Florida Section AWWA Fall 2019 Conference

Call for Papers

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Session Suggestion:	Future Water Supplies/Dealing with Emerging Contaminants
Paper Title:	Dealing with Widespread PFAS Contamination
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ABSTRACT for

FSAWWA 2019

Dealing with Widespread PFAS Contamination

Since May 2016 when EPA issued a lower drinking water health advisory level of 70 ng/L of combined perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), two poly- and perfluoroalkyl (PFASs) substances, 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) fire-fighting foams, has forced the City of Stuart to shut down some of their 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's down to non-detect levels from all of their groundwater supply wells. Construction of a 4.0/8.0 MGD IX system, partially funded by State Revolving Fund (SRF) loans, was completed in early June of 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 un-lined landfill, 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 paper will discuss some of the PFAS history, regulations, and lessons learned from a full-scale pilot project for the potable water supply system:

- PFAS Sources
- Health Risks from Exposure
- Exposure Entry Routes
    - Release of firefighting foams (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 the Unregulated Contaminant 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

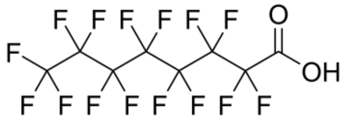
INTRODUCTION

Since May 2016 when EPA issued a lower drinking water health advisory level of 70 ng/L for combined PFOA and PFOS, two per- and polyfluoroalkyl (PFAS) substances, 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) fire-fighting foams forced the City of Stuart to shut down some of their 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's down to non-detect levels from all of their groundwater supply wells.

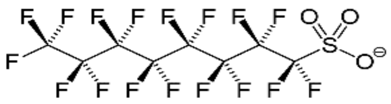
Construction of a 4.0/8.0 MGD IX system, partially funded by State Revolving Fund (SRF) loans, was completed in early June of 2019 and is undergoing full-scale testing using multiple types of IX resins and GAC mixes. Coupled with constantly changing regulations, the City continues to deal with cleanup of the AFFF and other contributing sources of contamination including an un-lined landfill, several industrial activities with other historical contaminations, and a nearby airport. 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.

BACKGROUND

Poly- and perfluoroalkyl substances (PFASs) are an environmentally persistent group of man-made chemicals that are being 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, but not limited to: fire-fighting foams, paper and cardboard coating materials 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 perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), have also been detected in the blood of animals in remote regions of the world. PFOA and PFOS are two of the most studied PFAS compounds and, therefore, regulated compounds, and belong to the perfluoroalkyl acids (PFAAs) family. PFAAs are stable chemicals made of a carbon backbone surrounded by fluorine atoms and an acid group located at the end of the carbon chain.



PFOA



PFOS

There are many sources of PFAS compounds, all man-made formulations of fluorinated compounds developed in the early 1950s, with continue to be manufactured to this day. A brief history of the development of these chemicals is provided below.

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, non-food 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.

1947	3M manufactures PFOA
1951	Dupont develops Teflon
1970	Air Force began using AFFF to fight fuel fires
2000	3M begins phase-out of 13 PFAS's including PFOA & PFOS
2001	Dupont consent decree – WV & OH
2006	Global Stewardship - Voluntary manufacturer reduction 2006, 95% removal by 2010, elimination by 2016
2009	Provisional HAL PFOA/PFOS 0.4/0.2 ug/L
2009	Superfund soil screening levels set – 60/6 mg/kg
2012	C8 Science panel links probable cancer to PFOA
2015	Hoosick Falls – Do Not Drink Order
2016	FDA no longer allows PFOA & PFOS to be added to food packaging
2016	EPA Lifetime HAL advisories of 0.07 ug/L for PFOA/PFOS

In recent years, numerous publications have appeared in which biological properties of PFAS's are described; however, these are generally limited to PFOA and PFOS. These two substances are mostly the only PFAS's that have been toxicologically examined in animal studies that would allow conclusions to be drawn about potential human toxicity. Data on short-chain PFASs 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's 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.

PFAS are distinct from other persistent and bioaccumulative organic compounds because of their importance as drinking water contaminants. PFAS exists predominantly as an anion under environmental conditions, does not bind well to soil, migrates readily from soil to groundwater, and is 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.

PFOA, specifically that is released to 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 is made or used; release of aqueous firefighting foams, particularly at military sites, airports, and fire fighter 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); 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 miles 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 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). 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 two miles of this facility (DuPont, 2009); contamination of the distant wells was likely due to air deposition (Post et al., 2012).

PFAS's 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 PFASs or its precursor compounds. These may include carpets, upholstered furniture, or textiles. These routes of entry may be of particular importance regarding the toxicology of per-fluorinated compounds in children because contact can occur indirectly by hand-to-mouth transfer or directly if an infant sucks on the product.

Another route that must be considered is inhalation of PFASs 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

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

PFAS has 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% of samples from 80 locations throughout the Cape Fear River (North Carolina) drainage basin, population 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 30 million), it was detected (> 1 ng/L) in 73% 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 miles downstream of the site of discharge from a fluorochemical manufacturing facility, with the highest levels (521-598 ng/L) in the six river miles furthest downstream (Hansen et al., 2002). In Germany, PFOA and other PFASs in organic material applied to agricultural land contaminated the Moehne and Ruhr Rivers, important sources of drinking water. PFOA was detected at up to 33,900 ng/L in a creek near the site of contamination upstream of these rivers, and at up to 519 ng/L in drinking water from the Moehne River (Skutlarek et al., 2006).

PFAS's 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. However, PFAS's can be removed from drinking water by granular activated carbon (GAC) or reverse osmosis (RO) (Rumsby et al., 2009; Bartell et al., 2010a; Tagaki et al., 2011; Eschauzier et al., 2012; Appleman et al., 2014; DWQI, 2015b). Therefore, unless specific treatment for removal of PFASs 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

PFAS are found in a wide range of consumer products that people use daily such as cookware, pizza boxes and stain repellants. Most people have been exposed to PFAS. 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. Studies indicate that PFOA and PFOS can cause reproductive and developmental, liver and kidney, and immunological effects in laboratory animals. Both chemicals have caused tumors in animals. 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; increased risk of thyroid disease;
- increased risk of decreased fertility;
- increased risk of asthma diagnosis;
- decreased response to vaccines

USEPA 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. Other States, however, have established some of their own criteria, and have established lower thresholds that they believe are more protective of public health.

The State of New Jersey, for instance, established a Drinking Water Quality Institute Health Effects Subcommittee to pursue development of a Maximum Contaminant Level (MCL) recommendation for PFOA on January 27, 2009 based on its potential health effects and its occurrence in New Jersey public water supplies (PWS). The USEPA 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 Health Effects Subcommittee agreed that the human data have limitations that preclude their use as the primary basis for risk assessment, it does not agree with USEPA 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 Health Effects Subcommittee therefore concluded that elevations in serum PFOA levels of the magnitude expected from ongoing exposure to 70 ng/L (the USEPA 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 below:

14 ng/L – Health-based MCL recommended by DWQI Health Effects Subcommittee

40 ng/L – NJDEP drinking water guidance (2007) based on older toxicology data

70 ng/L – USEPA Lifetime Health Advisory

Regulatory Review

The widespread detection of these chemicals and their persistence in the environment led the U.S. Environmental Protection Agency (EPA) to establish Provisional Health Advisory (PHA) values for PFOA and PFOS of 0.4 and 0.2 ug/L, respectively, and PFOS and PFOA were added to the EPA's Contaminant Candidate List 3 (CCL3) published in October 2009 (EPA 2009). Six of the perfluorinated compounds were also been added to the EPA's Unregulated Contaminant Monitoring Rule 3 (UCMR3). As a result of this testing, and with some of the history listed above 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.

