Perfluorinated compounds such as Perfluorooctanoic Acids in the environment, the effects, and the possibilities for novel remediation methods

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Abstract

Perfluorooctanoic Acid (PFOA) and related compounds such as perfluorooctane sulfonate (PFOS) are substances classified as persistent bio-accumulative compounds widely utilized across various manufacturing industries as surfactants, surface protectants and for chemical treatment of paper products. Much attention has been called to the use of such compounds in manufacturing when DuPont, manufacturer of Teflon®, Kevlar®, Corian® and other popular synthetic materials, agreed to pay a settlement with an American community to pay for toxicity studies. In recent years several publications have focused on Perfluorinated Compounds (PFC) in the environment in China and Tibet, as well as in South Africa. The effects on plant and animal communities ranging from human beings to zooplankton are currently elucidated. Soil studies have suggested that PFCs lower enzymatic activities inherent in soils and that PFCs exert transcriptional effects across multiple species as well which implies biological effects of PFCs have the potential to be rather widespread. Furthermore PFCs have been shown to accumulate in the tissues of plants in riparian communities in South Africa, of humans in Seattle Washington, and bird eggs in the Baltic Sea suggesting not only effects across diverse species but also multiple ecological ranges. While a group with the NIH and Emory University is currently trying to establish a link between PFOAs and gestational diabetes and others have linked toxicity of PFCs to the pancreas and other organs, there are other established links to toxicity in zooplanktonic communities as their consumers, *Daphnia magna* were thought to be quite sensitive. PFOA is toxic to them but not as toxic as once thought, this illustrate that PFCs are not just an issue for humans and environmental contamination with PFCs has much broader ecological implications. Due to the possible risks posed by these contaminants as well as their widespread use in industry, currently researchers are exploring methods for decontaminating water polluted by PFCs. Multiple chemical approaches are being explored for the task of decomposition of PFCs that include nanocatalysts, photochemical defluorination, plasma-liquid interface reactions and activated carbon bioreactors. As such this discussion is not only about the biological and ecological relevance of PFOA and related compounds but also possibilities for decontaminating new industrial waste as well as previously polluted ecosystems.

Perfluoroalkyl Compounds

Perfluoroalkyl compounds are a unique class of halogenated compounds, where main chain carbon atoms substituent hydrogen atoms have been replaced with fluorine, that are useful for manufacturing processes due to being both hydrophobic and lipophobic[1.] There are hundreds of known stable Perfluoronated compounds but of particular interest are Perfluorooctanoic acid (PFOA, Figure 1) and Perfluorooctanesulfonic acid (PFOS) which are used heavily in industrial applications, for forest fire fighting foam, or appear as degradation products and derivatives. Being both hydrophobic and lipophobic these compounds can serve as surfactants that repel both

Figure 1. Perfluorooctanoic acid [2.]
water and grease. While these compounds are highly useful due to their physical properties and thermal stability, that same stability lends well to survival PFOA and PFOS in the environment and as such they are known to be persistent in the environment, bioaccumulative across multiple species, and toxic with PFOS more so than PFOA [1,2.]

**Human Concern**

In December 2005 DuPont the manufacturer of such well known products such as Corian®, Kevlar®, and others including Teflon® reached a 16.5 million dollar settlement with the EPA. Teflon which is used in nonstick cookware and stain proof carpets and textiles was manufactured for some time in a process requiring the surfactant PFOA. Dupont was accused of not releasing health information about PFOA and as a part of its settlement launched a 5 million dollar study to determine whether PFOAs were being released as a degradation product of certain products or due to the use of PFOAs in manufacturing. The products tested would be kept secret however [3.] Dupont voluntarily entered into a phasing out of PFOA between 2010 and 2015 and claim at this time they no longer produce or utilized PFOAs according to their website.

Regardless of current utilization of Perfluoronated Compounds (PFC) human serum concentrations of PFOA, PFOS and other PFCs range from below the lower limit of quantitation (3.4 parts per billion (ppb)) to 175 ppb in a study of serum PFOS in elderly populations in the Seattle area, where an estimate of the 95% tolerance limit was set at 84.1 ppb [4.] While a study in the mid-Ohio Valley near Parkersberg West Virginia found that children, less than or equal to 5 years of age, of mothers who drank well water in the area near manufacturing plants had much higher PFOA serum concentration than their mothers likely due to exposure in utero and while breast feeding. The study was conducted between 2005 and 2006, individuals with documentation that they had drank water from PFOA contaminated districts had blood drawn and analyzed via HPLC-MS². The data of mothers was paired to their children and statistical analysis was performed. Serum levels of PFOA and PFOS in children in the area were found to remain about 42% higher than their mothers until at least 19 years of age although the PFOS data was reported
with low confidence [5.] These studies as well as others from around the world show that PFCs accumulate within the human body and may remain within the body for many years.

