

Treatment of Perfluorinated Alkyl Substances in Wash Water Using Granular Activated Carbon and Mixed- Media



Treatment of Perfluorinated Alkyl Substances in Wash Water Using Granular Activated Carbon and Mixed- Media

by

Jeffrey Szabo, John Hall and Matthew Magnuson
U.S. Environmental Protection Agency
Cincinnati, OH 45268

Sri Panguluri and Greg Meiners
CB&I Federal Services, LLC
Cincinnati, OH 45204

Interagency Agreement DW-89-92381801
U.S. Environmental Protection Agency Project Officer: John Hall
Office of Research and Development
Homeland Security Research Program
Cincinnati, OH 45268

Contract EP-C-12-014
U.S. Environmental Protection Agency Contracting Officer's Representative: Ruth Corn
Office of Research and Development
Homeland Security Research Program
Cincinnati, OH 45268

This page left intentionally blank

Disclaimer

The U.S. Environmental Protection Agency (EPA) through its Office of Research and Development funded and managed the research described herein under contract EP-C-12-014 with CB&I Federal Services, LLC and Interagency Agreement DW-89-92381801 with the Department of Energy. It has been subjected to the Agency's review and has been approved for publication. Note that approval does not signify that the contents necessarily reflect the views of the Agency. Any mention of trade names, products, or services does not imply an endorsement by the U.S. Government or EPA. The EPA does not endorse any commercial products, services, or enterprises.

The contractor role did not include establishing Agency policy.

Table of Contents

| | |
|---|-----|
| Disclaimer | ii |
| Table of Contents | iii |
| Acknowledgements | vi |
| 1.0 Introduction..... | 1 |
| 1.1 Background | 1 |
| 1.2 Project Objective..... | 1 |
| 1.3 WSTB System Description..... | 1 |
| 2.0 Description of Experiment and Apparatus..... | 4 |
| 2.1 Treatment Drum Setup..... | 5 |
| 2.2 Lagoon Contamination Procedure | 5 |
| 2.3 Contaminated Lagoon Water Treatment Procedure | 7 |
| 3.0 Analysis of Test Results | 11 |
| 4.0 Conclusions and Observations..... | 32 |
| 5.0 References..... | 33 |

List of Figures

| | |
|--|----|
| Figure 1. Schematic overview of the Water Security Test Bed (WSTB). | 2 |
| Figure 2. Aerial view of the Water Security Test Bed (WSTB)..... | 3 |
| Figure 3. Water Security Test Bed (WSTB) discharge lagoon..... | 3 |
| Figure 4. PFAS removal from water treatment train. | 4 |
| Figure 5. Rembind™ media mixed with sand. | 5 |
| Figure 6. Idaho National Laboratory fire truck AFFF eductor spray mechanism. | 5 |
| Figure 7. AFFF sprayed to contaminate lagoon water..... | 6 |
| Figure 8. AFFF contaminated lagoon water. | 7 |
| Figure 9. Plumbing setup for inlet flow control..... | 8 |
| Figure 10. Inlet flow control during testing. | 8 |
| Figure 11. Removal of PFBS from lagoon water using GAC and Rembind media. | 14 |
| Figure 12. Normalized PFBS concentration change with increasing treated water volume. | 14 |
| Figure 13. Normalized PFBS concentration change with increasing throughput (bed volumes). | 15 |
| Figure 14. Removal of PFBA from lagoon water using GAC and Rembind media. | 16 |
| Figure 15. Normalized PFBA concentration change with increasing treated water volume..... | 17 |
| Figure 16. Normalized PFBA concentration change with increasing throughput (bed volumes). | 17 |
| Figure 17. Removal of PFPA from lagoon water using GAC and Rembind media. | 18 |
| Figure 18. Normalized PFPA concentration change with increasing treated water volume. | 19 |
| Figure 19. Normalized PFPA concentration change with increasing throughput (bed volumes). | 19 |
| Figure 20. Removal of PFHxS from lagoon water using GAC and Rembind media. | 20 |
| Figure 21. Normalized PFHxS concentration change with increasing treated water volume. | 21 |

| | |
|--|----|
| Figure 22. Normalized PFHxS concentration change with increasing throughput (bed volumes). | 21 |
| Figure 23. Removal of PFHxA from lagoon water using GAC and Rembind media. | 22 |
| Figure 24. Normalized PFHxA concentration change with increasing treated water volume. | 23 |
| Figure 25. Normalized PFHxA concentration change with increasing throughput (bed volumes). | 23 |
| Figure 26. Removal of PFHS from lagoon water using GAC and Rembind media. | 24 |
| Figure 27. Normalized PFHS concentration change with increasing treated water volume. | 25 |
| Figure 28. Normalized PFHS concentration change with increasing throughput (bed volumes). | 25 |
| Figure 29. Removal of PFHA from lagoon water using GAC and Rembind media. | 26 |
| Figure 30. Normalized PFHA concentration change with increasing treated water volume. | 27 |
| Figure 31. Normalized PFHA concentration change with increasing throughput (bed volumes). | 27 |
| Figure 32. Removal of PFOS from lagoon water using GAC and Rembind media. | 28 |
| Figure 33. Normalized PFOS concentration change with increasing treated water volume. | 29 |
| Figure 34. Normalized PFOS concentration change with increasing throughput (bed volumes). | 29 |
| Figure 35. Removal of PFOS from lagoon water using GAC and Rembind media. | 30 |
| Figure 36. Normalized PFOA concentration change with increasing treated water volume. | 31 |
| Figure 37. Normalized PFOA concentration change with increasing throughput (bed volumes). | 31 |

List of Tables

| | |
|--|----|
| Table 1. Flowrates achieved through the media | 9 |
| Table 2. PFAS bulk water sampling at different times and locations | 9 |
| Table 3. Lagoon water quality sampling results | 11 |
| Table 4. List of PFAS compounds analyzed | 11 |
| Table 5. Average percent PFAS removal. | 13 |

Abbreviations

| | |
|-------|--|
| AFFF | aqueous film forming foam |
| ALS | ALS Environmental - Commercial laboratory in Kelso, WA |
| BWS | bulk water sample |
| CB&I | CB&I Federal Services LLC |
| COD | chemical oxygen demand |
| CSIRO | Commonwealth Scientific and Industrial Research Organization |
| EBCT | empty-bed contact time |
| EPA | U.S. Environmental Protection Agency |
| Ft | feet |
| GAC | granular activated carbon |
| gal | gallon |
| gpm | gallons per minute |
| hr | hour |
| IA | Interagency Agreement |
| INL | Idaho National Laboratory |
| L | liter |
| m | meter |
| min | minute |
| NTU | nephelometric turbidity units |
| PFAS | perfluorinated alkyl substances |
| PFBA | perfluorobutanoic acid |
| PFBS | perfluorobutane sulfonate |
| PFHA | perfluoroheptanoic acid |
| PFHS | perfluoroheptane sulfonate |
| PFHxA | perfluorohexanoic acid |
| PFHxS | perfluorohexane sulfonate |
| PFOS | perfluorooctanesulfonic acid |
| PFOA | perfluorooctanoic acid |
| PFPA | perfluoropentanoic acid |
| psi | pounds per square inch |
| QAPP | Quality Assurance Project Plan |
| TOC | total organic carbon |
| WSTB | Water Security Test Bed |

Acknowledgements

Contributions from the following individuals to the field work described in this report are acknowledged: Stephen Reese, Trent Armstrong, and Michael Carpenter of the Idaho National Laboratory. Jim Goodrich of the Environmental Protection Agency, who is the WSTB program manager.

Executive Summary

The U.S. Environmental Protection Agency's (EPA) National Homeland Security Research Center partnered with the Idaho National Laboratory (INL) to build the Water Security Test Bed (WSTB) at the INL test site outside of Idaho Falls, Idaho. The centerpiece of the WSTB is an 8-inch diameter drinking water pipe formerly in service at INL. The pipe was exhumed from the INL grounds and oriented in the shape of a small drinking water distribution system. The WSTB has service connections to simulate water demands, fire hydrants, and removable coupons to collect samples from the pipe interiors. Water from the WSTB pipe empties into a lined 28,000-gallon (105,980 L) lagoon which contains dirt, algae and organic matter, and was used for this study. Water from the lagoon can serve as "wash water," or water that is similar in nature to water flushed from a distribution system into an impoundment, water used to wash down a contaminated building, or water used to fight a fire.

This report summarizes the results from testing conducted to evaluate the treatment of large volumes of water containing perfluorinated alkyl substances (PFAS). Specifically, treatment for water contaminated by aqueous film forming foam (AFFF), which is used to fight very hot hydrocarbon based fires, as may arise from the response to petroleum spills and transportation accidents, was studied. Depending on the manufacturing process for the AFFF, the AFFF contaminated water can contain emerging contaminants such as perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), which are the subject of recent EPA health advisories. The AFFF selected for this study was a product widely used historically, and it contained PFOA and PFOS. The goal of the treatment was to reduce the PFAS concentration before disposal of the water (for example, in a sewer). The goal was not to reduce PFAS concentrations to drinking water advisory levels.

The WSTB pipe was not used for these experiments; instead, the WSTB discharge lagoon was contaminated with AFFF and the contaminated water was pumped through the treatment media then emptied into the bladder tanks. Treatment of the AFFF contaminated water was investigated via granular activated carbon (GAC) and mixed-media. Specifically, the Calgon Filtrasorb® 600 GAC and the Ziltek RemBind™ mixed-media were selected for evaluation.

The following is a summary of conclusions and observations about the performance and implementation of adsorptive treatment of AFFF contaminated water, based on the testing performed at the INL WSTB:

- The test results show that both GAC and RemBind™ are capable of removing various short-and-long chain PFAS with an efficiency greater than 99.9%, on average, over a 12-hour period, when the source water is spiked with firefighting levels of AFFF.
- The removal of shorter chains is of particular importance because newer AFFF products are formulated to eliminate longer chain PFAS. This suggests that water contaminated with newer AFFF formulations can also be successfully treated with these adsorbents, although this should be experimentally verified, especially for the site-specific water, which may contain substances that interfere or compete with PFAS adsorption.

- GAC media can accommodate a higher flowrate than the RemBind™ media. Up to 6.5 gallons per minute (gpm) (41.7 bed volumes) was achieved in two drums of GAC in series, while a total of 4 gpm (22 bed volumes) was achieved through two RemBind™ drums operated in parallel (2 gpm per drum). The RemBind™ media needs to be mixed with significant amount of sand to achieve operational flows in the field. Also, the low flow through and high pressure drop across the RemBind™ media drum may be too significant for the RemBind™ drums to be operated in series without an intermediate pump and storage mechanism. These factors impact the logistics of implementation of a RemBind™ based treatment system, if this adsorbent is chosen based on site-specific needs.
- For some PFAS, the data suggests that the first GAC drum in series (drum 1) was losing its adsorptive capacity, and breakthrough of PFAS was occurring. However, breakthrough was not observed in the second drum in series. Because such variations could impact utilization of the drums, this observation merits further investigation to enable the appropriate implementation of these drums at a specific site.

