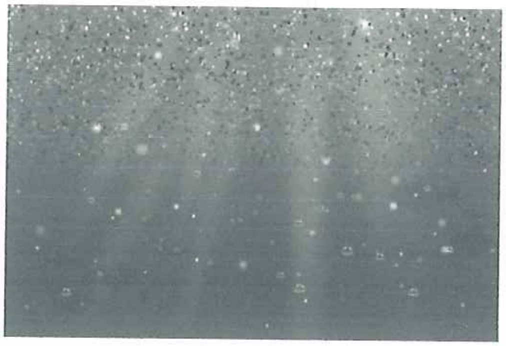
WATER ONLINE

Guest Column | April 13, 2021

The Microplastics And PFAS Connection

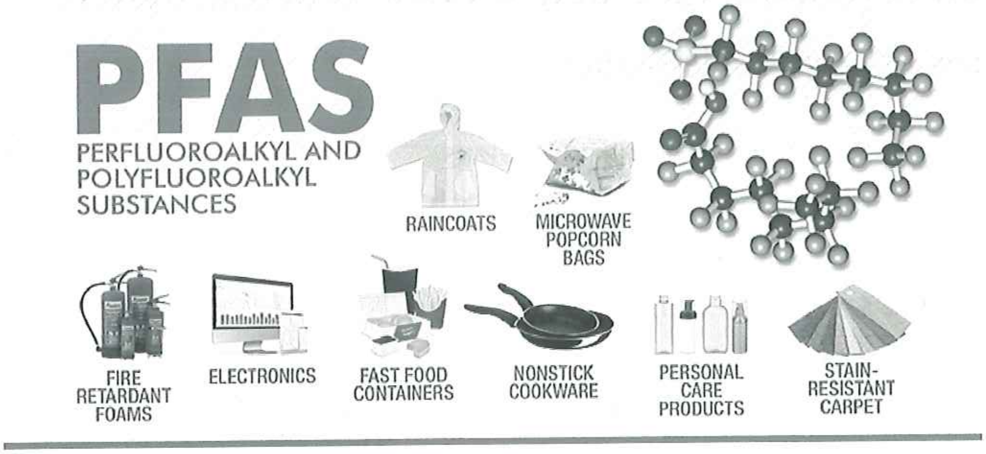
By Cayla Cook and Eva Steinle-Darling



Microplastics, small plastic particles with sizes ranging from 5 millimeters to 1 nanometer with various morphologies such as microfibers, fragments, pellets (nurdles), or microbeads, have received increasing attention, including upcoming statewide monitoring in California.

Per- and Polyfluoroalkyl Substances (PFAS) are a group of unique chemically stable compounds and, as a result, have made them highly valuable across a wide range of industrial, commercial, and military uses. However, this feature concomitantly makes them recalcitrant and persistent in nature — thus coined "forever" chemicals (Lindstrom et al. 2011, Buck et al. 2011). Recent developments in toxicology, coupled with significant political pressure, have put PFAS on the fast-track for regulation in drinking water and wastewater. While co-occurrence is well-known for a variety of contaminants like triclosan and triclocarban, the connection between microplastics and PFAS has not been studied in much detail despite being linked together in multiple ways. Not only can some PFAS occur as microplastics such as polyvinyl fluoride (PVF) and polytetrafluorethylene (PTFE), it is also used as a coating on synthetic textiles and plastic components that then break down to fiber- or particle-based macro-, meso-, or microplastics. Moreover, non-PFAS microplastics can involve PFAS at certain stages in their production process, for example polyvinyl chloride (PVC).

First, it is imperative to highlight that microplastics — similarly to PFAS — are not a single type of contaminant but a *suite* of contaminants. There are dozens of polymer types which alone consist of 4,283 additives including the well-known endocrine disruptor detected in human blood and urine, bisphenol-A (Groh et. al 2019; Vandenberg et al. 2014; Matsumoto et. al 2003). These additives include flame retardants, plastic stabilizers, and colourants, many of which are regulated in drinking water nationwide. Recent research has indicated that "most of the chemicals present in plastics (82 percent) cannot be identified using the … [National Institute of Standards and Technology] database and, thus, remain unknown" which would increase the associated compound list into perhaps the tens of thousands (Zimmermann et al. 2019). Some of these associated polymer types and additives are also, of course, PFAS.



