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Florida Water Resources JOURNAL

August 2020



Water Quality
and Disinfection

Dealing With Widespread Per- and Polyfluoroalkyl Substances Contamination

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Since May 2016, when the U.S. Environmental Protection Agency (EPA) issued a lower drinking water health advisory level of 70 ng/L for combined perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), two per- and polyfluoroalkyl substances (PFAS), a quiet city in Florida has been dealing with the challenges of widespread PFAS contamination.

Groundwater and soil contamination, primarily due to the use of aqueous film-forming foams (AFFF), which are used for firefighting, has forced the City of Stuart (city) to shut down some of its primary supply wells. Studies were immediately conducted and pilot testing was performed using granular activated carbon (GAC) and ion exchange (IX), resulting in the installation of a treatment system to remove PFAS down to nondetect levels from all groundwater supply wells.

Construction of a 4 to 8 mil-gal-per-day (mgd) IX system, partially funded by State Revolving Fund (SRF) loans, was completed in early June 2019 and is undergoing full-scale testing using multiple types of IX resins and GAC mixes. Coupled with constantly changing regulations, the city continues to deal with cleanup of the AFFF and other contributing sources of contamination, including an unlined landfill and several industrial activities with other historical contaminations.

Along with developing state regulations for PFAS contamination, which were never established prior to 2018 for PFAS in groundwater or soils, the challenges of changing regulations have forced the city to address a multitude of contamination sources and implement the best currently available technologies to deal with these contaminations.

This article will discuss some of the PFAS history, regulations, and lessons learned from a full-scale pilot project for the potable water supply system, including the following:

- ◆ PFAS Sources
- ◆ Health Risks From Exposure
- ◆ Exposure Entry Routes
 - Release of AFFF
 - Industrial
 - Groundwater - drinking water supply
 - Treated wastewater - public access reclaimed water
 - Stormwater runoff
 - Land application - biosolids
 - Food packaging
- ◆ Regulatory Review
 - Current regulations (Florida and other states) including Unregulated Contaminants Monitoring Rule (UCMR) program
 - Proposed and potential future regulations
 - EPA action plan (March 2019 update) review
- ◆ Treatment and Removal Technology Overview, Including IX, GAC, and Reverse Osmosis (RO)
- ◆ Pre- and/or Post-Treatment Opportunities
- ◆ Lessons Learned From Full-Scale Pilot Testing - Multiple IX and GAC Types Used

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employed in food packaging, ScotchGard™, and Teflon™. Drinking water is one route of exposure that may have led to increased concentrations in the blood serum of humans in most developed countries (USHHS, 2009), but some of these compounds, such as PFOA and PFOS, have also been detected in the blood of animals in remote regions of the world. The PFOA and PFOS are two of the most-studied, and, therefore, regulated, PFAS compounds, and belong to the perfluoroalkyl acids (PFAA) family. The PFAA are stable chemicals made of a carbon backbone surrounded by fluorine atoms and an acid group located at the end of the carbon chain, as shown in Figure 1.

There are many sources of PFAS compounds, all man-made formulations of fluorinated compounds developed in the early 1950s, which continue to be manufactured to this day. A brief history of the development of these chemicals, and how they affect humans, is provided in Table 1.

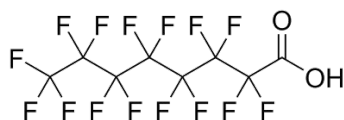
Exposure Entry Routes

There are a number of pathways through which PFAS contamination of humans can take place, including diet, drinking water, food contact materials, nonfood personal items, and indoor and outdoor air. Although a number of authors have attempted to calculate the contribution of these individual pathways to total contamination, the available data records are not presently adequate to allow sound conclusions to be drawn. There is, however, a general consensus that dietary uptake represents the largest contribution.

In recent years, the biological properties of PFAS have been detailed in numerous publications; however, these are generally limited to PFOA and PFOS. These two substances are mostly the only PFAS that have been toxicologically examined in animal studies that would allow conclusions to be drawn about

Background

The PFAS are an environmentally persistent group of man-made chemicals that are found in various types of water sources all over the world, including tap water. These chemicals have been used in a wide variety of industrial and consumer products, including the aforementioned AFFF, as well as paper and cardboard coating materials



PFOA



PFOS

Figure 1. Perfluorooctanoic acid and perfluorooctane sulfonic acid carbon chain.

potential human toxicity. Data on short-chain PFAS that are apparently being substituted for longer-chain molecules in industrial processes are only of a fragmentary nature.

Because of their solubility in water and the increasingly wide spectrum and volume of their use, these short-chain PFAS are starting to receive considerable study. This is particularly evident since they appear to be ubiquitously distributed throughout the water pathway and can thereby lead to an increased background contamination of the environment. Additionally, PFAS are being used in mixtures with varying compositions, making toxicological evaluations much more difficult. For this reason, standardized in vitro and in vivo methods should be used and further developed to allow reliable conclusions to be drawn concerning the toxicity of the individual substances, as well as of various PFAS mixtures. Consequently, an adequate toxicological evaluation of the total situation is presently not possible.

The PFAS are distinct from other persistent and bioaccumulative organic compounds because of their importance as drinking water contaminants. The PFAS exist predominantly as an anion under environmental conditions, do not bind well to soil, migrate readily from soil to groundwater, and are highly water soluble (Davis et al., 2007). These properties of PFAS differ from those of other persistent and bioaccumulative organic pollutants, such as polychlorinated dioxins and furans, polychlorinated biphenyls (PCBs), and pesticides, like chlordane and dichloro-diphenyl-trichloroethane (DDT). These other compounds are generally not significant as drinking water contaminants because they have a high affinity for soil and sediments, but low water solubility.

The PFOA that is specifically released into the environment can contaminate surface water and groundwater used as sources of drinking water. Sources of PFOA in the environment include discharge to air and water from industrial facilities, where it's made or used; release of AFFF, particularly at military sites, airports, and firefighter training facilities; disposal in landfills; discharge from wastewater treatment plants treating domestic and/or industrial waste; street runoff; stormwater runoff; land application of biosolids (sludge) from wastewater treatment plants treating industrial waste (Clarke and Smith, 2011; Lindstrom et al., 2011b; Sepulvado et al., 2011); and land application of wastewater from industrial sources (Konwick et al., 2008); and use of contaminated industrial waste as a soil amendment (Skutlarek et al., 2006; Hölzer et al., 2008).

As is the case for other groundwater contaminants, PFAS can reach drinking water wells via the well-established pathway of

migration of a groundwater plume that has been contaminated either directly from surface spills or by contaminated surface water mixing with groundwater drawn in by pumping wells. Unlike many other environmental contaminants, PFAS can also reach groundwater from air emissions from nearby industrial facilities, followed by deposition from air onto soil, and migration

through the soil to groundwater (Davis et al., 2007).

In West Virginia and Ohio, drinking water wells as far as 20 mi away were contaminated with PFOA by releases from an industrial facility, where it was used as a processing aid in fluoropolymer production. Groundwater contamination occurred via soil deposition

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Table 1. Development and Regulation Timeline for Per- and Polyfluoroalkyl Substances

1947	3M manufactures PFOA.
1951	Dupont develops Teflon.
1970	U.S. Air Force begins using AFFF to fight fuel fires.
2000	3M begins phase-out of 13 PFAS, including PFOA and PFOS.
2001	Dupont issues consent decree in West Virginia and Ohio.
2006	Global stewardship addresses issue, with voluntary manufacturer reduction in 2006, 95 percent removal by 2010, and elimination by 2016.
2009	Provisional health advisory level (HAL) for PFOA/PFOS set at 0.4/0.2 ug/L.
2009	Superfund soil screening levels set at 60/6 mg/kg.
2012	C8 Science panel links probable cancer to PFOA.
2015	Hoosick Falls, N.Y., issues do not drink order.
2016	Food and Drug Administration (FDA) no longer allows PFOA and PFOS to be added to food packaging.
2016	EPA lifetime HAL advisories of 0.07 ug/L set for PFOA and PFOS.

Table 2. Contaminants of Concern: City of Stuart Wells

Water Quality		Unit	Influent (range)	MCL/HAL
	Parameter			
	PFAS (PFOS)*	ug/L	0.051 - 0.470	-
	PFAS (PFOA)**	ug/L	0.014-0.052	-
	PFAS (PFOS + PFOA) (max)	ug/L	0.050 - 2.15	0.070
>	1,4-Dioxane**	ug/L	0.130	-
>	Methyl-tert-butyl-ether	ug/L	1.800	-
>	cis-1,2-Dichloroethylene (DCE)	ug/L	0.3-42.4	70.0
>	1,2 Dichloropropane (DCP)	ug/L	1.2-39.0	-
>	1,2,3-Trichloropropane (1,2,3-TCP)*	ug/L	1.0-23.8	-
>	Trichloroethylene (TCE)	ug/L	5.00	-
>	Tetrachloroethylene (PCE)	ug/L	0.65	3.0
>	Vinyl Chloride	ug/L	0.13	1.0
>	Chlorobenzene	ug/L	0.34	-
>	Benzene	ug/L	1.30	1.0

* UCMR 3 List

** UCMR 3 and UCMR 4 List

>Treatment currently in place

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of PFOA that had been emitted into the air followed by migration to groundwater, and, to some extent, recharge of the groundwater aquifer with contaminated surface water from the Ohio River (Steenland et al., 2009a; Shin et al., 2011). The PFOA was detected in public water supply wells in this vicinity at levels up to > 4000 ng/L (DuPont and URS Diamond Corporate Remediation Group, 2008) and in private wells at up to > 13,000 ng/L (Hoffman et al., 2011).

In New Jersey, PFOA was detected at up to 190 ng/L in shallow unconfined wells of a public water supply located near an industrial source (Post et al., 2009a), and at > 40 ng/L, with a maximum above 400 ng/L in 59 of 104 private wells within a radius of slightly more than 2 mi of this facility (DuPont, 2009). Contamination of the distant wells was likely due to air deposition (Post et al., 2012).

The PFAS may also enter the body by ingestion of dust and dirt particles and by contact with products that have been treated with substances that contain PFAS or their precursor compounds, which may include carpets, upholstered furniture, or textiles. These routes of entry may be of particular importance regarding the toxicology of perfluorinated compounds in children because contact can occur indirectly by hand-to-mouth transfer or directly to the mouth if an infant sucks on the product.

Another route that must be considered is inhalation of PFAS in indoor or outdoor air, as well as the inhalation of waterproofing sprays.

Dermal exposure may also occur by skin contact with PFAS-treated products.

Occurrence in Drinking Water

The PFOA and other PFAS occur in raw and finished drinking water from both groundwater and surface water sources in other parts of the United States and other nations around the world (reviewed by Mak et al., 2009; Post et al., 2012; Post et al., 2013). The PFAS are found in drinking water impacted by discharges from industrial facilities, release of AFFF, and other known sources of contamination, as well as where the source is unknown (Post et al., 2012).