1.0 Introduction

1.1 Background

The U.S. Environmental Protection Agency's (EPA) National Homeland Security Research Center has partnered with Idaho National Laboratory (INL) to build the Water Security Test Bed (WSTB) at INL in Idaho Falls, Idaho. The centerpiece of the WSTB is an 8-inch diameter drinking water pipe formerly in service at INL. The pipe was exhumed from the INL grounds and oriented in the shape of a small drinking water distribution system. The WSTB has service connections, fire hydrants, and removable coupons to collect samples from the pipe interiors. The WSTB has service connections to simulate water demands, fire hydrants, and removable coupons to collect samples from the pipe interiors. Water from the WSTB pipe empties into a 28,000 gallon lagoon that contains dirt, algae and organic matter. Water from the lagoon can serve as "wash water," or water that is similar in nature to water flushed from a distribution system into an impoundment, water used to wash down a contaminated building, water used to fight a fire, etc.

This experiment focused on treatment of large volumes of water contaminated with perfluorinated alkyl substance (PFAS), specifically aqueous film forming foam (AFFF). The aqueous film forming foam is used to fight very hot hydrocarbon based fires, as may arise from petroleum spills and transportation accidents. Water containing residual AFFF may need to be treated before disposal or discharge into a sewer system. The WSTB pipe was not used for these experiments; instead, the WSTB discharge lagoon was contaminated with AFFF and the contaminated water was pumped through the treatment media and emptied into the bladder tanks. Specifically, the Calgon Filtrasorb 600®¹ granular activated carbon (GAC) and the Ziltek RemBind™² mixed-media were selected as the treatment media. GAC is commonly used for perfluoro alkyl substances (PFAS) removal from water. Rembind is often used for PFAS removal from soil, but it was evaluated in this study to determine its applicability to water treatment.

1.2 Project Objective

The objective of the project was to simulate the treatment of wash-water contaminated with AFFF and containing perfluoro alkyl substances (PFAS). The PFAS include emerging contaminants such as perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), which are the subject of recent EPA health advisories (USEPA, 2016). Treatment options evaluated included GAC and the RemBind™ mixed-media. The goal of the treatment was to reduce the PFAS concentration before disposal of the water (for example, in a sewer). The goal was not to reduce PFAS concentrations to drinking water advisory levels.

1.3 WSTB System Description

The WSTB consists primarily of an 8-inch (20 cm) diameter drinking water pipe oriented in the shape of a small drinking water distribution system. The WSTB contains ports for service connections and a 15-foot (5 m) removable coupon section, designed to sample the pipe interior to examine the results from contamination/decontamination experiments on the pipe wall.

¹ Filtrasorb® is a trademark of Calgon Carbon Corporation, 3000 GSK Drive, Moon Township, PA

² RemBind™ is a trade marked powdered media developed by Ziltek Pty Ltd, Adelaide, Australia

(Coupons are excised samples of materials to be tested.) Figure 1 schematically depicts the main features of the WSTB.

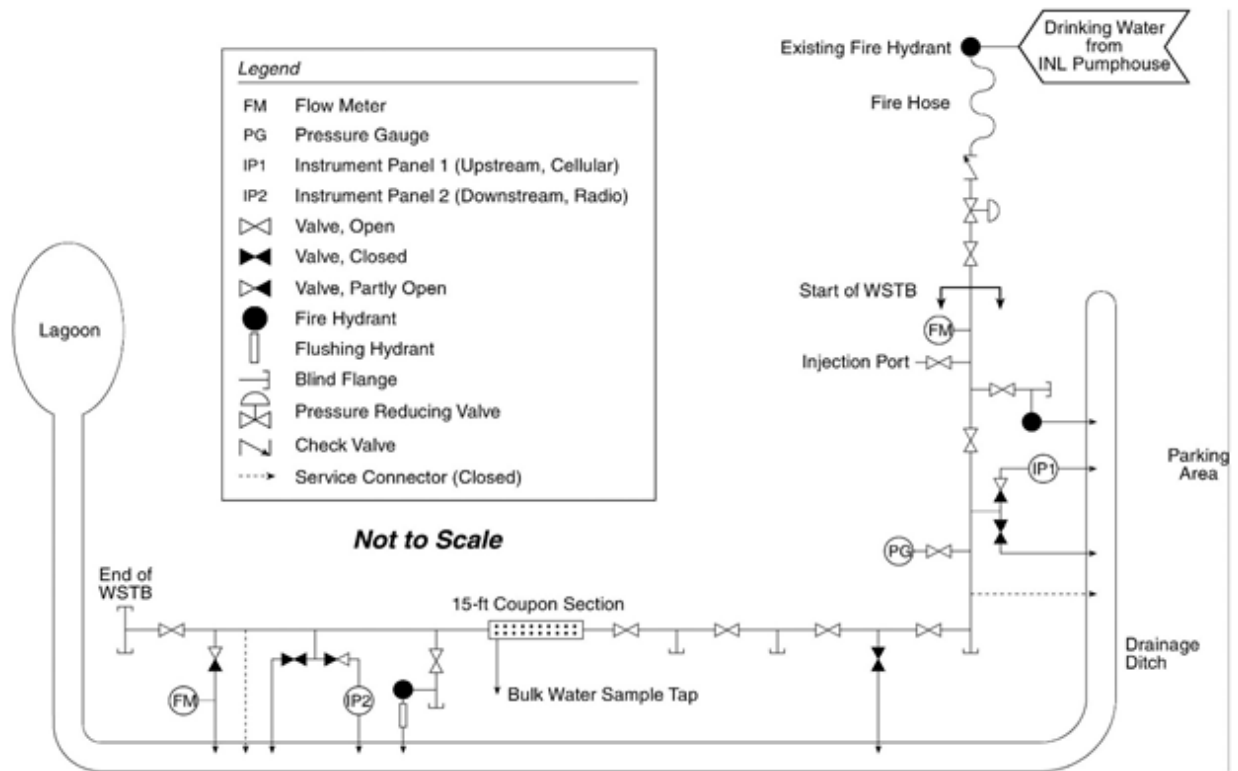


Figure 1. Schematic overview of the Water Security Test Bed (WSTB).

Figure 2 shows the aerial view of the WSTB. The lower right corner shows the upstream and system inlet; the upper left corner shows the lagoon which receives the water exiting the WSTB pipe.

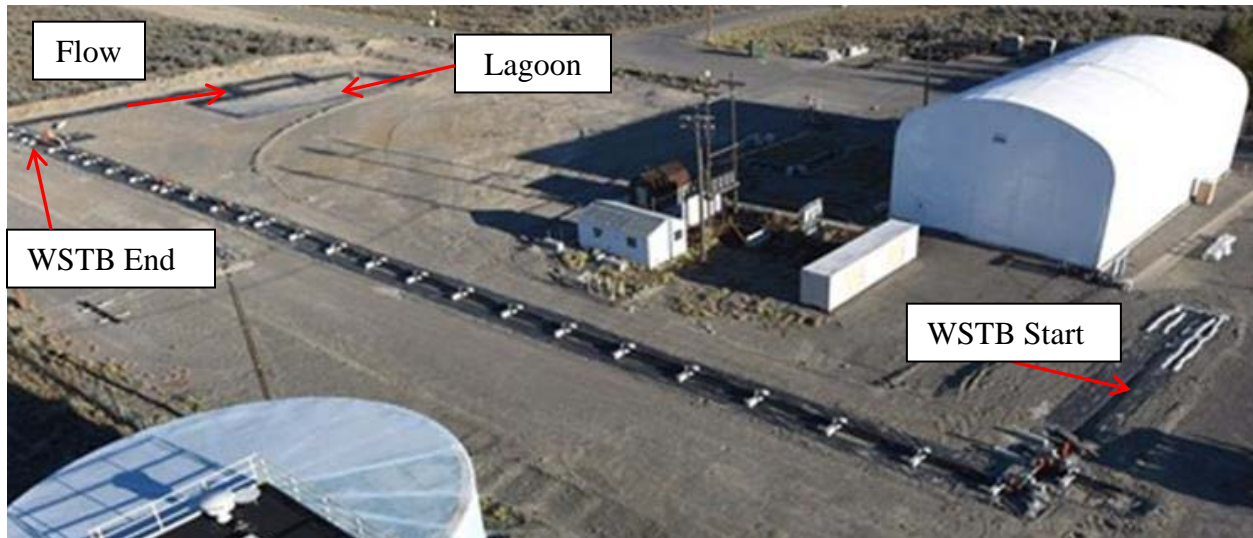


Figure 2. Aerial view of the Water Security Test Bed (WSTB).

Drinking water supplied to the WSTB is chlorinated ground water that also supplies the surrounding INL facilities. Other than chlorination, the groundwater is not treated further. The lagoon (Figure 3) has a total water storage capacity of 28,000 gallons (105,980 L). Water contained in this lagoon served as surrogate for “wash water” during this testing. Dirt and organic matter from the area surrounding the lagoon blows in water, and algae grows at the bottom. For this experiment, the lagoon was contaminated by spraying AFFF over its surface using a fire-fighting truck.



Figure 3. Water Security Test Bed (WSTB) discharge lagoon.

2.0 Description of Experiment and Apparatus

Figure 4 shows the experimental setup that was originally proposed (shown using blue flowlines) to individually test the performance of GAC and mixed-media (RemBind™) to remove PFAS from AFFF-contaminated water. However, during the initial setup of the drums and flow testing, it was determined that the RemBind™ media was not designed to handle the desired experimental flowrate (5 gallons per minute [gpm]) through the drums in series (see section 2.1 for more detail). Therefore, each RemBind™ drum was operated in parallel (shown using red flowlines in Figure 4), but the sampling locations and identification remained unchanged.

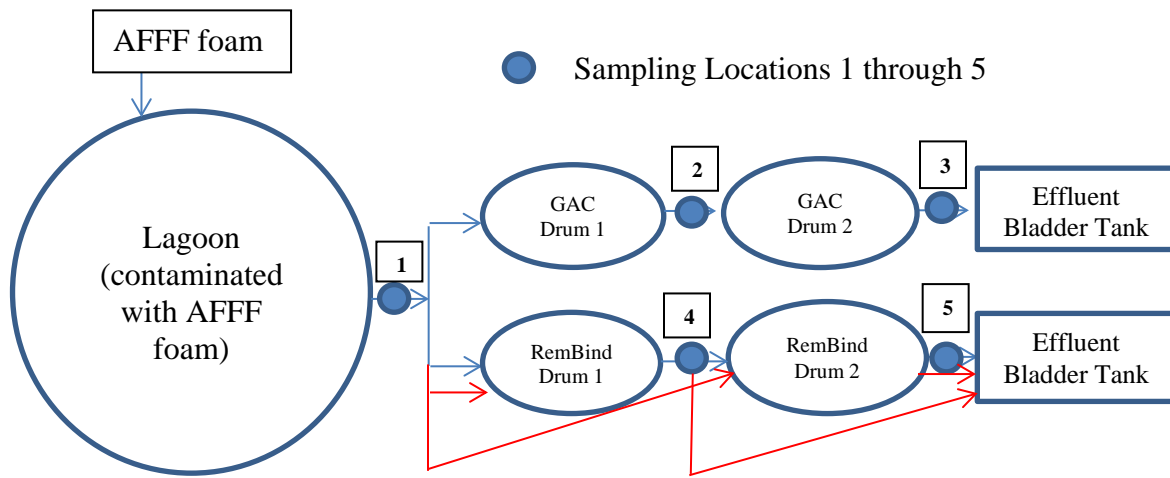


Figure 4. PFAS removal from water treatment train.

