

Rocky Hill Water Situation Section 2.

Case Study: PFAS removal. Horsham Township Pennsylvania.

Horsham Township first encountered PFAS contamination in its water supply 6 years ago in 2014 (before Rocky Hill had heard of PFAS) with levels of PFOS and PFOA at 200 ppt and 400ppt in 2 of its 15 wells, which were then taken out of service. In 2016, with the introduction of the EPA voluntary health guideline of 70 ppt for combined PFOA and PFOS, three more wells were also removed from service and efforts were then introduced to remediate these 5 wells by installing GAC adsorption filters.

In addition, as a result of active community pressure, the Township initiated a pilot study of a selective ion exchange system to investigate and establish the performance of ion exchange resins in further reducing trace PFOA and PFOS contamination levels down to zero (non-detectable) levels. The new goal then became the total elimination of PFAS contaminants from the drinking water.

The original intention was to insert the ion exchange process after a main GAC filtering system, so that the ion exchange system would be “polishing” the low levels of PFOA and PFOS contamination coming out of the GAC filters down to non detectable levels – basically relegating ion exchange to a final “clean-up” role following the commonly accepted method of GAC adsorption filtration. This was (and still is to a large extent) the usual role assigned to ion exchange.

They assigned one of their actual wells (#10) to this pilot study. The results were quite staggering. Rather than paraphrase, we here submit the original article published through Water Online, into the following text.

“Polishing PFAS To Non-Detect Levels Using PFAS-Selective Resin

Source: Purolite

Abstract

In mid-2016, shortly after the U.S. Environmental Protection Agency (EPA) revised the health guidelines for perfluorooctanoate (PFOA) and perfluorooctanesulfonate (PFOS) to 70 ng/L (or ppt), the township of Horsham, Pennsylvania, together with Horsham Water and Sewer Authority (Authority), the Township’s public water

supplier, set a goal of reducing these two contaminants to non-detect (ND) level in all drinking water supplied. To achieve this aggressive goal, the Authority installed granular activated carbon (GAC) filters on selected wells. A newly developed PFAS-selective ion exchange resin was installed downstream of the GAC filters on one well to evaluate the effectiveness of the resin in further polishing the water to the ND goal. After several months of operation, the GAC filters were bypassed and the resin continued to operate until the concentration of PFAS rose above the detection level. This case study provides details on the performance and consistency of both the GAC and the PFAS-selective resin in meeting the ND goal. A comparison is made of operating costs for both treatment options.

Background

Horsham Township is approximately 17 square miles in area and is located in southeastern Montgomery County, Pennsylvania. Horsham Water and Sewer Authority (the Authority) supplies drinking water to approximately 7,800 residential, commercial and industrial customers using 14 deep water wells and purchased water from two adjacent water suppliers. The Authority's supply wells are located in the Upper Reach Pennypack Creek, Park Creek and Warminster Subbasin-Little Neshaminy Creek subbasins of the Delaware River Watershed. Each of the Authority's supply wells is located within the Stockton Formation bedrock, which consists of shale, siltstone, and sandstone. The former Naval Air Station Joint Reserve Base Willow Grove is located in Horsham Township, PA.

In 2014, monitoring performed in accordance with the EPA's Third Unregulated Contaminant Monitoring Rule (UCMR3) revealed that 5 of the wells (Horsham Township, 2016) contained concentrations of several perfluoroalkyl substances (collectively called PFAS and pronounced as "p-fas"). Of these, perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) were found in two wells at concentrations approaching the EPA then Provisional Health Advisories of 200 ng/L and 400 ng/L respectively. These two wells were proactively taken out of service. Subsequent testing at lower minimum reporting levels than those prescribed by EPA under UCMR3 revealed the presence of PFAS at all 14 of the Authority's wells. In June 2016, one month after EPA issued a Lifetime Health Advisory of 70 ng/L (US EPA 2016) for the combined concentrations of PFOS and PFOA, the remaining three of the original five wells where PFAS was detected were removed from service. The Authority

began purchasing additional water from an adjacent water supplier and installed granular activated carbon (GAC) filters to remediate and return the five impacted wells to service. Responding to consumer concerns, the Township and Authority jointly adopted an aggressive short-term plan to reduce average PFOS/PFOA concentrations over its entire water system to non-detect levels by the end of 2016. Non-detect levels would be based on then-current laboratory methods and detection limits. A long-term plan was subsequently adopted, which included installation of PFAS treatment systems on ten wells and one interconnection with an adjacent water system (Horsham Township, 2016).

