Granular activated carbon for removal of perfluoroalkyl and polyfluoroalkyl substances (PFAS) from groundwater

Abstract

A full-scale treatment system was designed and constructed for removal of volatile organic compounds (VOCs) and metals from impacted groundwater at a contaminated site. Upon issuance of the discharge permit for the treatment system, state regulators unexpectedly included a numerical limit for total perfluoroalkyl and polyfluoroalkyl substances (PFAS) of 70 ng/L, and limits for several individual PFAS compounds (see Table 2). These substances are normally found extensively in groundwater around the US and are suspected of causing adverse health effects in humans when consumed. The treatment system consisted of granular activated carbon (GAC) and ion exchange (IX) processes as polishing steps for target contaminant removal, which are also primary technologies for PFAS treatment. Carbon selection proved critical to achieving and maintaining compliance with stringent effluent permit limits. Additionally, lead/lag configuration of the carbon vessels, sampling techniques, and establishment of the optimum carbon changeout frequency significantly contributed to the efficacy of the system.

Introduction

Perfluoroalkyl and polyfluoroalkyl substances (PFAS) are a group of man-made chemicals that includes perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS) and many other chemicals. PFAS have been manufactured and used in a variety of industries around the globe, including the United States, since the 1940s. PFOA and PFOS have been the most extensively produced and studied of these chemicals. Both chemicals are very persistent in the environment and in the human body they don't break down readily and they can accumulate in tissue over time. There is evidence that exposure to PFAS can lead to adverse human health effects.

https://www.epa.gov/pfas/basic-information-pfas)

The United States Environmental Protections Agency's (USEPA) 2016 health advisories were established to provide the public with a margin of protection from a lifetime of exposure to PFOA and PFOS from drinking water. USEPA established the health advisory levels at 70 parts per trillion (70 ng/l) for combined PFOA and PFOS.

The chief concern for consumption by humans is through drinking water. There are several options available for drinking water systems to lower concentrations of PFAS, including PFOA and PFOS in their drinking water supply. Contaminated wells can be shut off or reduced to limit the overall concentration in the water supply. Alternatively, water systems can treat for PFAS utilizing liquid granular activated carbon (LGAC), ion exchange resins and reverse osmosis, as well as other technologies. Coincidentally, the treatment system for this client contained both liquid granular activated carbon (LGAC) and ion exchange.

Materials and Methods

Water Source and Pre-Treatment

A full-scale system utilizing two 15,000 pound LGAC units in a lead-lag configuration were used to treat VOC and PFAS contaminated groundwater. The treatment was conducted at a temporary construction-contact water treatment plant where the groundwater was known to contain PFAS. The treatment system consisted of chemical oxidation, iron co-precipitation, filtration, LGAC and ion exchange resin. No discernable removal of PFAS was measured prior to the LGAC. The ion exchange resin used post LGAC showed potential for PFAS removal, however it was not utilized as the primary means of PFAS treatment. Average and maximum influent PFAS concentration are provided in Table 1.

Table 1 | **Feed water quality, Aug 2017 – Sep 2018**

Parameter	Average	Max
NEtFOSAA	<2.50	5
NMeFOSAA	<2.50	<2.50
Perfluoro-octanesulfonate	72.6	170
Perfluorobutanesulfonate	4.75	18
Perfluorodecanoic acid	122.5	480
Perfluorododecanoic acid	2.0	33
Perfluoroheptanoic acid	349.8	1300
Perfluorohexanesulfonate	10.2	41
Perfluorohexanoic acid	792	3500
Perfluorononanoic acid	104	380
Perfluorooctanoic acid	593	2400
Perfluorotetradecanoic acid	<0.75	<0.75
Perfluorotridecanoic acid	<0.75	<0.75
Perfluoroundecanoic acid	6.3	25
PFA Total	1993	7972

*All results in nanograms per liter (ng/L)

Discharge Limits

The discharge limits of the site where this treatment system was installed were set by the New Jersey Department of Environmental Protection (NJDEP). The permit equivalent included treatment limits for 14 PFAS compounds and a total PFAS limit of 70 nanograms per liter (ng/L). There were limits for five individual compounds, and a combined limit of 26 ng/L for the nine compounds not individually regulated. Table 2 summarizes those limitations.