Filtrisorb 600 GAC is made from select grades of bituminous coal to produce a high activity, durable, granular product capable of withstanding the abrasion associated with repeated backwashing, hydraulic transport, and reactivation for reuse. Activation is carefully controlled to produce a significant volume of different types of pores for effective adsorption of a broad range of high and low molecular weight organic contaminants (Calgon, 2015).

RemBind™ is a powdered reagent for the chemical fixation of organic and inorganic contaminants in soil. The product was developed by Ziltek in collaboration with Australian-based Commonwealth Scientific and Industrial Research Organization (CSIRO) and contains a proprietary blend of reagents (Ziltek, 2014). The main constituents of RemBind™ are:

- Activated carbon
- Aluminum hydroxide (amorphous)
- Kaolin clay and other proprietary additives

The AFFF used in this study was 3M's Light Water™ 3% concentrate (FC-203CF, St. Paul, MN). This formulation was used historically, and it contains PFOA and PFOS, which can be found as ground water contaminants at some sites, but are not in many modern AFFF formulations. The treatment effectiveness of each media type for this AFFF formulation was evaluated during this study.

2.1 Treatment Drum Setup

During initial setup of the treatment train shown in Figure 4, it was observed that 5 gpm was able to flow through the GAC drums, but that no flow was exiting through the RemBind™ lead drum when RemBind™ alone was in the drum. The vendor was immediately contacted and the ensuing discussions indicated that the media (which was finer than the GAC-media) provided by the vendor was not well suited for a flow-through setup. The media was designed for batch mode testing, where the media is mixed with water, and then water is removed after the desired contact time. As a potential solution, the vendor suggested that the RemBind™ drums be emptied, the media mixed with 50% sand (by volume) to increase the media porosity and then the RemBind™/sand mixture be put back in the drums. In addition, to prevent clogging, the bottom 4 inches of the drums were filled with pure sand before it was filled back up with the amended RemBind™ media. Figure 5 shows the RemBind™ media drum as refilled. The sand used in Figure 5 was swimming pool filter silica sand with a particle size of 0.43 to 0.85 mm.



Figure 5. Rembind™ media mixed with sand.

2.2 Lagoon Contamination Procedure

The AFFF contained in the 5-gallon tank was connected to an eductor mechanism as shown in Figure 6 for spraying.



Figure 6. Idaho National Laboratory fire truck AFFF eductor spray mechanism.

The eductor is a venturi jet device that uses pressurized water to entrain, mix and pump other

liquids such as the AFFF. The eductor consists of two basic parts: (1) the motive nozzle, which converts the water pressure energy to kinetic (velocity) energy, and (2) the suction chamber/diffuser section where the entrainment and mixing of water and AFFF takes place.

The eductor has a knob that is used to set the correct mix ratio based on concentration of the mix of AFFF (in this case 3%). The eductor also has a minimum pressure requirement (60 psi) which is necessary to generate sufficient suction force to deliver the proper mix of AFFF and water.

The INL fire department used their fire truck equipment to set up the eductor and spray five gallons of 3M's Lightwater 3% AFFF into the lagoon, as shown in Figure 7. The spray contamination of the lagoon water was completed in approximately 5 minutes.



Figure 7. AFFF sprayed to contaminate lagoon water.

The majority of the foam dissipated within two hours, with only some remnants remaining along the edges of the lagoon, as shown in Figure 8.



Figure 8. AFFF contaminated lagoon water.

Then, lagoon water was allowed to sit overnight prior to testing the next day. The lagoon was not actively mixed, and the remaining foam was no longer observed.

2.3 Contaminated Lagoon Water Treatment Procedure

The AFFF-containing lagoon water was pumped using a submersible pump through flexible tubing with flow controlled rotameters. Any unused water was bypassed back into the lagoon, and the flow of this water promoted mixing within the lagoon. The contaminated lagoon water was pumped from the lagoon and through the treatment drums at 5 gpm. However, as mentioned previously, the RemBind™ media containing drums were unable to handle the desired experimental flowrate while operating in series (due to an excessive pressure drop). Therefore, each of the RemBind™ containing media-drums were operated in parallel (as shown in Figure 4), but the sampling locations and identification remained unchanged. Treated water exiting the drums flowed into bladder tanks. The inlet flow control setup is shown in Figure 9 and Figure 10.

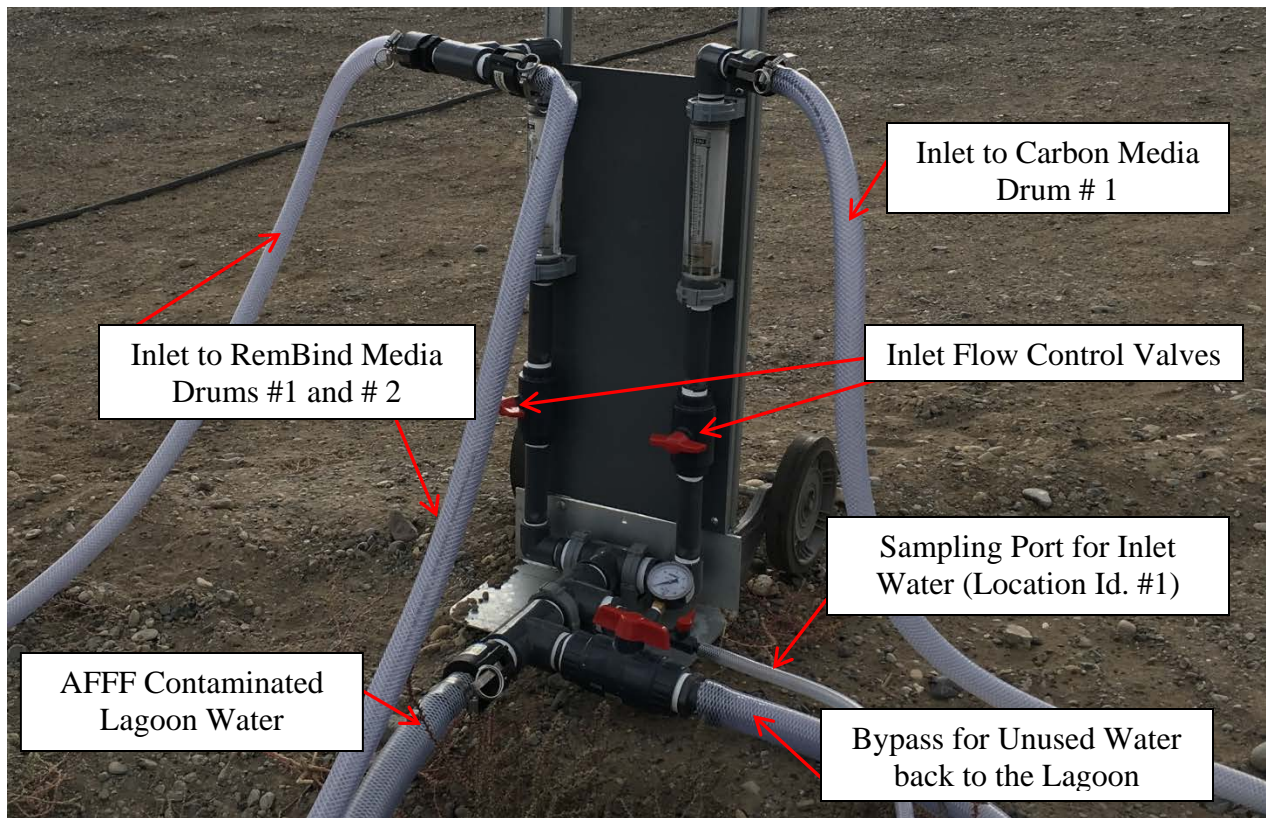


Figure 9. Plumbing setup for inlet flow control.



Figure 10. Inlet flow control during testing.

When the water treatment began, flow through the RemBind™ system was set to 1 gpm, or 0.5 gpm through each RemBind™ drum. The Calgon GAC containing drums in series were operated at the experimental design flowrate of 5 gpm. In the hours after the treatment began, flow was

gradually increased through the RemBind™ media. After each attempted flow adjustment, the flowrate was recorded. Table 1 contains a summary of flowrates and computed empty-bed contact times (EBCT) achieved throughout the test.

Table 1. Flowrates achieved through the media

| Time After Treatment Start (hr) | GAC Treatment (Drums in series) | | | | RemBind™ Media (drums in parallel) | | | |
|---------------------------------|---------------------------------|------------|----------------------|-----------------|------------------------------------|------------|----------------------|-----------------|
| | Flow (gpm) | EBCT (min) | Volume Treated (gal) | Bed Volumes (#) | Flow (gpm) | EBCT (min) | Volume Treated (gal) | Bed Volumes (#) |
| 0.08 | 5.0 | 22.0 | 25 | 0.2 | 1.0 | 110.0 | 5 | 0.0 |
| 0.50 | 5.0 | 22.0 | 150 | 1.4 | 1.0 | 110.0 | 30 | 0.3 |
| 1 | 5.0 | 22.0 | 300 | 2.7 | 1.0 | 110.0 | 60 | 0.5 |
| 3 | 6.5 | 16.9 | 1080 | 9.8 | 2.5 | 44.0 | 270 | 2.5 |
| 5 | 6.5 | 16.9 | 1860 | 16.9 | 4.0 | 27.5 | 750 | 6.8 |
| 7 | 6.5 | 16.9 | 2640 | 24.0 | 4.0 | 27.5 | 1215 | 11.0 |
| 9 | 6.5 | 16.9 | 3420 | 31.1 | 4.0 | 27.5 | 1695 | 15.4 |
| 12 | 6.5 | 16.9 | 4590 | 41.7 | 4.0 | 27.5 | 2415 | 22.0 |

EBCT: Empty Bed Contact Time (min) (Empty bed volume in gallons divided by flow rate in gallons per minute)

Bulk water samples (BWS) for PFAS analysis were collected throughout the experiment and are summarized in Table 2.

Table 2. PFAS bulk water sampling at different times and locations

| Time ID | Location/ID | | | | |
|-----------|--------------|-------------------|-------------------|------------------------|------------------------|
| | Inlet (BWS1) | GAC Drum 1 (BWS2) | GAC Outlet (BWS3) | RemBind™ Drum 1 (BWS4) | RemBind™ Drum 2 (BWS5) |
| 1 | 7:25 | 9:30 | 7:35 | 9:30 | 7:35 |
| 2 | 7:30 | 11:30 | 8:00 | 11:30 | 8:00 |
| 3 | 7:35 | 13:30 | 8:30 | 13:30 | 8:30 |
| 4 | 8:00 | 15:30 | 9:30 | 15:30 | 9:30 |
| 5 | 8:30 | 19:30 | 10:30 | 19:30 | 10:30 |
| 6 | | | 11:30 | | 11:30 |
| 7 | 10:30 | | 12:30 | | 12:30 |
| 8 | | | 13:30 | | 13:30 |
| 9 | 12:30 | | 14:30 | | 14:30 |
| 10 | | | 15:30 | | 15:30 |
| 11 | 14:30 | | 16:30 | | 16:30 |
| 12 | | | 17:30 | | 17:30 |
| 13 | 16:30 | | 18:30 | | 18:30 |
| 14 | | | 19:30 | | 19:30 |
| 15 | 18:30 | | | | |
| 16 | 19:30 | | | | |

BWS: Bulk Water Sample, or a sample of the water flowing into and out of the drums

From Table 2, a PFAS sample label ID of **BWS1-7** means the sample was collected at the BWS1 (location ID in “bold” is the Inlet) and at time ID **7**, which is 10:30 AM (for BWS1). Any blank

values in the table means no bulk water sample was collected at that location at that time ID/sequence. In addition to PFAS samples, periodic samples from lagoon were collected for quantifying some of the routine water quality parameters including pH, temperature, free chlorine, turbidity, specific conductivity, chemical oxygen demand (COD), and total organic carbon (TOC). The results from the testing are presented in Section 3.0.