In November 2016, after receiving a temporary permit from the Pennsylvania Department of Environmental Protection (PA DEP), the township installed a 50 gpm PFAS-selective ion exchange (IX) resin pilot downstream of an existing twin-tank GAC filtration system. The Authority wanted to evaluate the performance of the resin in consistently polishing the water from the GAC system to meet its goal of non-detect levels for PFOS and PFOA. This was the first permit issued by the state of Pennsylvania for treating PFAS in drinking water using ion exchange resin.

Influent Water Characteristics

During the test period from November 2016 to August 2018, the total influent PFAS concentration ranged from a minimum of 87 ng/L to a maximum of 147 ng/L, with an average of 108 ng/L. In addition to PFOS and PFOA, five additional PFAS species were present in the influent water. Both carboxylate and sulfonate type compounds (corresponding to acronyms in the Table ending with “A” and “S” respectively) were present. PFAS are grouped conveniently into two categories of short-chain PFAS (PFBS, PFHxA, PFHpA) and long-chain PFAS (PFHxS, PFOA, PFNA, PFOS) due to similar behavior in the environment (ITRC Fact Sheet Naming Conventions 2018). Short chain PFAS are defined as compounds containing less than 6 carbon atoms for sulfonate and less than 8 for carboxylate type compounds. Average influent values for PFOS and PFOA were 34 and 20 ng/L, somewhat lower than the combined guideline of 70 ng/L set by EPA (but still above the ND goal set by the Authority).

The background chemistry of the groundwater at the pilot site was considered by the Authority to be favorable for ion exchange. Total dissolved solids (TDS) ranged from 296 to 358 mg/L with sulfate at 8 to 23 mg/L, nitrate at 10 to 11 mg/L, alkalinity at 148 to 232 mg/L, and chloride at 35 to 50 mg/L. pH was approximately 7.5, TOC at 0.2 mg/L, suspended solids ranged from 0.5 to 0.6 mg/L, and 1,1-dichloroethane was detected in one sample at 37 ng/L.

The initial focus of the Authority was to remove PFOS and PFOA to ND, but the Authority also desired maximum removal of all short and long chain PFAS present in the well water.

At the near neutral pH of drinking water, PFAS molecules of the type shown in Table 1 are readily ionized, with the ionized “head” of the molecule becoming negatively charged (as an anion). This is shown in Fig.1 using PFOS as an example in which the “head” is the negatively charged sulfonic group. Consequently, a PFAS-selective resin with positively charged functional groups can readily bind with the negatively charged “head” of the molecule. The other end of the molecule is referred to as the hydrophobic (or water-hating) “tail,” consisting of several fluorine/ carbon bonds. PFAS-selective resins by nature are hydrophobic and can form adsorptive bonds with the hydrophobic tail of the molecule. This dual removal mechanism of ion exchange and adsorption allows for stronger bonds and greater possibility of reducing PFAS concentrations to ND levels.

Well #10, with a peak design flowrate of 100 gpm, was used for large-scale piloting at a reduced flowrate of 50 gpm under the terms of the permit from PA DEP. The water was first passed through a 20-micron suspended solids filter, then in series through 2 x 2.5-ft diameter stainless steel vessels, each vessel containing 20 cubic feet of bituminous GAC. Empty bed contact time (EBCT), or the time the water is in contact with the media before it is discharged, amounted to 2.8 minutes for each charge volume of GAC per vessel, or a total of 5.6 minutes for the two GAC vessels; linear velocity was approximately 10 gpm/ft². The Authority recognized that the design EBCT was lower than the 10 to 20 minutes specified in the PA DEP Public Water Supply (PWS) Manual. The linear velocity, even though it complied with the PWS design standards, was higher than the typical 4 gpm/ft² used for GAC. However, the Authority and PA DEP considered the design acceptable considering the relatively low levels of PFAS measured and the temporary nature of the pilot.

