‘FOREVER CHEMICALS’ – IT’S TIME FOR ACTION ON PFAS

PFAS are synthetic chemicals that have been shown to be extremely harmful to health and the environment, so PFAS-free alternatives have been developed. However, historical contamination remains a major concern and astonishingly many products still contain PFASs or use (and discharge) them in their manufacturing processes.

If you don’t like your eggs to stick to the frying pan, and you don’t want the grease in your take-away burger to leak, or if you want your furniture to be stain resistant, and your outdoor clothing to be both waterproof and breathable; you are almost certainly using products that still contain PFAS. So, should you worry? The short answer is ‘yes’, the long answer is:

Background

A large group of synthetic compounds known as the ‘Forever Chemicals’ are growing in notoriety as a result of their toxicity, persistence and ability to bioaccumulate. These chemicals are in a group termed per- and poly fluoroalkyl substances (PFAS), and in recent years have become the subject of intense media and regulatory attention, as a result of increasing instances of detection in drinking water above safe limits.

The actor Mark Ruffalo recently starred in the gripping 2019 film Dark Waters, in which he plays the role of real-life lawyer Robert Bilott in a fight against the chemical manufacturer DuPont. The film is based on a New York Times Magazine article “The Lawyer Who Became DuPont’s Worst Nightmare” by Nathaniel Rich, which itself was based on the book “Stain-Resistant, Nonstick, Waterproof and Lethal: The Hidden Dangers of C8” by Callie Lyons.

The titles of the film, article and book provide an insight into the subject matter which relates to pollution from PFOA - sometimes referred to as C8 (8 carbons in the molecule) - or perfluorooctanoic acid, which is a PFAS.

PFAS free waterproof clothing is now available from manufacturers such as Paramo

The problems associated with PFASs

PFASs are organofluorine chemical compounds that have multiple fluorine atoms attached to an alkyl chain. All PFASs persist indefinitely in the environment, either in their original form or after breaking down into a smaller number of ‘dead-end’ or terminal perfluorinated compounds. Long-chain PFASs bioaccumulate in humans and animals, with the more mobile short-chain PFASs accumulating in fruits and vegetables. Some PFASs are known to cause significant health impacts, but relatively few have been studied. Nevertheless, most are considered moderately to highly toxic, particularly for children’s development.

The most comprehensive epidemiological studies linking adverse human health effects to PFASs, particularly PFOA, come from the C8 Science Panel, which also featured in the Dark Waters film. The Panel measured PFOA blood serum concentration in 69,000 individuals from around DuPont’s Washington Works Plant and found a mean concentration of 83.0 ng/mL, compared to 4 ng/mL in a standard population of Americans. The Panel found that there was a ‘probable link’ between PFOA and kidney cancer, testicular cancer, thyroid disease, high cholesterol, pre-eclampsia and ulcerative colitis.

Why are PFASs manufactured?

Since the 1940s these chemicals have been used in a wide variety of consumer products and industrial applications because of their chemical and physical properties, including oil and water repellence, temperature and chemical resistance, and surfactant properties. PFASs have been used in firefighting foams, the manufacture of non-stick coatings for frying pans, food packaging, pharmaceuticals, pesticides, cosmetics, furniture and outdoor clothing, paints and photographic materials.

In many countries, certain PFASs have been replaced by alternative chemicals for which there is significantly less understanding of their environmental impact. For example, PFOS and PFOA have been largely replaced by other PFAS in the USA under a 2006 voluntary agreement brokered by the EPA with eight companies, including DuPont. So alternative PFASs are now found in many products; with PFOS and PFOA still found in products sourced from regions of the world where these chemicals are not yet banned.

With increasing pressure from environmental organisations, manufacturers are seeking alternatives to PFASs. For example, a leading manufacturer of outdoor clothing has said that they will ensure no PFCs of environmental concern are released in the manufacturing, use, and disposal of its products. It is not entirely clear what they mean by this because all PFASs are fluorinated and persistent, and PFASs are used in the manufacture of PTFE, with expanded PTFE still widely used as a waterproof and breathable fabric. The good news is that PFAS-free waterproof breathable outdoor products have been available from companies such as Páramo for many years.

Delipac sandwich pack – compostable, recyclable and PFAS-free

PFAS-free products

Páramo have completely eliminated PFAS from their lines. Instead of relying on forever chemicals to create an impermeable membrane, which Páramo founder Nick Brown likens to a “highly engineered plastic bag,” Páramo uses Nikwax, an all food-grade and non-persistent coating for outdoor gear. Brown says: “Páramo’s garments are ‘directional’ which means that the fabric fibers have been designed to push beaded water off their surface, in the way rain runs off a tiled roof. You can even wash your old jacket with Nikwax to re-waterproof it.”