Perhaps most surprising is the fact that one type of PFAS, polymeric PFAS, can break down into microplastics. This polymeric PFAS group consists of fluoropolymers, side-chain fluorinated polymers, and poly- or perfluoropolyethers (Lohmann et al. 2020). PTFE and PVF may occur as secondary microplastics in the environment or as intentionally produced primary microplastics (Bergmann et al. 2017; Ebnesajjad 2013). Due to their high density, environmental PTFE and PVF microplastics are more likely to settle into sediment which makes their removal more challenging. For example, if these particles are removed in wastewater treatment, then they are likely to be found in the solids or biosolids product.

Both landfills and wastewater treatment plants are concerned about microplastics and PFAS for a variety of reasons. While the science is still developing, PFAS groundwater contamination near landfills has been found to exceed local health-based guidance values, and microplastics have been found in landfill leachate, which have contaminated nearby groundwater (Minnesota Pollution Control Agency 2021; Pinjing et al. 2019; Karuppasamy et al. 2021). Concurrently, research and regulations have been developing for PFAS in biosolids in various states due to toxicity concerns while microplastics research has begun to indicate possible land accumulation or export to the nearby environment, select agricultural crop uptake, and other impacts (Corradini et al. 2019; Crossman et al. 2020; Sun et al. 2020). While PTFE and PVF represent a small portion of microplastics discovered in the environment, fluoropolymer microplastics may further contribute to environmental, groundwater, produce, or landfill PFAS levels without the necessary source control.

Plastics, paper products, and textiles are sometimes coated in nonpolymeric PFAS coatings that can be released. This side-chain fluorinated polymer group has been found to release nonpolymeric PFAS (Washington et al. 2015). Of these compounds formed, PFAS is specifically a concern with high density polyethylene (HDPE). In March 2021, the EPA released a memo stating that "PFAS compounds can be formed then partly leach" from plastics used in pesticide packaging (EPA Releases Testing Data Showing PFAS Contamination from Flourinated Containers, 2021). Additionally, fluoride and microplastic release from heated PFAS-coated paper products has recently been documented (Ranjan, Joseph, and Goel 2021). In short, PFAS coatings on plastic may be relatively common, with microplastic release possible on some packaging including food contact substances.

Beyond packaging, fluorotelomer-based polymers (FTPs) are a PFAS category used for water repellant or stain repellant clothing coatings which are often applied to polymeric textiles such as polyamide (PA) and polyester (PES). This water-resistant clothing can shed PFAS-coated microfibers during production or subsequent consumer washing. Early research indicates that the "largest fraction of fluorine is most likely present as durable water repellant polymer chemically bound to the fiber" indicating the co-occurrence of PFAS microplastics is widespread in textile washwater (Schellenberger et al. 2019). Moreover, many of these microfibers are not removed by wastewater treatment processes in either textile treatment facilities or municipal wastewater treatment plants (Ranjan, Joseph, and Goel 2021; Le Bihanic et al. 2020). An estimated ~0.7 tons of FTPs per year are emitted by outdoor rain jackets alone (Schellenberger et al. 2019).

In addition to polymeric PFAS and PFAS-coated plastics and textiles, PFAS can also adsorb onto microplastics in the environment then possibly desorb in aquatic species but not the human gut (Wang, Shih, and Li 2015; Islam et al. 2021; Bakir, Rowland, and Thompson 2014). Adsorption or association with more than 78 percent of the Environmental Protection Agency's priority pollutants further links macro-, meso-, and microplastics not just to PFAS, but other environmental contaminants such as polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethane (DDT), and pharmaceuticals (Rochman et al.

2013). Dependent upon the pH, salinity, and other factors, microplastics can adsorb to these hydrophobic contaminants and then desorb in more preferential conditions.