UCMR4 is currently underway, but does not include any of the PFAS family of contaminants. The fourth Unregulated Contaminant Monitoring Rule (UCMR 4) was published in the Federal Register on December 20, 2016. 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 conducted similarly to previous unregulated contaminant monitoring cycles every five years. In addition to PFAS compounds monitoring, seven specific PFAS analytes were nominated on the Contaminant Candidate List 5 for consideration in UCMR 5. Relative to the priority for PFAS compounds to be included, EPA officials indicated they would be awaiting input to assist the agency in making decisions on priority for monitoring. The EPA noted 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. 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’s 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 future of the City. The short-term solution involved analyzing, selecting, and implementing the treatment technologies available to treat and remove the currently present PFASs from the produced 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. Goals for the short-term evaluation include 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 PFASs and others listed in Table 1. This evaluation addresses the desktop analysis of multiple treatment alternatives.

Longer term raw water supply focused on alternative water sources should be evaluated in the future for sustainability, treatment feasibility, regulatory considerations, and financial efficiency for the City. Alternative water sources 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 Utility’s 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 1 provides a list of current and historical known contaminants that require advanced treatment beyond conventional lime softening and filtration.

Table 1 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 + PFOS) (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

* UCMR3 List
** UCMR3 and UCMR4 List
>Treatment currently in place

Prior to 2019, there was no known groundwater contaminant level established for PFAS's 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.

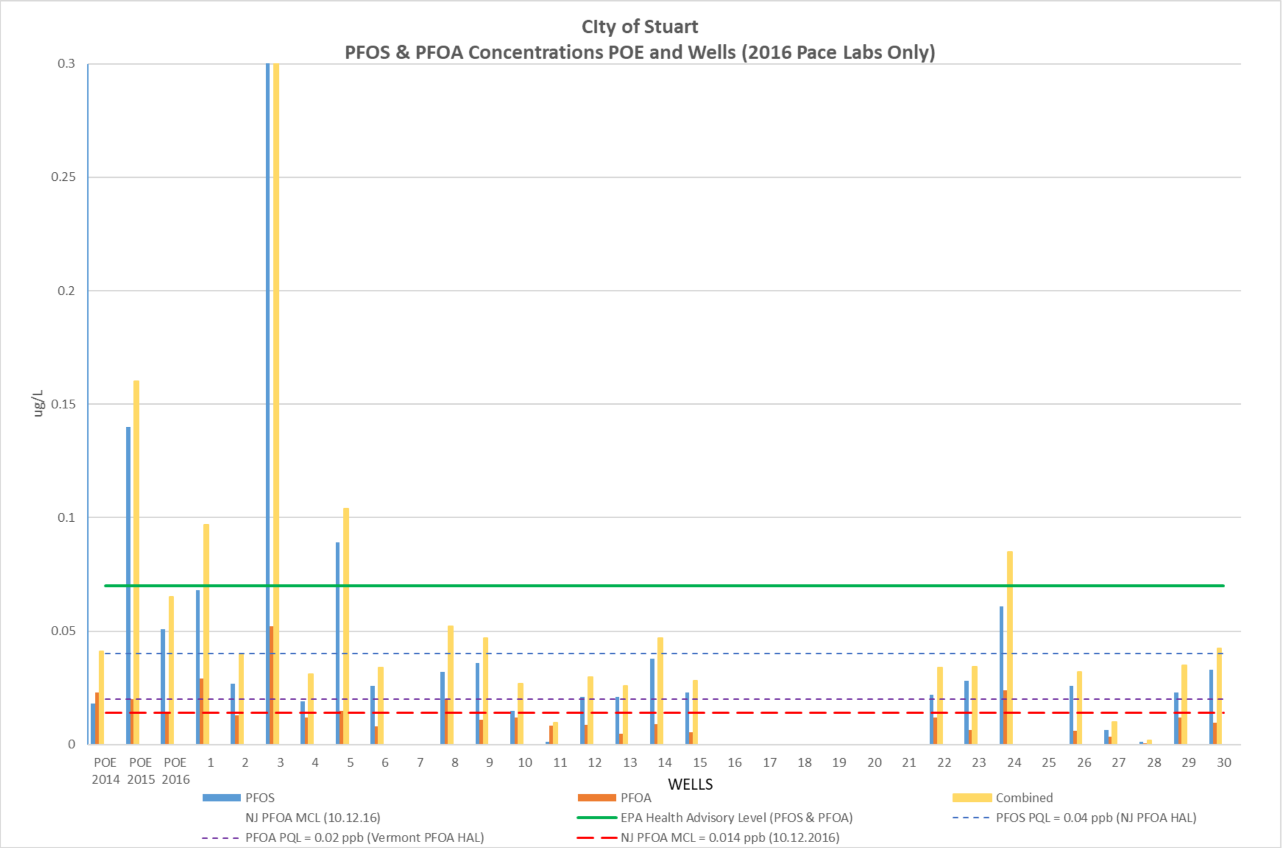
The short-term solution should include either replacing lost capacity from these wells with finished water from existing finish water interconnects, or restoring the functional use of the existing groundwater wells containing elevated PFAS levels with an alternative treatment method. Restoring capacity of the raw water supply wells containing PFAS levels above the Health Advisory Level (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's 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 PFASs found in the raw water. It is also evident from the water quality test results taken at the point of entry (POE) and individual wells that PFAS's are unaffected through the existing treatment plant. EXHIBIT 1 below depicts PFOA/PFOS levels in all of the wells as well as 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's included:

1. (An) Ion Exchange (AIX)
2. Granular Activated Carbon (GAC)
3. Membrane Treatment (RO and NF)
4. Other Treatment Methods: Chemical Oxidation/Reduction, Thermal and Electro-Chemical, Biological Treatment

EXHIBIT 1



Based on the research, literature review, and discussions with manufacturers, sorption processes (such GAC and AIX) and membrane treatment provide the most effective removal of PFAS's from water streams. Chemical oxidation, advanced oxidation and reduction processes, and thermal and electro-chemical processes are processes that show promise, but many of them are still in the research mode, have limitations, and 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's from the raw water, followed by reduction or removal of other known contaminants and upcoming UCMR's that may be of concern. The other volatiles and contaminants listed in Table 1 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 (IX)

Ion exchange is an exchange of ions between two electrolytes or between an electrolyte solution and a complex solution. Typical ion exchangers are ion exchange 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 exchange negatively charged ions (anions). Typical ion exchangers include softeners, which replace or remove calcium (hardness) with sodium.

Ion exchange resins from different manufacturers tend to deliver varying results on PFAS removal. Research indicates that fresh resin presents a 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 ion exchange has been shown to provide some removal of the PFASs. Generally, in the cases where ion exchange has provided some level of removal, the smaller versus larger carbon chains were removed at approximately 46% and 92%, respectively (Appleman, 2012). According to the WRF Web Report #4322, *Treatment Mitigation Strategies for Poly- and Perfluoroalkyl Substances*, 2016, Amberlite IRA-400 resin was found to have a higher capacity than GAC for both PFOS and PFOA removal. However, contact times for IX 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's that contained higher nominal organic matter (NOM) were more effectively removed using IX, possibly due to the interaction between the PFAS's and NOM.