PFAS free packaging is now available. For example, Delipac board contains no plastic and replaces the plastic coated/laminated paperboard that is used in food packaging. It is biodegradable, compostable and recyclable, and was recently tested and demonstrated to be free from PFAS. Delipac CEO Paul Spring says: “Our paperboard has been specifically developed for the food and beverage markets, and has been tested with reference to CEN/TS 15968 by LC/MS/MS for 33 different PFASs. It has also been shown to be free from the Substances of Very High Concern (SVHC) specified in the EU REACH regulation and the Waste Framework Directive.”

The sustainable packaging start-up Notpla is on a mission to make packaging disappear by pioneering the use of seaweed as an alternative to single-use plastic. Notpla developed ‘Ooho’, a flexible packaging for beverages and sauces, that does not contain any PFAs and is also 100% biodegradable, home compostable and can even be eaten. Commercial Director Tristan Kaye says: “To date, Oohos have replaced over 300,000 single-use plastic cups

and bottles at events such as the London Marathon (36k Oohos with Lucozade), Roland Garros (with Tropicana), the 2019 London Cocktail Week (Glenlivet Capsule with Pernod Ricard) or DGTL Festival (Lipton).

"Ooho can also be used for sauces and condiments for the take-away industry, and Notpla is currently working with a major international condiments manufacturer on the future of entirely natural sauce sachets."

Notpla is now challenging other applications of plastic such as the thin layer of plastic on board-based takeaway food boxes. Notpla coating is naturally biodegradable and provides both a grease-proof and water-resistant barrier, and is applied to a unique board that also incorporates agricultural grass. Both the Notpla board and coating are so natural that they will break down in the environment in less than a month, leaving no residue, and the company is now working with Just Eat Takeaway to make these boxes available to restaurants across the UK.

With respect to the testing of packaging materials Tristan says: "We think that current industry practice just doesn't go far enough; the end-consumer sees 'home-composting' as a great stamp of something being 'natural', but we know that the test is mostly about how quickly something breaks down to tiny pieces. It largely ignores what gets left behind. Everything we do we test in our labs with, what we think is the ultimate proof-test; worms. Our materials are entirely eaten by them, in some cases even before an orange peel."

PFAS-free sofa from IKEA

PFAS-free firefighting foam products are now commercially available, and are discussed in more detail below.

Commenting on its efforts to remove PFAS, a spokesperson from IKEA said: "We offer many PFAS free products such as detergents, oils, paints etc. All of our textiles, such as meter fabrics, table cloths and sofa covers are also free from PFAS. At IKEA we are passionate about responding to and offering our customers options based on their own ambitions, passions and needs. Whether it's the price, design, functionality, or materials, we are always searching for new and innovative approaches to strengthen our product range. IKEA's work on chemicals is aimed at avoiding any harmful effects on health and the environment, throughout the entire lifecycle of the product."

How do PFASs threaten humans?

According to Dr Ian Ross from Tetra Tech, the global consulting and engineering services provider, the main threat to humans is from drinking water. "PFASs can and do enter the food chain, but given the persistence and mobility of many PFASs, most of the contamination issues that we work on involve groundwater contamination where a significant source of PFAS remains, bleeding PFAS to ground for decades – such as at manufacturing sites or locations where firefighting foams have been used regularly for training purposes."

Large polymer PFASs such as PTFE are often considered to be too large to be taken up by our bodies, and therefore unlikely to cause us any harm. However, harmful non-polymer forms of PFAS are used in the production of PFAS polymers, and these harmful forms can be discharged into the environment, and can also be created as the polymers break down. Initially, PFOA and PFOS were the most commonly used PFAS in the production of these polymers, but they are now heavily restricted or banned due to their impacts on the environment and human health. Around ten years ago, these chemicals were replaced by 'GenX' (a short-chain PFAS substitute for PFOA in fluoropolymer production) and other similar chemicals. More recently, there has been an increase in the use of 'C6' PFAS in firefighting foams, some of which are themselves now under restriction or being considered for restrictions.

Notpla Just Eat Box

It is possible that there may be PFASs that are not directly harmful to humans or the environment, but the life-cycle of any product needs to be fully understood. Additionally, when it comes to potential harm; the absence of evidence should not be regarded as evidence of absence.