To bring this full circle, microplastics and PFAS are often found together in the environment and recent research has indicated that microplastics may increase PFAS toxicity (Pramanik et al. 2020; Le Bihanic et al. 2020; Sobhani et al. 2021). The co-occurrence of these two contaminants may come as a surprise to the public, utilities, or industries as each has historically been treated as an isolated issue; however, this is not always the case. Simultaneous microplastics and PFAS monitoring by utilities and industries can begin to shed light and increase knowledge on this co-occurrence. Moreover, source control of PFAS-coated textiles which shed microfibers could have a concurrent, positive impact on environmental and potable water quality. Increasing our understanding on their co-occurrence and considering concurrent mitigation strategies, including source control and treatment technologies, will lead to long-term sustainable solutions.

Cayla Cook is a Microplastics Lead and Staff Engineer with Carollo Engineers. She has a BSE in Civil and Environmental Engineering from Mississippi State University and an M.S. in Environmental Engineering from Arizona State University, where she studied smart polymers, biopolymer nanotechnology, microplastic analytical methods, and environmental and human health impacts of plastic and plastic-associated additives. Cayla spearheads all micro- and nanoplastic-related efforts at Carollo for water and wastewater. This includes investigating mitigation strategies including treatment technologies, implementing monitoring initiatives, and building a database to advance understanding of contamination.

Eva Steinle-Darling, PE, is a Vice President and Chief Technologist with Carollo Engineers. She has a BSE in Chemical Engineering from Princeton University and an M.S. and Ph.D. in Environmental Engineering from Stanford University, where she studied the removal of PFAS using nanofiltration membranes. Her work with Carollo focuses on advanced water treatment and reuse, including research, planning, feasibility studies, and design. Eva is leading Carollo's efforts to address clients' needs in responding to PFAS contamination in drinking water, wastewater, and recycled water. She also is working on several of Carollo's Water Research Foundation projects in which she is looking at, among many other things, the removal of PFAS through the advanced treatment train.

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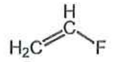
Vinyl Fluoride
CAS No. 75-02-5

Reasonably anticipated to be a human carcinogen
First Listed in the *Tenth Report on Carcinogens* (2002)



Carcinogenicity

Vinyl fluoride is *reasonably anticipated to be a human carcinogen* based on sufficient evidence of carcinogenicity in experimental animals. Both male and female rats exposed to vinyl fluoride by inhalation showed increased incidences of hepatic hemangiosarcoma, hepatocellular adenoma or carcinoma, and Zymbal gland carcinoma. Both male and female mice exposed to vinyl fluoride by inhalation showed increased incidences of hepatic hemangiosarcoma, bronchiolar-alveolar adenoma or adenocarcinoma, hepatocellular adenoma, and harderian gland adenoma. Female mice also showed an increased incidence of mammary gland adenocarcinoma (Bogdanffy *et al.* 1995, IARC 1995).

The tumor responses of laboratory animals to vinyl fluoride are similar to their responses to vinyl chloride, a known human carcinogen (IARC 1987), and to vinyl bromide, a probable human carcinogen (IARC 1986). A unique feature of vinyl chloride carcinogenicity is that vinyl chloride induces rare hepatic hemangiosarcomas in experimental animals and is causally associated with excess risk of liver hemangiosarcoma in epidemiological studies of exposed workers. The fact that vinyl fluoride, vinyl chloride, and vinyl bromide all induce rare hemangiosarcomas of the liver in experimental animals and induce the formation of similar DNA adducts suggests a possible common mechanism of carcinogenicity for all three of these chemicals.

No adequate human studies of the relationship between exposure to vinyl fluoride and human cancer were found.

Additional Information Relevant to Carcinogenicity

Vinyl fluoride is mutagenic in *Salmonella typhimurium* with the addition of a rat liver homogenate metabolic activation system. In addition, vinyl fluoride induces gene mutations and chromosomal aberrations in Chinese hamster ovary cells (with metabolic activation), sex-linked recessive lethal mutations in *Drosophila melanogaster*, and micronuclei in bone marrow cells of female mice (IARC 1995).