Given the research that had been conducted, ion exchange has the potential to provide removal of PFASs 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 require regular purchase of new resin
- Maintenance intensive with several mechanical transfer processes
- If regenerated, brine disposal includes waste of elevated chloride loaded waste stream through a dedicated force main to the deep injection well, resulting in significantly higher costs
- Higher capital installation costs than GAC

GRANULAR ACTIVATED CARBON (GAC)

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 liquid and solids phases. Activated carbon is an effective adsorbent because it is 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 granular activated carbon (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 PFASs in water sources. The testing researched has resulted in a variance of active removal rates and bed volumes. The carbon base material, loading rates, raw water contaminants, nominal organic matter (NOM) and total organic carbon (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 PFASs of concern for the City of Stuart.

In general, waters with TOC and NOM in the raw water significantly reduce the bed volumes to contaminant breakthrough. This results in more frequent regeneration and more costly operations. Relating to the City of Stuart's groundwater supply, organics are going to be present and are most likely going to reduce the longevity of each carbon load. It is anticipated that the frequency of full breakthrough would be around the 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-inch 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 is 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 the 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 pounds of GAC and require 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 above, 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 required for treatment
- Less maintenance than other treatment alternatives
- High percentage 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

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, nanofiltration (NF) membranes can be implemented to provide effective removal of the PFASs regulated by the UCMR 3 and UCMR 4. As with several other technologies listed within this analysis, the smaller carbon chain PFASAs such as perfluorobutanoic acid (PFBA) are more challenging to remove. NF membranes were observed to remove greater than 90% of the PFASs in both a flow through and recycled treatment approach (Appleman, 2012).

Where more effective treatment removal is needed, brackish water reverse osmosis (RO) membranes have shown to remove greater than 90% of all the contaminants listed and greater than 95% 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% of PFBAs found in the raw water, which are the smallest chain of PFASs. Therefore, membrane treatment provides the best available technology and highest removal efficiency of all the PFAS's down to the smallest molecular weight than the other treatment methods. While research indicates that membrane elements appear to reject the PFBAs, PFASs, and PFOAs at a high rate, it is suggested that the City pilot 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-inch 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 deep injection well (DIW) usage
- Direct force main required to convey concentrate to DIW for disposal
- New chemicals introduced to the plant operation (acid for pH adjustment, anti-scalant for membrane process)
- Capital expense is larger than other alternatives
- Operator interaction and instrument technician 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 standalone process or in addition to other forms of treatment such as GAC, IX, or together. These were not evaluated further, but were not ignored since this contamination is emerging and still being defined. EPA recently (July 2019) awarded $6 million in grants to research potential environmental impacts of PFAS substances in waste streams, including electron beam technology for the destruction of short-chain and perfluoroalkyl substances in groundwater, wastewater, sewage sludge, and soils.

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

Electrochemical oxidation destroys contaminants through two mechanisms: (1) direct anodic or (2) indirect oxidation. When contaminants are destroyed by direct anodic oxidation, contaminants 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 long life spans 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 by-products 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 PFASs, including polyfluoroalkyl compounds, can occur. Furthermore, only two studies have observed PFAS destruction when using electrochemical oxidation in the presence of aqueous film-forming foams (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 UV-induced oxidation are also promising treatment methods, but again, require similar research as electrochemical oxidation have not been fully developed into full-scale implementation.

Thermal degradation of PFAS's involve breaking the C–C and C–F bonds with high temperatures to produce perfluoroalkyl radicals that will subsequently decompose and form similar degradation products as photolytic treatment of PFASs. Thermal treatment methods include thermal chemical reactions, incineration, sonochemistry, sub- or super-critical, 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 PFASs including PFOS, ammonium perfluorooctanoate (APFO), and PFOA, has been successful at temperatures ranging from 600 degrees Celsius to 1,000 degrees Celsius (USEPA, 2003; Krusic and Roe, 2004; Krusic et al., 2005; Yamada et al., 2005; Taylor et al., 2014).

Sonochemical degradation of PFASs 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 psi) within its cavity. Highly reactive intermediates and radicals, including hydroxyl radicals, hydrogen atom, and oxygen atom, form during cavitation bubble collapse. This combination of highly reactive species and high temperatures and pressures has made sonolytic decomposition of PFASs successful, but again is only at the research level.

Microbial degradation of PFASs has only been observed to occur with polyfluoroalkyl substances. Several other studies have used different treatment methods to degrade PFASs, including ozonation under alkaline conditions, permanganate, and ball milling. Ozonation is a commonly used advanced oxidation processes (AOP) in at least one-third of water treatment plants (WTPs) in the United States. 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 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% PFOS, but with only 5% fluoride yield at elevated temperatures and very low Ph (65 degrees Celsius 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 at that point.

PILOT TESTING

Given the relatively minimal testing history and research completed on PFASs and the limited full-scale treatment systems that have been in operation, it was recommended that the City of Stuart 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 ion exchange (jar test level) as those technologies showed the most effective removal of PFASs in the research that has been conducted. The pilot testing will help to identify the operating costs related to regeneration of the GAC and ion exchange medias, 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.

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 of Stuart's Utility, it is 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 their existing deep injection well 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 one-pass through system if the level of treatment, or bed volumes, were greater than GAC and considered more feasible than GAC.