The water, after initial treatment by the two GAC vessels, was passed through a 2.5-ft diameter vessel containing 20 cubic feet of Purolite Purofine® PFA694E PFAS-selective resin – see Figure 2. Bed depths for both the GAC and resin media were approximately 34 inches. Sampling points were installed on the outlet of each vessel. An extra sampling point was installed in the resin polishing vessel at 2/3rd of the resin bed depth. This allowed monitoring corresponding to resin EBCT of 1.8 minutes at the 2/3rd sampling point and 2.8 minutes for the entire resin bed. The 2/3rd sampling point would provide advanced notice of PFAS breakthrough and be used to get an earlier estimate of operating capacity for the resin.



Figure 2. Well 10 Treatment System – Photo courtesy Altair Equipment and Horsham Water & Sewer Authority

System Performance

The entire system became operational on November 29, 2016. For reporting purposes, the Authority used a minimum reporting level (MRL) of 2.5 ng/L for each of PFOS and PFOA, based on MRLs provided by the laboratory completing the sample analyses; values below the MRL would be considered non-detect (ND). From start-up,

the concentration of PFOS and PFOA sampled at the 2/3rd sampling point of the resin bed remained consistently at non-detect levels until rising to 2.6 ng/L on day 394, then falling back below ND and then rising to 4 ng/L on day 472 – see Figure 3. In comparison, effluent water analyses from the first and second GAC vessels showed that ND was exceeded on day 58 from both vessels, rising to 30 ng/L and 20 ng/L from the first and second GAC vessels, respectively. This represents an operating capacity of 15,000 bed volumes based on the combined volume of GAC media in the two vessels (this is the same as 15,000 liters of water being treated by 1 liter of GAC).