Table 2 | **Individual PFA Discharge Limits**

Parameter	Limit
Perfluoro-octanesulfonate	70
Perfluoroheptanoic acid	15
Perfluorohexanoic acid	19
Perfluorononanoic acid	10
Perfluorooctanoic acid	40

*All results in nanograms per liter (ng/L)

Flow Rates

Flow rates varied throughout the course of treatment with the average value being 133 gallons per minute. The system was shut down from December 2017 to late March 2018 due to suspension of remediation activities at the site for the winter months.

Table 3 | **Average flow rates, Aug 2017 – Sep 2018**

Month	Weeks	Flow (gpm)
August-17	1-3	184
September-17	4-7	132
October-17	8-11	114
November-17	12-15	123
December-17		-
January-18		-
February-18		-
March-18	16	123
April-18	17-20	200
May-18	21-25	142
June-18	26-29	129
July-18	30-33	131
August-18	34-35	158
September-18	36	120
Average		133

LGAC

Two types of LGAC were used for this treatment, entitled Carbon A and B. The original carbon selected, Carbon A, was an 8 x 30 regenerated Bituminous Coal with an iodine number between 800 and 1,000. Carbon A was used in both the lead and lag stages for the first 11 weeks of system operation. Carbon B is also an 8 x 30 regenerated Bituminous Coal, however this carbon was previously used for potable water treatment. Carbon B was chosen for the first change out 11 weeks into the treatment system operation and was used for every subsequent changeout.

The primary differences of Carbon B are its origin and iodine number. The iodine number is used to create an adsorption isotherm for a given type of carbon that is indicative of its adsorption capacity. The higher the iodine number, the higher the anticipated adsorption capacity. Typically carbon has an iodine number range between 800 and 1000. While many suppliers offer regenerated 8x30 bituminous carbon in this range, one supplier was identified who differentiates between sources of returned carbon. As such they have the capacity to potentially provide a higher grade regenerated carbon when required for special applications. In this case, the potable 8x30 carbon was regenerated after being used for treating drinking water. The original application for this type of carbon would be final effluent polishing for removal of disinfection byproducts, which means minimal metals and inorganics (that do not get removed by regeneration) and also minimal fines (as this would have been an original requirement at the point of supply). The combination of these properties and the regeneration process used will result in an iodine number greater than 1,000, and possibly 25 percent higher than the standard 8x30 carbon.

Operating Strategy

Two 15,000-pound LGAC units were used for the duration of treatment. The two LGAC units were operated in series, in a lead-lag configuration. In this configuration, the flow is directed through the lead unit first which removes the bulk of the contaminants and then flows through the lag unit which is primarily used for polishing. Due to handling a majority of the contaminant load, the carbon in the lead unit reaches its capacity, and requires changing out before the lag unit. When it is determined that a carbon change is required, the lead unit is taken offline, emptied of the spent carbon, and refilled with fresh carbon. This unit, with the new carbon, is placed back online in the lag position, while the unit previously in the lag position is moved to lead. The changing of units between lead and lag is accomplished by adjusting valve positions to redirect flow. Rotating the units in this way allows for maximizing the lifespan of the carbon while still maintaining high effluent quality by always keeping the freshest carbon in the lag position for polishing prior to discharge.

The LGAC change out schedule that was used after the first 11 weeks was done to ensure compliance of the overall process until closure of the treatment plant. Figure 1 illustrates the LGAC changeout schedule and influent and effluent PFAS concentrations.

