Emerging contaminants: is the UK equipped for the challenges?

Ian Ross PhD, Jonathan Miles PhD, Jake Hurst (Arcadis), and Paul Gribble (ALcontrol Laboratories) outline the origin of the contaminants, emerging analytical methodology, regulatory responses and remediation options.

The definition and terminology associated with "emerging contaminants" has evolved rapidly in the past few years. Contaminants may be classed as "emerging" when the risk to human health and the environment is not entirely understood. As our knowledge of the fate, transport and toxicology of emerging contaminants advances, there is a need to be appropriately protective. As the science is often evolving much more rapidly than regulation, which can be geographically disparate, there is a risk that extensive exposure to emerging contaminants occurs before regulations are enforced.

Over the last 18 months, driven by detections in public water supplies and increasing health concerns, poly- and perfluoroalkyl substances (PFAS) are emerging as a challenging class of contaminants, one for which understanding of environmental behaviour is growing but management strategies are limited. This article is intended to raise awareness about this class of compounds and highlight that the current management toolkit is inadequate to appropriately assess PFAS in order that risks and liabilities can be effectively managed.

PFAS are a product of the synthetic chemical industry. Their unique properties such as their ability to repel both water and oils, high thermal stability and surface tension effects, have seen many thousands of new fluorinated molecules produced and used across a huge range of industrial applications and consumer products. PFAS totally resist biodegradation, making them almost ubiquitous in the environment; and some tend to bioaccumulate within the food chain, raising health concerns.

PFAS are a very diverse class of chemicals comprising thousands of differing compounds, united by the common structural element of a fully fluorinated alkyl chain, known as the perfluoroalky group. The whole PFAS molecule may be either fully (per-) or partly (poly-) fluorinated, but each compound always contains a perfluoroalkyl group .

The presence of the perfluoroalkyl group means that they all share a similar environmental fate in that they biotransform to make common daughter products, perfluorinated compounds which are extremely persistent and likely to contaminate aquifers for millions of years to come.

In the UK, awareness has primarily focused on two perfluorinated compounds, perfluorooctane sulphonic acid (PFOS), and perfluorooctanoic acid (PFOA), which, with the exception of certain high profile incidents such as the Buncefield Oil Terminal fire, have largely remained under the radar of contaminated land professionals. Additional perfluorinated compounds exist that have longer or shorter perfluoroalkyl chain lengths and these are collectively termed perfluoroalkyl acids (PFAAs).

Attention on PFAS in the UK is likely to increase, as detections in drinking water above regulatory guidelines are now reported across the world, particularly in the US, Australia, Germany, and Scandinavia. Stories of PFAS contamination are appearing regularly in the press including internationally recognised media such as the New York Times and Time magazine. Coming on top of the Flint, Michigan, water crisis, questions are now repeatedly being asked about the quality of America's drinking water supply. During January 2016 the village of Hoosick Falls in New York State had the distinction of being the first declared Superfund site due to the presence of PFOA in drinking water. Probable health effects linked to PFOA include high cholesterol, ulcerative colitis, thyroid disease, testicular cancer, kidney cancer, and pregnancy-induced hypertension[2].

A number of high profile lawsuits involving industrial manufacturers and users of PFAS have also hit the news increasing awareness of the scale and magnitude of potential liabilities.

With the increasing media attention, many regulators globally are focusing on the protection of drinking water supplies, where conventional treatment technologies, such as granular activated carbon (GAC) are available but potentially ineffective for many PFAS and generally costly due to its inefficiency.

Typical analytical methods to measure PFAS just assess the concentration of PFOS, PFOA and PFAA's, with maybe a handful of precursors and do not reflect the concentrations of total PFAS. The complexity of the chemistry of PFAS in multiple products has been elucidated and described in multiple academic publications[1,3,4] and it is clear that conventional analytical methods fail to measure the vast majority of PFAS.

We describe the evolution of advanced analytical tools to comprehensively measure PFAS using differing innovative scientific approaches which provide elegant and pragmatic solutions to assess and this manage impacts from PFAS.