Vinyl fluoride likely is metabolized in a manner similar to vinyl chloride: oxidation via cytochrome P450 to fluoroethylene oxide, followed by rearrangement to 2-fluoroacetaldehyde, which is oxidized to fluoroacetic acid. Human, rat, and mouse liver microsomes metabolize vinyl fluoride at similar rates (Cantoreggi and Keller 1997).

Vinyl fluoride metabolites form covalent DNA adducts. Inhalation exposure of rats and mice to vinyl fluoride produced a dose-related increase in the formation of the promutagenic adduct N^2,3-ethenoguanine in their liver DNA (Swenberg *et al.* 1995).

No available data suggest that mechanisms by which vinyl fluoride induces tumors in experimental animals would not also operate in humans.

Properties

Vinyl fluoride is a colorless gas with a faint ether-like odor. It is insoluble in water and soluble in alcohol, ether, and acetone. Vinyl fluoride is extremely flammable and will form explosive mixtures with air. It can form hazardous polymers when heated. A fire containing vinyl fluoride can generate highly toxic hydrogen fluoride gas (HSDB 2001). Vinyl fluoride reacts with alkali and alkaline earth metals, powdered aluminum, zinc, and beryllium (IARC 1995).

Use

Vinyl fluoride is used primarily in the production of polyvinyl fluoride and other fluoropolymers. Polymers of vinyl fluoride are resistant to weather and have great strength, chemical inertness, and low permeability to air and water. Polyvinyl fluoride is laminated with aluminum, galvanized steel, and cellulose materials and is used as a protective surface for the exteriors of residential and commercial buildings. Polyvinyl fluoride laminated with various plastics has been used to cover walls, pipes, and electrical equipment and inside aircraft cabins (IARC 1995).

Production

Vinyl fluoride was first prepared in the early 1900s by reaction of zinc with 1,1-difluoro-2-bromoethane. Modern preparation of vinyl fluoride involves reaction of acetylene and hydrogen fluoride in the presence of a mercury-based or aluminum-based catalyst (IARC 1995). Annual U.S. production is approximately 3.3 million lb (HSDB 2001). The U.S. Environmental Protection Agency (EPA), through the Office of Pollution Prevention and Toxics, listed vinyl fluoride in the high production volume chemical list in 1990, indicating that annual production exceeded 1 million lb (EPA 1990). Only one U.S. manufacturer of vinyl fluoride was identified (HSDB 2001).

Exposure

Exposure to vinyl fluoride in the environment will occur by inhalation, because vinyl fluoride released into the environment exists as a gas (IPCS 1993).

Occupational exposure to vinyl fluoride occurs primarily by inhalation (HSDB 2001). Skin and eye contact can occur among workers handling liquid vinyl fluoride. Handling liquid vinyl fluoride also would cause frostbite (IPCS 1993).

Occupational exposure to vinyl fluoride was studied in a manufacturing and polymerization facility in the United States. In eight personal air samples taken at the manufacturing facility, concentrations of vinyl fluoride generally were less than 2 ppm (3.76 mg/m^3). In one personal sample, however, the concentration of vinyl fluoride was 21 ppm (39.5 mg/m^3). Vinyl fluoride concentrations in seven personal samples taken in the polymerization facility ranged from 1 to 4 ppm (1.88 to 7.52 mg/m^3). In four general working areas, the vinyl fluoride concentrations ranged from 1 to 5 ppm (1.88 to 9.4 mg/m^3) (IARC 1995).

Regulations

DOT

Vinyl fluoride is considered a hazardous material and special requirements have been set for marking, labeling, and transporting this material

EPA

Clean Air Act

Prevention of Accidental Release: Threshold Quantity (TQ) = 10,000 lbs

Guidelines

ACGIH

Threshold Limit Value - Time-Weighted Average Limit (TLV-TWA) = 1 ppm

NIOSH

Ceiling Recommended Exposure Limit = 5 ppm
Recommended Exposure Limit (REL) = 1 ppm

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