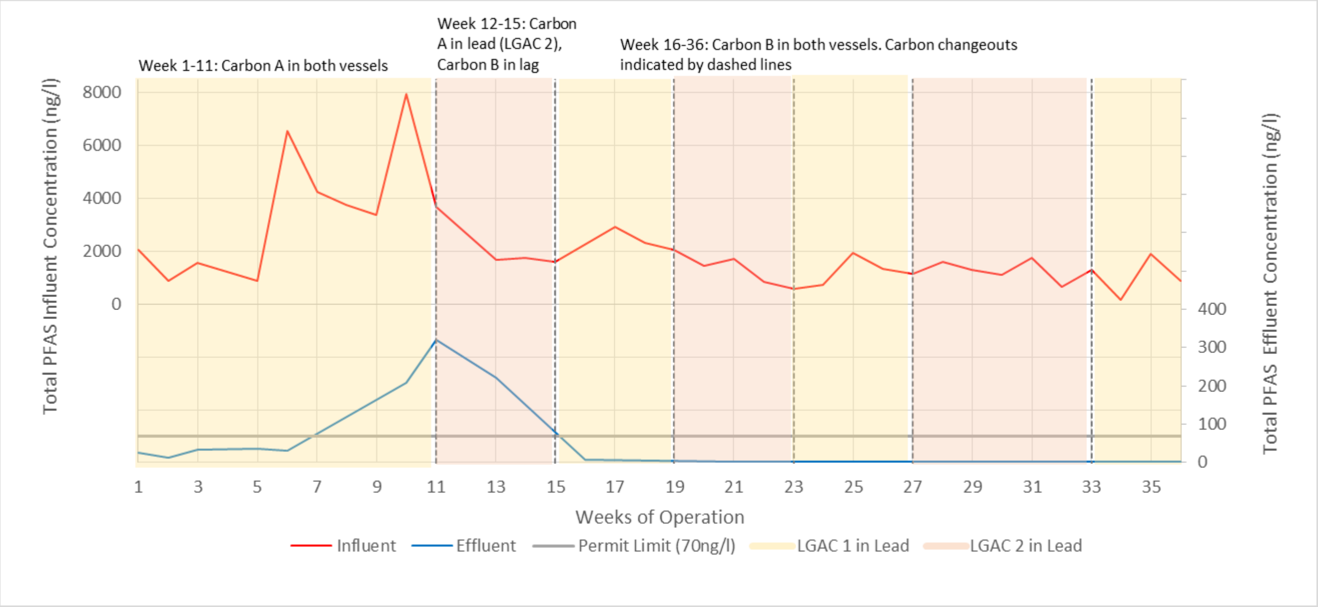
Sampling Procedures

All samples were analyzed via a certified lab with one week turnaround time using EPA Method 537 version 1.1 - DETERMINATION OF SELECTED PERFLUORINATED ALKYL ACIDS IN DRINKING WATER BY SOLID PHASE EXTRACTION AND LIQUID CHROMATOGRAPHY/TANDEM MASS SPECTROMETRY (LC/MS/MS).

One week turnaround of the samples proved to be a hindrance due to the low effluent limits and the rapid breakthrough of the PFAS. This was counter-acted by the changeout procedure discussed in the *Results and Discussion section*.

Sampling procedures and locations were reviewed by Envirogen Operations staff to assure that no PFAS were being introduced at the time the sample was taken. Hygiene habits were evaluated and it was determined that no form of shampoo, conditioner or body wash should be used by the sampler on the morning of a sampling event. Powder free nitrile gloves were deemed to be acceptable and were changed after collecting samples at each sample point. In addition, field blanks were added to the sampling roster to confirm that these procedures and site conditions were not a cause of any elevated PFC levels.

Figure 1 | **Influent and Effluent Total PFAS Concentrations with Carbon Change outs**



Results and Discussion

Total PFAS

Table 4 shows the certified lab data for total PFAS during the entirety of treatment plant operation. During the first 11 weeks, 15.8 million gallons of ground water were processed and 87 grams of PFAS were removed via the lead LGAC. This results in a loading rate of 5.86 milligrams of total PFAS per pound of Carbon A. Another 60 grams were removed by the lag vessel. At week 11, and 87 grams adsorbed, Carbon A was still able to remove PFAS, however the system was not operating in compliance with discharge limits.

