

A Critical Review of a Recommended Analytical and Classification Approach for Organic Fluorinated Compounds with an Emphasis on Per- and Polyfluoroalkyl Substances (PFASs) in Integrated Environmental

When regulators and researchers seek to identify organic fluorinated compounds in environmental media such as groundwater or soil to determine if the compounds have potentially adverse effects, it is imperative to use the right analytical method for the task.

The question must match the method; the method must match the matrix.

“A Critical Review of a Recommended Analytical and Classification Approach for Organic Fluorinated Compounds with an Emphasis on Per- and Polyfluoroalkyl Substances (PFAS),” published October 3, 2020 in *Integrated Environmental Assessment and Management*, concluded that analytical techniques that identify organic fluorine coupled with targeted chemical analysis will yield the information needed to identify public health or environmental hazards.

Organic fluorinated compounds are so widespread that almost any water or soil analysis will detect their presence. What such analysis won't tell you, however, is whether these fluorinated compounds came from a pesticide, a pharmaceutical, the fluoride in our toothpaste, a non-polymeric PFAS or a polymer. In other words, the presence of fluorine alone does not give any information about the specific fluorinated compound that may be present, nor does it equate to the existence of a hazard.

So they can set and enforce thresholds for public health and environmental safety, regulators must identify, quantify and characterize fluorinated compounds in drinking, surface and ground water, soil, sediment and air. The current regulatory regime for fluorinated compounds differs widely among continents, countries and even municipalities. At the root of this inconsistency is how we measure and test for fluorinated compounds and what standards we apply to assess risk. The end result is different regulatory limits for the same chemical often in the same matrix.

To achieve a consistent regulatory scheme, we must apply robust, reproducible and scientifically validated methods to differentiate organic from inorganic fluorinated compounds, and among the many types of organic fluorinated compounds.

Thousands of organic or carbon-containing fluorinated compounds, mostly synthetic, are in use around the world every day as industrial chemicals, pesticides, pharmaceuticals or veterinary drugs. Fluorinated compounds are in our medicine cabinets in drugs such as Lipitor and Celebrex, in our flat screen televisions as liquid crystal displays and in our fire extinguishers. Production and use of some of these products send fluorinated compounds into the environment which may then be detected by non-targeted analytical methods.

Per- and Polyfluoroalkyl Substances or PFAS also contain fluorine, but they are structurally, chemically and toxicologically different from the compounds mentioned above. PFAS are carbon chains in which all or most Hydrogen (H) atoms are replaced with Fluorine (F) atoms plus a perfluoroalkyl group. PFAS can be either polymers or non-polymers, and there are more than 4,700 of them.

Within the PFAS classification, there are also significant differences in structure, stability, toxicology and molecular weight. These differences are instrumental in determining the environmental fate of different PFAS.

For example, perfluorooctanoic acid (PFOA) is a non polymer PFAS; a perfluoroalkyl acid (PFAA). Like many other PFAAs, PFOA has a low molecular weight and is water soluble. It can dissolve in water and be dispersed in air, enabling it to travel far from its point of manufacture, use or disposal. It also has a long biological half-life. PFAAs like PFOA may be found in surface water, groundwater and drinking water.

In contrast, high molecular weight fluoropolymers such as polytetrafluoroethylene (PTFE) and fluorinated ethylene propylene (FEP) are very high molecular weight polymeric PFAS. They are insoluble in water and are most likely to be found near their point of use or disposal. They do not degrade under environmental conditions. These fluoropolymers are unlikely to be present in water resources.

Another type of polymer PFAS, side chain fluorinated polymers, also have high molecular weights and limited mobility, but they can degrade over time in the environment to non polymer PFAS, which can then become mobile and impact water resources.

While valid analytical chemistry measures can detect the presence of PFAS in the environment, they cannot determine unequivocally the source of the PFAS.

Misattribution of sources may unnecessarily alarm the public or prompt ineffective regulation. Incorrect comparisons between analytical measures and regulatory limits may create the appearance of hazard where none exists.

To properly harmonize a global regulatory scheme, it is essential to differentiate among the chemicals and measure them with robust, reproducible and validated methods according to a universal standard. In other words, we must all work from the same rule book. Clear, unambiguous, hazard-based criteria should be established before a regulatory authority sets a limit for a PFAS substance.

Our research found widely accepted analytical measures for only a limited number of organic fluorinated substances, such as PFAA in drinking water, while standards for other environmental matrices were undefined. To close this regulatory gap, it is essential to match the analytical method to the goal of the analysis.

Analytical methods exist to determine all fluorine in a sample as well as confirm the existence and identity specific PFAS. Some fluorine-containing compounds, such as non-polymer PFAS, can be detected by multiple methods, while others, such as calcium fluoride can be detected only by total fluorine methods. The method used must also correspond with the matrix. A test that is efficacious for water may not work for blood or textiles.

Knowing the purpose of the analysis, such as determining the extent of an accidental release of a fluorinated chemical into a river or monitoring airborne emissions at a manufacturing facility, and how the results will be interpreted and used will inform the analytical approach.

To effectively protect public health and the environment, efforts must focus on those fluorinated compounds that pose the greatest risk. That requires an understanding of exposure pathways and a standard measure for the concentration of the substance.