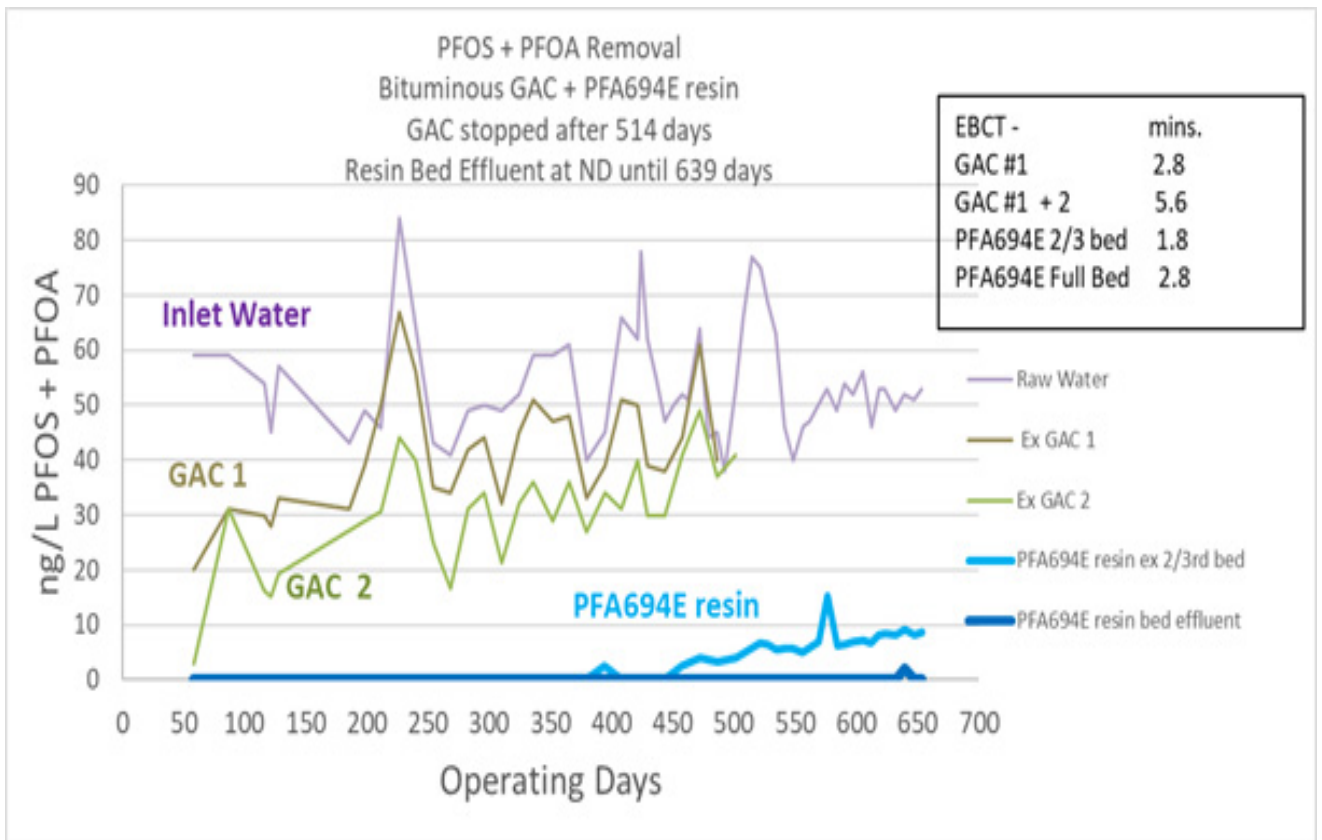


Fig. 3 Combined PFOS / PFOA Breakthrough

Once the PFOA concentration reached 2.6 ng/L at the 2/3rd sampling point for the resin, the treated water from the resin was diverted to waste while the system continued to operate to allow full evaluation of the treatment system to breakthrough, while maintaining compliance with the PA DEP permit. On day 514, with permission from PA DEP, the two GAC vessels were taken out of service while the raw water was routed directly to the resin vessel which continued to operate. In this way, the performance of the resin could be evaluated without pretreating with the GAC. The resin operated for 639 days

before PFOA was detected at a concentration of 2 ng/L of PFOA in an effluent sample from the resin bed. At that point the concentrations of PFBS, PFHxS, and PFOS were still at non-detect levels. Operating capacity of the resin at that point was equivalent to treating 511,000 bed volumes (BV) of water based on 2/3rd of the resin volume, or 329,000 BV based on the entire volume of resin.

Even though PFOS and PFOA were the initial targets for reduction, non-detect levels were achieved for all PFAS in the outlet water from the resin vessel. For conciseness, only total PFAS breakthrough graphs are shown in Figure 4, but the order of breakthrough observed was PFHxA < PFHpA < PFOA < PFNA < PFBS < PFHxS < PFOS.

