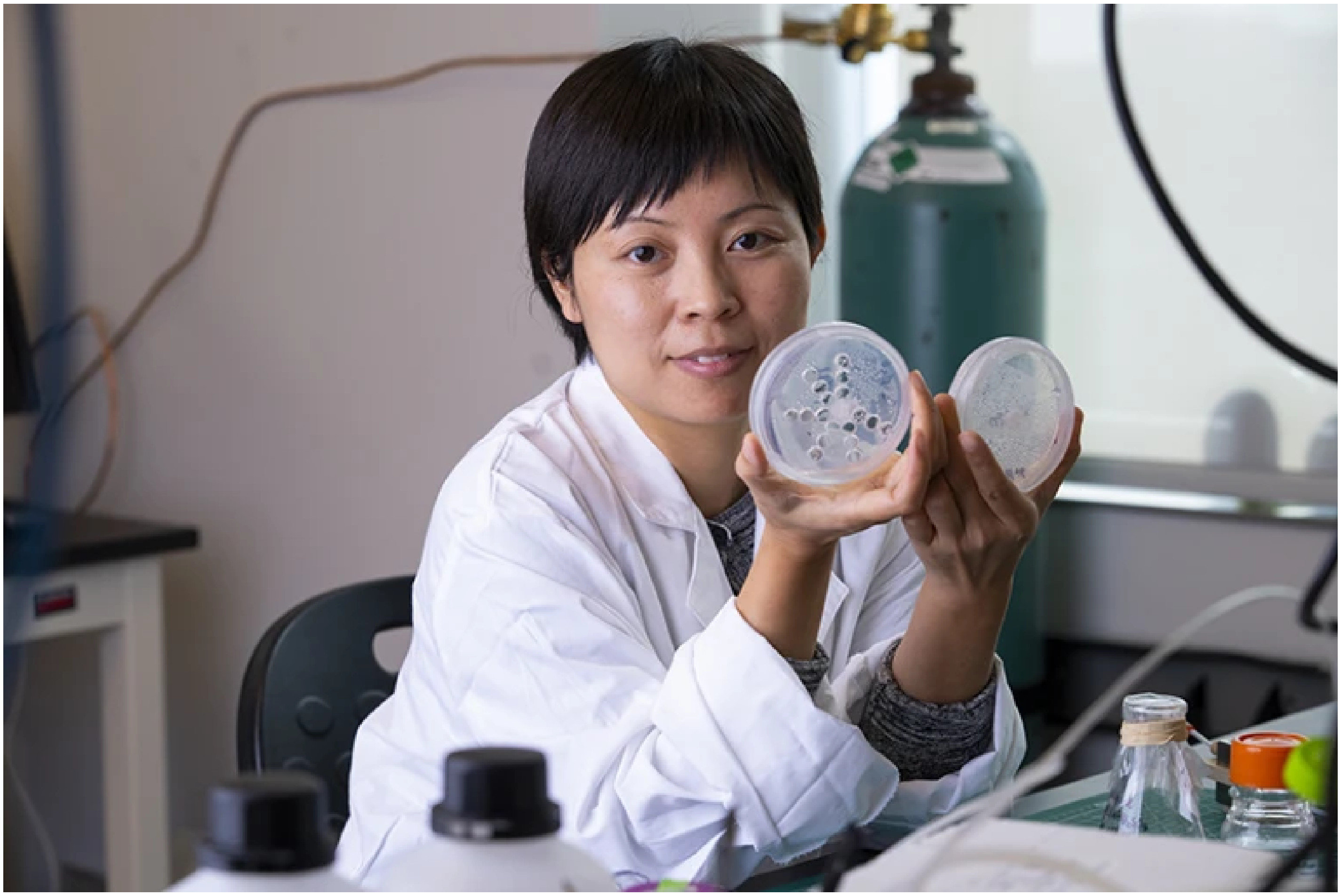
The substances also accumulate in people, and are thought to contribute to reproductive issues, impaired immune function and even cancer. Over the past two decades, concern about these forever chemicals has grown, leading to the imposition or proposal of regulations to cap their presence in water in the United States, the European Union and the United Kingdom.

But 'forever' might be a shorter time than previously thought. Scientists, including Thagard, are developing methods to break down PFAS into fluoride and carbon dioxide, which are not dangerous in the small amounts produced. These approaches to degrading the molecules have arisen in the past few years and could become widely available in just a few more. The big questions are where in the water cycle to deploy them, and which method makes the most economic sense.