The PFAS have been detected at high frequency in some river basins that are important sources of drinking water. For example, it was detected (> 1 ng/L) in 82.3 percent of samples from 80 locations throughout the Cape Fear River (N.C.) drainage basin (population of 1.7 million), at a median of 12.6 ng/L and a maximum of 287 ng/L (Nakayama et al., 2007). In the Upper Mississippi River drainage basin in the midwestern U.S. (population of 30 million), it was detected (> 1 ng/L) in 73 percent of 88 locations, with a median of 2.07 ng/L and a maximum of 125 ng/L. In the Tennessee River in Alabama, PFOA levels were 395+128 ng/L in samples from the 35 river mi downstream of the site of discharge from a fluorochemical manufacturing facility, with the highest levels (521-598 ng/L) in the 6 river mi furthest downstream (Hansen et al., 2002).

In Germany, PFOA and other PFAS in organic material, which were applied to agricultural land, contaminated the Moehne

and Ruhr Rivers, important sources of drinking water. The PFOA was detected at up to 33,900 ng/L in a creek near the site of contamination upstream of these two rivers, and at up to 519 ng/L in drinking water from the Moehne River (Skutlarek et al., 2006).

The PFAS are not effectively removed from drinking water by conventional treatment processes, such as coagulation/flocculation, sand filtration, sedimentation, medium-pressure ozonation, aeration, chloramination, and chlorination; the PFAS can, however, be removed from drinking water by GAC or RO (Rumsby et al., 2009; Bartell et al., 2010a; Tagaki et al., 2011; Eschauzier et al., 2012; Appleman et al., 2014; DWQI, 2015b). Unless specific treatment for removal of PFAS is in place, concentrations of PFAS detected in raw drinking water can be considered to be representative of concentrations in finished drinking water.

Health Risks From Exposure

The PFAS are found in a wide range of consumer products that people use every day, such as cookware, pizza boxes, and stain repellants; therefore, most people have been exposed to them. Certain PFAS can accumulate and stay in the human body for long periods of time. There is evidence that exposure to PFAS can lead to adverse health outcomes in humans. The most-studied PFAS chemicals are PFOA and PFOS and it's been shown that they can cause reproductive and developmental, liver and kidney, and immunological effects in laboratory animals. Both chemicals have also caused tumors in animals.

The PFOA and PFOS are linked to a number of health effects, including:

- ◆ Liver damage
- ◆ Kidney damage
- ◆ Increased cholesterol levels
- ◆ Pregnancy-induced hypertension
- ◆ Certain types of cancer and increased risk of thyroid disease
- ◆ Increased risk of decreased fertility
- ◆ Increased risk of asthma diagnosis
- ◆ Decreased response to vaccines

The EPA acknowledges that associations of PFOA and numerous health endpoints are observed in these human populations and that associations with some effects have consistently been found in multiple human studies. Some states, however, have established some of their own criteria, and have established lower thresholds that they believe are more protective of public health.

New Jersey, for instance, established a Drinking Water Quality Institute (DWQI) Health Effects Subcommittee to pursue development of a maximum contaminant level

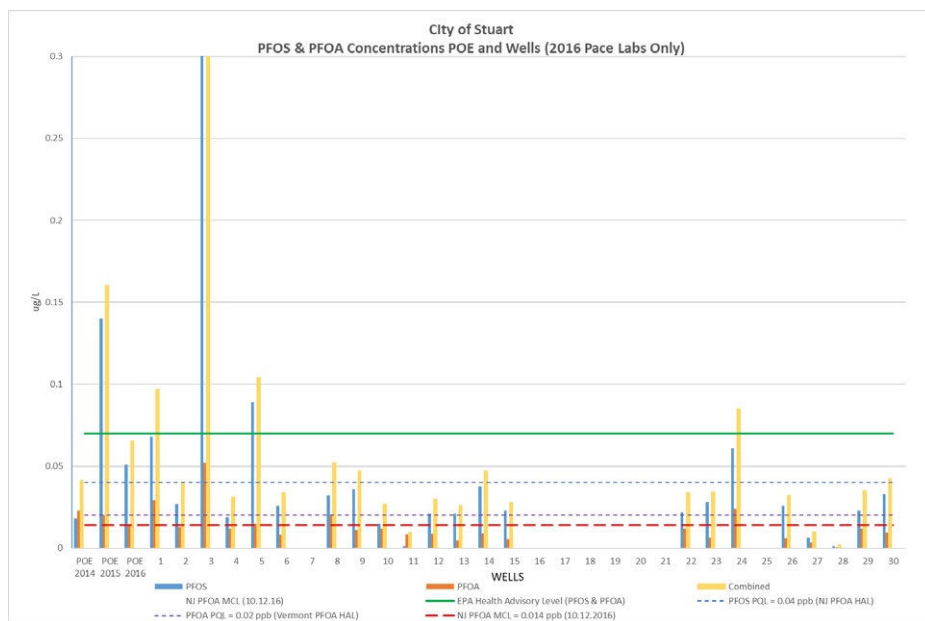


Figure 2. Contaminant concentrations.

(MCL) recommendation for PFOA on Jan. 27, 2009, based on its potential health effects and its occurrence in New Jersey public water supplies. The EPA states that, while these human studies are useful for hazard identification, they cannot be used quantitatively because the PFOA exposures at which the associations were observed are unknown or highly uncertain. Although the subcommittee agreed that the human data have limitations that preclude their use as the primary basis for risk assessment, it does not agree with EPA that the serum PFOA concentrations and PFOA exposures associated with human health effects are highly uncertain or unknown.

Several health effects, some with evidence supporting multiple criteria for causality, are associated with PFOA exposures at serum levels well below those that would result from exposure to 70 ng/L in drinking water. The subcommittee therefore concluded that elevations in serum PFOA levels of the magnitude expected from ongoing exposure to 70 ng/L (EPA Health Advisory) in drinking water are not desirable and may not be protective of public health.

New Jersey therefore established much lower criteria as listed:

14 ng/L – Health-based MCL recommended by DWQI Health Effects Subcommittee
 40 ng/L – N.J. Department of Environmental Protection (DEP) drinking water guidance (2007) based on older toxicology data
 70 ng/L – EPA lifetime health advisory

Regulatory Review

The widespread detection of these chemicals and their persistence in the environment led EPA to establish provisional health advisory (PHA) values for PFOA and PFOS of 0.4 and 0.2 ug/L, respectively, and PFOA and PFOS were added to the EPA Contaminant Candidate List 3 (CCL 3) published in October 2009 (EPA, 2009). Six of the perfluorinated compounds were also added to the EPA UCMR 3. As a result of this testing, and with some of the history and health risks associated with PFAS compounds, EPA greatly reduced the health advisory levels in May 2016 and issued a provisional health advisory of 0.07 ug/L for combined PFOS and PFOA.

The UCMR 4 is currently underway, but does not include any of the PFAS family of contaminants. The UCMR 4 was published in the Federal Register on Dec. 20, 2016. The UCMR 4 requires monitoring for 30 chemical contaminants between 2018 and 2020 using analytical methods developed by EPA and consensus organizations. This monitoring provides a basis for future regulatory actions to protect public health.

The EPA is considering UCMR 5 to be

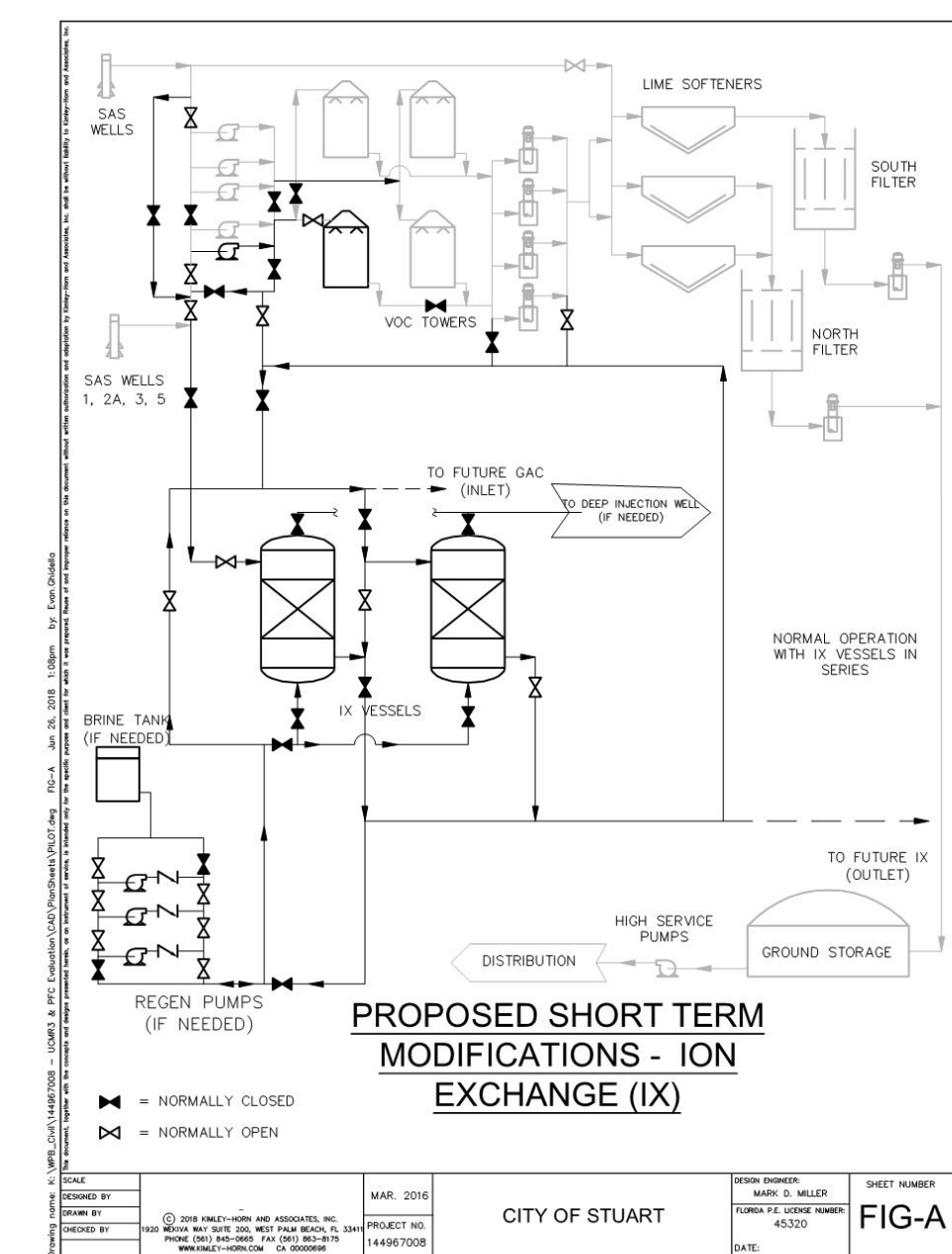


Figure 3. Breakthrough curves at different resin depths versus bed volumes.

conducted similarly to previously unregulated contaminant monitoring cycles every five years. In addition to PFAS compounds monitoring, seven specific PFAS analytes were nominated on the CCL 5 for consideration in UCMR 5. Relative to the priority for PFAS compounds to be included, EPA officials indicated that they would be awaiting input to assist the agency in making decisions on priority for monitoring. The EPA noted that the agency did not have health advisories for many PFAS compounds, but that did not preclude the agency from monitoring them under UCMR 5, which would be useful in developing such advisories. The UCMR 5 monitoring would begin in January 2023 and be completed by 2026.