Unlike many other toxins, humans can only slowly excrete some PFASs, so levels build as an exposed person ages, if exposure continues - from tap water for example. Human biomonitoring has detected a range of PFAS in the blood of European citizens. Whilst the levels of PFAS, PFOA and PFOS are decreasing, levels of more 'novel' PFASs are increasing. In some areas, concentrations of PFOA and PFOS in the most exposed citizens were above proposed benchmark levels for adverse effects in humans.

PFAS in the environment

The persistence and mobility of PFASs are the key factors behind their ubiquitous presence in the environment. PFASs have been detected in air, soil, plants and biota, with the highest levels found in areas close to industrial production, manufacturing and application sites. In many cases this has led to the contamination of water, accumulation in plants, and increases in human dietary exposure.

A case study by the World Health Organization (WHO) documents PFAS contamination of the drinking water of the Veneto region in Italy. Industrial activity in the area had polluted both surface waters and ground water, as well as the drinking water of approximately 127,000 citizens (WHO, 2017). Monitoring conducted by the authorities of the Veneto Region found PFOS in 63-100% of the locations sampled and PFOA in 100% of the sites; exceeding the EU drinking water limit by a factor of 130 for PFOS and 66 for PFOA in samples taken in the Veneto Region.

Since the 1960s, Aqueous Film-Forming Foams (AFFFs) containing PFAS have been commonly employed in firefighting procedures and in associated training activities. As a result, PFAS has accumulated in the soil and groundwater at many airports, military sites, petrochemical plants and firefighting locations. Contaminated surface and groundwater can travel well beyond the original source area, with some PFAS plumes impacting more than 250 km2 of groundwater (Yingling 2015). Many firefighting organisations are therefore transitioning to fluorine free firefighting (F3) foams. Writing in International Airport Review magazine in 2019, Dr Ian Ross concluded: "The growing concerns regarding drinking water impacts from PFOS, PFOA and PFHxS, are driving a dramatically increased regulatory, media and political focus on the wider class of PFASs. At the same time the performance of F3 foams at extinguishing fires has markedly improved such that its performance is comparable to AFFF. So now the balance between the perceived risk of transitioning to F3 foams, versus the potential harm caused and liabilities associated with continued use of PFAS based foams, makes evaluation of how to move away from C8 and C6 PFAS based foams a wise commercial decision.

"Transitioning to the new generation F3 foams is a positive step if airports have not already made this choice, as they are now effective for fire extinguishment and have negligible long term environmental hazards."

Manufacturers of PFAS-free firefighting foam products can now apply to be 'GreenScreen Certified' and one of the first companies to do so was Angus Fire, based in Yorkshire, UK. Global Product Manager David Plant says: "We offer a wide range of fluorine free foams, and have done so for a number of years. We have carried out many large-scale fire tests with LASTfire and some of the major oil companies to prove efficacy, and the GreenScreen Certification will support our products' environmental credentials. We now have many users of our PFAS-free products around the world including some of the major chemical and oil & gas companies, as well as airports, military and municipal fire and rescue services."

PFAS remediation

Granular activated carbon (GAC) is commonly employed as an adsorbent to remove PFAS from soil and liquids. However, given the mobility and persistence of PFASs, the scale of treatment can be large (and costly), and the remediation process may need to run for several years. Once the GAC has been exhausted it may be regenerated at a high temperature to destroy PFAS compounds that were adsorbed by the carbon.

Alternative techniques have also been developed. For example, the foam fractionation process utilises micro-bubbles of air to extract PFASs. Multistage foam fractionation columns are employed to remove more than 99% of PFAS from liquids such as groundwater and leachate.

PFAS regulations

PFOS and PFOA are listed under Annex A of the Stockholm Convention on persistent organic pollutants (POPs). Parties to the Convention (which includes most countries) should therefore eliminate the production and use of these chemicals.

In Europe, PFOS is restricted under the EU POPs Regulation (2019). PFOA and its precursors are currently restricted under the REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) regulation (2006), including their presence in products made or imported into the EU. This will soon be replaced by a new restriction under the POPs Regulation, which will have more limited derogations, following a decision taken at the Stockholm Convention.

In September 2020, the European Food Safety (EFSA) set a new safety threshold for the PFAS – a group tolerable weekly intake (TWI) of 4.4 nanograms per kilogram of body weight per week. The announcement reported toddlers and other children as the most exposed population groups, and exposure during pregnancy and breastfeeding is the main contributor to PFAS levels in infants.

