Rocky Hill Water Situation.   Section 1

Defining the Problem: The Aquifer has Low Levels of PFOS

Following the TCE contamination of the Rocky Hill aquifer in the 1980's a remedial program was established by the NJDEP for the aquifer under Superfund jurisdiction. In this program a remedial well (referred to as GWTF #1) was established in a small building in the Montgomery North shopping center, adjacent to the Santander bank.

This GWTF #1 installation utilizes the so-called pump and dump procedure where the aquifer is continuously pumped through a Granular Activated Carbon filter and the effluent discharged to the storm drains.   In the US EPA 2016 EPA report on the remedial program it was stated that more than 300 million gallons of water had been pumped from the Rocky Hill aquifer in this manner, from two primary source areas at a combined 44 gallons per minute. Groundwater monitoring has been continuously conducted by NJDEP at the GWTF #1 location.

The important point here is that GWTF #1 is using the Rocky Hill aquifer and the GWTF #1 measurements of PFAS contaminants can be compared directly with ours from the Rocky Hill Water Facility (RHWF).

The RHWF uses aeration extraction that cannot remove PFAS organic contaminants (because they have no significant vapor pressure) and therefore the output tests from the RHWF show the PFAS levels that are in the input water from the aquifer.

It turns out that the test results for GWTF #1 match our RHWF results exactly, and we can include them as an extra data set. They are independent measurements of the same aquifer. The actual test results (taken from NJDEP- Drinking Water Watch) are compiled and presented on the following pages.

A) Levels of PFNA in the Rocky Hill Aquifer are Non-Detectable (ND)

For PFNA the NJ MCL is set at 13 parts per trillion (ppt).
The results all indicate non-detectable (ND), less than 2ppt- the detectability limit.
All the test labs can agree when there is zero detectable signal.

PFNA in the Aquifer (Perfluorononanoic Acid in ng/L)

RHWF	GTRWF #1	Date	Lab
<2	<2	1/14/20	Lancaster Labs
<2	<2	10/22/20	Lancaster Labs
<2	<2	8/6/20	Lancaster Labs
<1.8		2/21/20	Lancaster Labs
<2	<2	4/21/20	Aqua Pro-Tech Labs
<2		4/24/20	Alpha Analytical Inc

Aquifer content using data from Lancaster Labs= 1.97 +/- 0.07
Aquifer content using all 10 values = 1.98 +/- 0.06   **A+**
NJDEP requirement = 13

B) Levels of PFOA in the Aquifer are Below the NJDEP Requirement

The NJDEP requires MCL levels of PFOA to be 14 ppt. RHWF and GWTF tests are in total agreement for the 6 results from Lancaster labs, and even for the 2 higher results (13.4 and 13.7ppt) from the Aqua Pro-Tech Labs.
The 17.4ppt result from Alpha Analytical Inc. we consider to be an outlier, and the GWTF#1 data set simply does not include it.
On the basis of the 9 data points, including the outlier, the average is 12.5ppt, which is still within the 14ppt MCL for PFOA.

PFOA in Aquifer (Perfluoroctanoic Acid in ng/L)

RHWF	GWTF #1	Date	Lab
11	11	1/14/20	Lancaster Labs
11	11	10/22/19	Lancaster Labs
12	12	8/6/20	Lancaster Labs
13.4	13.7	4/21/20	Aqua Pro-Tech
17.4		5/7/2019	Alpha Analytical

Aquifer content using data from Lancaster Labs= 11.33 +/-0.51
Aquifer content including all 9 values= 12.5 +/- 2.11   ✔
NJDEP requirement = 14

We can get this Non-Detectable (ND)
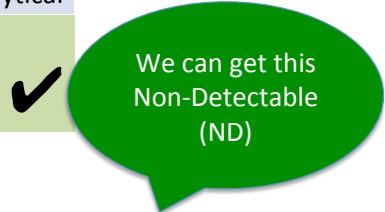
C) Levels of PFOS in the Aquifer Exceed the NJDEP requirement by 3 ppt

The NJ DEP MCL level for PFOS is set at 13ppt. Once again the 6 results from the Lancaster Labs are totally consistent. The results from Aqua Pro-Tech are consistent but 32% higher than the GWTF#1 average of 16ppt from Lancaster Labs and 15% higher than the RHWF average of 16.7ppt. Once again the 25.4ppt result from Alpha Analytical Inc. is considered to be an outlier, while the GWTF #1 data set does not include it.

Based on the 6 results from Lancaster Labs the average is 16.33ppt with a standard deviation of +/- 1.21ppt. When including the Aqua Pro-Tech data, the average becomes 17.3 +/_ 1.99ppt. These results exceed MCL compliance by less than 3ppt within the error (variance) of the measurements.