Approach

The city's existing groundwater supply had limitations due to challenges with other historical contaminants, including the presence of PFAS and some of the emerging contaminants of concern. Accordingly, the approach to the city's water supply concerns revolved around achieving compliance for the existing water source and customers, as well as a sustainable supply for the city's future.

The short-term solution involved analyzing, selecting, and implementing the treatment technologies available to treat and remove the currently present PFAS from the produced

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water prior to distribution. The focus of this evaluation supports the short-term alternatives available to achieve such treatment and enable the city to achieve compliance. The goals for the short-term evaluation included the paramount compliance with UCMR regulations, followed by minimizing the capital and operation expenses for the short-term solutions.

The long-term approach involved implementing a consistent and reliable treatment

method to remove emerging contaminants or securing a sustainable water source free of contaminants beyond traditional salinity and organic contaminants.

The current water supply is derived from the surficial aquifer, which has limited withdrawal capacity and is highly scrutinized by the South Florida Water Management District (SFWMD) due to its influence on the surrounding water table. In addition, its close proximity to the surface yields it as suspect to contamination from

surface application of chemicals and reclaimed water. Specifically, these contaminants include the PFAS and others, which are listed in Table 2. This evaluation addresses the desktop analysis of multiple treatment alternatives.

Longer-term raw water supply focused on alternative water sources that should be evaluated in the future for sustainability, treatment feasibility, regulatory considerations, and financial efficiency for the city. Alternative water sources that were identified can be used as the sole source of supply water, or used in combination with the existing surficial influenced wells or another alternative supply. Once one or multiple sources are identified and committed, treatment pilots should be engaged to demonstrate successful treatment, as well as operational feasibility, to support operational commitments to the city's utility staff and financial resources.

The existing surficial aquifer is a limited source of raw water, and the city does not have any alternative water supply sources other than interconnects with neighboring utilities. Additionally, the existing surficial aquifer has a number of existing contaminants that further limit the withdrawal capacity and, with the recent discovery of PFAS contaminants, further limits the utility's ability to meet future water system demands and drinking water standards. Table 2 provides a list of current and historical known contaminants that require advanced treatment beyond conventional lime softening and filtration.

Prior to 2019, there was no known groundwater contaminant level established for PFAS that would trigger corrective cleanup actions or potential funding at the PFAS levels measured in the wells. Additionally, the use of reclaim water for irrigation and continued recharge of the surficial aquifer has no regulations for these emerging contaminants; however, reclaim water quality standards are currently under review by the regulatory agencies, which may trigger monitoring and/or potential treatment for these emerging contaminants. Subsequently, the city's actions should address these contaminants in both the drinking water and potential discharge to the wastewater treatment system to minimize any discharge of these contaminants to the environment.

The short-term solution should include either replacing lost capacity from these wells with finished water from existing finish water interconnects, or restoring the functional use of the existing groundwater wells containing elevated PFAS levels with an alternative treatment method. Restoring capacity of the raw

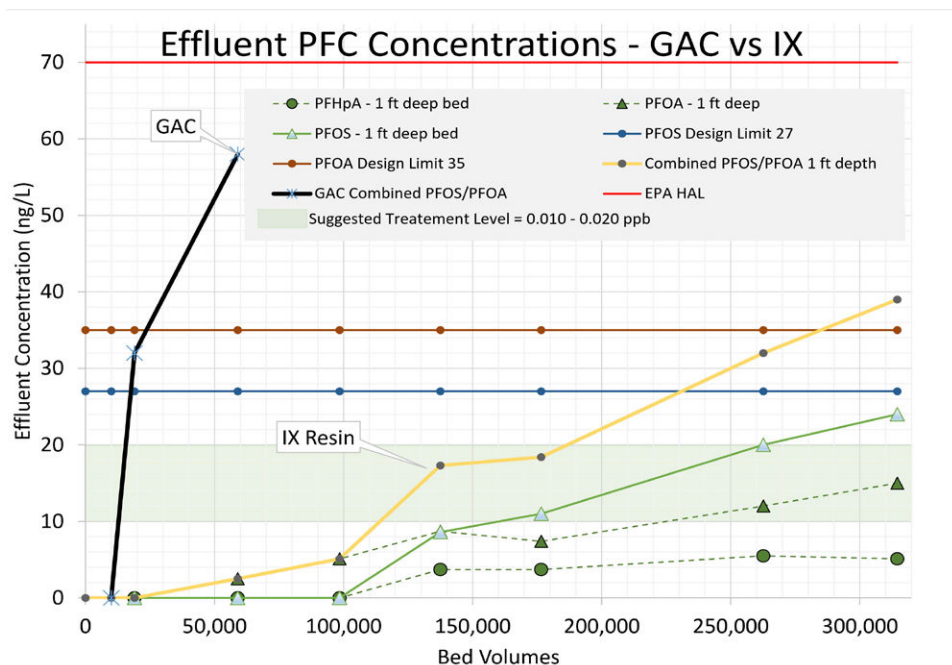


Figure 4. Granular activated carbon versus ion exchange.

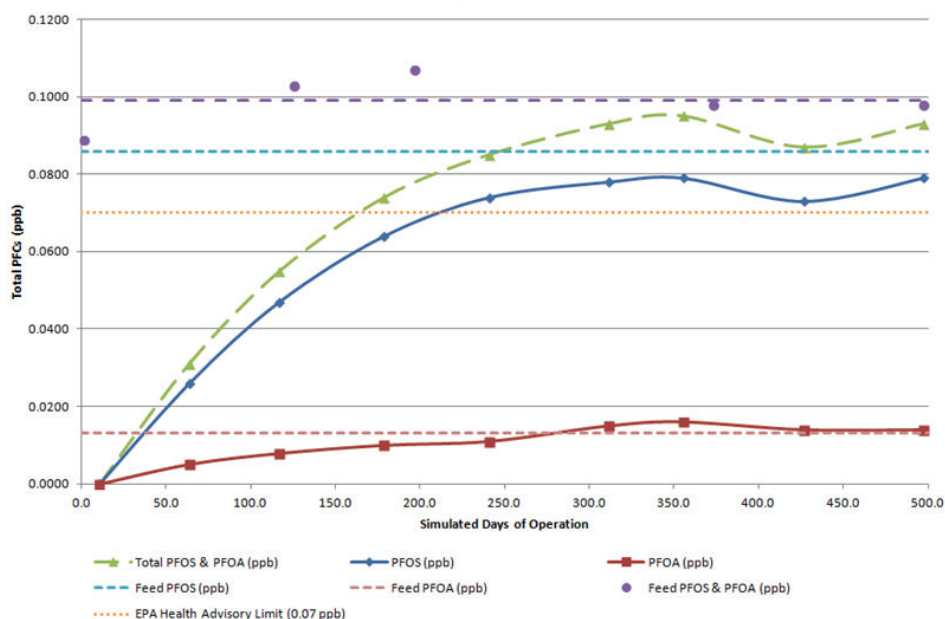


Figure 5. Perfluorooctanoic acid and perfluorooctane sulfonic acid versus simulated days of operation.

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water supply wells containing PFAS levels above the HAL must include an advanced treatment method not currently used at the existing facility. Pilot testing using the most cost-effective, best-known track record of reducing PFAS was developed and implemented to identify design criteria, operational experience, and capital and operating costs associated with the selected treatment option.

The existing treatment system provides conventional treatment, consisting of aeration

and air stripping of volatile organic compounds, lime softening, filtration, and disinfection. Conventional filtration and lime softening have limited effectiveness removing PFAS found in the raw water. It's also evident from the water quality test results taken at the point of entry (POE) and individual wells that PFAS are unaffected through the existing treatment plant. Figure 2 depicts PFOA and PFOS levels in all of the wells, as well as at the point of entry, indicating that the existing conventional treatment system is ineffective at removing these

constituents. As such, conventional treatment is not an option for continued treatment and reduction of these emerging contaminants; therefore, alternative treatment options were researched and evaluated that would effectively remove these contaminants in a cost-effective manner.

Viable treatment methods known at the time to be effective at removing PFAS include:

1. An ion exchange (AIX)
2. GAC
3. Membrane treatment: RO and nanofiltration (NF)
4. Other treatment methods: chemical oxidation/reduction, thermal and electrochemical, biological

Based on the research, literature review, and discussions with manufacturers, sorption processes (such as GAC and AIX) and membrane treatment provide the most-effective removal of PFAS from water streams. Chemical oxidation, advanced oxidation and reduction processes, and thermal and electrochemical processes are processes that show promise, but many of them are still in the research mode, have limitations, and have no full-scale track record. Each one is site-specific and may be complementary and more effective as combined systems, but may be more suitable in wastewater streams where other interferences exist. These treatment methods were not evaluated further due to their more research-driven techniques and limited full-scale installations that exist for the treatment of groundwater.

The primary treatment goal is to remove the PFAS from the raw water, followed by reduction or removal of other known contaminants and upcoming UCMRs that may be of concern. The other volatiles and contaminants listed in Table 2 are the secondary goal of implementing a new treatment process.

Total organic carbon (TOC) reduction with a new treatment process is also a benefit that would improve the disinfection byproduct results in the finish water. The benefit of reducing TOC levels has a two-fold effect: addressing the short-term treatment goals, and allowing long-term continued use of the system.

Ion Exchange

The IX is an exchange of ions between two electrolytes, or between an electrolyte solution and a complex solution. Typical ion exchangers are IX resins (functionalized porous or gel polymer), zeolites, montmorillonite, clay, and soil humus. Ion exchangers are either cation exchangers that exchange positively charged ions (cations) or anion exchangers that

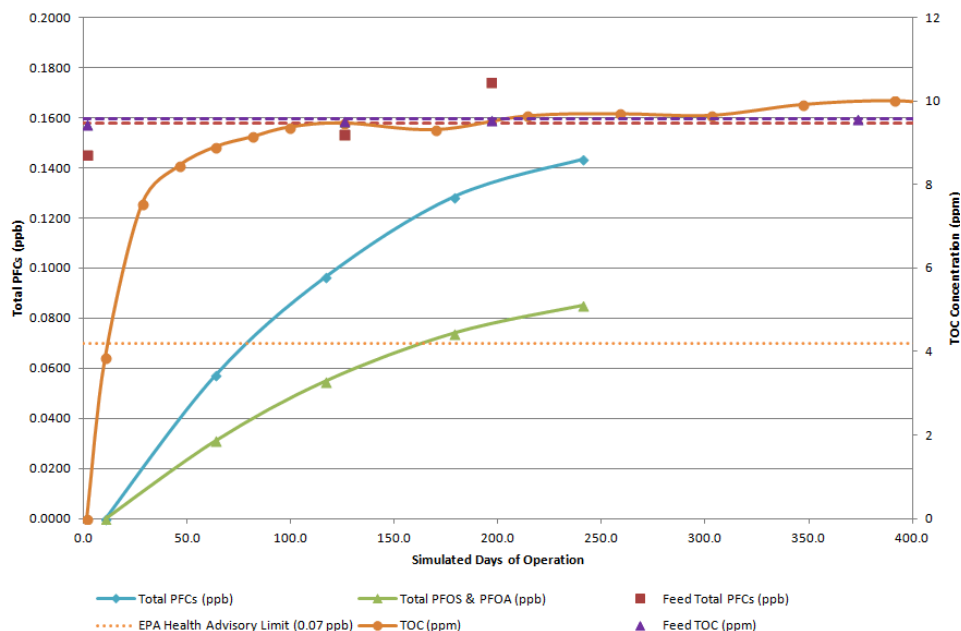


Figure 6. Perfluorinated chemicals and total organic carbon versus simulated days of operation.