3.0 Analysis of Test Results

The results from routine water quality samples indicated that the addition of AFFF caused an increase in turbidity, COD and TOC levels of the lagoon water. These data are summarized in Table 3. It should be noted that TOC, COD, turbidity and pH increased upon introduction of the AFFF into the lagoon water. The observed increase in temperature throughout the day is due to the sun shining on the lagoon surface, which heats the water. The lagoon water cools off at night.

Table 3. Lagoon water quality sampling results

| Date/Activity | Clock Time | Related PFAS Sample ID | pH | Temp. (C) | Free Chlorine (mg/L) | Turb. (NTU) | Specific Cond. (µs/cm) | COD (mg/L) | TOC (mg/L) |
|---------------------------|------------|------------------------|------|-----------|----------------------|-------------|------------------------|------------|------------|
| 9/19/2016 Background | 7:25 | BWS 1-1 | 8.2 | 12.8 | | 0.50 | 507 | 36 | 2.92 |
| | 8:45 | NA | 8.34 | 12.3 | | | | | |
| | 9:15 | NA | | | 0.09 | | | | 0.75 |
| T6 (4 hours) | 11:30 | BWS 1-8 | | | | 1.57 | 491 | 269 | 75.44 |
| | 14:05 | NA | 8.72 | 22.7 | | | | | |
| T10 (8 hours) | 15:30 | BWS 1-12 | | | | 1.49 | 495 | 271 | 81.49 |
| | 18:45 | NA | 9.04 | 19.5 | | | | | |
| T14 (12 hours) | 19:30 | BWS 1-16 | | | | 1.47 | 484 | 278 | 81.37 |
| 9/20/2016 Restart pumping | 9:00 | NA | 8.50 | 12.0 | 0.09 | | | | |

TOC: Total Organic Carbon; COD: Chemical Oxygen Demand

PFAS samples were analyzed using EPA method 537, which was modified with an expanded list of 36 analytes (listed with CAS Registry Number[®] in Table 4) (Shoemaker, et al. 2009). The expanded list included some of the degradation PFAS precursors such as fluorotelomers. TOC was measured via EPA Method 415.3 (Potter and Wimsatt, 2005). COD was measured using Hach Method 8000 (Hach, 2014a). Free chlorine was measured using Hach Method 10102 (Hach, 2014b). Turbidity measurements were conducted according to Standard Method 2130 (APHA, 1999). Specific conductivity was measured according to the Thermo Scientific Orion Versa Star user's manual (Thermo Scientific, 2014). pH measurements were conducted according to the Extech 407220 pH meter user's manual (Extech, 2016). Temperature was measured by immersing a National Institute of Standards and Technology (NIST)-traceable thermometer in the water sample.

Table 4. List of PFAS compounds analyzed

| Analyte | CAS Number/ID |
|---|---------------|
| 2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol | 1691-99-2 |
| 2-(N-methylperfluoro-1-octanesulfonamido)-ethanol | 24448-09-7 |
| 6:2 Fluorotelomer sulfonate | 27619-97-2 |
| 8:2 Fluorotelomer sulfonate | 8:2FTS |

| Analyte | CAS Number/ID |
|---|--------------------|
| d7-N-MeFOSE (Surr) | d7-N-MeFOSE (Surr) |
| d9-NEtFOSE (Surr) | d9-NEtFOSE (Surr) |
| N-ethylperfluoro-1-octanesulfonamide | 4151-50-2 |
| N-methylperfluoro-1-octanesulfonamide | 31506-32-8 |
| Perfluorobutane Sulfonate | 45187-15-3 |
| Perfluorobutanoic Acid | 375-22-4 |
| Perfluorodecane Sulfonate | 335-77-3 |
| Perfluorodecanoic Acid | 335-76-2 |
| Perfluorododecanoic Acid | 307-55-1 |
| Perfluoroheptane sulfonate | 375-92-8 |
| Perfluoroheptanoic Acid | 375-85-9 |
| Perfluorohexane Sulfonate | 108427-53-8 |
| Perfluorohexanoic Acid | 307-24-4 |
| Perfluoro-n-[1,2,3,4,5-13C5] nonanoic acid | PFNNAC13 |
| Perfluoro-n-[1,2,3,4-13C4] butanoic acid | PFBTAC13 |
| Perfluoro-n-[1,2,3,4-13C4] octanoic acid | PFOCAC13 |
| Perfluoro-n-[1,2-13C2] decanoic acid | PFDCAC13 |
| Perfluoro-n-[1,2-13C2] hexanoic acid | PFHXAC13 |
| Perfluoro-n-[1,2-13C2]dodecanoic Acid | PFDDAC13 |
| Perfluoro-n-[1,2-13C2]undecanoic Acid | PFUDAC13 |
| Perfluorononanoic Acid | 375-95-1 |
| Perfluoro-n-tetradecanoic acid | 376-06-7 |
| Perfluoro-n-tridecanoic acid | 72629-94-8 |
| Perfluorooctane Sulfonate | 45298-90-6 |
| Perfluorooctanoic Acid | 335-67-1 |
| Perfluorooctylsulfonamide | 754-91-6 |
| Perfluoropentanoic Acid | 2706-90-3 |
| Perfluoroundecanoic Acid | 2058-94-8 |
| S_6:2 Fluorotelomer sulfonate-13C2 | 13C2-6:2FTS (Surr) |
| S_N-ethyl-d5-perfluoro-1-octanesulfonamide | d5-NEfFOSA (Surr) |
| Sodium perfluoro-1-[1,2,3,4-13C4] octanesulfonate | NAPFOcSLFN8C13 |
| Sodium perfluoro-1-hexane[18O2]sulfonate | 18O-PFHS |

Overall, 43 samples were analyzed for the suite of PFAS. Only 18 of the 36 analytes listed in Table 4. List of PFAS compounds analyzed were detected in one (or more) of the samples. The following nine compounds were the most common PFAS detected in the inlet to the treatment media.

1. Perfluorobutane Sulfonate (PFBS)
2. Perfluorobutanoic Acid (PFBA)
3. Perfluoropentanoic Acid (PFPA)

4. Perfluorohexane Sulfonate (PFHxS)
5. Perfluorohexanoic Acid (PFHxA)
6. Perfluoroheptane sulfonate (PFHS)
7. Perfluoroheptanoic Acid (PFHA)
8. Perfluorooctane Sulfonate (PFOS)
9. Perfluorooctanoic Acid (PFOA)

Of these nine detected compounds, the top four compounds PFOS (82.1%), PFHxS (12.8%), PFHS (2.6%) and PFOA (0.7%) represent a combined total of 98.2% of the inlet loading. A summary of the average percent removal observed over the 12-hour treatment study is presented in Table 5.

Table 5. Average percent PFAS removal.

| PFAS | GAC Average % Removal | Rembind Average % Removal |
|-------------|--------------------------------------|--|
| PFOS | 99.986% | 99.991% |
| PFOA | 99.997% | 99.996% |
| PFBS | 99.999% | 99.996% |
| PFBA | 99.991% | 99.990% |
| PFHS | 99.999% | 99.997% |
| PFHA | 99.983% | 99.996% |
| PFHxS | 99.9997% | 99.997% |
| PFHxA | 99.985% | 99.994% |
| PFPA | 99.989% | 99.994% |

Figure 11 shows the individual treatment system performance for PFBS. Figure 12 and Figure 13 show the normalized PFBS concentration plotted against the total volume treated and bed volumes treated. On average, the GAC media achieved a removal efficiency of 99.999%, and the RemBind™ (one drum) achieved 99.996% removal efficiency. The upward trajectory of the resulting effluent concentration by an order of magnitude from the GAC Drum 1 effluent may be an indicator that the GAC media is becoming spent and breakthrough is observed. The black straight line at the bottom in the following set of figures (Figure 11 through Figure 37) represents the limit of detection for the specific compound shown in the individual graph.

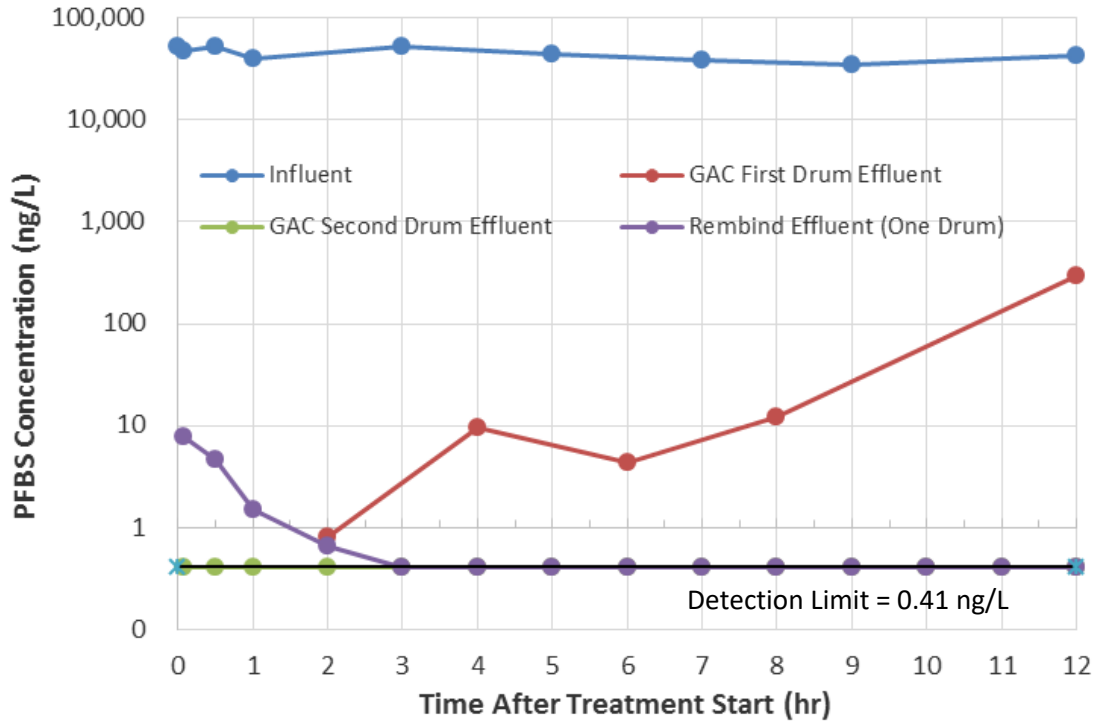


Figure 11. Removal of PFBS from lagoon water using GAC and Rembind media.