Table 4 | Weekly Concentration of Total PFAS – Influent, Lead GAC Effluent and Lag GAC Effluent

Week	1	2	3	4	5	6	7	8	9	10	11	12
Influent	2061	873	1548	NS	876	6568	4274	3747	3384	7978	3689	NS
Lead Eff.	NS	NS	NS	NS	354	1989	2091	1928	1748	7451	2300	NS
Lag Eff.	NS	24	29	47	NS	155	370	468	394	2456	1167	NS

Week	13	14	15	16	17	18	19	20	21	22	23	24
Influent	1692	1743	1593	NS	2926	2316	2071	1447	1708	838	587	737
Lead Eff.	608	552	759	NS	55	242	12	17	28	33	1	4
Lag Eff.	3	12	15	NS	ND	31	ND	ND	ND	3	3	3

Week	25	26	27	28	29	30	31	32	33	34	35	36
Influent	1927	1355	1161	1603	1299	1118	1760	663	1316	170	1911	897
Lead Eff.	8	9	3	4	4	4	19	22	3	4	5	3
Lag Eff.	4	3	3	3	3	3	3	3	3	3	3	12

*All results in nanograms per liter (ng/L) **NS – Not Sampled ***ND – Non-Detect ****Change out week

Upon changing over to Carbon B in either vessels, similar, or slightly lower total loading rates were found averaging 2.87 mg/lb carbon, but the removal efficiency for individual compounds was much higher.

As previously discussed, the less than ideal turnaround times for PFAS samples, the rapid breakthrough of PFAS and the scheduling concerns with performing the LGAC change outs resulted in having to schedule change outs on a predictive basis using operational data. The focus of predictive scheduling of change outs was to maximize carbon usage while minimizing risk of out-of-compliance discharge. Therefore, it was decided that the carbon in the lead LGAC would be replaced at the estimated date of breakthrough. Breakthrough, in this instance, is defined as when effluent from the lead LGAC vessel exceeds the permit limits.

This approach resulted in a carbon change every 4 weeks after the initial eleven weeks of treatment. This schedule was adjusted based on flow and influent concentrations, increasing time between changeouts when flow or influent concentration dropped. Table 5 shows the actual LGAC change out schedule. The letters represent the type of carbon used and the numbers represent each carbon change.

Table 5 | LGAC Change Out Schedule

Week of Change out	Lead	Lag	Weeks in Service
0	A1	A2	11
11	A2	B1	4
15	B1	B2	4
19	B2	B3	4
23	B3	B4	4
27	B4	B5	6
33	B5	B6	3

After the schedule was put in place, no exceedance of the permit equivalent of 70 ng/L was observed for total PFAS. From week 13 and onward, the max lag LGAC effluent concentration was 31 ng/L. The lead LGAC did not consistently meet discharge limits until week 19, at which time, the highest level of total PFAS was 33 ng/L.

The change out frequency, based solely on total PFAS, could have been decreased. However, individual compound restrictions proved to be the limiting factor.

Perfluoroheptanoic Acid (PFHpA)

PFHpA was one of three main contributors to the total PFAS, but was not a factor driving when carbon change outs were performed. On

Table 6 | **Weekly Concentration of Perfluorohexanoic Acid (PFHxA)**

Week	1	2	3	4	5	6	7	8	9	10	11	12
Influent	650	270	590	NS	290	2200	1200	1300	1200	3500	1700	NS
Lead Eff.	NS	NS	NS	NS	170	910	930	810	830	3500	1200	NS
Lag Eff.	NS	8	21	34	NS	110	240	290	270	1500	710	NS

Week	13	14	15	16	17	18	19	20	21	22	23	24
Influent	750	720	690	NS	1100	900	790	610	610	350	250	310
Lead Eff.	340	300	380	NS	27	160	7	11	20	24	ND	1
Lag Eff.	ND	5	7	NS	ND	13	ND	ND	ND	ND	ND	ND

Week	25	26	27	28	29	30	31	32	33	34	35	36
Influent	700	520	400	650	490	420	760	290	540	54	960	360
Lead Eff.	4	5	ND	1	3.5	5.0	12	15	ND	ND	1	ND
Lag Eff.	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	7

*All results in nanograms per liter (ng/L) **NS – Not Sampled ***ND – Non-Detect ****Change out week

average, PFHpA contributed to 16.7% of total PFAS.