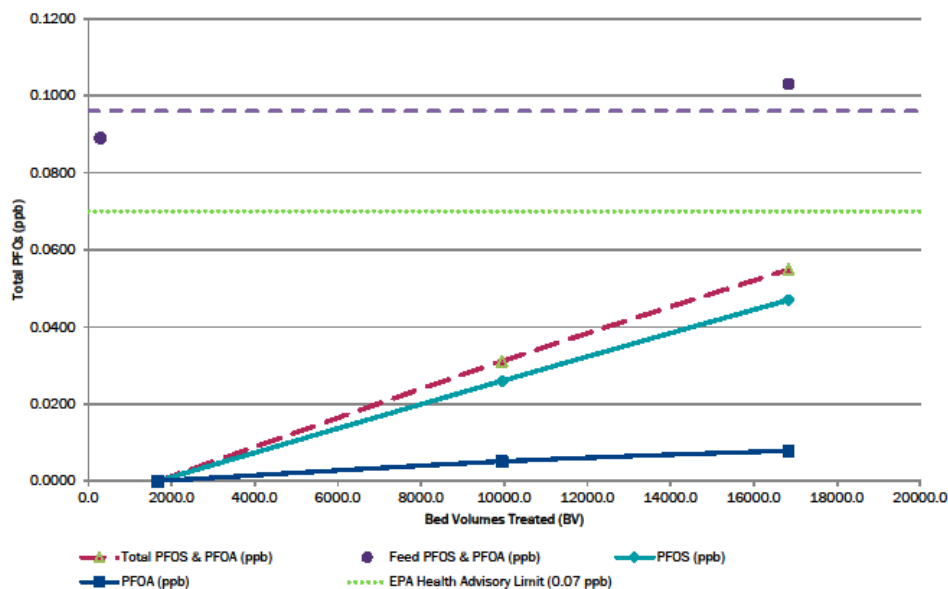


Figure 7. Perfluorooctanoic acid and perfluorooctane sulfonic acid versus bed volumes treated.

exchange negatively charged ions (anions). Typical ion exchangers include softeners that replace or remove calcium (hardness) with sodium.

The IX resins from different manufacturers tend to deliver varying results on PFAS removal. Research indicates that fresh resin presents higher removal efficiency than continuous regeneration approaches (Appleman, 2012). The removal efficiency is estimated to be largely based on molecular weight of the carbon chains. The longer chains, such as PFOS, typically have better removal efficiency in cases where IX has been shown to provide some removal of the PFAS.

Generally, in the cases where IX has provided some level of removal, the smaller versus larger carbon chains were removed at approximately 46 and 92 percent, respectively (Appleman, 2012). According to the 2016 Water Research Foundation (WRF) Web Report #4322, "Treatment Mitigation Strategies for Per- and Polyfluoroalkyl Substances," Amberlite IRA-400 resin was found to have a higher capacity than GAC for both PFOS and PFOA removal. The contact times for IX, however, are much longer than typical bed volumes used for conventional IX treatment, and conventional regeneration techniques were not sufficient to regenerate the resins.

Other studies have indicated waters contaminated with PFAS that contained higher nominal organic matter (NOM) were more effectively removed using IX, possibly due to the interaction between the PFAS and NOM.

Given the research that had been conducted, IX has the potential to provide removal of PFAS and should be considered on a case-by-case basis, compared to the contaminants present and the utility's goals.

Some of the advantages of using IX include:

- Specific, yet partial removal of contaminants with select media.
- Requires low operating pressures.
- No hazardous chemicals required for treatment.

The disadvantages include:

- Significantly less contaminant removal compared to other alternatives.
- Potential to lose resin and requires regular purchase of new resin.
- Maintenance-intensive, with several mechanical transfer processes.
- If regenerated, brine disposal includes waste of an elevated chloride-loaded waste stream through a dedicated force main to the deep injection well (DIW), resulting in significantly higher costs.
- Higher capital installation costs than GAC.

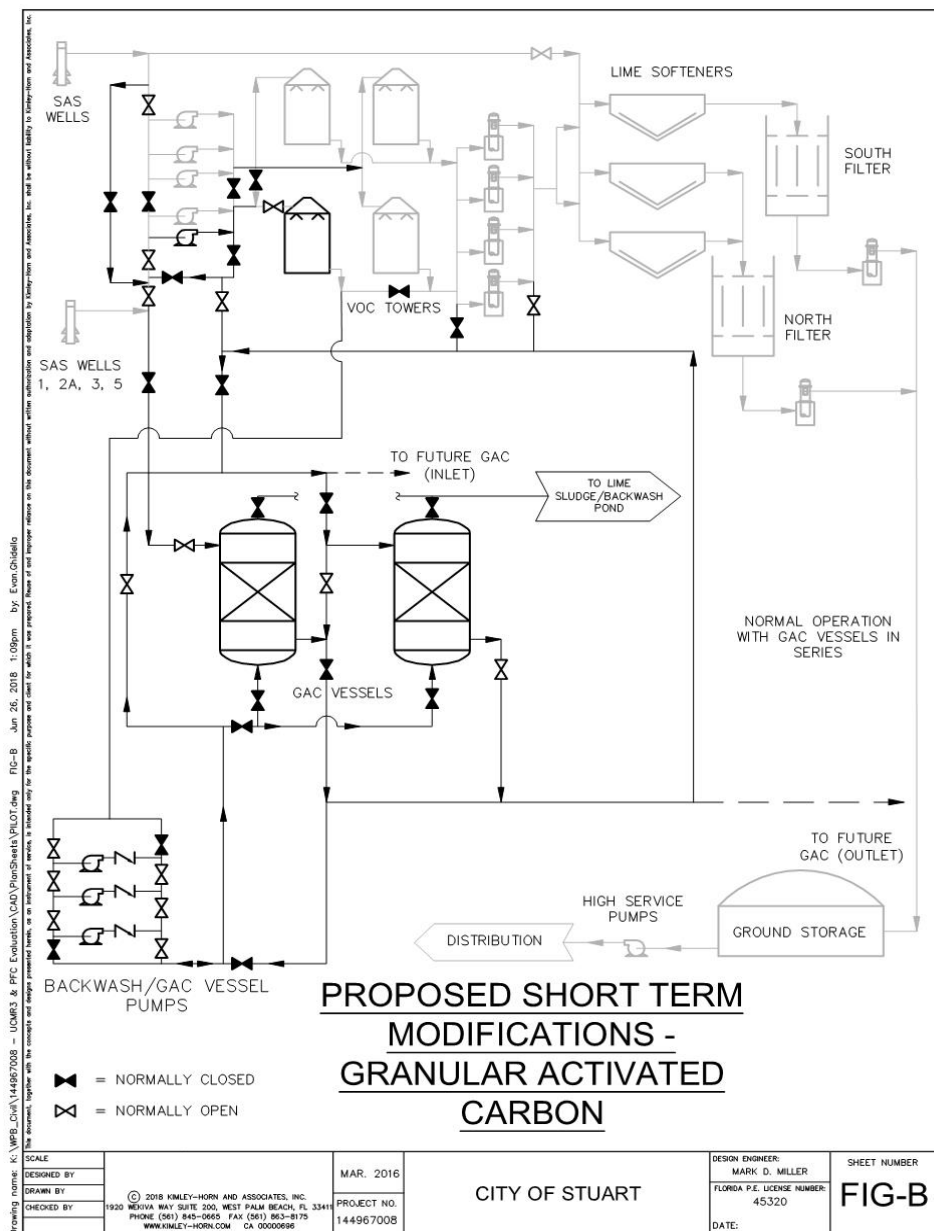


Figure 8. Granular activated carbon process flow diagram.

Granular Activated Carbon

Activated carbon is commonly used to adsorb natural organic compounds, taste and odor compounds, and synthetic organic chemicals in drinking water treatment. Adsorption is both the physical and chemical process of accumulating a substance at the interface between the liquid and solids phases. Activated carbon is an effective adsorbent because it's a highly porous material and provides a large surface area where contaminants may adsorb. The two main types of activated carbon used in water treatment applications are GAC and powdered activated carbon (PAC). Further,

there are other types of GAC, including coconut, wood, and coal-based.

Multiple carbon manufacturers and carbon bases (of their carbon components) have been utilized to effectively remove PFAS in water sources and the testing research has resulted in a variance of active removal rates and bed volumes. The carbon base material, loading rates, raw water contaminants, NOM and TOC, and granule size have all contributed to the length of run time, removal of specific contaminants, and regeneration frequency. Despite the variations in these criteria, the treatment technology overall is effective at removing PFAS of concern to the city.

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In general, waters with TOC and NOM in the raw water significantly reduce the bed volumes to contaminant breakthrough, which results in more-frequent regeneration and more-costly operations. Relating to the city's groundwater supply, organics are going to be present and are most likely going to reduce the longevity of each carbon load. It's anticipated that the frequency of full breakthrough would be around 10,000 bed volumes (Appleman, 2012).

At the pilot scale, small columns of GAC can be exposed to a steady stream of raw water to simulate the actual operating conditions of the utility. Pilot testing is typically completed

using 4-in. columns filled with a known quantity of GAC. As the water is processed through the GAC, the water quality parameters are analyzed on the treated side of the GAC media. As the specific parameters of concern consume the GAC adsorption sites within the media, they will be identified in the treated water. This is termed as the initial breakthrough and the beginning stages of degrading removal of the specified contaminant.

At this point, the carbon will become less efficient at removing the contaminant and the engineering analysis can be used to determine the percentage of breakthrough that can be allowed, while maintaining compliance with

the regulatory conditions. Once the GAC reaches its limit for obtaining regulatory compliance, it's considered exhausted and requires regeneration or replacement with virgin media. This process reveals the design parameters for the full-scale design and operation of the GAC treatment process and can be scaled up directly to the full-scale treatment.

At full-scale treatment design and operation, the process is administered in the same fashion. The pressurized carbon vessels are much larger and hold from 20,000 to 40,000 lbs of GAC, requiring backwash cycles as the pressure buildup in the vessel typically escalates prior to the exhaustion of the carbon media. The breakthrough of the contaminants is observed similarly to the breakthrough described for the pilot-scale operation. The frequency of regeneration is similar to the process observed in the pilot scale adjusted for the quantity of flow at the full-scale treatment. As noted, the full-scale treatment and operation closely resembles the process experienced in the pilot-scale treatment and operation.

Some of the advantages of using GAC include:

- ◆ Proven technology with numerous installations.
- ◆ Requires low operating pressures.
- ◆ No chemicals are required for treatment.
- ◆ Less maintenance than other treatment alternatives.
- ◆ High percentage of removal of specific contaminants.
- ◆ Can be designed for full or partial removal of contaminants.
- ◆ Regenerated GAC minimizes operational costs.
- ◆ Capital expense for installation is low compared to other alternatives.
- ◆ Allows hardness and alkalinity through for treated water stability.