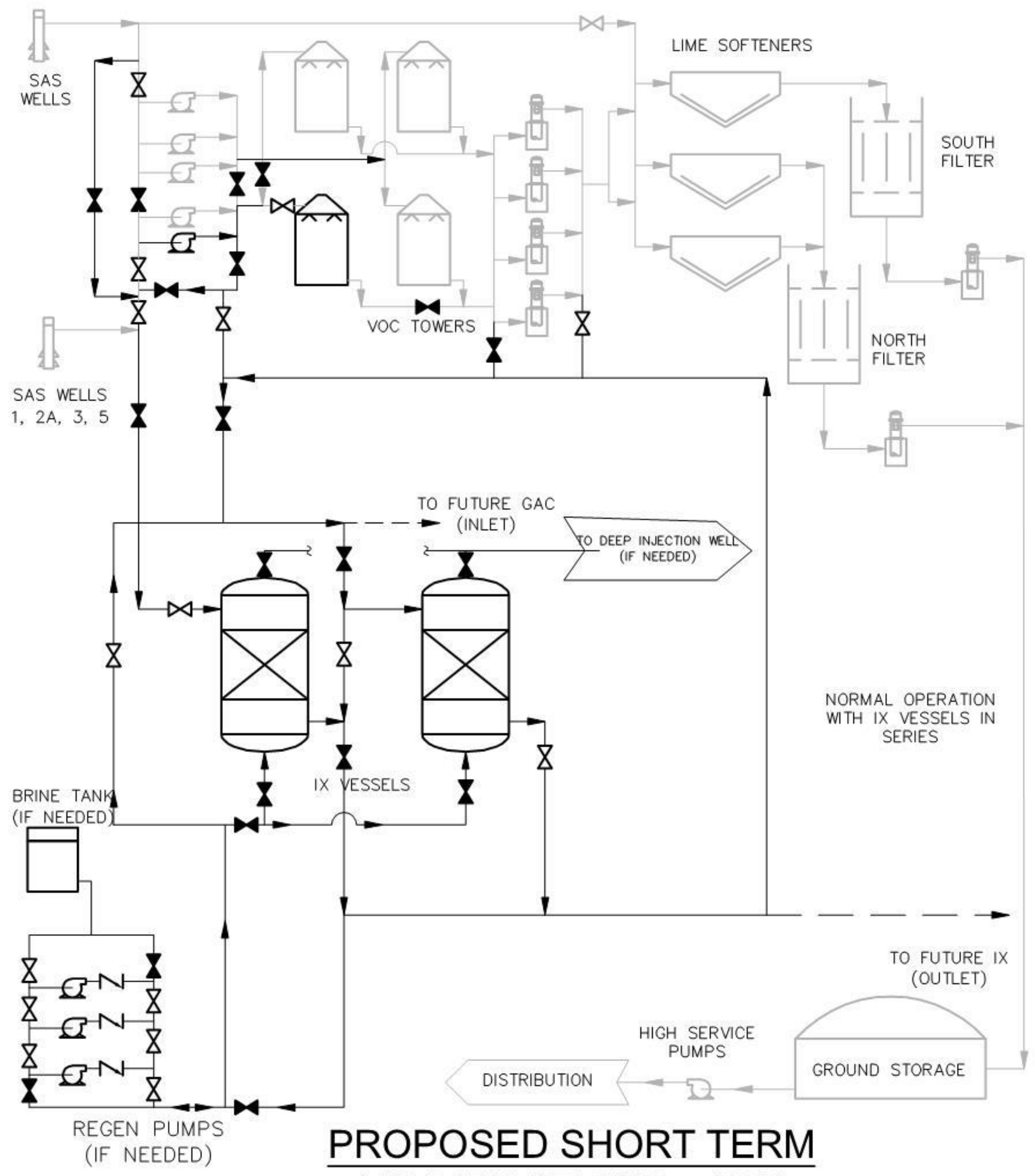
1. ION EXCHANGE PILOT TESTING

Ion exchange treatment was at first believed to be too expensive due to the disposal of the waste brine regenerant. Concentrating the PFAS's 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 reclaim water. Therefore, the waste would have to be piped separately to the WWTP where it could be pumped and disposed of via the deep injection well (DIW). The DIW 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 ion exchange 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's.

Figure 2 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 PPT. Typically, the break-even costs of GAC versus IX are in the range of 4:1, with GAC being four times less expensive per cubic foot than IX. Exhibit Fig-A below illustrates the GAC process flow diagram**.**

- Similar to the GAC testing, the feed contained an average TOC concentration of 10 mg/L (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.
- EXHIBIT 2 indicates the bed volumes to provide sufficient treatment are greater than 200,000, assuming PFAS level breakthrough is less than the 38 PPT design level.
- Based on extensive literature review, laboratory testing capabilities, on-going research, and stricter water quality requirements in other states, it is recommended the City target treatment removal levels less than 10 ng/L up to 20 ng/L combined PFOS/PFOA.
- With these lower target removal levels, it is anticipated IX can remove PFAS's up to 120,000 bed volumes.



PROPOSED SHORT TERM MODIFICATIONS - ION EXCHANGE (IX)

⧓ = NORMALLY CLOSED

⋈ = NORMALLY OPEN

Drawing name: K:\WPB_Civil\144967008 – UCMR3 & PFC Evaluation\CAD\PlanSheets\PILOT.dwg FIG-A Jun 26, 2018 1:08pm by: Evan.Ghidella

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MAR. 2016
PROJECT NO. 144967008

CITY OF STUART

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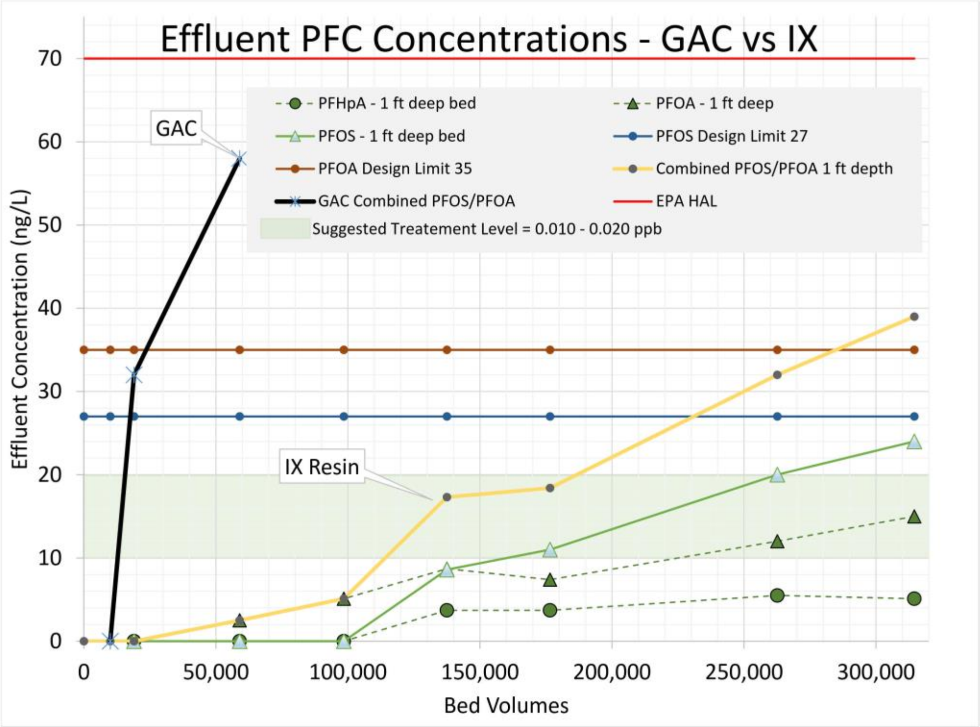
SHEET NUMBER
FIG-A

EXHIBIT 2



2. GAC PILOT TESTING

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 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 (CCC) by taking a water sample from the respective supply well, and sending the sample to the manufacturer's lab 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's and ACT's aren't anticipated to be 100% 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 are provided below in Figures 1 through 3, Accelerated Column Test (ACT) Study: Removal of Perfluorinated Compounds from Groundwater using Filtrasorb 400 12x40 Activated Carbon, prepared December 5, 2016. Exhibit Fig-B below 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 PFASs, as well as TOC and color removal. The column test simulated a 10-foot-diameter vessel containing 20,000 lbs. of granular activated carbon operating at 500 gallons per minute. This system and operation conditions simulated a 9.3 minute effective bed contact time (EBCT) based upon A.D. packing density, and 10.8 minute EBCT after backwashing. At completion, the ACT simulated 500 days of operation.

Figure 1 below shows the plotted breakthrough curves for PFOS and PFOA versus simulated days of operation. Figure 2 below 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 gallons treated. See Figure 1 below for plotted breakthrough curves for PFOS and PFOA versus simulated days of operation.

- 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 detection limit for TOC after ~11 simulated days of operation, which equates to a carbon use rate of 2.66 lbs. / 1,000 gallons treated.

- TOC achieved 50% breakthrough after ~20 simulated days, which equates to a carbon use rate of 1.45 lbs. / 1,000 gallons treated. The initial breakthrough for color was observed at the same time and reached 50% of feed at ~73 simulated days of operation.