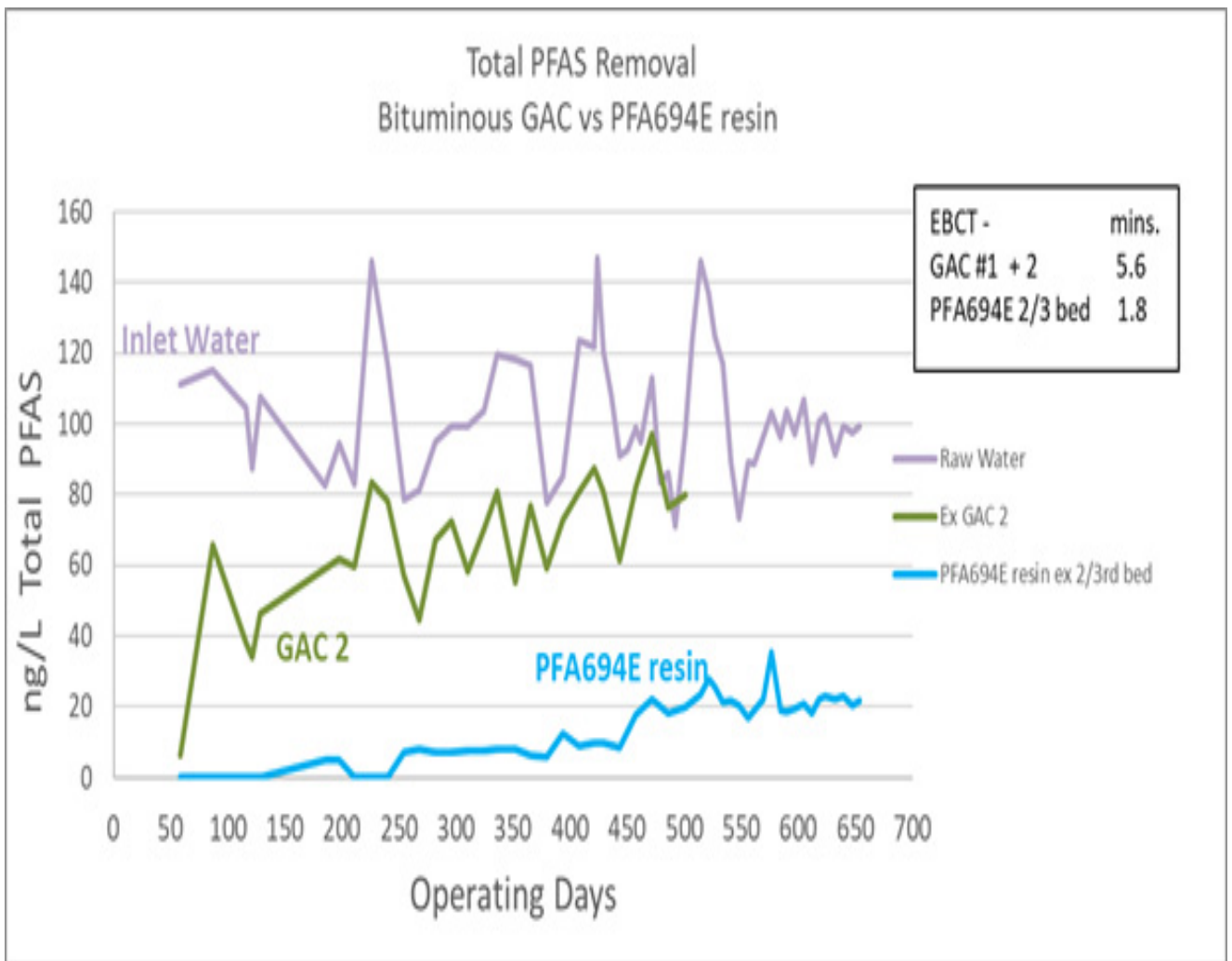


Fig. 4 Combined Breakthrough of Total PFAs

The Authority has since received a modified permit from PA DEP to operate a twin-tank resin-only system. The system was installed in mid-October 2018 and continues to operate today. This system will be further evaluated as the basis for design and construction of permanent, resin-only treatment systems at this well and two other wells that are part of the Horsham Water and Sewer Authority water supply.

Operating Cost of proposed full system

The operating costs for GAC and resin were compared for a permanent full-scale system designed for a peak flow rate of 100 gpm. In each case, a pair of lead-lag vessels would be used to hold the respective media. Design for ion exchange includes 1x20-micron cartridge filter followed by 2 x 4-ft diameter vessels with resin bed depth of 36 inches and EBCT of 2.8 minutes. Design for GAC includes 1x20-micron cartridge filter followed by 2 x 6-ft diameter vessels with GAC bed depth of 60 inches and EBCT of 10.6 minutes. Annual operating cost, including replacement media, labor, trucking, spent media profiling and incineration is estimated at approximately \$8,000 and \$15,000 respectively for ion exchange and GAC. These estimates are based on very conservative operating capacity estimate of 350,000 bed volumes for a lead-lag pair of resin vessels while a generous capacity of 34,000 bed volumes is assumed for the GAC system. Operating costs are estimated at \$0.16 and \$0.29 per 1000 gallons of water treated by the resin and GAC systems, respectively. Larger vessels needed for the GAC system will further add to the cost of using GAC versus the PFAS-selective resin.

Conclusion

The desire of Horsham to reduce PFOA and PFOS to non-detect levels, instead of merely complying with US EPA's guideline of 70 ng/L, is a first for the water treatment industry.

Field piloting of Purolite's Purofine PFA694E PFAS-selective resin demonstrated that the entire suite of PFAS present in the well water (PFBS, PFHxA, PFHpA, PFHxS, PFOA, PFNA and PFOS) were effectively reduced to non-detect levels while operating with very short EBCT of 1.8 minutes and treating 511,000 bed volumes of water (639 operating days). The very short EBCT required for the resin means that more compact ion exchange vessels can be used compared to GAC for a full-scale treatment system, resulting in much smaller footprint, headspace and capital cost.

Prior to piloting, the relatively low concentrations of PFAS in the inlet water was expected to favor adsorptive media like GAC. However, operating capacity for the PFAS-selective resin was shown to be more than 30 times higher than for GAC, demonstrating the superiority of the ion exchange removal mechanism for consistently reducing ionized PFAS to non-detect levels.

After the GAC system was stopped, the resin continued to perform consistently on its own. Based on this, PA DEP recently permitted the Authority to treat the water with just two PFAS-selective resin vessels in series, eliminating the GAC system and allowing for a system that met the ND goal of the Township and the Authority.”