The disadvantages include:

- ◆ Spent carbon must be regenerated offsite.
- ◆ GAC is consumed by hydrogen sulfide (H_2S), iron, dissolved organic carbon (DOC), and TOC, which can reduce the removal efficiency and significantly shorten the regeneration cycles, resulting in increased operating costs.
- ◆ Iron can blind over the media, greatly reducing the treatment effectiveness of the GAC.
- ◆ Operational expenses may be higher than the other alternatives due to the frequent estimation of regeneration cycles.

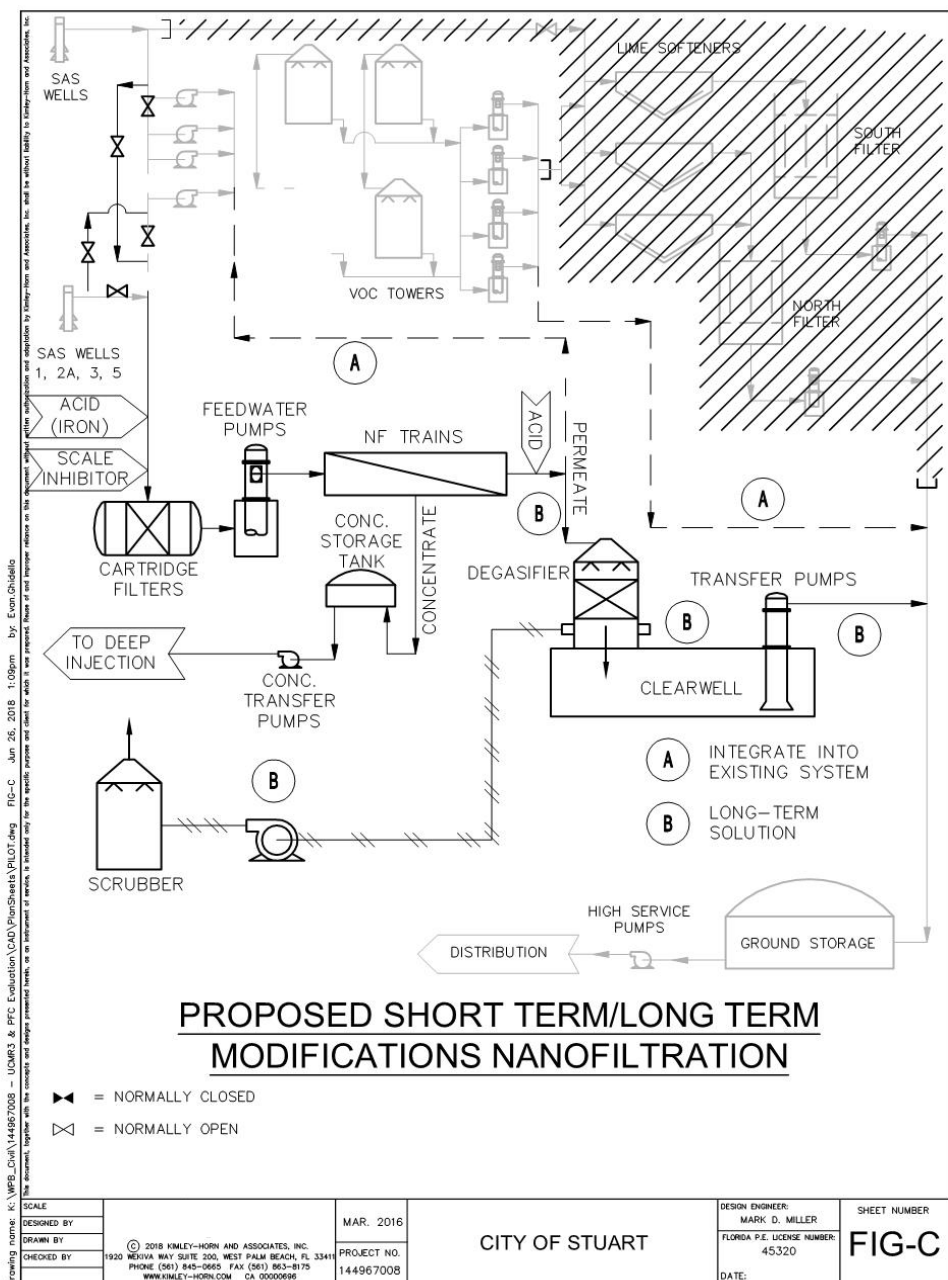


Figure 9. Membrane process flow diagram.

Continued on page 38

Membrane Treatment

Research suggests that membrane treatment is a viable option for removal of the contaminants listed in the UCMR 3 and the suggested contaminants in the drafted UCMR 4; however, there is no known full-scale membrane treatment system that is currently in operation and that demonstrates consistent reliable rejection of these contaminants. Depending on the level of treatment desired and the contaminants present, NF membranes can be implemented to provide effective removal of the PFAS regulated by UCMR 3 and UCMR 4.

As with several other technologies listed within this analysis, the smaller-carbon chain PFAS, such as perfluorobutanoic acid (PFBA), are more challenging to remove. The NF membranes were observed to remove

greater than 90 percent of the PFAS in both a flowthrough and recycled treatment approach (Appleman, 2012).

Where more-effective treatment removal is needed, brackish water RO membranes have shown to remove greater than 90 percent of all the contaminants listed, and greater than 95 percent of all contaminants listed over the molar mass of 300 g/mol (Appleman, 2012). Even with the molar mass driving most of the rejection abilities, the RO membrane is estimated to remove greater than 95 percent of PFBA found in the raw water, which is the smallest chain of PFAS; therefore, membrane treatment provides the best available technology and highest removal efficiency of all the PFAS down to the smallest molecular weight than the other treatment methods.

While research indicates that membrane elements appear to reject the PFBA, PFAS, and PFOA at a high rate, it's suggested that

the city pilot the membrane elements to confirm the rejection rates, as well as compare the performance of elements from different manufacturers.

At the pilot scale, a single-element testing unit can be utilized to show rejection characteristics of selected membranes. The performance can be quickly compared by simulating the projected recovery of multiple elements within the full-scale system. Typical single-element pilot tests focus on the lead and tail elements of the system, as well as a representative middle element within the membrane train. Samples taken from the raw feed stream, permeate, and concentrate can be analyzed to monitor the respective performance from the membrane elements. If further testing is desired to simulate the full membrane train's performance and any fouling potential, a pilot-scale membrane test can be initiated using 4-in. elements mocking the projected staging array.

Some of the advantages of using membrane treatment include:

- ◆ High percentage of removal of contaminants.
- ◆ Continuous operation of consistent treatment quality.
- ◆ Automated process controls for operators.
- ◆ Lowest operating costs compared to the comparable alternatives.
- ◆ Can be tested at a small scale to identify the effective removal of contaminants.

The disadvantages include:

- ◆ Concentrate disposal is required, resulting in increased DIW usage.
- ◆ Direct force main is required to convey concentrate to DIW for disposal.
- ◆ New chemicals are introduced to the plant operation (acid for pH adjustment, antiscalant for membrane process).
- ◆ Capital expense is larger than other alternatives.
- ◆ Operator interaction and instrument technician are required for day-to-day operation.

Other Treatment Options

The following methods of treatment are primarily research-driven and show some degree of effectiveness, either as a standalone process or in addition to other forms of treatment, such as GAC and IX, either separately or together. These were not evaluated further, but were not ignored, since this contamination is emerging and still being defined. In July 2019, EPA awarded \$6 million in grants to research potential environmental impacts of PFAS substances in waste streams, including electron beam technology, for the destruction

Table 3. Raw Water Parameters

City of Stuart - Design Raw Water						
	Detected range	units	HAL/ MCL	units	Design Raw Water (ug/L)	Target Reduction (ug/L)
Methyl-tert-butyl-ether	1.8	ug/L	U	ug/L	1.8	-
1,1-Dichloroethane	0.23	ug/L	U	ug/L	0.23	-
Chloromethane	0.38-0.51	ug/L	U	ug/L	0.51	-
Tetrachloroethylene (PERC)	0.65	ug/L	0	ug/L	0.65	-
1,2-Dichlorobenzene	0.25	ug/L	600	ug/L	0.25	-
Benzene	1.3	ug/L	0	ug/L	1.3	-
Vinyl Chloride	0.8-12.5	ug/L	1	ug/L	1.3	-
cis-1,2-Dichloroethylene	0.3-42.4	ug/L	70	ug/L	40	-
trans-1,2-Dichloroethylene	1.1	ug/L	0.1	ug/L	1.1	-
Chlorobenzene	0.34	ug/L	100	ug/L	-	-
Perfluorooctanesulfonic acid (PFOS)	0.051-0.470	ug/L	0.070	ug/L	0.500	ND (0.0025)
Perfluorooctanoic acid (PFOA)	0.014-0.052	ug/L	0.070	ug/L	0.100	ND (0.0012)
Perfluorononanoic acid (PFNA)	0.011-0.014	ug/L			0.014	-
Perfluoroheptanoic acid (PFHpA)	0.0035-0.027	ug/L			0.027	-
Perfluorohexanesulfonic acid (PFHxS)	0.011-0.26	ug/L			0.26	-
Perfluorobutanesulfonic acid (PFBS)	0-0.041	ug/L			0.041	-
Perfluoro-1-hexanesulfonic acid	0.015-0.47	ug/L			0.47	-
Perfluoro-1-octanesulfonic acid	0.046-0.38	ug/L			0.38	-
Hydrogen Sulfide (Total)	0.1 - 0.8	mg/L			0.6	-
Sulfate	10 - 25	mg/L	250		15	-
Chloride	25 - 60	mg/L	250		50	-
Nitrate	<8	mg/L	10		5	-
Alkalinity (as CaCO ₃)	210 - 310				280	-
TOC	3.7 - 10.4	mg/L			8.0	-
Iron	0.04 - 0.65	mg/L	0.3	mg/L	0.5	-
Color	15 - 40	CU	15	CU	30	-
pH	7.0 - 7.6				7.4	-
Calcium Hardness (as CaCO ₃)	280 - 350				300	-
TDS	320 - 410	mg/L	500	mg/L	410	-
Existing Contaminants (VOC's)						
Parameters to Remove						

of short-chain and perfluoroalkyl substances in groundwater, wastewater, sewage sludge, and soils.

Based on research, advanced oxidation processes (AOP), such as chemical oxidation, electrochemical oxidation, ultraviolet treatment, photolysis, photocatalysis, activated persulfate oxidation, and other oxidative reduction processes, appear to be successful in degrading PFAS, especially PFOA and PFOS.

Electrochemical oxidation destroys contaminants through two mechanisms: direct anodic or indirect oxidation. When contaminants are destroyed by direct anodic oxidation, they will adsorb onto the anode surface and are destroyed by an electron transfer reaction. In indirect oxidation, contaminants are destroyed in solution by oxidation through strong oxidants generated by cathodic electrochemical reactions. This process has been used to treat many different contaminants, including phenols, dyes, and endocrine-disrupting chemicals.

Electrochemical oxidation can have a long life span and is versatile, energy-efficient, automated, and cost-effective. It can also be used on different volumes of gases, liquids, and solids, and is relatively easy and inexpensive to construct and operate. There are a wide variety of electrode materials that can be used; however, their cost is a major limitation, as well as the difficulty of building the electrodes compared with other electrode materials. In general, electrochemical oxidation has some limitations.