- Figure 3 below indicates the bed volumes to provide sufficient treatment are greater than 20,000. Assuming 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's to less than the EPA limit of 70 ppt.

The ongoing RSSCT column testing being conducted was determined to be inconclusive since it appeared 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 of the following issues should be considered in the design of a proposed GAC system. Some of these 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 which occurs will blind over the top layers of GAC, further reducing the absorption capability of the GAC. Therefore, it is 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% through the towers based on field testing and, since some of the TOC's 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.

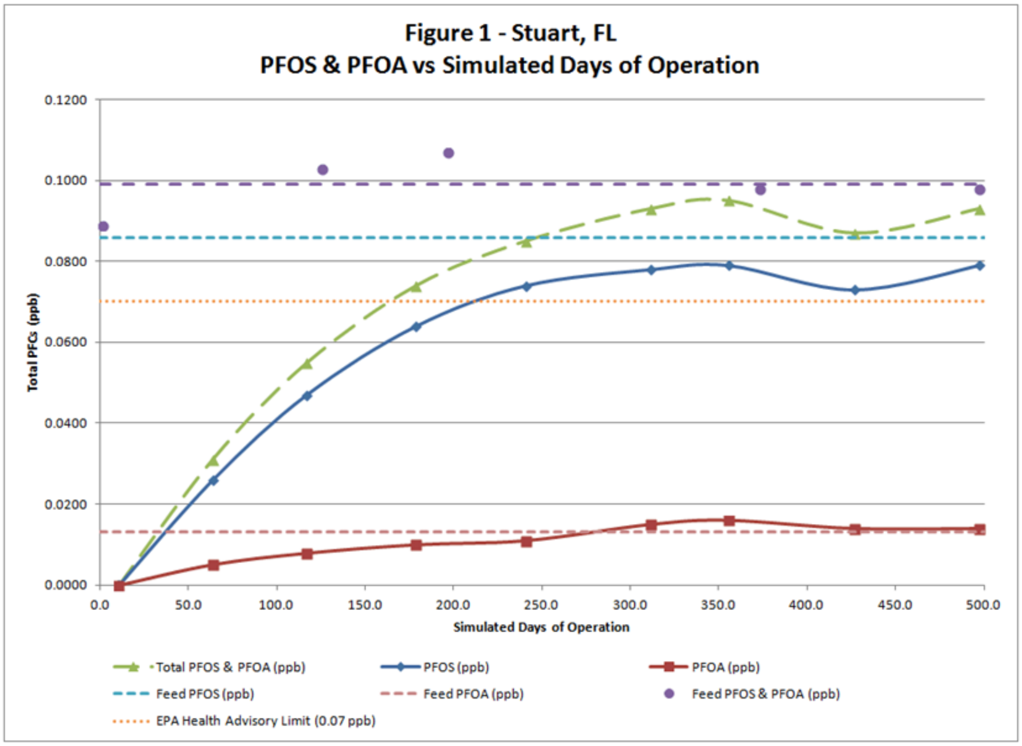


Figure 1 - Stuart, FL
PFOS & PFOA vs Simulated Days of Operation

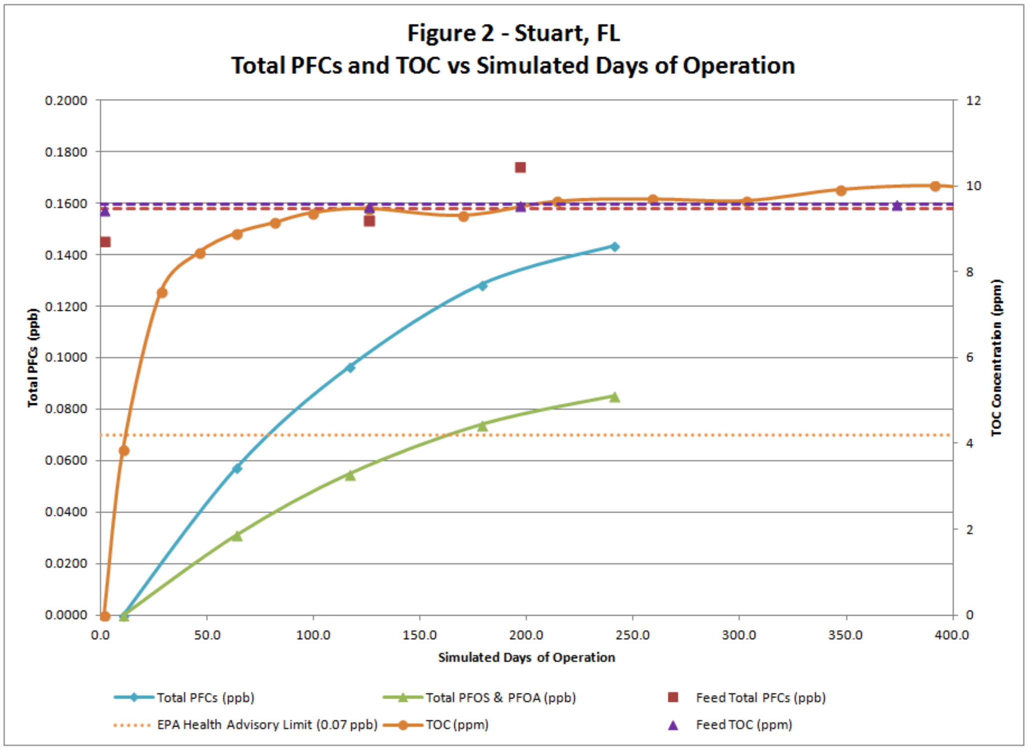


Figure 2 - Stuart, FL
Total PFCs and TOC vs Simulated Days of Operation