A Challenging Class of Contaminants

Developed in the 1950's many distinct types of PFAS were synthesised for use in a very large range of applications, including as stain repellents for textiles, and carpeting, non-stick cookware, uses in electronics and photographic industries, water and oil resistant coatings for food packaging (eg. pizza boxes), hydraulic fluids, electroplating, and mist suppressants. They are also major components of the class B (flammable liquid) firefighting foams known as Aqueous film forming foam (AFFF) and other fluorinated foams which have been used in training exercises and fire incidents, most notably at airports, petrochemical, civil and military facilities.

Due to releases over time it is now recognised PFAS are ubiquitous in the environment at very low concentrations, having been detected in food, surface water and groundwater, soils, and in many human and wildlife populations. This ubiquity is due to the chemical characteristics that make them so useful and also impart significant stability to these chemicals in the natural environment. Whereas many

man-made chemicals will biodegrade under natural conditions PFAS do not show any indication that they will biodegrade whatsoever. Polyfluorinated PFAS do partially transform in the environment and are thus termed precursors. Precursors produce "dead end" perfluorinated daughter products, the PFAAs, including PFOS and PFOA, which are extremely persistent and can be more mobile in groundwater than the precursors they originated from.

Discrete high concentration sources of PFAS may include fire training areas, manufacturers of derivative products (such as waterproof fabrics, packaging etc.) and landfills where domestic waste impregnated with PFAS will migrate into leachate. PFAS plumes can migrate very significant distances from the initial source zones, with plumes spanning miles in length being reported. The complexity of the PFAS chemistry and the surface active nature of PFAS can also lead to significant PFAS mass in the source zone, slowly contributing to the evolving plume.

Global trends in replacement & regulation

PFOS was added to Annex B of the Stockholm Convention in 2009 as it was classified as persistent, bioaccumulative and toxic. It has been reported by European regulators that PFOA will be added to the Stockholm convention during 2016.

The manufacture and use of PFOS and PFOA which both contain 8 carbon atoms has, with some exceptions, largely been phased out in the western world. Replacement has often come in the form of shorter chain PFAS containing between 4 and 6 carbons (e.g. perfluorohexanoic acid (C6) or perfluorobutane sulphonate (C4)) which have been shown to be less bioaccumulative[5]. However, there is limited available scientific information on the toxicology of shorter chain species and all PFAS, including both long and short chain molecules, are environmentally persistent. If drinking water is impacted with long or short chain PFAS there is still the potential for continued daily exposure, even if the short chain PFAS are excreted rapidly. The shorter chain compounds are more mobile in groundwater than the longer chain molecules and are also much more difficult and expensive to remove from water using current commercially available treatment technologies.

Regulatory standards are extremely low; for example, the European Annual Average Environmental Quality Standard for PFOS in inland surface waters is 0.65ng/L, based on modelling which assumes a conservative

amount of freshwater fish is ingested. Globally numerous fishing lakes have been closed as a result of PFAS impacts.

In the UK, Drinking Water Inspectorate guidance (October 2009) sets out a multi-tiered approach restricting concentrations of PFOS and PFOA to 0.3µg/L in its most stringent tier. The US Environmental Protection Agency has recently issued long-term exposure Health Advisory Limits of 0.07µg/L for combined PFOS and PFOA in drinking water resulting in guidance values significantly below the UK standards and potentially indicating the direction of travel for future UK regulation. In addition, more comprehensive regulations are developing to cover PFAS in certain U.S. states and European countries (e.g., Germany, Sweden and Denmark) that include the short chain replacements for PFOS and PFOA.

Understanding PFAS Fate and Transport – The Problem of "Dark Matter"

In PFAS containing commercial products such as AFFF there are a few hundred identified polyfluorinated compounds in addition to the PFAAs. Considering all manufactured PFAS formulations there are thousands of precursors. These precursor compounds will all, given time, biotransform to produce perfluorinated compounds, the PFAAs such as PFOS and PFOA, which do not transform further and therefore persist in the environment; this is illustrated as a funnel [Figure 2]. Therefore, there are conceptual & analytical challenges to overcome when considering how to assess soil, sediment and groundwater contaminated with PFAS as there are thousands of additional analytes to consider (termed "dark matter"), not just PFOS, PFOA or the PFAAs.