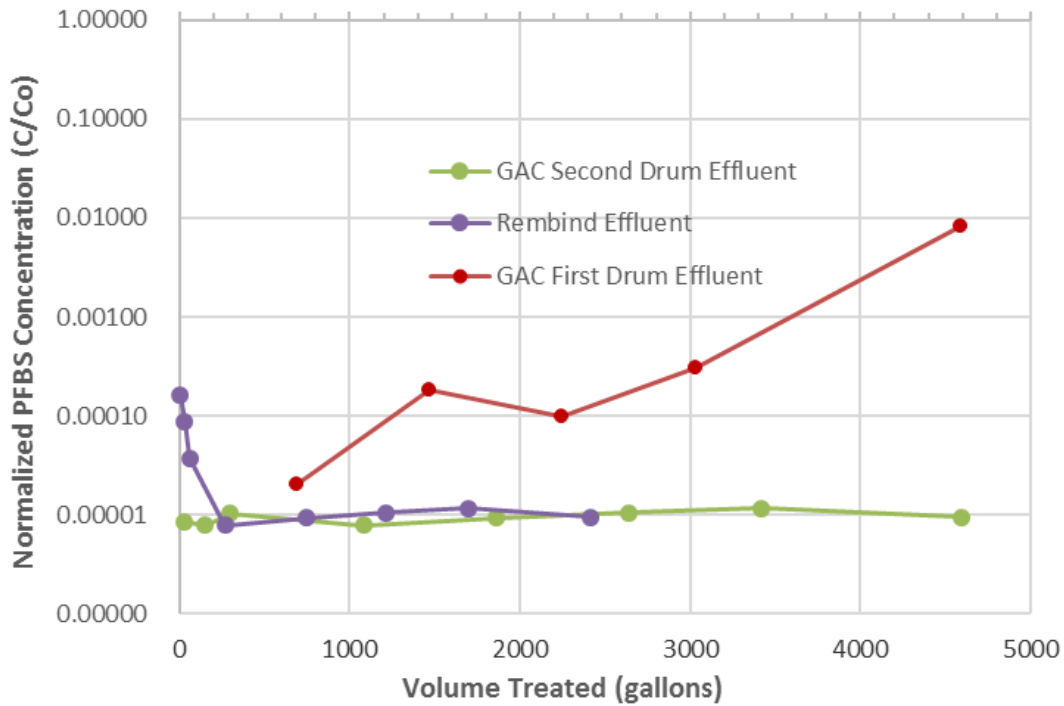


Figure 12. Normalized PFBS concentration change with increasing treated water volume.

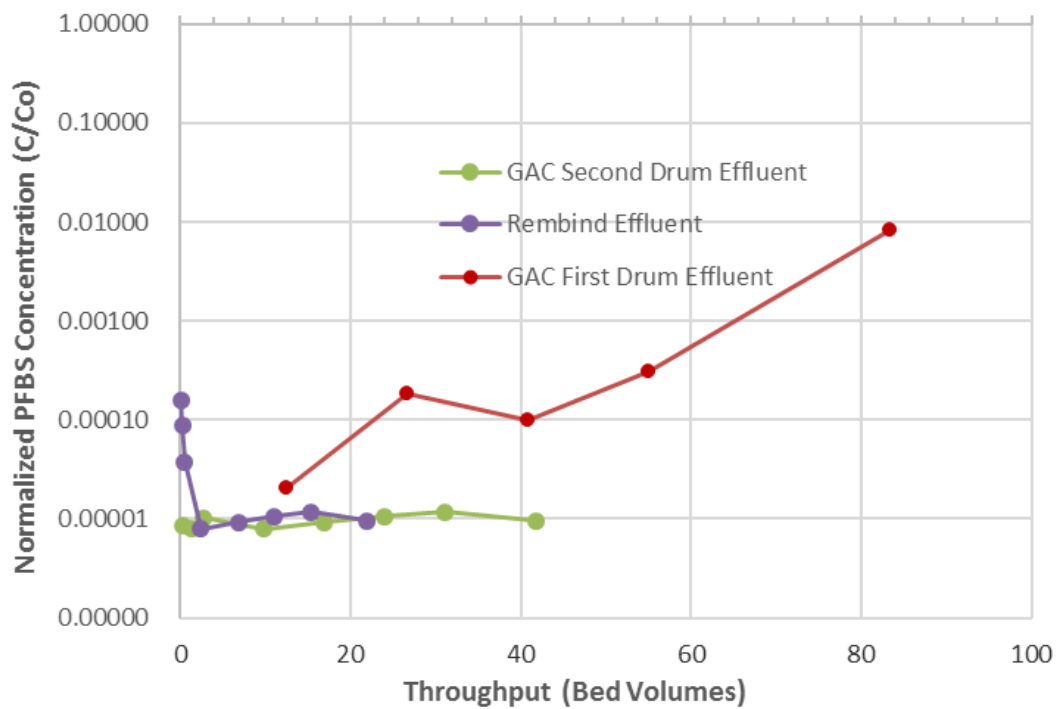


Figure 13. Normalized PFBS concentration change with increasing throughput (bed volumes).

Figure 14 shows the individual treatment system performance for PFBA. Figure 15 and Figure 16 show the normalized PFBA concentration plotted against the total volume treated and bed volumes treated. On average, the GAC media achieved a removal efficiency of 99.991%, and the RemBind™ (one drum) achieved 99.990% removal efficiency. Similar to PFBS, the upward trajectory of the GAC effluent from Drum 1 may be an indicator that the GAC media is becoming spent.

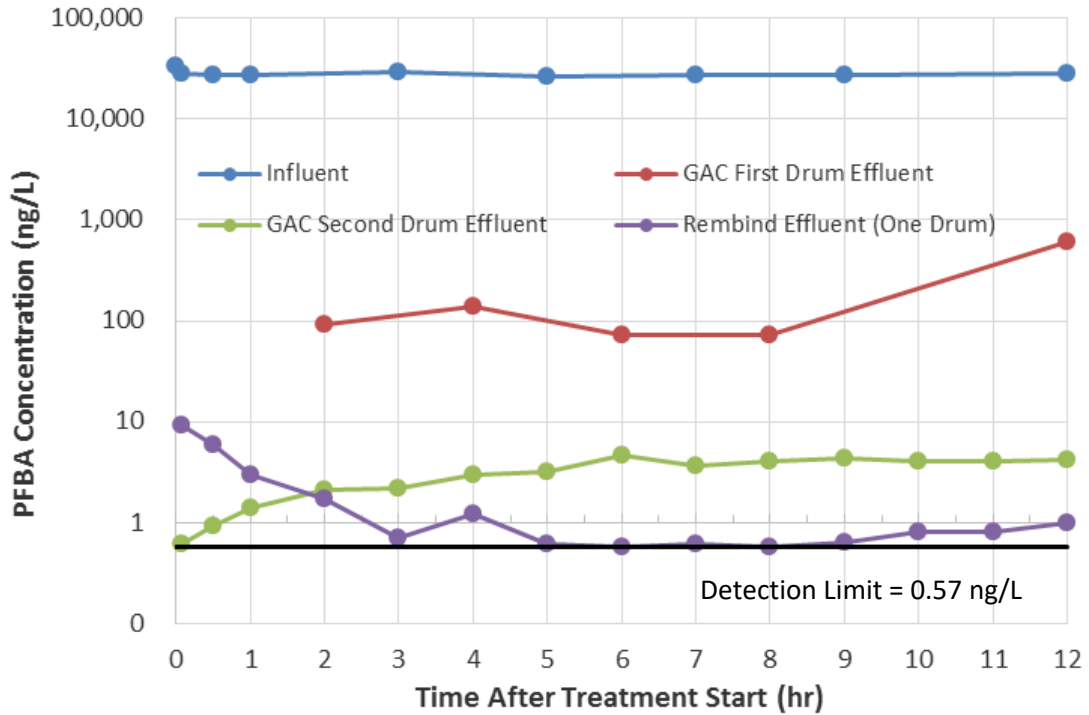


Figure 14. Removal of PFBA from lagoon water using GAC and Rembind media.

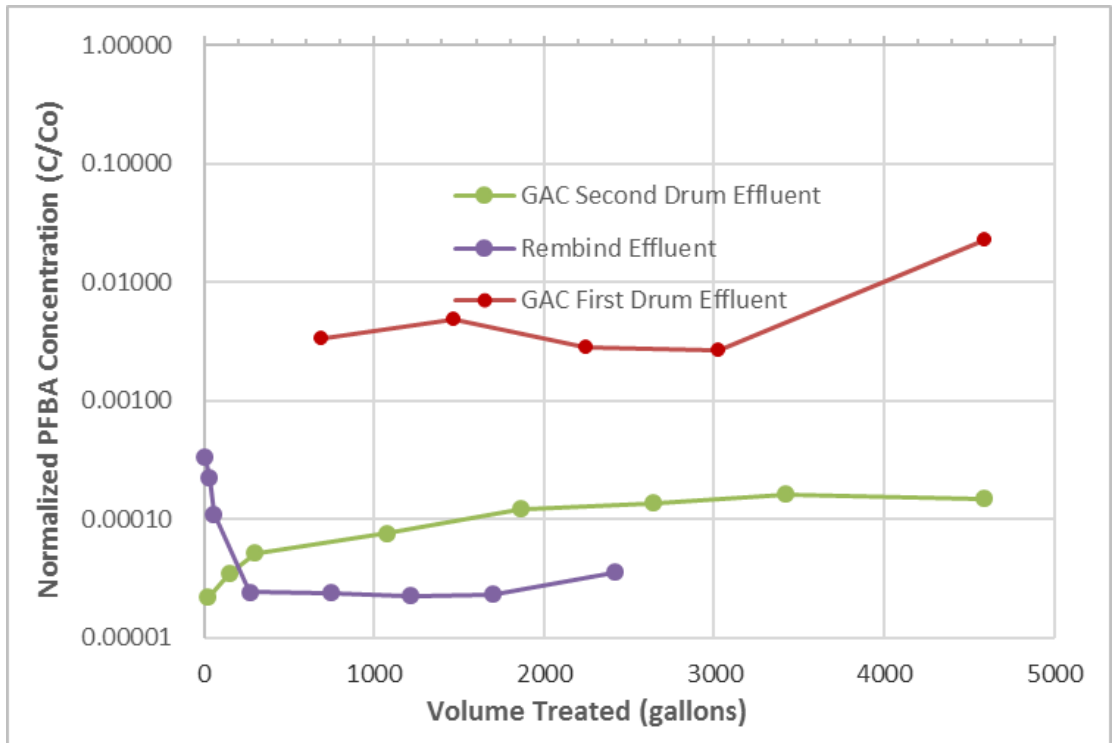


Figure 15. Normalized PFBA concentration change with increasing treated water volume.