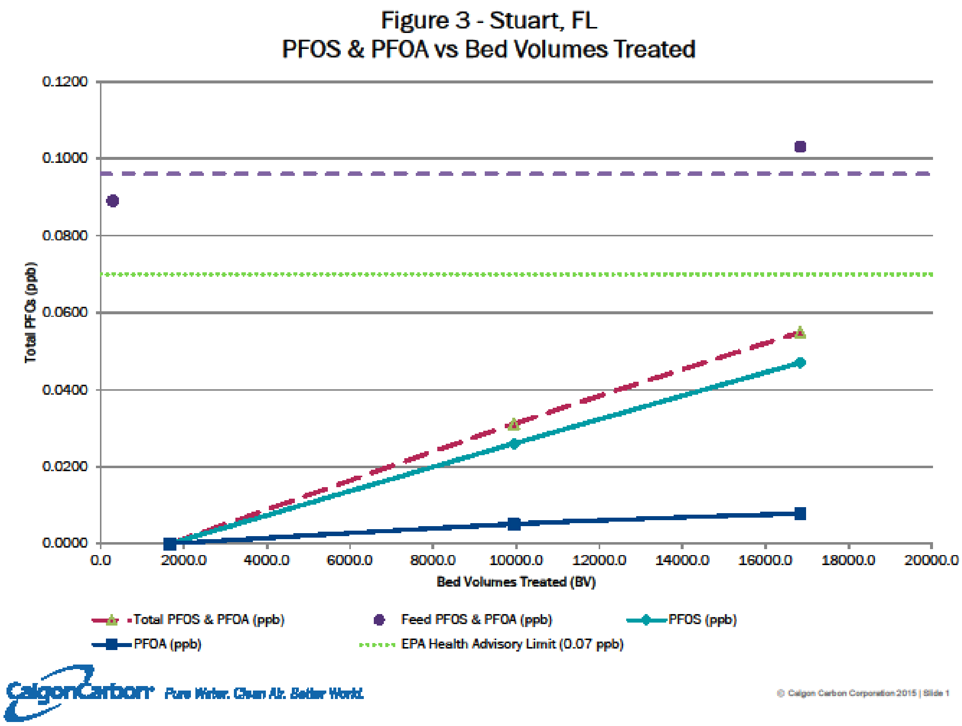
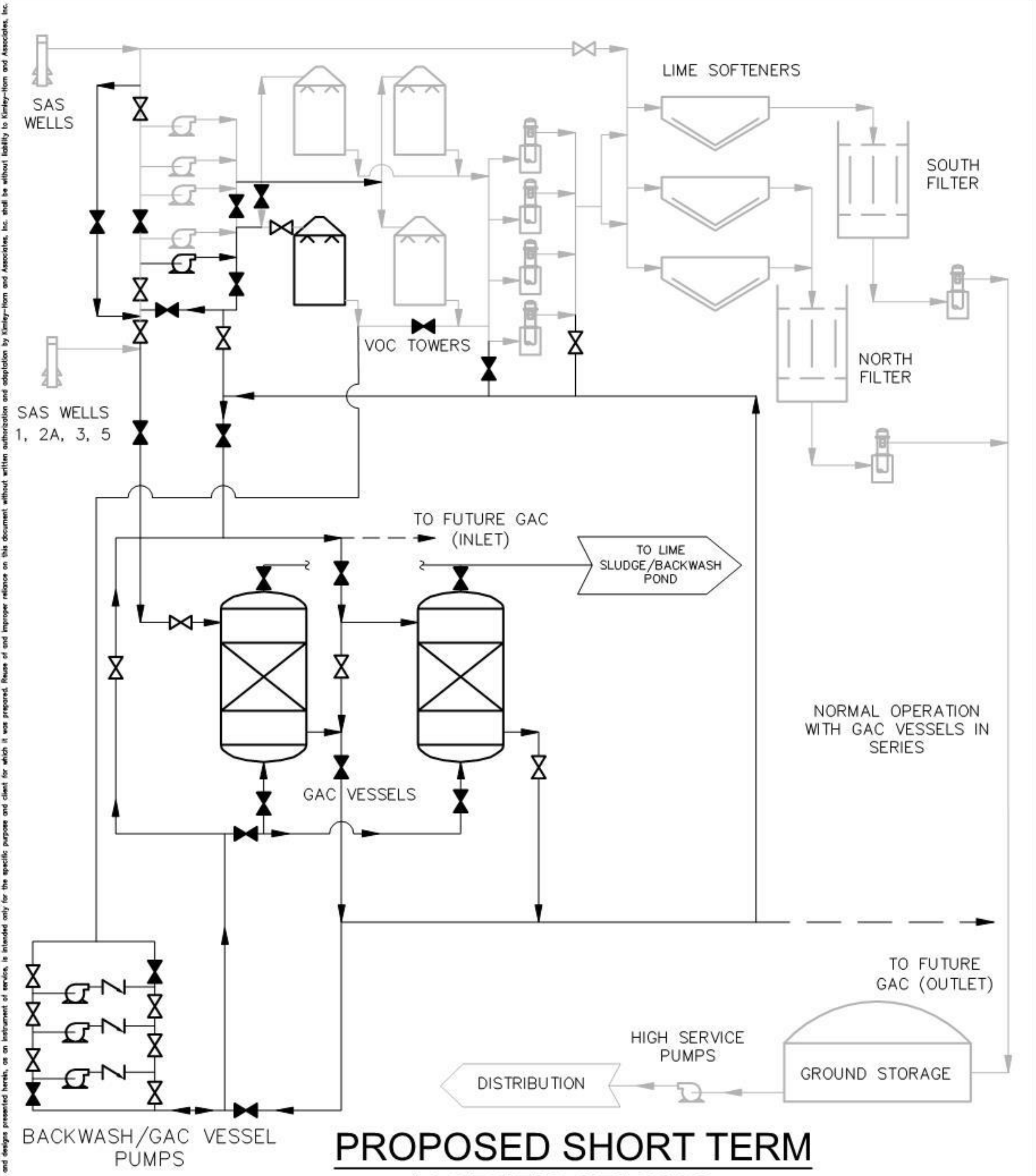


Figure 3 - Stuart, FL
PFOS & PFOA vs Bed Volumes Treated



⧓ = NORMALLY CLOSED

⋈ = NORMALLY OPEN

PROPOSED SHORT TERM MODIFICATIONS - GRANULAR ACTIVATED CARBON

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MAR. 2016

PROJECT NO.
144967008

CITY OF STUART

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DATE:

SHEET NUMBER
FIG-B

3. MEMBRANE TREATMENT (NOT PILOTED)

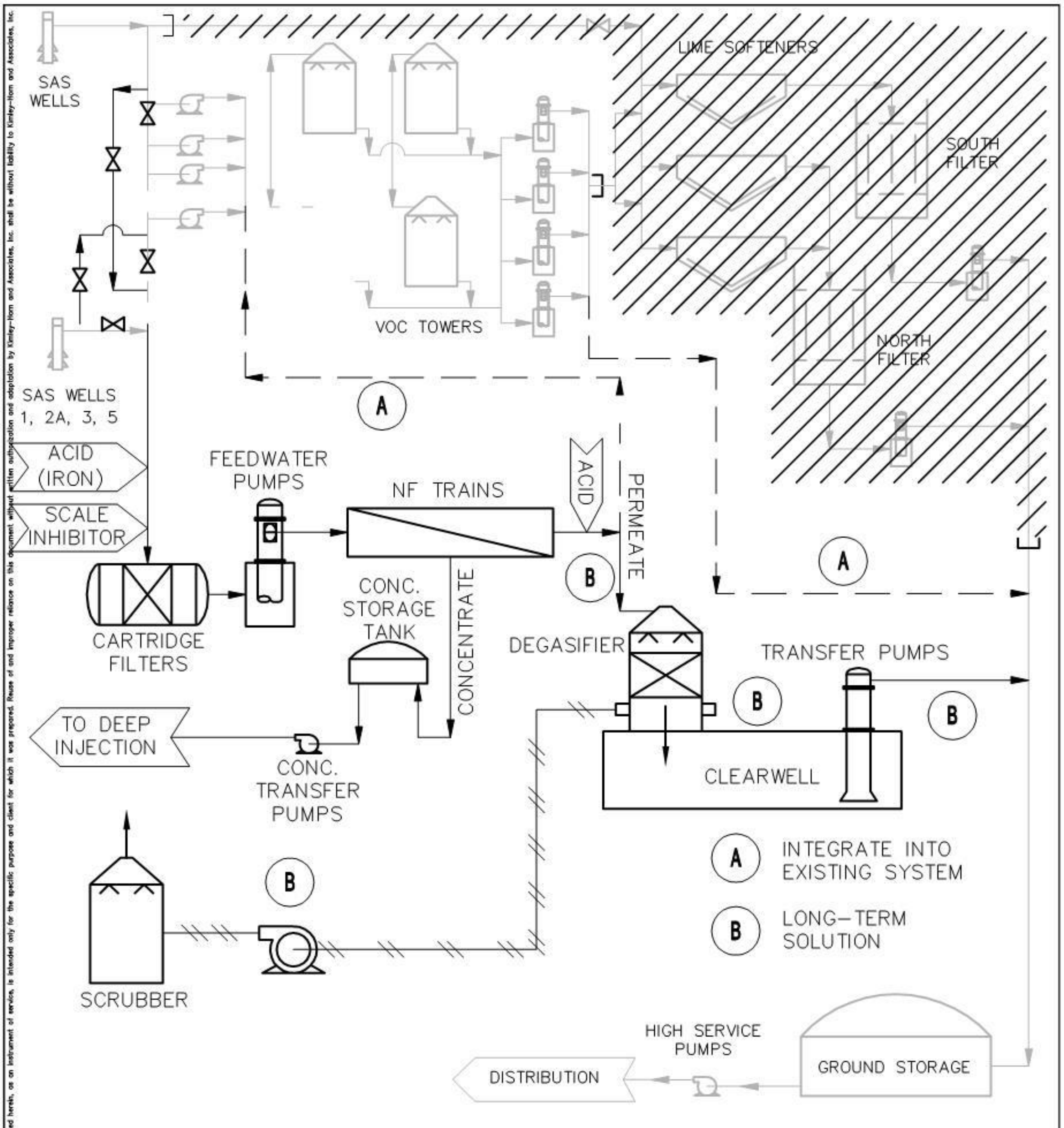
Reverse osmosis (RO) treatment has been identified as a more effective treatment alternative for removing PFASs, mostly due to the molecular weight cutoff for membrane rejection compared to the relatively large molecular weight of the PFASs. Across all sizes of carbon chains, the removal has been identified as greater than 90% for most contaminants and over 95% for the remainder of the PFASs. Pilot testing for RO is very similar to the steps described for nanofiltration (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.

