

# Resilient Water Treatment Technologies and Challenges for the Removal of Emerging Contaminants - Perfluorinated Compounds

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## ABSTRACT

Due to their global presence, persistence, and adverse health effects, perfluorinated compounds (perfluoroalkyl and polyfluoroalkyl substances PFASs) have become major chemical of concern for drinking water supplies worldwide. Presence of these PFCs in various geographical regions and environmental matrices across globe has been well documented in literature. This range from drinking water in New Hampshire, USA to arctic ice to surface waters in Asia, and Europe to aquatic life, and so on. Presence of long chain, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) have received greater attention from the drinking water utilities in recent years in United States. US EPA has recently issued a revised health advisory for PFOA and PFOS concentrations to 70ng/L. Corresponding health advisory for shorter chain (C4-C7) perfluorinated compounds is 300-7000ng/L. This widespread nature of these contaminants has made a strong need for identifying appropriate and resilient water treatment technologies that can be incorporated in existing drinking water infrastructure. Detection and accurately quantifying these chemicals of concern at such low level (ng/L) pose a bigger analytical challenge for researchers. There is a strong need to develop more cost-effective ways to determine such contaminants so that these PFCs can be monitored on a more regular basis. PFOA and PFOS's low volatility and high water solubility makes it harder to effectively and efficiently remove these contaminants using many conventional treatment technologies. This paper outlines major treatment technologies that can be incorporated in existing water infrastructure. Two major such technologies are adsorption (granulated and powdered activated carbon) and membrane filtration (reverse osmosis, nanofiltration etc). Concentrated brine generation during water treatment limits the use of membrane filtration in water scarce areas. Adsorption using activated carbon has proved to be effective in removing these perfluorinated compounds. Presence of such GAC/PAC systems in existing drinking water treatment trains make these technologies more attractive. New advances in carbon materials has further improved the removal efficiencies of PFOA and PFOS. However, disposal of spent media (carbon) may pose a greater threat as incinerating such material requires energy. To make such process energy efficient, more research is required to develop novel sorbents for PFOA and PFOS removal.

**Keywords:** p PFOA, PFOS, emerging contaminants, adsorption

## 1 INTRODUCTION

Occurance of perfluoroalkyl and polyfluoroalkyl substances (PFAS) have been widely reported in literature. These chemicals are a class of chemicals that are characterized by a carbon backbone. Arrangement of replacement of hydrogen atoms in these carbon backbone differentiate per and poly PFAS. Carbon backbone in which hydrogen atoms have been completely (per-) or partially (poly-) replaced by fluorine.

Between 2000 and 2002, PFOS was voluntarily phased out of production in the U.S. by its primary manufacturer. In 2006, eight major companies voluntarily agreed to phase out their global production of PFOA and PFOA-related chemicals, although there are a limited number of ongoing use.

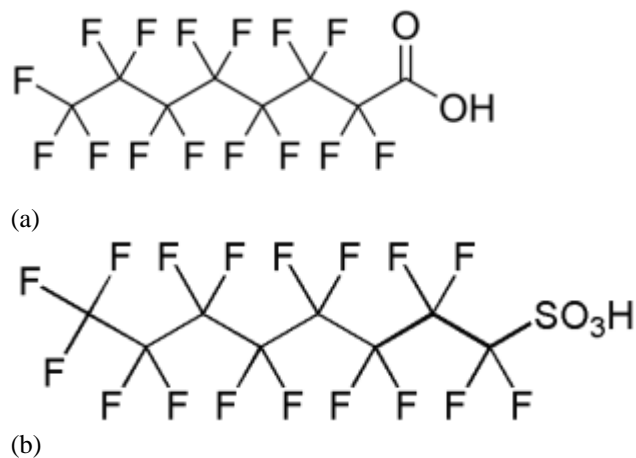


Figure 1: The structure of Perfluorooctanoic acid (a) and Perfluorooctanesulfonic acid (b)

Fluorine is the most electronegative element in periodic table. PFOA has a log K<sub>oc</sub> of 2.06 and does not easily adsorb to sediments or aquifer materials; therefore, it tends to stay in the water. Due to its high mobility in water, PFOA has been found in surface water, ground water, and drinking water. Because of its persistence, and low

volatility in ionized form, it can be transported long distances to the Arctic [1-2].

## 2 GEOGRAPHICAL OVERVIEW

Although PFCs are primarily used in United States but occurrence and detection of these compounds have now been reported worldwide. Table 1 list some major occurrence worldwide.

Table 1: Detection of PFCs in various environmental matrices around the world

Country	Key Outcome
Australia	Highest average level of PFOs in human blood
Canada	PFCs in 3 arctic lakes
China	Highest average level of PFOs in human blood
Denmark	Immune suppression due to PFOA/PFOS in childrens
France	27% public water system contain PFOS
Germany	PFC detected in water; consumed by >5M people
Greenland	Rising PFC in polar bears
India	15 PFCs detected in River Ganges
Italy	High levels of PFCs in water
Japan	High levels of PFCs in water, food
Norway	12 PFCs found in food and beverages
South Africa	100% samples from 3 rivers found positive for PFOA/PFOS
Spain	
Sweden	Elevated levels of PFCs near military bases
UK	Airborne PFOA in Manchester
USA	PFCs in public water supply and private wells
Vietnam	PFC found in 98%-100% Vietnamese women giving birth

\*www.theintercept.com [3]

Similar PFCs had been detected and reported in US public water supplies and private wells. Table 2 list some of major such occurrences in US waters.