PFOS in Aquifer (Perfluoroctane Sulfonic Acid in ng/L)

RHWF	GWTF #1	Date	Lab
15	15	1/14/20	Lancaster Labs
17	16	10/22/19	Lancaster Labs
18	17	8/6/19	Lancaster Labs
19.2	21.2	4/21/20	Aqua Pro-Tech
25.4		4/29/19	Alpha Analytical Inc
Aquifer content using data from only Lancaster Labs= 16.33 +/- 1.21 Aquifer content (excluding outliers)= 17.3 +/- 1.99 NJDEP requirement = 13			

✗

We can get this Non-detectable (ND)

Summary: RHWF has trace levels of PFOS that can be removed to ND levels.
These results indicate that the PFAS contaminants in the Rocky Hill aquifer are at trace levels, the PFNA contaminant being non detectable (ND).
The residual PFAS contaminations can be totally removed using selective extraction procedures. These PFAS chemicals are extremely dangerous and **we aim to totally eliminate them from our drinking water.**
We describe how this can be done innovatively and economically for Rocky Hill.

Defining the Solution

1) The Adsorption Process as a Possible Solution

Adsorption is basically a surface phenomenon, and should not be confused with absorption which is a bulk volume property.

The material most commonly used in adsorption systems is granular activated carbon (GAC) sometimes referred to as activated charcoal because it was initially produced by burning wood under conditions of restricted combustion with reduced oxygen and leaving mostly carbon. The use of charcoal to extract impurities from water and to visibly clean drinking water goes back many centuries.

The production and use of granular activated carbon is now the basis of major industries, and GAC is now used extensively in air filtration and water purification. The mechanism of adsorption depends on the attraction between atoms and between molecules at very short distances. The attractive forces are very short range, and are known as Van der Waals forces. They are quite weak forces.

In the case of a contaminant molecule (or any other molecule) in water being adsorbed by GAC, the adsorption occurs at the interface between water and carbon. The more surface area there is of carbon, the better the chance of getting adsorption. At the interface there is the competition between the molecule being adsorbed as a result of the Van der Waals attractive forces or being retained in the water phase because of a preferred solubility.
Therefore, very soluble molecules or dissolved salts are not adsorbed.

The secret of GAC lies in the very large surface areas that can be generated through the activation processes used in its manufacture. These are largely proprietary, but involve high temperature (without ignition) oxidation procedures to condition and expand and fracture the carbon. These processes are so well managed that the pore size, the number of pores and the pore size distribution can be largely controlled so that the activated carbon can essentially be optimized for particular applications. The generally quoted description of GAC is that 1 gram of it has an effective surface area of a football field (1000 square meters).

The mechanism is that a molecule will get adsorbed into a suitable crevice or pore in the carbon and will be surrounded and trapped. These pores are therefore trapping sites. The forces involved are the molecular Van der Waals forces. These are not selective ionic forces, and any molecule can be trapped.

Problems with GAC Adsorption

The requirement of very close interaction distances (because of the short range attraction forces) poses severe restrictions on the actual working situations.
It is simply a question of a contaminant molecule being able to find and access a trapping site on the carbon surface. The preferred conditions for this would be thin surface films of water interacting slowly with large areas of carbon, or even recirculating over the carbon, in an attempt to find viable trapping sites.

This scenario is inconsistent with the practical need to pump significant volumes of water in a water facility. The answer is generally to increase the amount of GAC.

There are many design parameters that are applied to this situation, but the most basic and important one is the so-called empty bed contact time (EBCT) relating the water flow rate and the necessary volume of GAC material for effective adsorption. Based empirically on many pilot studies of simulated and real systems, the working rule of thumb is that EBCT for GAC should be more than 10 minutes.

If we apply this to a system pumping 100 gallons per minute (representing an average medium sized water facility) this indicates a needed GAC **minimum** volume of 1000 gallons = 3,785 liters = 3.785 cubic meters. With a bulk GAC density of around 2000 kg per cubic meter, the **minimum** needed weight of GAC is then 7570 kg = **8.34 tons US**. This gives an appreciation of the considerable amount of GAC actually needed in such systems.

In spite of the above requirements, many municipalities adopted adsorption with GAC to remove volatile organic compounds (VOC) contamination from their water systems (we used aeration) and are now also using it for PFAS removal, and are tolerating the expense of replacement of large amounts of activated carbon on a routine basis.

PFAS Breakthrough, and Lead-Lag operation

The use of tons of activated carbon in large filter tanks poses logistical problems involving flat bed trucking of filter tanks with expended carbon to be reactivated and replaced. This involves significant refurbishment costs, and also expensive "down-time" at the water facility.

To reduce the effects of these problems a lead-lag approach has been widely adopted. A single large tank system can be replaced by a system of smaller tanks in series (generally two in a set) that can be used in a "lead–lag" configuration. The EBCT (contact time) parameter and the needed flow rate can be maintained with two filter tanks in series. Also, not only are the smaller tanks much easier to handle but the down-time disruption of the water facility can be anticipated and managed more effectively.

The output from the "lead" filter is monitored for contaminant output and when contaminant **breakthrough** is indicated the lead filter is moved off-line and the lag filter substituted in its place (by valve control in the pipework) and the operation continued using only the single filter tank. The lead filter tank can then be recharged with new GAC and brought back into operation as the new lag filter, avoiding any costly shut-down or disruption of service. We would use this approach.