Production of toxic byproducts may also occur when treating PFAS-contaminated wastewater mixed with other harmful substances, including chlorine gas, hydrogen fluoride, bromate, perchlorate, and absorbable organic halides. Future research is needed for these options, since degradation of different PFAS, including polyfluoroalkyl compounds, can occur. Furthermore, only two studies have observed PFAS destruction when using electrochemical oxidation in the presence of AFFF-impacted or PFAS-contaminated synthetic groundwater.

More studies need to be conducted with environmental matrices to determine whether electrochemical oxidation is suitable for PFAS remediation. Photolysis, photocatalysis, activated persulfate oxidation, and other ultraviolet (UV)-induced oxidation are also promising treatment methods, but again, require similar research, as electrochemical oxidation has not been fully developed into full-scale implementation.

Thermal degradation of PFAS involve breaking the carbon-carbon (C-C) and carbon-fluorine (C-F) bonds with high temperatures to produce perfluoroalkyl radicals that will subsequently decompose and form similar

Table 4. Ion Exchange System Design Criteria	
Pretreatment:	Bag Filters (10 micron)
PFC Treatment Capacity:	75% Full Scale (WTP = 6 mgd MDF) 4.0 mgd (2,800 gpm)
Number of Vessels:	4 w/ 1 O/S
Vessel Diameter:	12 ft
Vessel Area:	113 sq ft
Orientation:	Lead/Lag (series)
Loading:	12.4 gpm/sqft 700 - 1,400 gpm/vessel
Vessel SW Depth:	9 ft (8.0 – 10.0 ft)
dP across vessel:	1.5 – 2 psi/ft bed 5.25 – 10 psi
Empty Bed Contact Time (EBCT) resin:	2.4 – 3.0 minutes
Resin Depth:	4 ft – 5 ft
Resin Volume:	452 cft/vessel 565 cft/vessel (max) 1,808 - 2,260 cft TOTAL
Topping/Guard Depth:	0 - 1 ft
Topping/Guard Volume:	113 cft/vessel 452 cft TOTAL
Resin Types:	Purolite - PFA694E DOW - Dowex PSR2 Calgon - CalRes 2301, CalRes 2304
Topping Type:	Ion Exchange Resin Granular Activated Carbon (GAC)
Desired Treatment Capacity (to nondetect)	
Design:	80,000 Bed Volumes
Maximum projected:	150,000 Bed Volumes

degradation products as photolytic treatment of PFAS. Thermal treatment methods include thermal chemical reactions, incineration, sonochemistry, sub- or supercritical, microwave-hydrothermal, and high-voltage electric discharge, all of which are still in research modes.

Incineration is one of the most common ways to destroy hazardous compounds and to reduce waste, but can result in harmful emissions. Incineration of PFAS, including PFOS, ammonium perfluorooctanoate (APFO), and PFOA, has been successful at temperatures ranging from 600 to 1,000°C (USEPA, 2003; Krusic and Roe, 2004; Krusic et al., 2005; Yamada et al., 2005; Taylor et al., 2014).

Sonochemical degradation of PFAS is another treatment process that occurs through the application of ultrasound to an aqueous medium. When ultrasound is applied, cavitation bubbles form during the rarefaction (negative pressure) portion of sound waves. The cavitation

bubbles will implode, creating extreme temperatures and pressures (14,000 pounds per sq in. [psi]) within a cavity. Highly reactive intermediates and radicals, including hydroxyl radicals, hydrogen atoms, and oxygen atoms, form during cavitation bubble collapse. This combination of highly reactive species and high temperatures and pressures has made sonolytic decomposition of PFAS successful, but again, is only at the research level.

Microbial degradation of PFAS has only been observed to occur with polyfluoroalkyl substances. Several other studies have used different treatment methods to degrade PFAS, including ozonation under alkaline conditions, permanganate, and ball milling. Ozonation is a commonly used advanced AOP in at least one-third of water treatment plants (WTPs) in the U.S. Ozonation of PFOA and PFOS was viable within 4 h when pretreating with O₃ at pH 4–5, followed by pH adjustment to 11, but

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Capital and Operating Costs

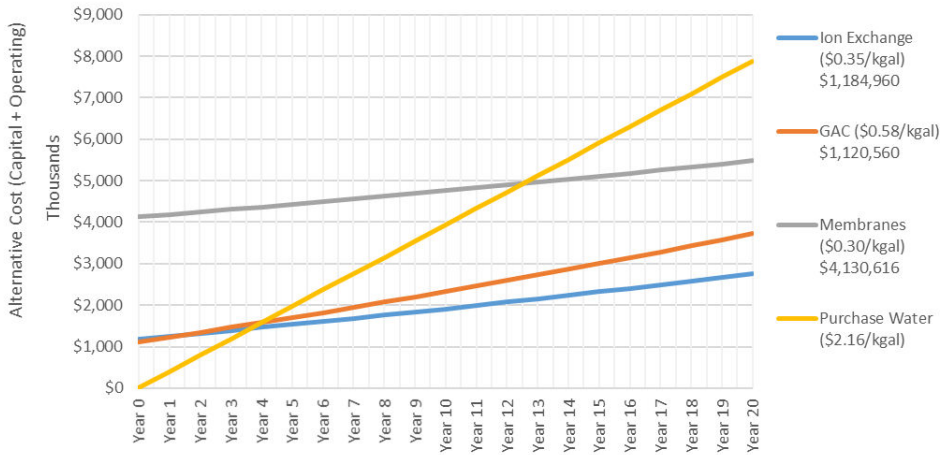


Figure 10. Facility capital and operating costs.

Table 5. Long-Term Economic Differential

Treatment Alternative	Capital Cost	Annual Operating Cost	20-Year Net Present Value (NPV): Capital and Operating Cost
Ion Exchange	\$ 1,184,960	\$ 67,069	\$ 2,526,335
GAC	\$ 1,120,560	\$ 111,143	\$ 3,343,410
Membranes	\$ 4,130,616	\$ 57,488	\$ 5,280,366
Local Utility	\$ N/A	\$ 394,200	\$ 7,884,000

Continued from page 39
environmental matrices containing humic acid may inhibit ozonation (Lin et al., 2012a).

Permanganate is also widely used as an oxidizing agent for iron and manganese, taste and odor control, microorganism control, and degradation of other hazardous pollutants. Permanganate removed about 50 percent PFOS, but with only 5 percent fluoride yield at elevated temperatures and very low pH (65°C and pH 4.2). Although complete PFOS decomposition could not be achieved, degradation efficiency of permanganate improved with increasing temperatures and was not inhibited by the addition of organic acids, including oxalic, tartaric, succinic, citric, and humic acid.

In general, most of these advanced treatment options are still considered research and do not have any known full-scale installations with any proven operational track record; therefore, further consideration of these treatment options was deemed not feasible or recommended.

Pilot Testing

Given the relatively minimal testing history and research completed on PFAS and the limited full-scale treatment systems that have been in operation, it was recommended that the city perform a pilot test immediately to identify the best method of treatment for the utility. Specific technologies to be tested include GAC, NF, low-pressure RO, and IX (jar test-level), as these technologies showed the most-effective removal of PFAS in the research that has been conducted. The pilot testing will help to identify the operating costs related to regeneration of the GAC and IX media, as well as the feed pressures effective for membrane treatment. Further, design specifics can be identified to support the preliminary and final design of the full-scale treatment.

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Table 6. Resin and Hybrid Systems

CITY OF STUART - IX PFAS TREATMENT SYSTEM															
VESSEL 1 - Calgon	Polymer Structure	Volume (ft) ³	Weight (lbs)	VESSEL 2 - Evoqua	Polymer Structure	Volume (ft) ³	Weight (lbs)	VESSEL 3 - Purolite	Polymer Structure	Volume (ft) ³	Weight (lbs)	VESSEL 4 - Resintech	Polymer Structure	Volume (ft) ³	Weight (lbs)
CALRES 2304	Gel - 100% N-Tri-Butyl Amine	459	-	Resin PSR2 Plus	Styrene-divinylbenzene	564	-	PFA694E	Polystyrene crosslinked with divinylbenzene	425	17,850	SIR-110-HP	Styrene-divinylbenzene	452	18,532
Filtrisorb 400		106.6	3,200					A502P	Macroporous polystyrene crosslinked with divinylbenzene	148	-	AGC-30-AW	Coconut Shell	113	3,107
Total		565.6	3,200	Total		564	0	Total		573	17,850	Total		565	21,639



Figure 11. Start-up of the system.



Figure 12. Sand and foulant on bag filters.

Continued from page 40

It was important to dedicate the pilot testing to the worst-case supply to ensure that the desired level of water quality can be obtained, as well as develop a conservative review of the capital and operating costs. In the city's utility, it was recommended to identify the worst-case source water and commence the pilot testing at that location. Should the well not present access for pilot testing onsite, a split stream of the water supply can be plumbed to the nearest available area for operating the various pilot testing units.

Initially, pilot testing IX was not conducted due to the significantly higher capital costs associated with constructing a separate pipeline to the wastewater treatment plant (WWTP) for disposal of spent brine regenerant to the WWTP, and additional costs and handling of salt and brine for the regeneration. Simply disposing of the spent regenerant to the WWTP would create higher-than-desired salinity in the treated wastewater effluent used in the city's reclaim system. Conversion of its existing DIW to accept industrial waste was also a cost that, at the time, was not considered feasible. Disposal of concentrated solution of PFAS was also an unknown, since there were no regulations in place that might consider concentrated PFAS as hazardous waste; however, piloting IX was reconsidered as a pass-through system if the levels of treatment, or bed volumes, were greater and considered more feasible than GAC.

Ion Exchange Pilot Testing

The IX treatment was at first believed to be too expensive due to the disposal of the waste brine regenerant. Concentrating the PFAS and elevating the salt content in the waste stream did not make this option feasible, since the waste could not be disposed of via sanitary sewer because most of the treated wastewater was reused for reclaimed water. The waste, therefore,



Figure 13. Bag filter vessel.

would have to be piped separately to the WWTP where it could be pumped and disposed of via the DIW, but it would also have to be modified to receive the waste stream, requiring it be converted to an industrial-rated DIW. Capital and operating costs would therefore be higher for IX versus GAC.

Based on the significant additional costs to install a separate pipeline from the WTP to the WWTP for brine waste disposal, and the additional costs and handling of salt and brine feed system, AIX was initially not pursued further; however, continued pilot testing was conducted by Evoqua as a trial to test some of the IX resins that exhibited PFAS adsorption. As pilot testing continued with several types of IX resins (specifically, Dowex PSR2), in addition to being the most-effective of the ones being tested, the removal efficiency and long-term

removal presented IX to be the most apparent cost-effective treatment method for removal of PFAS.

Figure 3 illustrates the plotted breakthrough curves for PFOS and PFOA at different resin depths versus bed volumes. Compared to GAC, the breakthrough of combined PFOA and PFOS was more than 20 times longer than GAC using the design limit of 38 parts per trillion (ppt). Typically, the breakeven costs of GAC versus IX are in the range of 4:1, with GAC being four times less expensive per cu ft than IX.