Treatment technologies by themselves won't completely solve the problem of PFAS pollution. For one thing, the number of possible molecules based on the carbon–fluorine bond is vast, making it difficult to know for certain whether a particular method can tackle each one. "There are new ones being put on the market each year," says Timothy Strathmann, a civil and environmental engineer at the Colorado School of Mines in Golden. It can also be difficult to measure some of these molecules, especially at low concentrations. The sheer number of possible molecules, plus their stealthiness, are an ongoing challenge, Strathmann says. "This is why we need to also keep up with our ability to detect and sense these chemicals. Because if you don't know what you're looking for, you don't find it."

Electrical zapping

Thagard's water-treatment technique relies on electrical discharge plasma[1]. She puts water contaminated with PFAS in a reactor and pushes bubbles of argon gas through it. The PFAS is attracted to the interface between the water and the bubbles, and rides them to the surface of the water. The atmosphere above the water is also argon — chosen because it has a high density of electrons. High-voltage pulses of electricity flow between electrodes near the surface of the water, knocking electrons loose from the argon atoms and turning the insulating gas into a conducting plasma.



Environmental biochemist Susie Dai is using a fungus to help break down 'forever' chemicals. Credit: Michael Miller, Texas A&M AgriLife

The process delivers enough energy to break the carbon–fluorine bonds. If any PFAS is left, it's at concentrations too low to detect, below the parts-per-billion level. The fluoride and carbon dioxide that are produced from the disintegration of PFAS are absorbed by the water, but in amounts that Thagard says are too small to be concerning. However, the mechanism that causes the bonds to break — something that was never expected to happen — is still unclear. "The science is largely unknown," she says. "We are doing extensive research from the fundamental side."

Thagard and her colleagues carried out a field test on PFAS-polluted water at Wright–Patterson Air Force Base, outside Dayton, Ohio, in 2019 and showed that they could treat 4 litres of water and reduce the amount of PFAS to below the health-advisory level of the US Environmental Protection Agency in a couple of minutes[2]. That was using a crude system, she says; an optimized reactor could treat about 40 litres per minute. The US military has been funding research, including Thagard's work, into cleaning up PFAS because the long-time use of firefighting foams has contaminated many bases.

Thagard is chief executive of DMAX Plasma, a start-up firm she founded in Potsdam to commercialize the technology. The start-up has sold small systems to military and industrial customers. Its standard treatment unit, the company says, requires less electricity than most household electric ovens. With some engineering work, Thagard says that the systems could be scaled up to meet the needs of water-treatment plants.

Under pressure

Another effort to destroy PFAS is being led by Aquagga, a water-treatment start-up company in Tacoma, Washington, in collaboration with Strathmann. It is using a technique called hydrothermal alkaline treatment (HALT), which involves adding an alkaline substance such as sodium hydroxide to the PFAS and heating it to 350 °C under high pressure (roughly 160 times atmospheric pressure)[3]. Under these conditions, the hydroxide draws the fluorine to itself and destabilizes the PFAS molecules. Using high-resolution mass spectrometry, the researchers found that after treating a sample of water containing PFAS they had extracted as much fluoride as should have been bound up in the PFAS to begin with — suggesting it had all been broken down.

In the absence of destructive technologies, PFAS in water systems has been filtered out and sent to landfill or an incinerator. But even burning doesn't destroy all the PFAS, which can be spread by smoke or ash from the incinerator or leach out of landfill. Neither process results in the substances being removed from the environment permanently, the way that the destructive approach does.

Some sort of filtration or separation process to increase the pollutant-to-water ratio will probably be a step in any PFAS-destructive technology. "You're not going to treat a million gallons with the destructive process," Strathmann says. Indeed, the HALT method that Aquagga is developing works with PFAS that has been caught by an activated-carbon filter. So far, the pilot versions can treat only around 4–8 litres of concentrated PFAS per hour, but the company is working to scale that up. It's taking orders for systems that can treat up to 75 litres per hour and developing ones that will treat nearly 600 litres per hour.

Some attempts to destroy PFAS have only succeeded in breaking long-chain molecules into smaller ones with fewer than six carbon atoms. The HALT method seems to be more versatile. "This process applies across the full spectrum, from the very shortest chains, with only one carbon, all the way to the longest chain we've tested", with ten carbon atoms, Strathmann says. That means it should destroy any PFAS, even those that regulatory agencies have not yet listed as of concern[4,5].