While it is certainly interesting that PFCs may remain in the body for many years, that fact bears no clinical significance without knowing what its effects may be. Animal models suggest that PFC exposure may reduce circulating thyroid hormones either by affecting the thyroid hormone production or by displacing thyroid hormone from serum albumin, but studies on humans with non occupational exposure including a study on New York State anglers who consumed potentially contaminated fish show no statistically significant relationship between thyroid hormones and PFOA/PFOS levels and only weak relationship between thyroid hormones and PFDAs [6.] Work continues on determining PFC effect on PFCs and thyroid function as there has been statistically significant relationships found within human populations with occupational PFC exposure.[6.] Other possibilities for effects of PFCs as demonstrated in animal models include developmental neurotoxicity of PFOS in rats as well as other developmental effects such as reduced fetal weight, cleft palate, anasarca, and cardiac defects [7, 8.] While early this year a group of scientists from NIH and Emory University published brief preliminary results of a study linking pre-gravid serum concentrations of PFOA to Gestational Diabetes Mellitus with increasing risk with increased concentration [9.] At this time researchers continue to increase our understanding of the impacts of human exposure to PFCs.

**Greater Ecological Impact**

Contamination by PFCs is not confined to isolated areas around factories, although contamination is increasing in growing economies such as China[10,11,12,] but is also prevalent in habitats around the world. PFCs have been detected in marine and freshwater habitats from human inhabited areas to remote areas such as the arctic [13.] In an analysis of Guillemot Eggs from the Baltic sea collected annually from 1968 until 2003 it was found that there was an increasing amount of PFOS. Eight individuals from each time were sampled by LC-MS², in 1968 guillemot eggs contained 25 ng PFOS/ g of wet weight which peaked in 1997 at 1324 ng/g wet weight[13.] Guillemot are an avian species that preys on migratory fish in the Baltic Sea, and while this may support the spread of PFCs by water PFCs can also travel through
the atmosphere to remote locations. A group from Lancaster University, the Chinese Academy of Sciences and the Max Planck Institute extracted snow cores from 3 locations across the Tibetan Plateau which support this claim. Snow cores were dated using $\delta^{18}O$ ratios to select samples from 1980-2010 (2010 samples were fresh snow gathered at sites). Samples were then analyzed by HPLC (with all Teflon components removed to prevent contamination) and ESI-MS$^3$. Researchers found highest concentrations of PFOS with varying levels of other PFCs. The temporal and spatial deposition of PFCs suggested that PFCs were carried through the atmosphere on westerly winds [14.]

**Effects on Wildlife**

With knowledge that PFCs are widespread in nature at this point in time researchers are attempting to determine the effects of PFOA and other PFCs on soils, plants and animals. Soil is a very complex and often forgotten environment. The microbiota of soil is responsible for functions from the turnover of organic material to supporting the growth of plants. A team in eastern China revealed a dose dependent inhibition of important soil enzymes. The enzymes tested were phosphatase, catalase and urease. Such enzymes catalyze biochemical reactions which detoxify the soil and mediate nutrient conditions for microbiota and plants in the soil. The team suggests that these enzymes, specifically catalase, can act as an effective indicator of PFC contamination as well toxicity to soil environments [15.]

In 2008, Colombo et al. sought to use standardized tests to determine toxicity of PFOA in the form of ammonium perfluorooctanoate (APFO) to three freshwater organisms, *Pseudokirchneriella subcapitata* (green algae), *Daphnia magna* (the water flea), and *Oncorhynchus mykiss* (rainbow trout). What was found was levels of 316 mg/l of APFO for *D. magna* to 1000 mg/L of APFO for *O. mykiss* using the same testing procedures were required for observable toxicity. They mention however it may be the amount of un-ionized ammonia in solution that played a role in the observed toxicity. They also conclude based on data from other outdoor studies where PFOA existed at less than 70mg/L that under non spill conditions toxicity is not a risk[16.] Similar results were found in another study looking at *daphnia magna*, though researchers acknowledged their study was only across 21 days and more thorough field studies over longer time periods should be conducted[17.] Both studies had results that conflict with earlier studies.
that suggested a much lower concentration of PFOA was required for toxicity to *D. magna* though they point to differences in lab tests that may account for earlier discrepancies.