Perfluorooctanoic Acid (PFOA)

PFOA was the second of three main contributors representing 29.3% of total PFAS. It, along with perfluorohexanoic acid, were the first two to break through the LGAC. PFOA, with a higher effluent limit of 40 ng/L, was considered an indicator of breakthrough but was not the limiting factor driving carbon exchanges.

Perfluorohexanoic Acid (PFHxA)

PFHxA is the third and largest contributor to total PFAS at 39.3%. PFHxA has a discharge limit of only 19 ng/L, and with an influent range of 823.8 ng/L to 3,500 ng/L, removal rates from 78%, to as high as 99%, are necessary to maintain compliance. As such, concentrations of PFHxA in the lead LGAC effluent were determined to be the limiting factor driving carbon exchanges. Table 6 shows the concentration of PFHxA throughout the treatment period.

After the changeout schedule was implemented from week 12 onward, no exceedance of PFHxA occurred at the effluent of the lag LGAC. While concentrations above the effluent limit occurred post lead LGAC, these exceedances were manageable by the lag LGAC. Figure 2a shows the influent and effluent concentrations of PFOA, PFHpA, and PFHxA. Figure 2b shows the effluent concentrations of these compounds from week 19 to termination of treatment in relation to permit limits.

Figure 2a | Influent and Lead LGAC Effluent Concentrations of permitted PFAS compounds