Making PFAS dark matter visible - new analytical methods

Conventional analysis for PFAS compounds is typically based on the US EPA Method 537, a drinking water method designed to measure twelve PFAS down to ~0.01µg/L. There is variability in the suite of compounds typically included within conventional analysis which generally include only common PFAA's and a handful of known polyfluorinated precursors for which standards are available. The quantification of branched PFOS isomers is also not frequently undertaken.

The key limitation in conventional PFAS analysis is that the thousands of compounds comprising PFAS dark matter have, to date, been undetectable due to the sheer number of these compounds, low awareness of

their presence and knowledge of chemical structures and lack of individual standards. Therefore, the full extent of PFAS impacts from precursors and their eventual dead end daughter products and their associated long term liabilities have not been able to be assessed.

To address this analytical challenge **Arcadis**, in conjunction with **ALcontrol** Laboratories, has recently commercialised a method called the Total Oxidisable Precursor (TOP) assay[6, 7] which is able to quantify the total PFAS mass within a sample and provide information of the perfluorinated carbon chain lengths present in the precursors at low detection limits (c. 2 ng/l and 1 µg/kg).

The TOP assay allows quantification of the sum PFAS including PFAA precursors by converting them to detectable PFAAs, via an oxidative digest. This allows the PFAAs evolved from the precursors to be measured by conventional LC-MS/MS. The digest represents a similar, but accelerated, conversion of precursors to PFAAs as dead end products. PFAAs are produced by the TOP assay digest from precursors, is as observed via microbial metabolism in the environment over many years and in vivo in higher organisms, but not exactly the same dead end PFAAs may form via each process. The TOP assay also provides indicative data regarding the perfluoroalkyl chain length of the precursors, which can assist with assessing their potential to bioaccumulate.

The value of this approach is clear. TOP assay testing of real world samples from PFAS impacted sites starkly illustrates that precursors represent a significant component of contaminant mass currently not being addressed [Figure 3]. By conducting PFAA analysis before and after the sample matrix is digested, it is possible to assess both the free PFAAs and the PFAAs which were hidden in the form of precursor
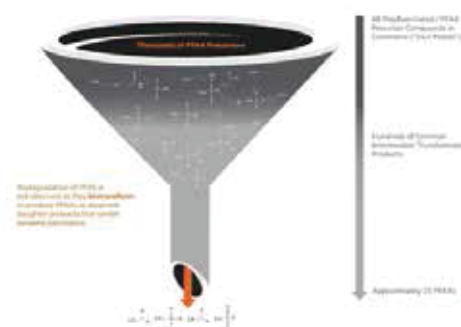
Figure 2: Aerobic Precursor Biotransformation Funnel. Source: Arcadis

compounds, currently not detectable by conventional means. In groundwater and soil samples from a PFAS impacted source zone, a 75% and 240% increase in sum PFAS concentration, respectively, were revealed upon application of TOP assay. It is also noted that the more mobile, shorter chain PFAAs currently becoming the focus of regulation globally are much more visible in the digested sample.

Arcadis also tested two further analytical techniques which assess the total organofluorine content of a sample, namely particle induced gamma emission spectroscopy (PIGE) and adsorbable organic fluorine (AOF). These methods do not speciate PFAS into perfluoroalkyl chain lengths or have detection limits in the ng/L range, so are not as sophisticated or sensitive as the TOP assay. Correlations in total PFAS concentrations from multiple samples were variable when PIGE was compared with AOF and TOP assay, indicating PIGE needs further development. An excellent correlation was observed between AOF and TOP assay demonstrating that TOP assay can comprehensively assess total PFAS concentrations [Figure 4].

Water treatment and remediation options

In terms of remediating existing contamination, typical water treatment responses to address PFAS use activated carbon, however, sorption capacities are low especially for short chain compounds which reach breakthrough very rapidly. Treatment volumes are high due to the diffuse and low concentration nature of groundwater plumes and regeneration of the carbon is also challenging (requiring elevated temperatures >1000ºC). This makes treatment with GAC costly in terms of carbon use compared to more traditional contaminants.