The occurrence of breakthrough is of crucial concern in the use of adsorption filters. It is indicative of the situation that all the trapping sites are now saturated.

This is not any failure of the GAC material, which in fact is the most effective material known in being able to provide enormous surface area and enormous numbers of trapping sites for adsorption, it is due to the Van der Waals forces being fundamental forces of attraction between any molecules, so that any and all types of molecules can be trapped in adsorption processes.

In the case of surface water sources there are multiple contained forms of naturally occurring dissolved organic molecules, generally at levels of mg/L -parts per million. These are normally quite natural and are not considered harmful, but they will all be adsorbed by GAC.

Organic molecules in aquifer water supplies are generally at measurable levels of hundreds of ppb (parts per billion). The PFAS contaminant molecule levels are at ppt (parts per trillion). In the aquifer water mix there are therefore hundreds of thousands of organic molecules for each PFAS molecule candidate searching for trapping sites, which therefore rapidly become fully saturated with organic molecules. The PFAS contaminants are then not adsorbed and break through the GAC filter.

This logically indicates that GAC adsorption is certainly **not** the optimal method of eliminating trace levels of contaminant molecules (like PFAS at ppt levels).
The PFAS molecules are treated like any others in the adsorption process and are massively outnumbered by all the other molecules.
The game then becomes one of costly and frequent replacement of large amounts of GAC on a regular basis due entirely to saturated adsorption by other molecules.

To eliminate PFAS trace contamination from our water supply we therefore need to employ some other approach that somehow enhances PFAS extraction. One answer lies in the PFAS molecule itself.

The long chain perfluoro molecules have carbon atoms bonded together and linked to fluorine atoms forming closed structures. The body of the molecule is then hydrophobic (water repellant). However, the "head" of the molecule chain is comprised of the functional group so, with PFOS for example, it would be comprised of the sulphonic acid group O2=S-OH with the molecule attachment to the sulphur atom. In water such PFAS molecules are ionized with the functional groups (SO3 for PFOS) being negatively charged anions.

These anions can be captured by Ion Exchange using anion exchange resins. The ion exchange process involves the stronger and longer-range ionic (electrostatic) forces. The PFAS hydrophobic fluorinated carbon chain structure could of course also be adsorbed on the surfaces of hydrophobic resin as described earlier.
So, we now have two separate capture mechanisms for the PFAS molecules.

It will be seen that ion exchange resins can be direct replacement for GAC in filtration systems. The EBCT parameters can be much less than for GAC and the required amount of resin material therefore also very much less than for GAC.

2) The Ion Exchange Solution for PFAS and for Rocky Hill

A descriptive article on ion exchange that is well worth reading has been generated by Rohm and Haas a specialty chemical company producing polymers and acrylics and now a subsidiary of Dow Chemical Company, and by Lenntech a Dutch company specializing in water treatment systems.
https://www.lenntech.com/Data-sheets/Ion-Exchange-for-Dummies-RH.pdf

The title "Ion Exchange for Dummies" is quite misleading. The article is very informative. Ion exchange resins have been around for a long time and are well established and are now becoming increasingly complex and specialised.
It is ironic that a preferred solution to removing PFAS organic polymer contaminants in water could actually depend on organic polymers.

From the above article it is seen that polymer resins can be produced as porous gel spheres of less than 1mm diameter (about the consistency of coarse sand) and they can be embedded on their outer structure with chosen ion radicals which are then fixed permanently onto the resin spheres, in the maximum numbers possible.

The resin can then be activated (as an example) by immersion in brine solution containing Sodium Na + cations and Chlorine Cl – anions.
With certain selected positive-charged cation functional groups fixed on the resin, the anions (Cl-) would be attached and therefore (in this example) Cl- would be the mobile ion that can be exchanged in this anion exchange resin, which is therefore named for the mobile ion. The resin is activated by loading the exchange ions.

This is a totally different process than for adsorption as previously described for GAC. Whereas the adsorption process is indiscriminate, applying to any molecules, the ion exchange process only applies to charged ions.

In actual fact the exchange resin polymer is itself hydrophobic and capable of adsorption so any molecule interacting closely with the resin surface pores can be adsorbed. So there is a small adsorption component as well as ion exchange.

Intuitively one would think that this small adsorption component with ion exchange resins could not possibly be comparable to the massive adsorption process with granular activated carbon, and it would indeed be a very desirable situation if the dominant influence of dissolved organic molecules was somehow reduced.

Organic C-H bonding groups are symmetrical and non-polar, and theoretically organics should not be water soluble. However the attachment of hydroxyl OH- and other functional groups changes all that so that in reality dissolved organic hydrocarbons are polar **and ionized**. In fact the fluorinated PFAS organic molecules are themselves an example of this. They are quite soluble, though hydrophobic.
These ionized organic molecules can now create a saturation problem for ion exchange.   It is necessary to evaluate and then to minimize this effect.
In the next Section (2) we will describe a recent field study on PFAS trace level extraction using selected ion exchange resins in an actual Municipal water facility. The case study presents a real and very practical solution for the Rocky Hill PFAS situation.