**Future Directions**

While there are differing opinions on the effects of PFCs, there is likely more to the story that we are not seeing. It may a reliance on human epidemiological studies to guide current research on the effects of PFCs, when a molecular approach may be more appropriate. A study looking at activation of Peroxisome Proliferation Activation Receptor alpha (PPARα) in vivo using microarray and RT-PCR showed that specific PFC exposure resulted in different levels of gene expression in rat hepatocytes [18.] And in a study published earlier this year it was shown that mice exposed to different levels of PFOA over a 28 day period expressed different sets of miRNAs at differing levels depending on the dose of PFOA they received [19.]

This evidence may suggest that PFCs are not causing direct damage to organs or tissues, but instead are influencing gene expression in a deleterious fashion. Rather than looking at the symptoms of occupationally exposed workers and environmentally exposed organism, suggesting that PFCs are the culprit or that they are directly causing the observed symptoms we should be looking at the transcriptomes of the exposed individuals showing signs of toxicity. By comparing the gene expression of affected and exposed individuals to similar individuals with low environmental levels of PFCs it may be possible to elucidate the effects of PFCs at the molecular level and work up through the cellular and biochemical pathways to see if PFCs have any sort of toxicity or whether it could be a number of environmental factors working in concert.

**Novel Remediation Methods**

Due to the unique nature of PFOA, it is resistant to biochemical degradation in the environment, oxidation and reduction. There are currently multiple catalytic techniques being studies to remove PFOA from the environment. TiO₂ is a well recognized photocatalyst, which are considered promising due to
low energy requirement, but is ill suited for degradation of PFCs and current efforts are geared to finding more effective photocatalysts. Ga$_2$O$_3$ (Gallium(III) Oxide) has been shown effective as a photocatalyst for degradation of PFOA. An exciting method for increasing the efficiency of Ga$_2$O$_3$ catalysis was elucidated that involved forming sheaf like nanostructures of Ga$_2$O$_3$ generating a surface area of 36.1 m$^2$/g and significantly increasing the effectiveness of the catalyst (15 times greater under UV light (254 nm) and 42 times under vacuum UV light (185 nm).) This method was proven effective using sewage water from a municipal waste water plant [20].

More recently the same group out of Tsinghua University published a method for generating a In$_2$O$_3$ meso-microporous nanoplates yielding a specific surface area of (156.9 m$^2$/g). The In$_2$O$_3$ nanoplates reduced the $t_{1/2}$ to 4.4 minutes under UV light while their Ga$_2$O$_3$ only reduced the $t_{1/2}$ of PFOA to 9.6 minutes under Vacuum UV. There is also no mention of a requirement for acidic conditions which may mean this catalyst will function without the need for adding an acid to wastewater for treatment[21.]

Published shortly after a team from South China University of Technology developed a photocatalytic system using vacuum ultraviolet light and Iron(III) ions to defluorinate PFOA under acidic conditions [22.] While the VUV/Fe$^{3+}$ system is not as effective, it is efficient and it is likely that a large scale Iron(III) photocatalyst system would cost far less than an In$_2$O$_3$ system.

Catalytic systems would need to deal with large flow volumes and may not contact enough PFOA molecules to be considered effective for remediation. A solution may be to remove PFOAs from wastewater and deal with the sludge separately by photocatalysis or some other means. And at the same time as the catalysts are being identified a team from Yangzhou University produced a membrane bioreactor that with 100mg/L of powdered activated carbon is able to remove 90% of PFCs from waste water. The caveat to their system is that it operates currently at 10 L/(m$^2$•hr)[23.]

While there are many rather high tech methods in the works some suggest using the natural ability of organisms to absorb and accumulate PFCs. It has been suggested that wetland plants which have been reported to accumulate pollutants such as atrazine and nitroglycerin would work well for remediation of PFCs. Laboratory tests indicate that wetland plants would in fact accumulate PFCs in the natural
environment so field studies were conducted in South Africa to test the susceptibility of riparian wetland plants to perfluorooctanoic acid for use in bioremediation of PFCs. Researchers found high levels of PFOA compared to previous studies which they contribute to the high PFOA concentration present in the soil. They also looked at root systems and soil conditions. It was found that more complex root systems and lower salinity were optimum for PFOA uptake by wetland plants, wetland plants may be beneficial for plans to manage PFC contamination[24.]

What the chemical remediation plant of the future may look like is a constructed riparian wetland holding area for incoming waste water. Waste water could then be flowed at a controlled rate into Powdered Activated Charcoal Membrane bioreactors and back into the environment. The pipes moving wastewater between stations could be lined with VUV/photocatalyst systems to decompose as much of the PFCs and other harmful chemicals as possible. While this may not be the actual solution to widespread contamination by PFCs it would be obviously be prudent to consider an integrated remediation technique in future efforts.
References