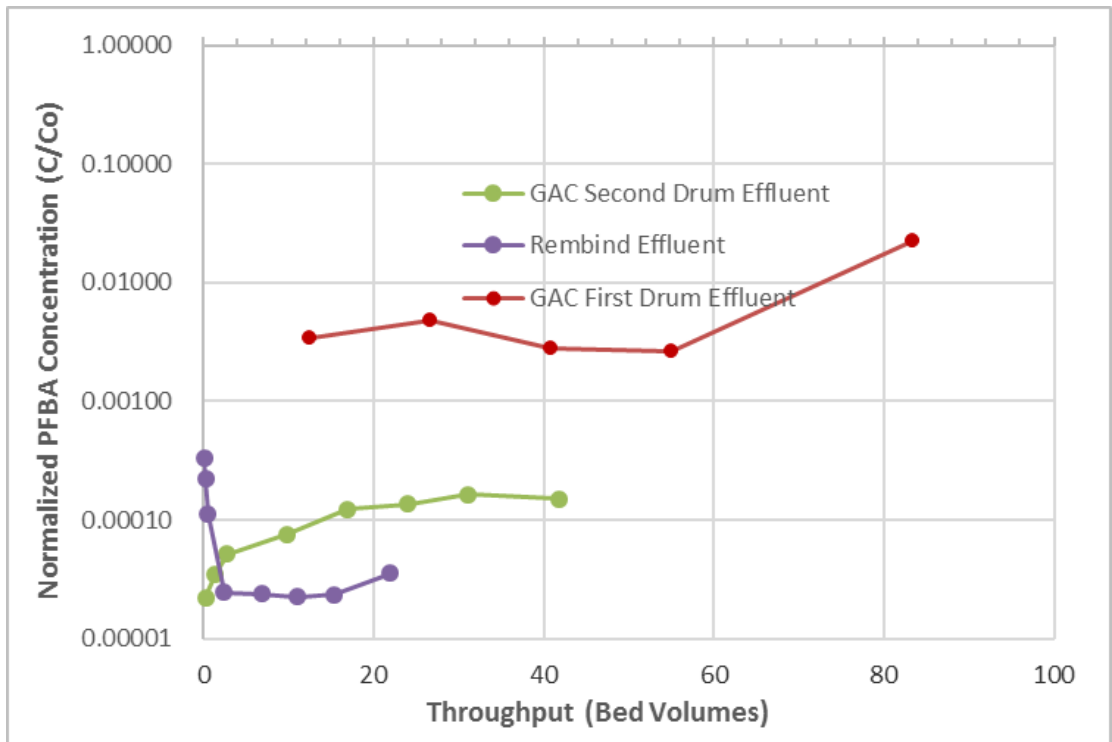


Figure 16. Normalized PFBA concentration change with increasing throughput (bed volumes).

Figure 17 shows the individual treatment system performance for PFPA. Figure 18 and Figure 19 show the normalized PFPA concentration plotted against the total volume treated and bed volumes treated. On average, the GAC media achieved a removal efficiency of 99.989% and the RemBind™ (one drum) achieved 99.994% removal efficiency. Similar to PFBS and PFBA, the upward trajectory of the GAC effluent from Drum 1 may be an indicator that the GAC media is becoming spent.

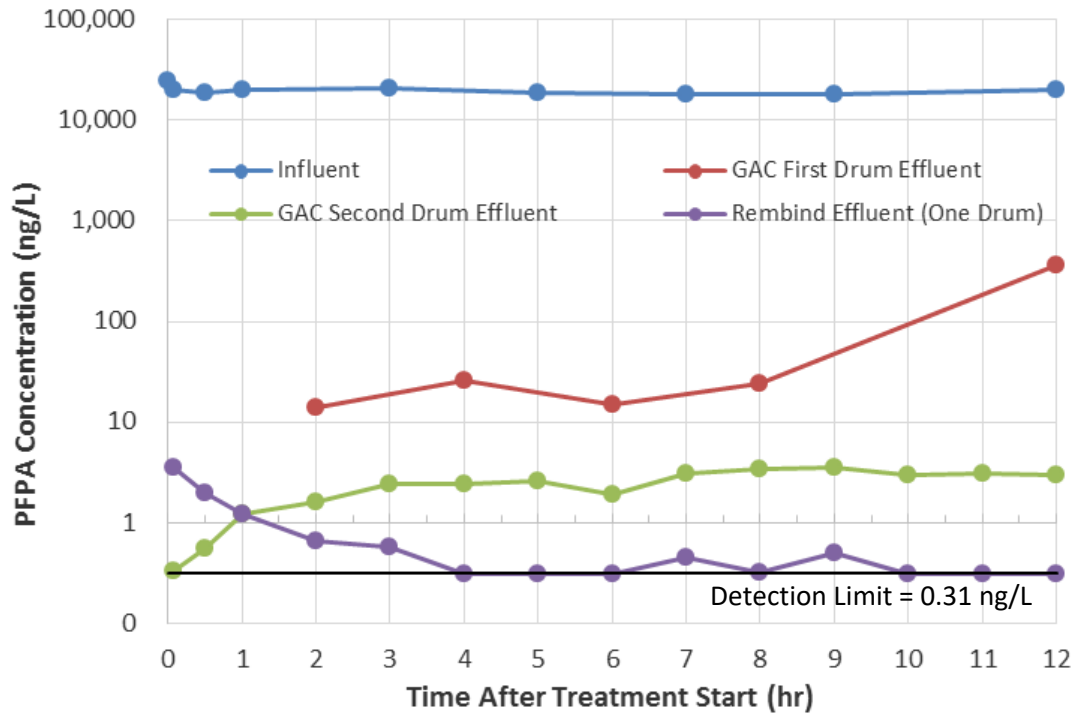


Figure 17. Removal of PFPA from lagoon water using GAC and Rembind media.

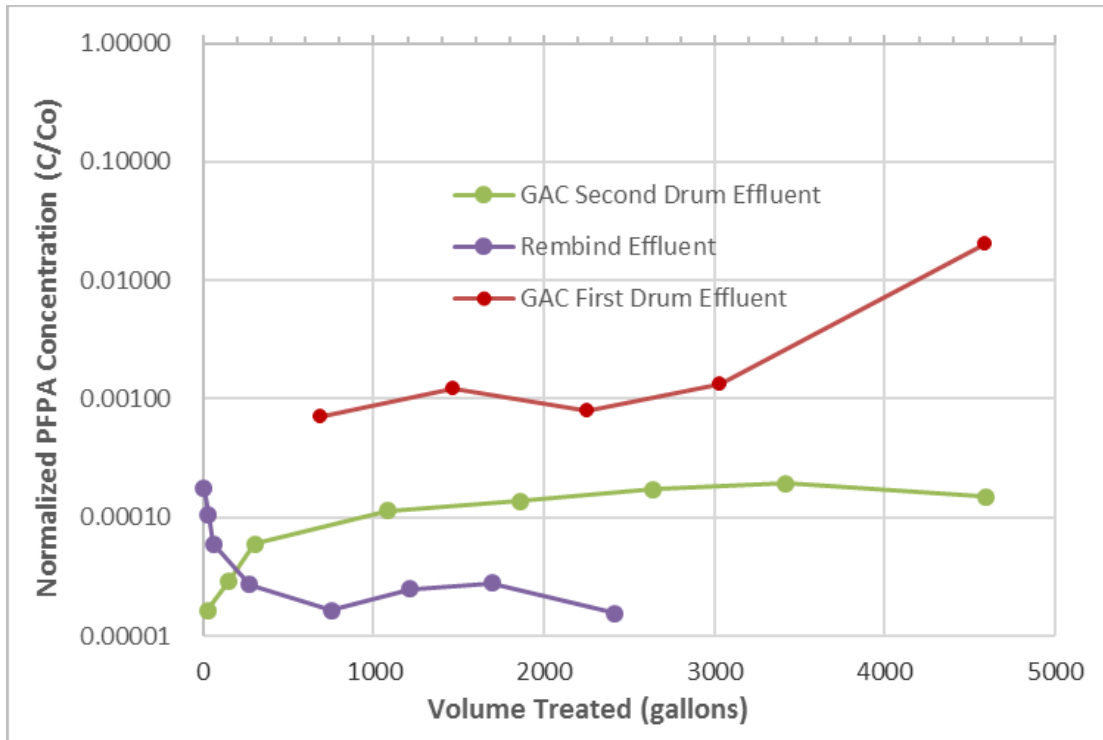


Figure 18. Normalized PFPA concentration change with increasing treated water volume.

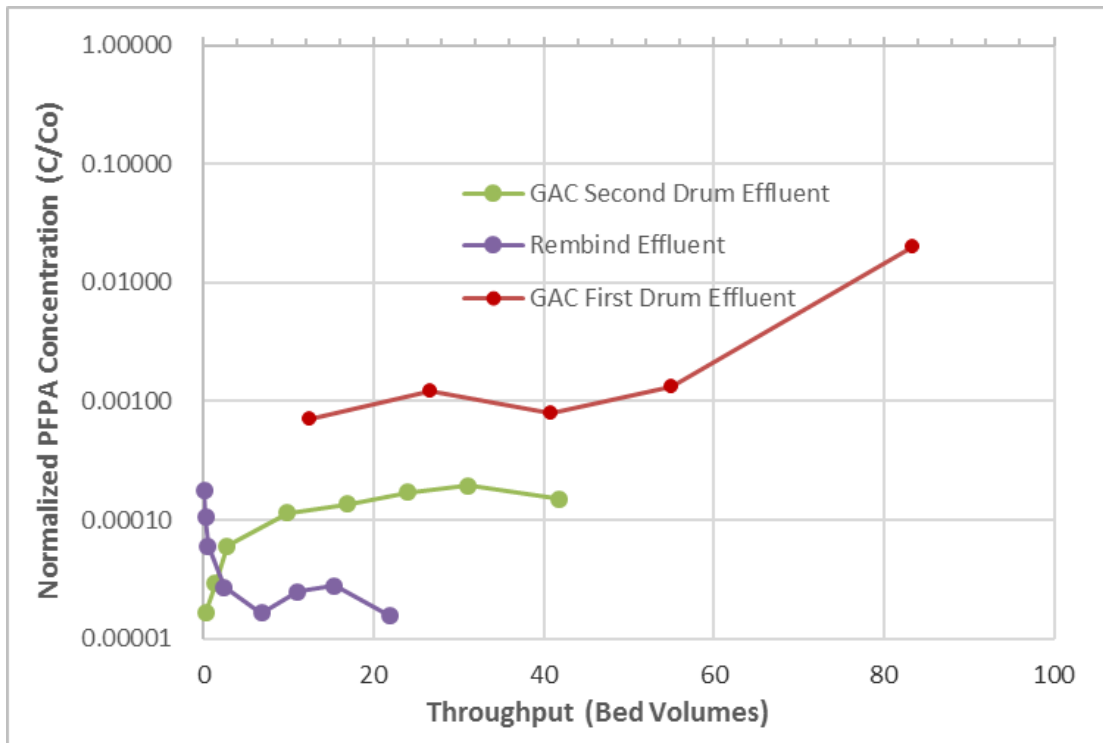


Figure 19. Normalized PFPA concentration change with increasing throughput (bed volumes).

Figure 20 shows the individual treatment system performance for PFHxS. Figure 21 and Figure 22 show the normalized PFHxS concentration plotted against the total volume treated and bed volumes treated. On average, the GAC media achieved a removal efficiency of 99.9997% and the RemBind™ (one drum) achieved 99.9967% removal efficiency. Similar to the PFBS, PFBA, and PFPA graphs, the upward trajectory of the GAC effluent from Drum 1 may be an indicator that the GAC media is becoming spent.