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 re-stabilization needed. Research indicates high removals (greater than 95% rejection) of PFASs which should be confirmed on the actual water source. To test the NF membrane's rejection capabilities, analyzing a single element's 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-inch element pilot configured with concentrate staging and potentially inter-stage boost pumps as required to simulate full-scale treatment conditions. Exhibit Fig-C below 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's, the design of an IX treatment system used to treat PFAS's 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 PFA's 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 non-detect once there is a breakthrough, resin regenerated OR removed and disposed of, and lag 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 PFAS treatment system only rated for 4 MGD. Up to 2 MGD of bypass to the VOC towers (current operation) could be provided through either a dedicated pump or control bypass valve.
- Pre-chlorination 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. (Refer to PROCESS FLOW DIAGRAM below).
- The IX system was designed to allow full treatment of the raw water system since detectable levels of PFAS's exist in the majority of supply wells
- Other volatiles and contaminants were not expected to affect the IX resin were listed and tested to confirm little to no impact on the PFAS removal effectiveness.
- Other volatiles and contaminants were not expected to affect the IX resin were listed and tested to confirm little to no impact on the PFAS removal effectiveness.



PROPOSED SHORT TERM/LONG TERM MODIFICATIONS NANOFILTRATION

⧓ = NORMALLY CLOSED

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MAR. 2016
PROJECT NO.
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CITY OF STUART

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MARK D. MILLER
FLORIDA P.E. LICENSE NUMBER:
45320
DATE:

SHEET NUMBER
FIG-C

The system should also be designed to accommodate existing contaminants, such as VOC's without impacting PFAS removal efficiency, including the following raw water parameters:

TABLE 2

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	-
Alkalininty (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

The following design criteria was 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 breakthrough of PFAS's before they are detected. Since there is no on-line continuous monitoring of PFAS's test equipment currently available, this is the preferred method of operation.

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 non-detect)

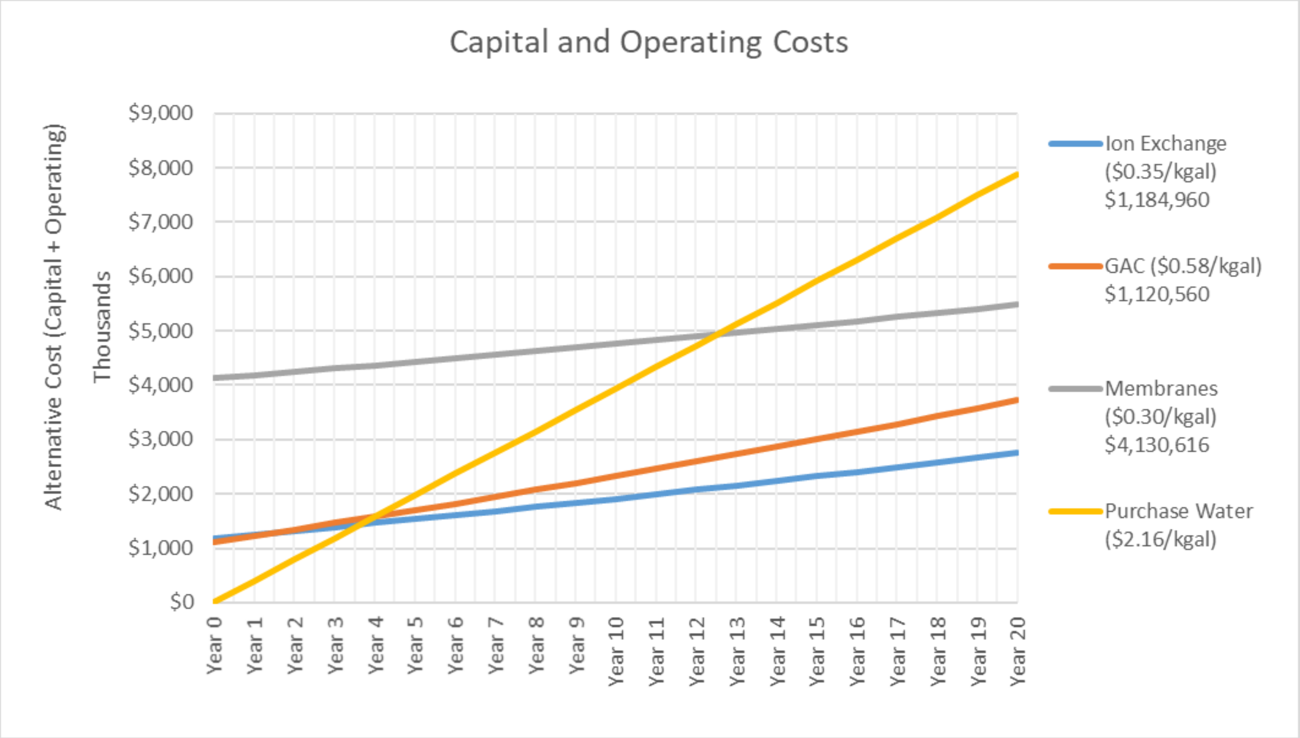
Design	**80,000 BV (Bed Volumes)**
Maximum projected	**150,000 BV (Bed Volumes)**

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 expense and operational expense.