Figure 4 illustrates the following findings:

- ◆ Similar to the GAC testing, the feed contained an average TOC concentration of 10 mg/L parts per mil (ppm) and an average apparent color of 25. The resin treatment appeared to be unaffected by these constituents, assuming the iron was not oxidized and suspended material did not foul the resin.
- ◆ The bed volumes providing sufficient treatment are greater than 100,000, assuming the PFAS-level breakthrough is less than the 38 ppt design level.
- ◆ Based on extensive literature review, laboratory testing capabilities, ongoing research, and stricter water quality requirements in other states, it's recommended that the city target treatment removal levels less than 10 ng/L and up to 20 ng/L for combined PFOS/PFOA.
- ◆ With these lower target removal levels, it's anticipated IX can remove PFAS up to 80,000 bed volumes.

Granular Activated Carbon Pilot Testing

The GAC pilot testing offers a great deal of flexibility in performing tests quickly and efficiently. The pilot-testing recommendation includes securing a four-column GAC pilot, where multiple carbon manufacturers and

Table 7. Ion Exchange Resin Testing

City of Stuart Ion Exchange Resin Testing																					
6/7/2019 Sampled																					
SGS Job Number:	FA64947																				
		Vessel 1					Vessel 2					Vessel 3					Vessel 4				
	units	INF	25%	50%	75%	EFF		25%	50%	75%	EFF		25%	50%	75%	EFF		25%	50%	75%	EFF
Perfluorooctanesulfonic acid (PFOS)	ug/L	0.143	U	U	U	U		U	U	U	U		U	U	U	U		U	U	U	U
Perfluorooctanoic acid (PFOA)	ug/L	0.0141	U	U	U	U		U	U	U	U		U	U	U	U		U	U	U	U
Perfluorononanoic acid (PFNA)	ug/L	0.004	U	U	U	U		U	U	U	U		U	U	U	U		U	U	U	U
Perfluoroheptanoic acid (PFHpA)	ug/L	0.006	U	U	U	U		U	U	U	U		U	U	U	U		U	U	U	U
Perfluorohexanesulfonic acid (PFHxS)	ug/L	0.051	U	U	U	U		U	U	U	U		U	U	U	U		U	U	U	U
Perfluorobutanesulfonic acid (PFBS)	ug/L	0.008	U	U	U	U		U	U	U	U		U	U	U	U		U	U	U	U
Hydrogen Sulfide (Total)	mg/L	0.10				0.11					0.10					0.10					0.10
Sulfate	mg/L	17.7				18.8					18.6					16.4					18.1
Chloride	mg/L	20.7				21.9					22.4					22.4					22.0
Nitrate	mg/L	0.025				0.025					0.025					0.025					0.025
Alkalinity (as CaCO ₃)		265				264					265					265					266
TOC	mg/L	6.2				0.95					3.3					0.80					1.4
Iron	mg/L	0.419				0.449					0.433					0.432					0.216
Color	CU	10				5*					5*					5*					5*
pH		7.4				7.6					7.4					7.5					7.4
Calcium Hardness (as CaCO ₃)	mg/L	246				274					275					263					248
TDS	mg/L	348				339					322					327					336
Bed Volumes (Total)						1,421					1,378				5,065				1,205		1,378
Combined PFOS/PFOA (PPT)		157.1				U					U				U				U		U
* 5 mg/l is mdl																					
U= Undetected																					

* 5 mg/l is mdl

U= Undetected

City of Stuart Ion Exchange Resin Testing																					
9/9/2019 Sampled																					
SGS Job Number:	FA67960																				
		Vessel 1					Vessel 2					Vessel 3					Vessel 4				
	units	INF	25%	50%	75%	EFF		25%	50%	75%	EFF		25%	50%	75%	EFF		25%	50%	75%	EFF
Perfluorooctanesulfonic acid (PFOS)	ug/L	0.101	0.107	0.04	0.01	U		0.05	U	U	U		0.125	0.040	0.05	U		0.13	0.02	0.02	U
Perfluorooctanoic acid (PFOA)	ug/L	0.012	0.011	0.01	U	U		0.01	U	U	U		0.012	0.01	0.010	U		0.01	0.01	0.01	U
Perfluorononanoic acid (PFNA)	ug/L	0.002	U	U	U	U		0	U	U	U		0.002	U	U	U		0	U	U	U
Perfluoroheptanoic acid (PFHpA)	ug/L	0.006	0.006	0	U	U		0	U	U	U		0.007	0.01	0.01	U		0.01	0	0	U
Perfluorohexanesulfonic acid (PFHxS)	ug/L	0.029	0.027	0.01	U	U		0.01	U	U	U		0.031	0.01	0.01	U		0.03	0	0.01	U
Perfluorobutanesulfonic acid (PFBS)	ug/L	0.008	0.007	0	U	U		0	U	U	U		0.008	0	0	U		0.01	U	U	U
Hydrogen Sulfide (Total)	mg/L	0.14				0.10					0.10					0.12					0.10
Sulfate	mg/L	19.4				18.3					18					17.9					17.9
Chloride	mg/L	24.4				21.9					21.9					21.9					22.0
Nitrate	mg/L	0.025				0.025					0.025					0.025					0.025
Alkalinity (as CaCO ₃)		256				257					256					256					256
TOC	mg/L	6.5				5.5					5.6					6.2					5.6
Iron	mg/L	0.43				0.48					0.45					0.47					0.47
Color	CU	20				15					15					15					15
pH		7.3				7.4					7.4					7.3					7.3
Calcium Hardness (as CaCO ₃)	mg/L	278				280					274					286					282
Ammonia	mg/L	0.37				0.38					0.39					0.36					0.38
TKN	mg/L	0.47				0.44					0.46					0.55					0.48
TDS	mg/L	358				366					358					372					346
Bed Volumes (Total) *						17,065					14,564					16,728					16,193
Bed Volumes (PFAS Resin)						21,028					14,564					22,554					20,241
Combined PFOS/PFOA		113	118			U					U			137		U					U
* 5 mg/l is mdl																					
U= Undetected MDL is 0.0019 ug/l																					

* 5 mg/l is mdl

U= Undetected MDL is 0.0019 ug/l

carbon bases can be compared, and conducting a rapid small-scale column test (RSSCT). Onsite monitoring and sampling will be required to ensure that all PFAS parameters can be tracked, as the media exhausts its adsorption capabilities.

Additional pilot testing was recommended and completed by Calgon Carbon Corporation by taking a water sample from the respective supply well and sending the sample to the manufacturer's laboratory to complete an accelerated column test (ACT), which can provide a more-rapid insight into the carbon's removal capabilities than a column test stand. While the RSSCT and ACT aren't anticipated to be 100 percent scalable to the full-scale treatment, they should give a strong indication as to the water quality expectations, regeneration frequency, and anticipated breakthrough timeframes.

The results from the ACT, "Accelerated Column Test Study: Removal of Perfluorinated Compounds From Groundwater Using Filtrasorb 400 12x40 Activated Carbon," prepared on Dec. 5, 2016, are provided in Figures 5 through 7. Figure 8 illustrates the GAC process flow diagram.

The ACT was conducted using Calgon's F-400 12x40 activated carbon to determine the bed life for reduction of PFAS, as well as TOC and color removal. The column test simulated a 10-ft-diameter vessel containing 20,000 lbs of GAC operating at 500 gal per minute. This system and operation condition simulated a 9.3-minute effective bed contact time (EBCT) based on A.D. packing density, and a 10.8-minute EBCT after backwashing.

At completion, the ACT simulated 500 days of operation.

Figure 5 shows the plotted breakthrough curves for PFOS and PFOA versus simulated days of operation. Figure 6 shows the plotted breakthrough curves for TOC and color versus simulated days of operation.

The following conclusions can be drawn from the data generated in this ACT:

- ◆ The feed contained average PFAS concentrations of 86 and 13 ppt for PFOS and PFOA, respectively, for a combined average of 99 ppt.
- ◆ The column effluent achieved initial breakthrough above the minimum detection limit after 60 simulated days of operation. The combined effluent concentrations for PFOS and PFOA reached higher than 70 ppt after nearly 180 simulated days of operation, equating to a carbon use rate of 0.16 lbs GAC per 1,000 gal treated.
- ◆ The feed contained an average TOC concentration of 9.6 mg/L ppm and an average apparent color of 23.
- ◆ The column effluent achieved initial breakthrough above the detection limit for TOC after ~11 simulated days of operation, which equates to a carbon use rate of 2.66 lbs/1,000 gal treated.
- ◆ The TOC achieved 50 percent breakthrough after ~20 simulated days, which equates to a carbon use rate of 1.45 lbs/1,000 gal treated. The initial breakthrough for color was observed at the same time and reached 50 percent of feed at ~73 simulated days of operation.
- ◆ Figure 7 indicates that the bed volumes

to provide sufficient treatment are greater than 20,000. Assuming that the influent concentration of the PFOS/PFOA combined is nearly four times the ACT results, the bed volumes are expected to be less than 10,000 to provide sufficient treatment of PFAS to less than the EPA limit of 70 ppt.

The ongoing RSSCT column testing being conducted was determined to be inconclusive, since it appeared that the elevated TOC levels greatly impacted the PFAS removal capability of the GAC. Ongoing pilot testing using AIX in series was subsequently conducted and found to be successful.

Some of the early testing data suggests several issues should be considered in the design of a proposed GAC system. Some of these issues include:

- ◆ Iron and TOC levels will affect PFAS treatment negatively. Competition for the carbon sites exists when elevated levels of iron and TOC exist, reducing the carbon's absorption ability for PFAS removal. Additionally, any oxidized form of iron that occurs will blind over the top layers of GAC, further reducing its absorption capability; therefore, it's important to prevent oxidation of iron prior to the GAC beds.
- ◆ The existing volatile organic compound (VOC) towers may improve GAC performance, since they appear to reduce overall iron levels in the raw water through the tower packing. Iron levels appear to decrease by more than 50 percent through the towers based on field testing and, since

Continued on page 46



Figure 14. System color reduction.

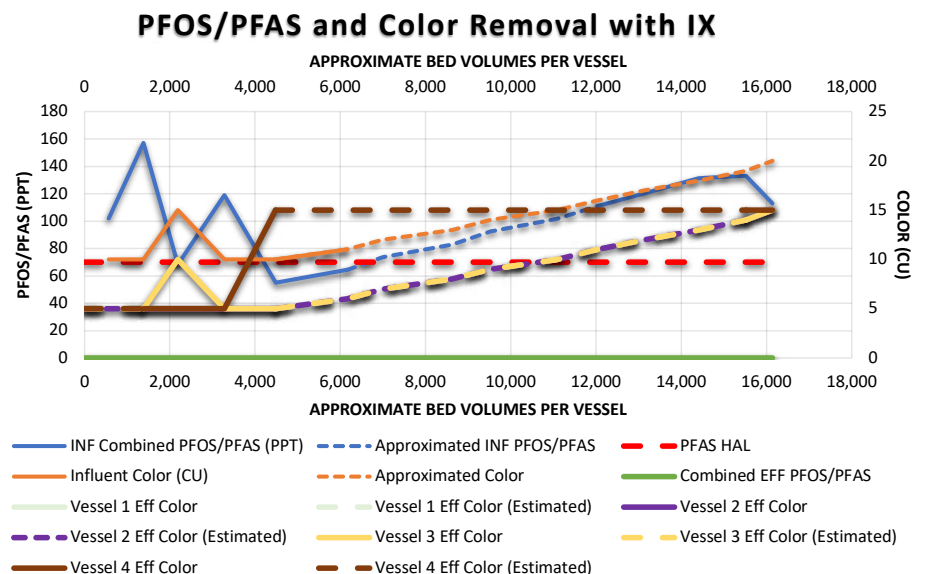


Figure 15. Perfluorooctanoic acid and perfluorooctane sulfonic acid and color removal with ion exchange.