A number of other PFASs are on the REACH list of Substances of Very High Concern (SVHCs). In June 2019, GenX was the first chemical added to the SVHC list on the basis of its persistent, mobile and toxic properties posing a threat to drinking water and the environment. Several PFASs are on the Community Rolling Action Plan for evaluation over the coming years.

In the USA, the Toxic Substances Control Act (TSCA) requires the EPA to evaluate the safety of existing chemicals via a three-stage process: prioritization, risk evaluation, and risk management. However, the US edition of the Guardian newspaper is running a campaign known as 'Toxic America' comparing regulations in the US with the EU; it says the REACH laws: "require manufacturers to prove to regulators that a product is safe before it can be used. The US has similar rules for new chemicals entering the market but no such precautionary principles for the thousands of potential toxins already in use."

You can even wash an old jacket with Nikwax to re-waterproof it

The Biden administration seems to be ramping up action in chemicals such as PFAS. For example, in May 2021 the US EPA added new PFAS compounds to its Drinking Water Treatability Database. "As EPA scientists and researchers evaluate technologies to remove PFAS from drinking water, we believe it's important to share this information," said the EPA's Jennifer Orme-Zavaleta. "This is exactly the kind of work that our new Council on PFAS is working to support so that our federal, state, local, and Tribal partners have the information and tools they need to help protect our nation's drinking water from PFAS and other contaminants."

The Drinking Water Treatability Database presents an overview of different contaminants and possible treatment processes to remove them from drinking water. With this update, the EPA added treatment information for eleven PFAS compounds, which brings the total number of PFAS in the database to 37, including PFOA and PFOS.

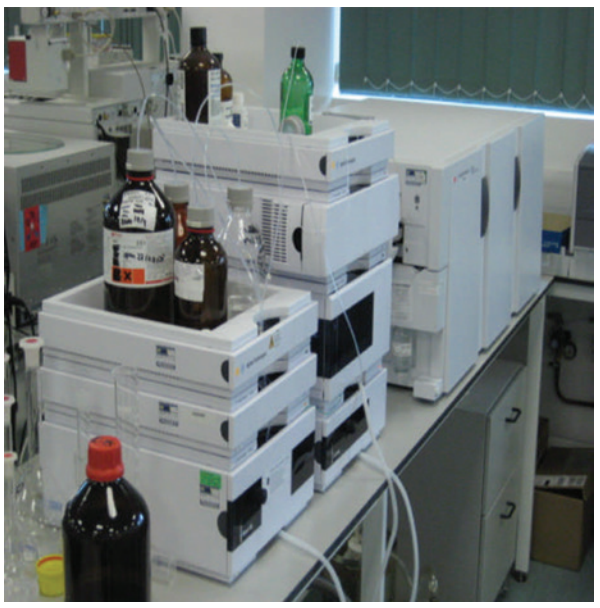
Certain PFASs are authorised by the US Food & Drug Administration (FDA) for limited use in cookware, food packaging, and food processing equipment. This includes grease-proofing agents in fast-food wrappers, microwave popcorn bags, take-out paperboard containers, and pet food bags.

PFOSs and their derivatives are included as a priority hazardous substance under the EU Water Framework Directive (2013), with a very low Environmental Quality Standard (AA-EQS) limit value of 0.65 ng/L (0.00065 µg/L) for inland surface waters and 0.13 ng/L for seawater.

The EU recently revised the Drinking Water Directive (2020/2184) and reduced the acceptable level to 100ng/L for 20 types of PFAS and 500 ng/L for all PFASs.

Writing in the UK edition of the Guardian newspaper, Rachel Salvidge reports: "the drinking water inspectorate (in the UK) has only set the 10ng/L limit for PFOS and PFOA, and there are no limits on the wider group of chemicals. In contrast, Denmark has a limit of 100ng/l for the total of 12 PFAS, with lower levels proposed for PFOS of 3ng/L; Sweden has set a 90ng/L for the sum of 11 PFAS; and Bavaria has regulated 13 individual PFASs to a range of limits between 0.1 micrograms (µg)/L and 10µg/L.

In February 2021 the US EPA announced that with the final Regulatory Determinations for PFOA and PFOS, they will implement the national primary drinking water regulation development process for these two PFASs. The Regulatory Determinations also outline avenues that the agency is considering to further evaluate additional PFAS chemicals and provide flexibility for the agency to consider groups of PFASs.