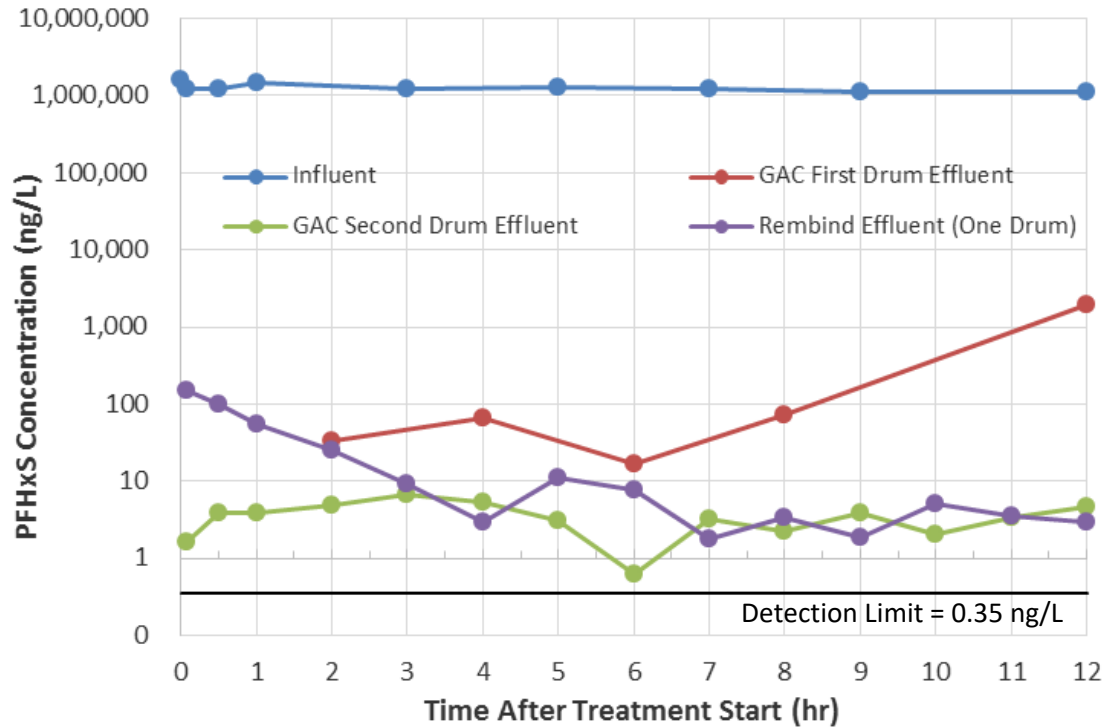


Figure 20. Removal of PFHxS from lagoon water using GAC and Rembind media.

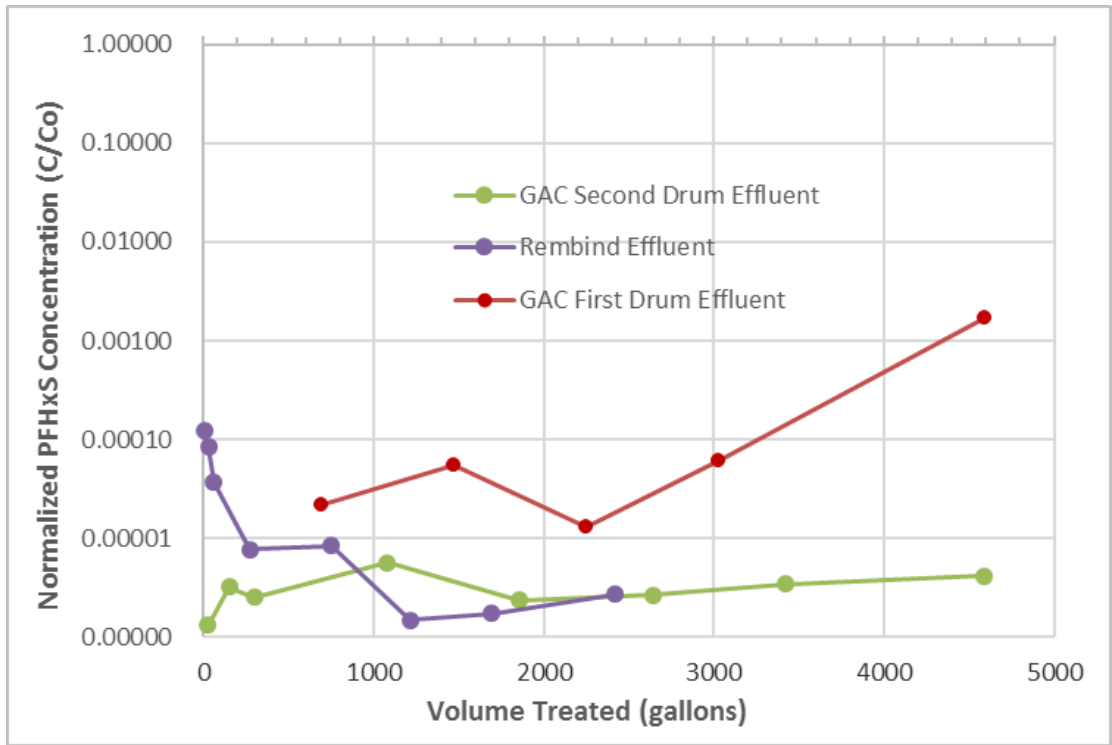


Figure 21. Normalized PFHxS concentration change with increasing treated water volume.

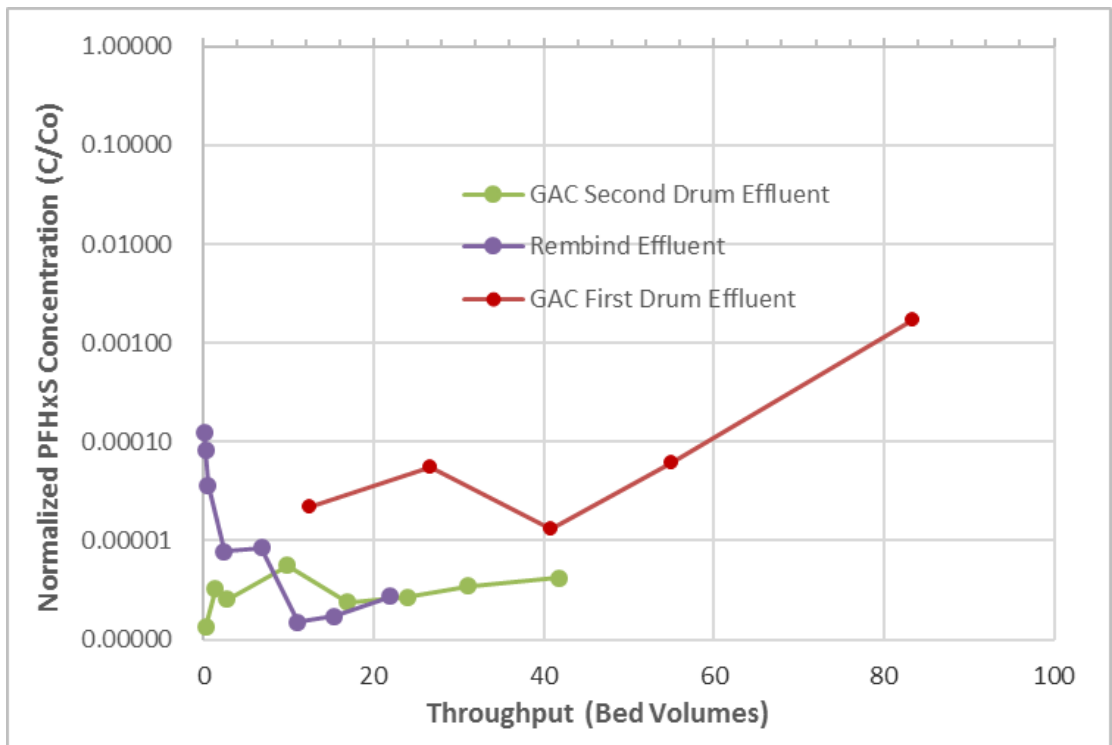


Figure 22. Normalized PFHxS concentration change with increasing throughput (bed volumes).

Figure 23 shows the individual treatment system performance for PFHxA. Figure 24 and Figure 25 show the normalized PFHxA concentration plotted against the total volume treated and bed volumes treated. On average, the GAC media achieved a removal efficiency of 99.985%, and the RemBind™ (one drum) achieved 99.994% removal efficiency. Similar to the previous graphs, the upward trajectory of the GAC effluent from Drum 1 may be an indicator that the GAC media is becoming spent.

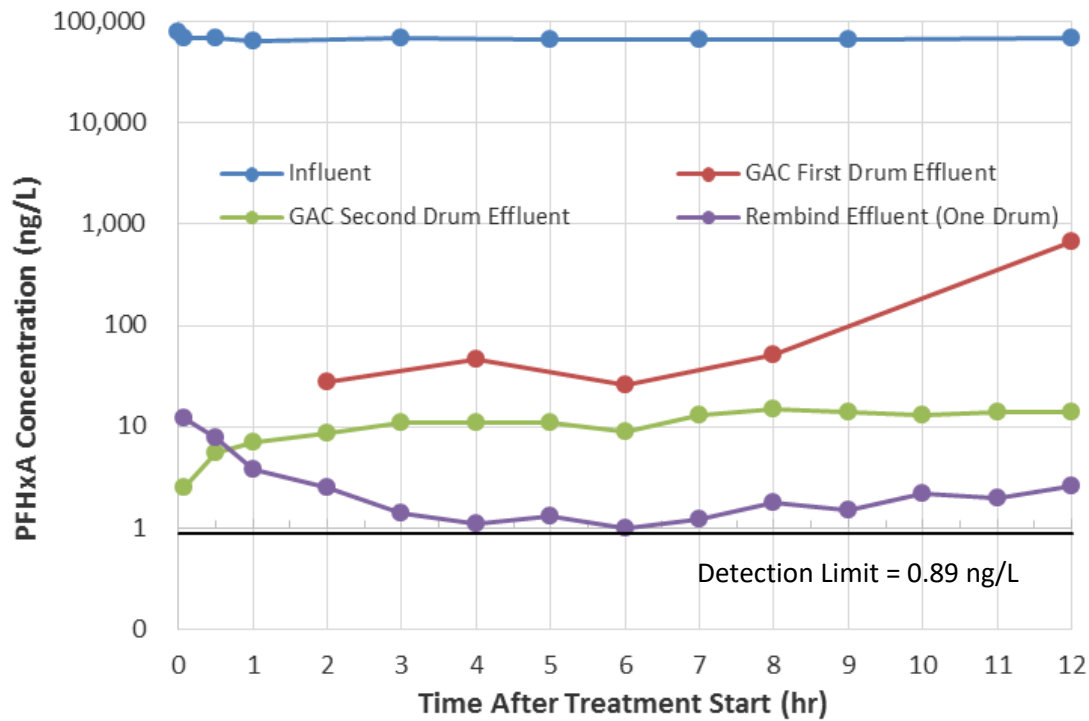


Figure 23. Removal of PFHxA from lagoon water using GAC and Rembind media.