Continued from page 44

some of the TOCs are bound up with iron, may also reduce TOC levels through the towers. Historically, the VOC towers are cleaned regularly due to the buildup of foulants that may be a conglomeration of iron, sulfide (converted to sulfur), and organics; therefore, the proposed GAC piping confirmation should include operating the GAC vessels in series after the VOC towers.

Membrane Treatment (Not Piloted)

An RO treatment has been identified as a more-effective treatment alternative for removing PFAS, mostly due to the molecular weight cutoff for membrane rejection, compared to the relatively large molecular weight of the PFAS. Across all sizes of carbon chains, the removal has been identified as greater than 90 percent for most contaminants and over 95 percent for the remainder of the PFAS. Pilot testing for RO is very similar to the steps described for NF, with the exception of the membrane used for piloting. Generally, the units available to test NF are also capable of producing the higher pressures needed to operate RO membranes.

The NF offers a low-operating-cost membrane treatment alternative due to its low driving pressures and lower rejection, which helps stabilize the permeate stream, with minimal post-treatment restabilization needed. Research indicates high removals (greater than 95 percent rejection) of PFAS, which should be confirmed on the actual water source.

To test the NF membrane's rejection capabilities, analyzing a single-element performance can be completed quickly and efficiently using a single-element test unit fed with raw water. Additional multi-element pilot testing, with concentrate staging, is necessary to identify representative full-scale feed pressures, fouling conditions, recovery optimization, and further water quality confidence. These tests are typically achieved through a 4-in. element pilot configured with concentrate staging and potentially interstage boost pumps, as required to simulate full-scale treatment conditions.

Figure 9 illustrates the membrane system process flow diagram.

Evaluation and Design

Based on pilot testing of the IX resin, and the fact that the resin should not be regenerated to remove the PFAS, the design of an IX treatment system used to treat PFAS through a one-pass throughput to exhaustion was developed, with some of the following criteria:

- ◆ The resin should not be backwashed once initially installed, as it alters the chromatographic profile across the resin bed and can result in early breakthrough of PFAS and shorter service life.
- ◆ Prefiltration is necessary to prevent buildup of suspended solids on the resin and blinding over of the resin (10–50 micron [µm] bag filters recommended).
- ◆ Lead/lag operation is recommended to maintain effluent PFAS levels below nondetect once there is a breakthrough, resin is regenerated or removed and disposed of, and the lag is put into lead service.
- ◆ Acrylic-based resins shed TOC better when considering regeneration with brine and removal of NOM; therefore, regeneration should not be implemented for PFAS removal.
- ◆ Since the PFAS treatment system is only rated for 8 mgd, up to 4 mgd of bypass to the VOC towers (current operation) could be provided, through either a dedicated pump or control bypass valve.
- ◆ Prechlorination of the IX resin was not recommended by any of the resin manufacturers and can break down the resins; therefore, the location of the IX system within the existing treatment system should be before chlorination, or prior to the VOC towers.
- ◆ The IX system was designed to allow full treatment of the raw water system, since detectable levels of PFAS exist in the majority of supply wells.
- ◆ Other volatiles and contaminants not expected to affect the IX resin were listed and

tested to confirm little to no impact on the PFAS removal effectiveness.

The system should also be designed to accommodate existing contaminants, such as VOCs, without impacting PFAS removal efficiency, including the raw water parameters in Table 3.

The design criteria in Table 4 were developed based on resin manufacturer performance data and pilot-test results. In general, the treatment system should include lead/lag operation, where treatment vessels are operated in series, providing the ultimate barrier to preventing any breakthroughs of PFAS before they are detected. Since there is no online continuous monitoring of PFAS test equipment currently available, this is the preferred method of operation.

The three treatment alternatives considered for the utility's WTP were each projected to remove the emerging contaminants to an acceptable level based on UCMR regulatory compliance. The recommendations have been based on the ability to achieve treatment compliance for the utility, as well as capital and operational expenses.

Based on the combination of capital and operating costs, it was recommended that the utility pursue an IX treatment alternative for this facility. Although the GAC treatment alternative provides the lowest initial capital cost for the three alternatives, the operating costs for IX clearly provide a more-rapid return on investment, as compared to GAC, due to frequent carbon changeout with the GAC option. The net return on investment shows that IX is the most cost-effective treatment alternative beyond one to two years of operation.

Additionally, IX provides the necessary treatment capabilities to effectively remove the emerging contaminants from the raw water supply, coupled with the flexibility to increase removal through increasing the media regeneration frequency. The annual operating expenses are slightly more than the membrane treatment alternative; however, the capital cost differential doesn't support the short-term or even long-term (20 years) application of membrane treatment.

Figure 10 highlights the operational and capital expenses for operating the facility over the course of 20 years. As shown, GAC provides the second most cost-effective solution for the city's treatment. Since this option will most likely be a short-term solution to the city's demand, purchasing water from a nearby utility is the most cost-effective short-term solution (three years +/-), even though the operating costs are much higher than one of the treatment options. The long-term economic differential is

Table 8. Treatment Costs

Treatment Volume	Treatment Level	Operating Cost
< 25,000 BV	Nondetect	>\$1.44 /kgal
80,000 BV – >150,000 BV	10 – 20 ng/L	\$0.25 - \$0.45/kgal
>250,000 BV	> 30 ng/L	< \$0.18 /kgal

shown numerically, with the net present value, in Table 5.

Implementation and Start-Up of System

Funding for this project was not readily available and, therefore, the city had to pursue loans through the Florida SRF program, with partial forgiveness based on project qualifications. As a result, the project included unique stipulations, such as the Federal American Iron and Steel Act, which requires only American-made steel, and the application of Davis-Bacon wages for labor used in construction of the project.

The design of the system was dependent on limited pilot-test data using one RCCT with GAC, and IX rapid column testing using one IX resin. Additionally, since the supply wells that contained elevated PFAS (PFOS and PFOA) levels above the EPA HAL were removed from service, it was critical to expedite completion of a treatment system in order to restore plant capacity (Figure 11).

The system was to provide immediate reduction and removal of PFAS from the raw water, but also provide a competitive means of comparing alternative resins for future replacement when the resins become exhausted, so that each of the four vessels were loaded with different resins from different manufacturers. In addition, with elevated TOC levels, the manufacturers were given the opportunity to load a “topping” layer of IX resin (or GAC) to reduce the TOC levels prior to the raw water loading up the IX resin designed specifically for PFAS removal. The resulting “hybrid” would then be used to evaluate the overall PFAS removal effectiveness of each system. Table 6 shows the installed IX resins and hybrid systems of each of the system vessels.

Typical with all construction projects, the start-up had some challenges that required extended flushing of the raw water mains to remove suspended and oxidized materials. Pretreatment using 10-20 micron bag filters (Figure 12) to remove suspended material were plugged quickly when the system was started up and the bag filters were first loaded, which resulted in frequent shutdowns in order to replace the bag filters (Figure 13). Adjustments to the wellfield operation were conducted to minimize oxidation of iron and sulfide within the raw water once the raw water main was flushed.

Once the suspended material issue was resolved and bacteriological clearance was achieved, the system was brought online. Initial water quality sampling was performed and immediate color reduction was observed. Color

reduction, shown in Figure 14, also resulted in an impact on chlorine demand, significantly reducing chlorine dosage after the IX system was placed into service.

The initial data collected included other water quality parameters, which are listed in Table 7. The six PFAS constituents tested were per the UCMR 3 list, although only PFOS and PFOA are currently regulated in Florida. Given the potential for additional PFAS parameters that will be added as part of UCMR 5, additional PFAS constituents should be sampled for testing.

The results shown illustrate that PFAS removal has continued up to just below 20,000 bed volumes down to nondetect on the effluent of each vessel. Color and TOC reduction were very effective with fresh resin, but slowly increased with the bed volumes. The PFAS concentrations over time increased from nondetect up to background levels throughout the vessel depths. Figure 15 illustrates the trends over time and bed volumes with respect to influent and effluent color, and PFOS/PFOA removal.

Conclusions

Continued testing and monitoring of the system will be performed until breakthrough of PFOS/PFOA occurs. Once breakthrough is achieved, unit costs for IX resin and total bed volumes will be used to determine the most-economical resin to use for replacement. An approximate estimation of treatment volume expected, and the resulting operating costs, were provided based on the treatment-level goals. A goal of 80,000 bed volumes down to 10-20 ng/L ppt was established to determine expected operating costs for the system.

Based on extensive literature review, laboratory testing capabilities, ongoing research, and stricter water quality requirements in other states, the basis of design is to target treatment removals to less than 10 ng/L and up to 20 ng/L combined PFOS/PFOA, which will be used to determine when the IX resin has reached exhaustion and should be replaced. Although these target treatment values are well below the current EPA HAL of 70 ng/L and minimum reporting levels of 40 ng/L and 20 ng/L for PFOS and PFOA, respectively, targeting lower values is prudent for treatment and recommended for long-term sustainability of the wellfield.

It's also important to note that most laboratories can only detect perfluorinated chemicals (PFCs) in the range of 2.9 to 14 ng/L and are allowed up to a 30 percent error (EPA Method 537M); therefore, until detection levels change, using lower target values would not be practical, limit the number of laboratories capable of measuring PFCs, and greatly increase treatment costs (Table 8). At the time of this

writing (mid-2019), Eurofins-Lancaster Labs has been reporting a quantitation limit of 1.7 ppt and a detection limit of 0.43 ppt on the samples used for groundwater.

The TOC and organics have a significant effect on PFAS removal capacity using GAC and IX resins by reducing the capability of the materials to adsorb PFAS contaminants. Waters with lower TOC levels have more capacity to remove these constituents, resulting in lower operating costs and more options for cost-effective treatment.

Disposal of spent resins or GAC with saturated PFAS concentrations is typically through incineration, which allows the PFAS to break down to their original states. At the time of this writing, landfills with energy-to-waste capability, which allows the material to be incinerated at high temperatures, is the disposal method of choice. Should EPA or other state regulatory agencies consider the materials classified as hazardous waste, limited treatment options may result, just based on economics. The use of GAC may be limited if this occurs, since the material cannot maintain its National Science Foundation (NSF) rating when the majority of GACs are regenerated and reused.

The PFAS contaminations will continue to present challenges for removal from known point sources to unknown industrial and man-made sources. These chemicals are persistent in the environment, since they have both hydrophilic and hydrophobic properties, and will continue to be detected in all sorts of utility streams, including water, wastewater, reclaim water, and biosolids. With increasing pressure to lower PFAS standards, laboratory equipment technology that can detect levels down to ppt, and pending regulations (UCMR 5) to measure more PFAS constituents down to even lower detection levels, the future for dealing with PFAS in the environment will continue to draw attention.

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