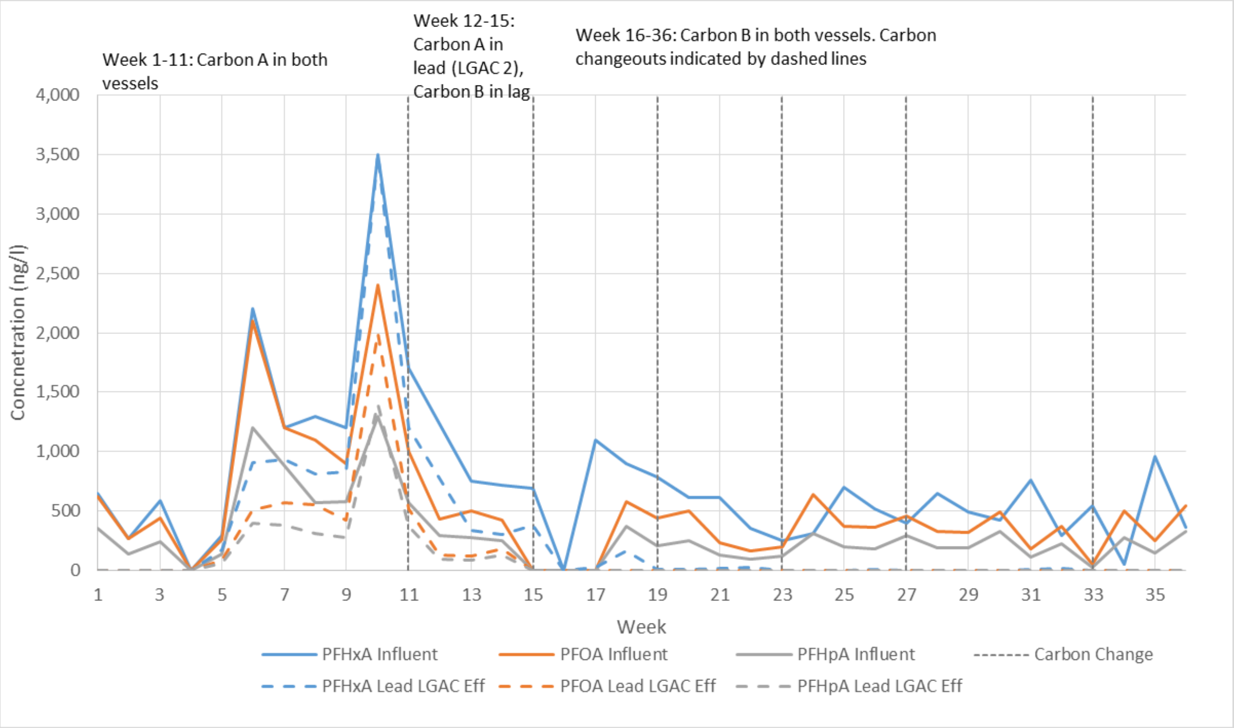
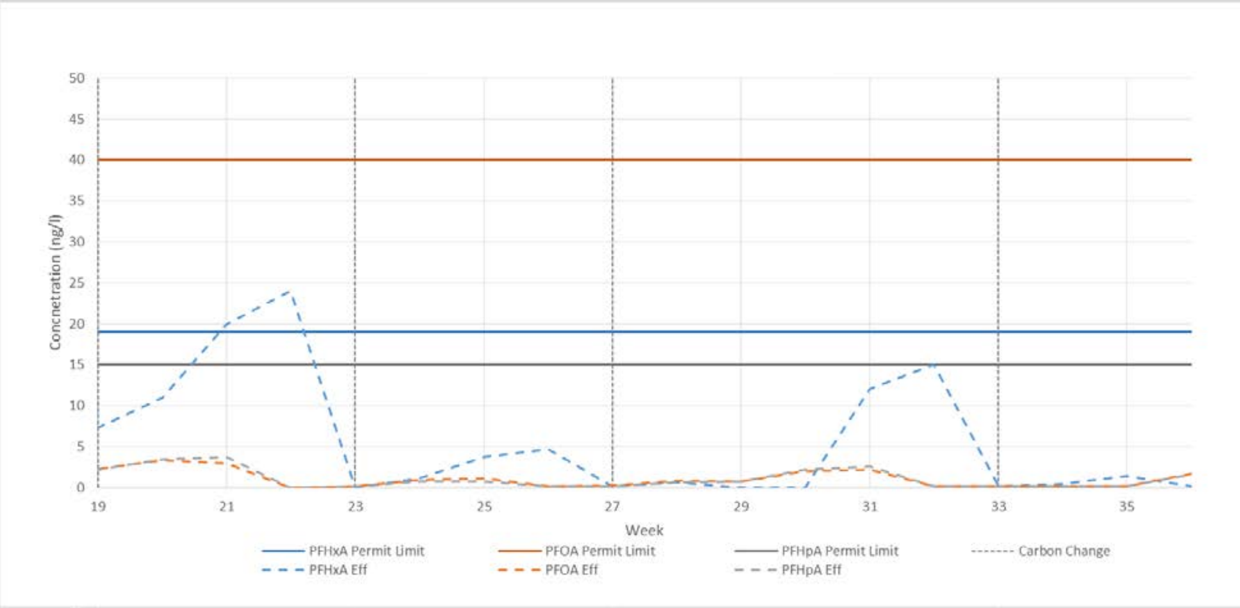


Figure 2b | Lead LGAC Effluent Concentrations of Permitted PFAS Demonstrating Use of PFHxA Levels as Indicator of Need for Carbon Change



Conclusions

Groundwater contaminated with a variety of PFAS compounds was effectively treated using specially selected activated carbon and operated in a lead-lag configuration.

Carbon changeout frequency was managed conservatively to assure compliance with stringent discharge limits. This was necessitated by extended turnaround times for receiving certified laboratory data for samples which did not allow for real time assessment of breakthrough. Upon establishment of the proper changeout frequency, full compliance was accomplished across the range of PFAS compounds in the water.

Savings in carbon usage were achieved by moving the unspent lag carbon to the less critical lead position to allow complete exhaustion.

Additional critical learnings around sampling procedures and techniques contributed to the collection of reliable influent and effluent data for a true determination of system efficacy.

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