Alternative sorbents including silica, activated clays, and ion exchange resins are also being developed but have challenges around regeneration or the management of high concentration/low volume liquid waste streams and, to date, have not significantly replaced GAC as a treatment of choice. Reverse osmosis has also been trialled, but it is the only technology currently proven to reliably remove the very short chain PFAA from solution but is very expensive and not widely used.

Soil treatment methods include landfill (which risks just transferring the problem elsewhere), stabilization or capping using binding reagents to prevent leaching, and also soil washing which obviously requires a water treatment solution for the eluent. Destroying PFAS in soils is currently limited to high temperature incineration at >1000ºC which is prohibitively expensive. **Arcadis** has recently developed a technology to destroy PFAS in situ using a remedial technology known as ScisoR© (smart combined In-Situ Oxidation and Reduction) which has shown initial promising results at laboratory scale.
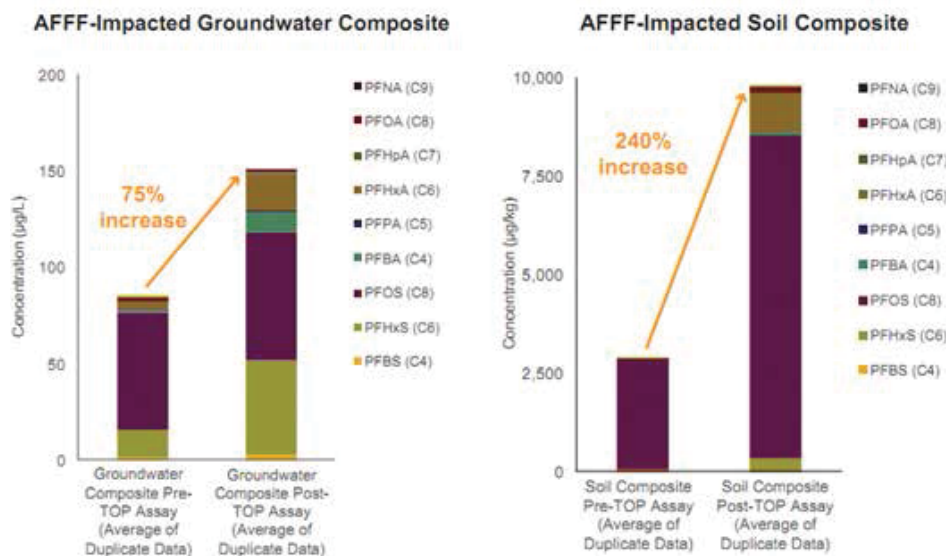
An issue coming into focus

This is a fast moving area where the science continues to develop rapidly. Globally, regulatory standards are playing catch up with advancing science and, in the US, public opinion is questioning why it took so long to act when the risks of PFOS and PFOA have been known for many years. Exposure levels for PFOS and PFOA are under review and in many cases are being extended to include shorter chain PFAAs, which are still
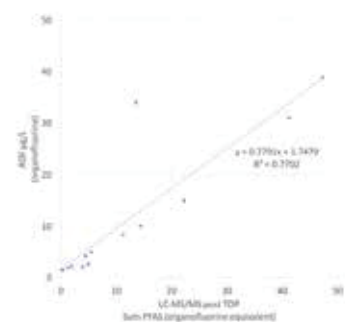
Figure 4 Correlation between TOP assay and AOF. Source: Arcadis

in widespread use and used increasing as replacements for longer chain PFAAs. Like the US, parts of the UK rely on drinking water from groundwater sources, and whilst the UK has not currently responded to global trends around PFAS, the direction of travel appears to be clear.

As expanded regulatory scrutiny is almost certain, industry will demand appropriate responses are developed cost effectively. The established toolkit will not work to adequately manage the risks of PFAS in the environment. Bespoke approaches in thinking and technology are required, TOP assay is one such new tool allowing practitioners to understand the full extent of PFAS contamination for the first time. Further tools will be needed to provide technically robust and cost effective solutions to meet the challenges of PFAS.

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Figure 3 Commercial top assay data from a fire training area. Source: Arcadis