A sound technique

In addition to heated chemicals or bright plasma, high-frequency sound waves might also provide the energy needed to break up the molecular chains, by knocking the fluorine atoms loose. Jay Meegoda, a civil and environmental engineer at the New Jersey Institute of Technology in Newark, is among those working on this approach — known as sonolysis. He sends sound waves at a frequency of about 1 megahertz into a concentrated solution of PFAS[6]. This ultrasound creates bubbles in the water that are only a few nanometres across.

Meegoda keeps pouring acoustic energy into the solution until the bubbles become unstable and implode. That releases a burst of energy, raising the temperature of the water that immediately surrounds the bubbles to 5,000 °C for about 10 nanoseconds. Although brief, the heating "is good enough to break all the molecular bonds", Meegoda says. Everything in the immediate vicinity of the bubble gets broken down to individual atoms, even the water. Hydrogen and oxygen atoms quickly recombine as water. Carbon atoms from the PFAS join with oxygen to become carbon monoxide, and then carbon dioxide. Fluorine atoms form fluoride ions.

Meegoda is working with Tetra Tech, an engineering services company in Pasadena, California, and hopes to run a pilot project with his technology in 2024. He expects to see some sort of PFAS degradation technology, whether his own or another, on the market in about two years.

Meegoda, Strathmann and Thagard, along with many other researchers, are focused on degrading PFAS at existing water-treatment facilities, where the chemicals would have to be concentrated before destruction. But Michelle Crimi, a civil and environmental engineer and a colleague of Thagard's at Clarkson, is taking the attack closer to the source. She wants to use a version of sonolysis to handle polluted ground water. Her idea is to build horizontal wells at contaminated areas, such as air-force bases or industrial sites, where there is already a high concentration of PFAS. "We don't want to treat extremely low concentrations and huge volumes of drinking water indefinitely," Crimi says. "That's super expensive." As the ground water slowly flows through the well — it could take two days to traverse a 46-centimetre well — an ultrasound system hits it with sound waves at frequencies in the mid-kilohertz range[7]. In the same way as Meegoda's sonolysis system, the sound waves deliver enough energy to create bubbles in the water and break apart the PFAS molecules. The water would then continue on its natural course, into rivers, lakes or the aquifers that feed more-familiar vertical wells. "Our goal is to stop the contaminated water from reaching the drinking-water wells," Crimi says.

Crimi has co-founded a start-up company — RemWell in Potsdam — to commercialize her technology. She launched a field test in late October at Peterson Space Force Base in Colorado Springs, Colorado, to gather data on how well the system works.

Let it rot

Leaning towards a more naturalistic approach, Susie Dai, an environmental biochemist at Texas A&M University in College Station, is working on a technique using bioremediation, which relies on living organisms to break down the PFAS. "Bioremediation is typically cheaper than any other chemical or mechanical process, because you have an organism that's growing by themselves do the work," she says.

Dai starts with maize (corn) stover — the leaves, stalks and cobs that remain after the maize is harvested. She separates its two main components: the cellulose that makes up plant cell walls and fibres, and the lignin that gives the stalks their stiffness. She then modifies the lignin by treating it with polyethylenimine to add functional groups, then mixes it back together with the cellulose to form a fibrous, organic filter material that can catch and hold the PFAS molecules[8]. Finally, Dai adds a fungus called *Irpex lacteus*, or white-rot, that commonly grows on fallen trees. The fungus devours the PFAS, using enzymes to break it down into more benign molecules. It also eats the filter material.

Dai still needs to measure whether the fungus fully breaks down all of the contaminant and produces pure fluoride, or leaves behind some chains. “I think it’s pretty promising if PFAS are disappearing from the environment,” she says. “It is still important for us to know what the degraded products are, but it’s less important than the removal of the parent molecule.” She is looking for a site where she can test her technology under real-world conditions.

Crimi would like to see the producers of PFAS pollution take further steps to shoulder the costs of cleaning up the problem, which tends to disproportionately affect lower-income communities. “It’s tricky with PFAS, because the solutions are really just emerging. There’s still a lot of work to do to really inform what is the most sustainable and cost-effective way to address the big problem,” she says.

Still, she’s optimistic that the world won’t be stuck with forever chemicals eternally. “I always say, ‘Forever no more.’” Scaling up the various techniques now under development would turn that hope into a cleaner-water reality.

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