PFAS analysis has been one of the fastest areas of growth for ALS laboratories

How to measure PFAS

PFASs are challenging contaminants to measure because most cannot be detected by conventional analytical techniques. Furthermore, many applications involve complex mixtures of PFAS chemicals. Nevertheless, PFOS (perfluorooctane sulfonic acid) and PFOA (perfluorooctanoic acid) are the best known examples and have become a major focus of regulatory attention.

Conventional methods allow for the analysis of around 15-20 different compounds (e.g. US EPA Method 537), which means that many compounds will remain undetermined. These include a significant number of polyfluoroalkyl substances which, under certain conditions, can be converted into perfluoroalkyl acids (PFAAs). Several PFAA precursors containing a C8-perfluoroalkyl chain, including C8 sulphonamide compounds and 8:2 fluorotelomer alcohols, have been shown to partially transform to PFOA.

The behaviour of PFAS can vary depending on the composition of the sample; the presence of co-contaminants, and the impact of remediation activities. So, a new analytical approach, known as the 'TOP Assay', was launched in 2015 by ALS, the global testing, inspection, certification and verification company, in collaboration with Dr. Ross.

Explaining the importance of the Total Oxidisable Precursor (TOP) Assay, Geraint Williams from ALS says: "The analysis of PFASs has been one of the fastest areas of growth for our specialist laboratories in recent years. This demand has come from areas where PFAS concentrations are likely to be at their greatest, such as at fire training areas where firefighting foams have been used extensively.

"Extremely low levels of detection are necessary, which would be beyond the capability of most laboratories, but here at ALS we have developed a method using liquid chromatography with tandem mass spectrometry (LC-MS/MS) to meet these requirements. Polyfluoroalkyl substances have the potential to transform in the environment to ultimately create PFAAs. It is extremely difficult to identify many of the PFASs present in complex mixtures because of the lack of availability of analytical standards for many proprietary polyfluoroalkyl substances."

The TOP Assay has become a powerful tool in the analysis of PFAAs and difficult to measure PFASs. Chemically oxidative conditions are created to convert precursors in the sample to PFAAs. This is achieved by hydroxyl radicals, which are formed under heated alkaline conditions with potassium persulfate and sodium hydroxide prior to incubation.

The difference in concentration of PFAAs in the pre- and post-oxidized samples provides an estimate of the unidentified precursors. The TOP Assay also provides an indication of the perfluoroalkyl chain length of the precursors, which can assist in the assessment of PFAS contamination and the potential for bioaccumulation.

Geraint emphasises the importance of measuring branched and linear isomers of PFOS: "If these are not reported, the results might be underestimating PFOS concentrations by 20-30% depending on the original manufacturing process," he explains. "The presence of linear and branched isomers also has implications for partitioning, transport and bioaccumulation."

PFAS – should we worry?

International bans on widely used long-chain PFASs have led to their substitution with a large number of shorter chain PFASs. Several of these alternatives are now under regulatory scrutiny in the REACH Regulation because of the concern they pose for the environment and for human health. However, with thousands of chemicals falling into this group, it will never be possible to fully assess the toxicology of each. It is therefore important that regulatory pressure is applied to prevent organisations from developing and utilising chemicals without prior understanding of their toxicity, persistence and ability to bioaccumulate.

For most of us, the main pathway for us to bioaccumulate PFASs is by the ingestion of contaminated water or food, so we will need to seek confirmation from food, beverage and drinking water providers that their products are 'safe'.

The environmental charity, Fidra, has been calling for the removal of PFAS since testing revealed widespread use in UK food packaging. In February 2021, Fidra delivered almost 12,000 signatures to the CEO's of the UK supermarkets Aldi, ASDA, Co-op, Iceland, Lidl, Morrisons, Marks and Spencer, Tesco, Sainsbury's and Waitrose, urging action to remove these highly persistent chemicals from food packaging.

Respondol fluorine free (F3) foam concentrate for extinguishing and securing all types of flammable liquid fires and Class A incidents

In response Fidra announced that 5 out of the 10 supermarkets approached are now actively working with suppliers to reduce PFAS use, with both Morrisons and Marks and Spencer aiming to remove PFAS from own brand food packaging by the end of 2021, and Iceland already free of PFAS across all own brand products.

PFASs are already ubiquitous in the environment and are detectable in the blood of most people. However, the main sources of PFASs are locations at which there are or have been high concentration levels, so a major factor in reducing exposure will be public demand for alternative firefighting foams and for products that do not contain PFAS.

The recent publicity, including the Dark Waters film, will help to raise the public perception of this issue, and if consumers start to look for 'PFAS free' or 'PFC Free' products (that are labeled as such), the motivation for manufacturers to find alternatives will increase.

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