Based on the combination of capital and operating costs, it was recommended the Utility pursue ion exchange (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 change out with the GAC option. The net return on investment shows 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 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. The graph below highlights the operational and capital expense for operating the facility over the course of 20 years. As shown in the capital and operating costs figure, 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 (3 years +/-) even though the operating costs are much higher than one of the treatment options. The long-term economic differential is graphically depicted in EXHIBIT 3 below and numerically with the net present value shown in TABLE 3.

EXHIBIT 3



IMPLEMENTATION & START-UP OF SYSTEM

Funding for this project was not readily available and, therefore, the City had to pursue loans through the Florida State Revolving Fund (SRF) loan program with partial forgiveness based on project qualifications. As a result, the project included unique stipulations, such as including the Federal American Iron and Steel Act requiring only American-made steel, and 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 & 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.

TABLE 3

Treatment Alternative	Capital Cost	Annual Operating Cost	20-Year 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
Martin County Utilities	$ N/A	$ 394,200	$ 7,884,000

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. Therefore, each of the four (4) vessels were each 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. Below in TABLE 4 are the installed IX resins and hybrid systems of each of the system vessels.

TABLE 4

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
Filtrasorb 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

STARTUP OF SYSTEM

Typical with all construction projects, startup had some challenges that required extended flushing of the raw watermains to remove suspended and oxidized materials. Pretreatment using 10-20 micron bag filters 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 bag filters. Adjustments to the wellfield operation were conducted to minimize oxidation of iron and sulfide within the raw water once the raw watermain was flushed.

SAND & FOULANT ON BAG FILTERS

BAG FILTER VESSEL

Once the suspended material issue was resolved and bacteriological clearance was achieved, the system was brought on-line. Initial water quality sampling was performed and immediate color reduction was observed. Color reduction shown below also resulted in an impact on chlorine demand, significantly reducing chlorine dosage after the IX system was placed into service.

IX SYSTEM COLOR REDUCTION

Initial data collected included other water quality parameters listed below. The six PFAS constituents tested were per the UCMR3 list, although only PFOS and PFOA are regulated currently in Florida. Given the potential for additional PFAS parameters that will be added as part of UCMR5, additional PFAS constituents should be sampled for 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**
Alkalininty (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**
* 5 mg/l is mdl																		
U= Undetected																		

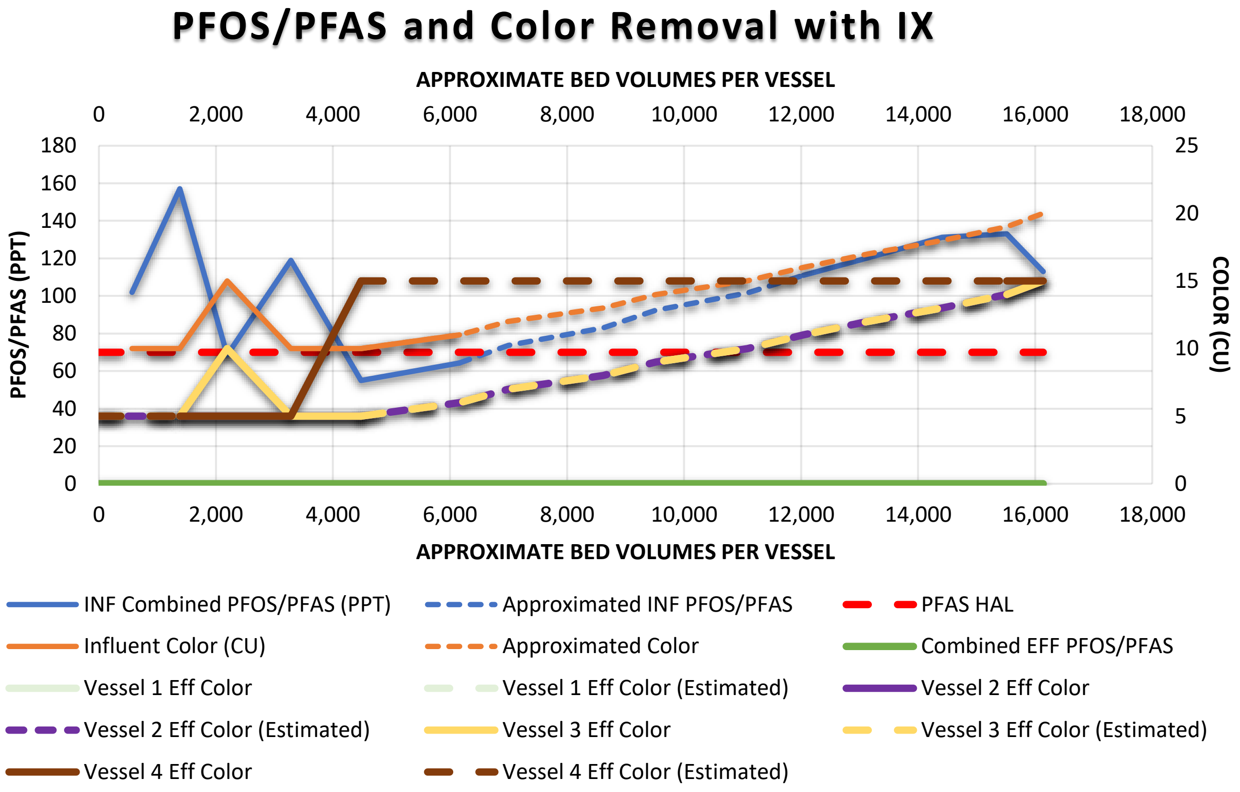
City of Stuart Ion Exchange Resin Testing

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**
Alkalininty (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																		

The results shown above illustrate PFAS removal has continued up to just below 20,000 bed volumes (BV) down to non-detect on the effluent of each vessel. Color and TOC reduction were very effective with fresh resin, but slowly increased with BV's. PFAS concentrations over time increased from non-detect up to background levels throughout the vessel depths. EXHIBIT 4 illustrates the trends over time and BV's with respect to influent and effluent color, and PFOS/PFOA removal.

EXHIBIT 4



CONCLUSIONS

Continued testing and monitoring of the system will be performed until breakthrough of PFOS/PFOA will occur. Once breakthrough is achieved, unit costs for IX resin and total BV's at which breakthrough occurred 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 was provided based on the treatment level goals. A goal of 80,000 BV down to 10 – 20 ng/L (ppt) was established to determine expected operating costs for the system.

Treatment Volume	Treatment Level	Operating Cost
• < 25,000 BV	Non-Detect	>$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

Based on extensive literature review, laboratory testing capabilities, on-going research, and stricter water quality requirements in other states, the basis of design is to target treatment removals to less than 10 ng/L 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 is also important to note that most laboratories can only detect PFC’s in the range of 2.9 to 14 ng/L and are allowed up to 30% error (EPA Method 537M). Therefore, until detection levels change, using lower target values would not be practical, would limit the number of laboratories capable of measuring PFC’s, and would greatly increase treatment costs (see table above). At the time of this paper writing, Eurofins-Lancaster Labs has been reporting a quantitation limit of 1.7 ppt and detection limit of 0.43 ppt on the samples used for groundwater.

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’s to breakdown to their original states. At the time of this paper 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 material 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 NSF rating since the majority of GAC’s are regenerated and reused.

PFAS contaminations will continue to present challenges for removal from known point sources to unknown industrial and man-made sources of contamination. 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, lab equipment technology that can detect levels down to parts per trillion, and pending regulations (UCMR5) 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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