Analysis of the Horsham study and relevance to Rocky Hill

This case study is important because it is one of the first such studies and relates to an actual municipal water system rather than being a laboratory controlled pilot study. Many laboratory pilot studies are often criticized as not being representative of real world conditions and scale. This study has direct relevance to a proposed ion exchange system for Rocky Hill. There is a lot of similarity in the levels of PFOS and PFOA (though Rocky Hill's trace levels are lower) and in aquifer parameters.

The first striking thing in the study is the apparent breakdown collapse of the GAC filtration after only 58 days of operation, in both the lead and lag GAC filters at the same time.

This can only be due to a very high level of dissolved organic material (DOM) or to an inadequate volume of GAC for the flow rate (50 gpm). Both of these issues have been discussed in the previous [Section 1](#).

The question of dissolved organic molecules is of primary importance and will be mentioned again in more detail later in the next Section (3), however in this study the DOM was a measured quantity (0.2mg/L) in the initial evaluation of the water quality and it was considered favorable, and it would certainly be below the low

range of DOM concentrations in the Canadian study of Dixit et al with DOM rich water sources and ion exchange (mentioned later). So the issue here is simply an inadequate amount of GAC.

The minimum volume of GAC for a flow rate of 50 gpm, and based on the rule of EBCT of 10 minutes minimum contact time, is 67 cubic feet. Each carbon filter had only 20 cubic feet of GAC for a total of only 40 cubic feet. So, the system is considerably undersized for GAC at the proposed flow rate.

It is claimed in the text that the 2.8 minutes contact time for each GAC filter was appreciated as being below the required and recommended 10 to 20 minutes total, but was considered adequate and acceptable for this short duration pilot study. However, if there is not adequate contact time the required conditions of close contact at the carbon-water interface needed by the short range Van der Waals forces is not met, and there is little or no adsorption.

If there is inadequate adsorption there is no point in having GAC adsorption filters. The only way to get satisfactory GAC adsorption would have been to reduce the flow rate to lower than 30 gallons per minute (say 25 gpm), or of course to double the amount of GAC.

As it turns out the data are now more interesting in evaluating the performance of ion exchange. The GAC filters both indicated breakdown around day 57 after which the PFAS effluent from both filters gradually increased up to the level of the incoming water as shown in Fig3 for combined PFOA+PFOS, and Fig 4 for total PFAS. The input PFAS levels from the well are varying quite widely, showing significant contaminant fluctuations. The output from the filters replicates this activity.

Basically the ion exchange resin had been handling input levels of total PFAS (Fig 4) well above 60 ppt for quite a long time before the GAC filters were finally disconnected at day 528, when the effluent from the filters matched the input contaminant level. The GAC filters were then essentially transparent. After this point the ion exchange resin then carried on alone and handled the input water directly, at the 50 gallons per minute flow rate, for more than another three months until the pilot study was ended at 639 days.

The PFOA and PFOS output from the 2/3 tap point of the ion exchange filter (simulating a lead filter configuration) is labeled PFA694E resin in Fig 3. The output from the total ion exchange filter is shown as the lowest line that flatlines along the zero level axis up to day 639 when there was a small suggested blip at 2 ppt for PFOA and the study was ended.

The Fig 4 for total PFAS contaminants does not show this bottom line for total PFAS output, but it is the same as for Fig 3, namely zero level until day 639.

This is exceptionally good performance considering it is based on only a single filter of 20 cubic feet of ion exchange resin, handling input PFAS contaminant levels ranging from 60 ppt to above 100 ppt and reducing them down to non detect (ND) output level for almost 2 years.

This provides good verification of the value of using the longer range ion attraction forces (compared to the short range molecular forces) to reduce the long contact time restrictions that are characteristic of GAC.

It also demonstrates that the selective ion exchange resin used in this case study (Purofine PFA694E) has a sufficiently high ion exchange capacity to handle quite high levels of PFAS contaminant extraction while using reasonable volumes of resin material.

Also, most importantly, the results demonstrate (as we hoped) that the ion exchange resin does not seem to get bogged down with DOM (dissolved organic material) to anywhere near the same degree observed for GAC.

The bulk costs of the selected resin and of a suitably selected GAC seem to be comparable, the cost difference then being due to the fact that the volume of required resin is considerably less than the required volume of GAC. This is reflected in the cost estimates mentioned in the article for a proposed full scale system to operate at 100 gallons per minute.

The next Section (3) describes an ion exchange system design for the Rocky Hill facility.