Table 2: Major occurrences of PFOA in drinking water in USA

Site	Highest Level (µg/ L)	Year
Hoosick Falls, NY	983	-
North Bennington, VT	40-2880	-
Parkersburg, WV	0.0412	2014
Vienna, WV	0.056	2007
North Jersey, NJ	0.14	2006-08
Little hocking, OH	7.2-14	2002-05
Oakdale, MN	0.9	2004-08

United States EPA has established a lifetime drinking water health advisory levels at 70 parts per trillion (ppt) or ng/L for PFOA. However many US states have issued their own guideline values. These guideline values varies from state to state ranging from 0.02 to 2 µg/ L. Table 3. shows more recently some US states have further lowered their health advisories.

Table 3. State Guideline Values for PFOA

State	Guideline Value (µg/ L)	Source
Delaware Department of Resources and Environmental Control	0.4	DNREC (2016)
Maine Department of Health and Human Services	0.1	Maine DHHS (2014)
Michigan Department of Environmental Quality	0.42	Michigan DEQ (2013)
Minnesota Department of Health	0.3	MDH (2009)
New Jersey Department of Environmental Protection	0.04	NJDEP (2014)
North Carolina Division of Water Quality	2	NCDEQ (2013)
Vermont Agency of Natural Resources	0.02	Vermont ANR (2016)

\*US EPA [4]

## 3 PROBLEM OVERVIEW

Due to their widespread occurrence in various environmental matrices (air, water, soil, snow, fish, oceans, ice, humans etc) and adverse health and environmental impacts, these compounds have received great attention from researchers across the globe. Unique physical and chemical properties of these PFCs makes them extremely stable which in turn, prevents their destruction in the troposphere resulting in their accumulation in the atmosphere [5-6]. Such processes also add to global warming

River water and lake water are predominantly used as raw water for US public water supply systems. However in a recent US EPA report, detection of PFCs in Tennessee River (< 25–598 ng/L), Mississippi River (< 1.0–125 ng/L), Lake Erie (21–47 ng/L), Lake Ontario (15–70 ng/L), the Conasauga River (253–1,150 ng/L) and Altamaha River (3.0–3.1 ng/L) watersheds in Georgia have raised concern on such raw water sources [7-10].

## 4 TECHNOLOGICAL SOLUTIONS

Detection of PFCs in US public and private drinking water supplies have prompted a strong need for developing appropriate treatment technologies. Some of US states have lowered the PFCs health advisory or permissible limit to an extent that is only achievable using advanced environmental analytical instrumentation. Such sophisticated analytical instrumentation makes monitoring, detection and development of treatment very expensive.

Like any other chemical contaminants, treatment of PFCs compounds also rely on its physical and chemical characteristics. As evident from Figure 1, the carbon-fluorine bond present in PFOA/PFOS makes such compounds exceedingly resistant to biodegradation, hydrolysis, oxidation, and photolysis.

Due to strength of C-F bond, biodegradation (aerobic and anaerobic) have been found ineffective for the removal of PFOA and PFOS. This leaves adsorption, ion exchange resins, and high-pressure membranes as the technologies that can be effective.

Numerous existing and new treatment technologies have been tested to a varying degree of success. This include membrane processes, advanced oxidation processes, ion exchange, adsorption. Membranes (low and high pressure) processes have been found effective in treatment of PFCs however due to their high water rejection and energy input. Their use is very limited to specific applications. High pressure nanofiltration and reverse osmosis can reject not only particulates but also dissolved constituents. Use of such technologies is not very feasible in water scarce areas. Addition of minerals is also required in membrane processes.

Most of the existing drinking water oxidation or disinfection technologies have been shown to be ineffective in treatment of PFOA or PFOS in water. This is primarily due to strong C-F bond. Advanced oxidation processes (AOP) utilize hydroxyl radicals to destroy PFOA/PFOS. AOPs convert more toxic to a less complex compounds. These processes are limited by low removal rates and high capital and operational costs.

Activated carbon adsorption - Both powdered activated carbon (PAC) and granular activated carbon (GAC) have been tested to a varying degree of success. Depending on the type of carbon, dose, and contact time, PAC effectiveness varies. PAC is usually applied before or within the conventional treatment process whereas GAC is applied as a filtration step. Numerous studies have shown GAC to be shown effective for the treatment of PFOA and PFOS [11-15]. GAC is most common and effective (>90% removal) treatment technologies for the PFCs. Dual filter design has been tested at OH and WV plants. Adsorption of

PFCs on carbon depends on the surface area, hence coating of carbon surface has also been adopted in some studies. Some of such carbon based products are commercially available now. This include PerfluoroAd®, Evoqua Bituminous, Anthracite, and coconut carbon. AquaCarb CX series carbon combines the benefits of an activated carbon with the high micropore structure of coconut shell, with faster kinetics comparable to bituminous coal.

Point of use (POU) water treatment devices are installed at an individual tap, faucet, or outlet and reduce contaminants at that one point-of-use. POU water filters have also gained a growing attention due to their use at private wells and places not served with public water systems. Olsen and Paulson [16] had investigated 14 such POU devices for their effectiveness for removing PFCs. Eleven POU devices removed all PFCs in the field test to below quantifiable detection limits. Such POU devices require periodic replacement of media to maintain effectiveness and sanitary reasons.

## 5 CHALLENGES

Selection of an appropriate technology for PFCs removal is a challenging task especially considering the type of source, required level of treatment, financial aspects, and technology efficacy. Many of existing public water supplies are considering GAC based system due to their familiarity with such GAC systems, their effectiveness for PFCs, and easy incorporation into the existing water treatment plant processes. Most of the adsorption based treatment technologies concentrate PFCs in the adsorbent media. Once this media is exhausted, their regeneration, or disposal poses other environmental risks. More research is required to come up with a sustainable solution for the removal of PFCs.

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