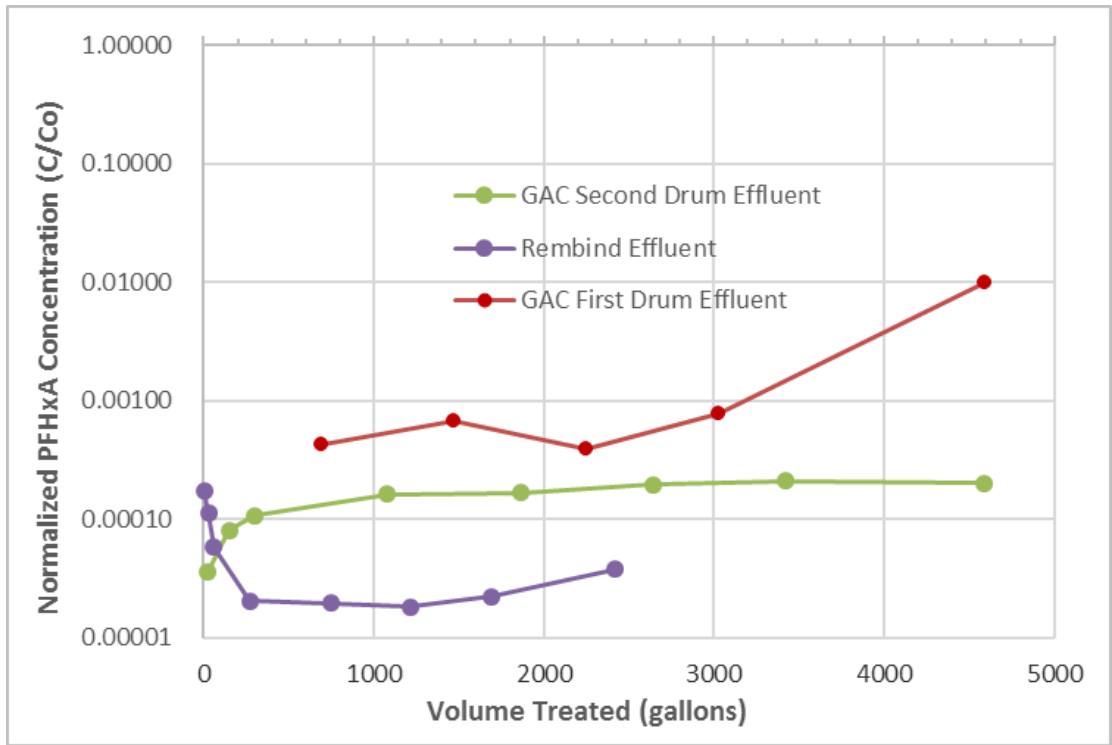


Figure 24. Normalized PFHxA concentration change with increasing treated water volume.

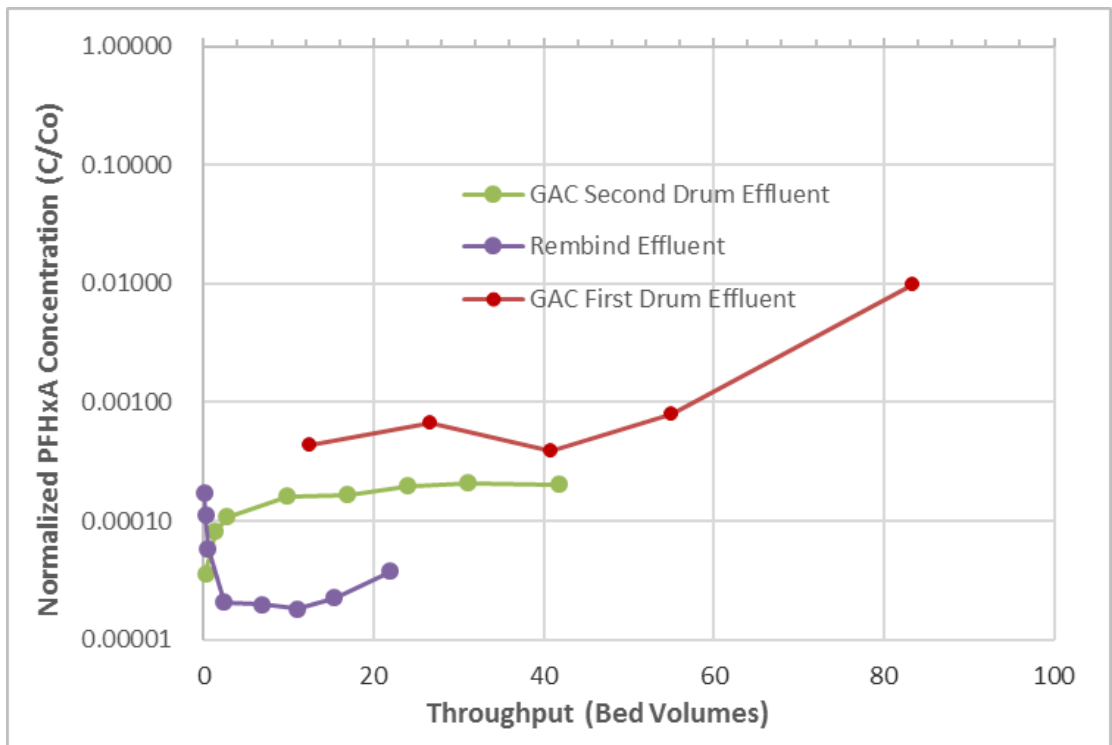


Figure 25. Normalized PFHxA concentration change with increasing throughput (bed volumes).

Figure 26 shows the individual treatment system performance for PFHS. Figure 27 and Figure 28 show the normalized PFHS concentration plotted against the total volume treated and bed volumes treated. On average, the GAC media achieved a removal efficiency of 99.999% and the RemBind™ (one drum) achieved 99.997% removal efficiency. Similar to the previous graphs, the upward trajectory of the GAC effluent from Drum 1 may be an indicator that the GAC media is becoming spent.

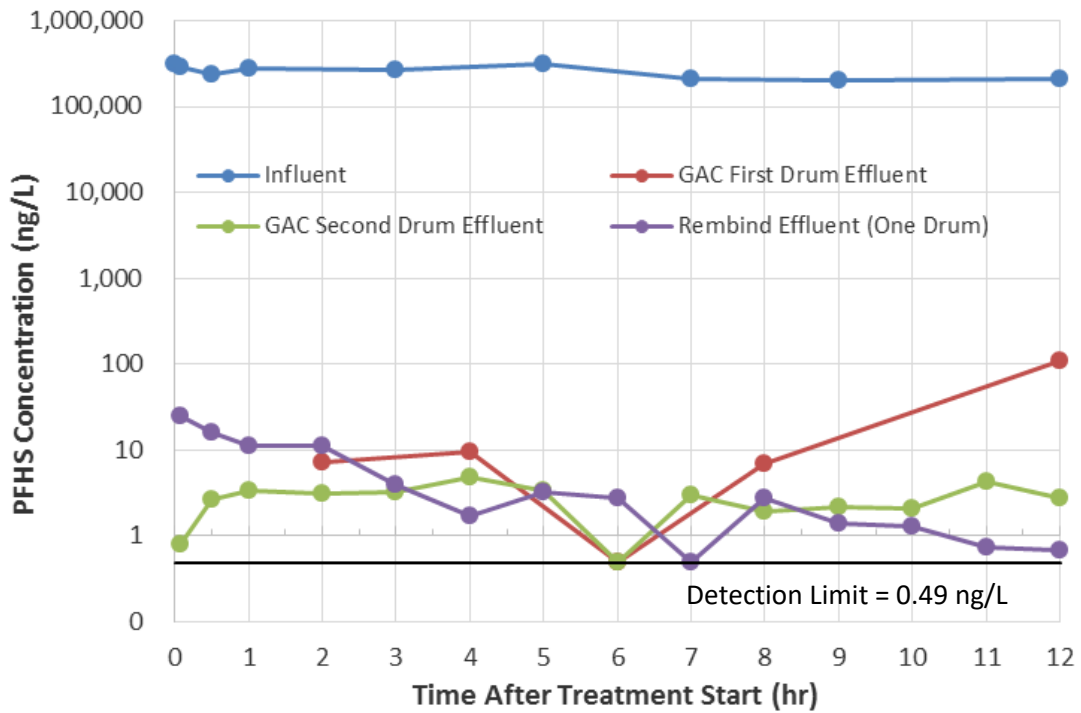


Figure 26. Removal of PFHS from lagoon water using GAC and Rembind media.

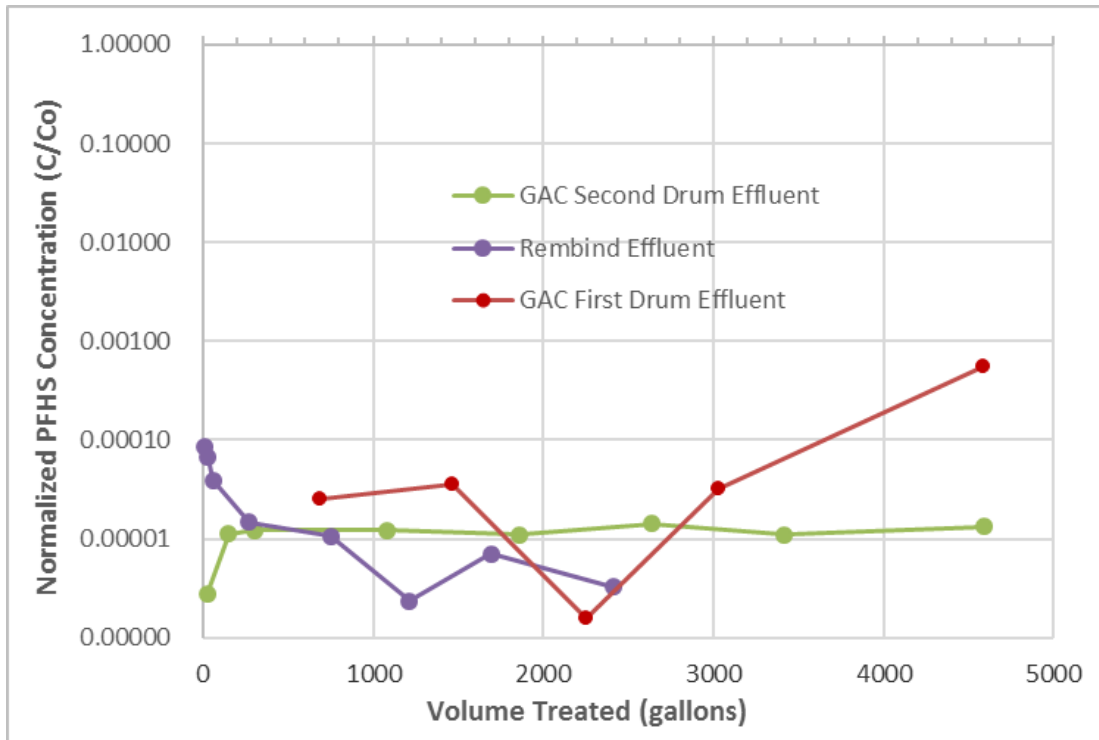


Figure 27. Normalized PFHS concentration change with increasing treated water volume.

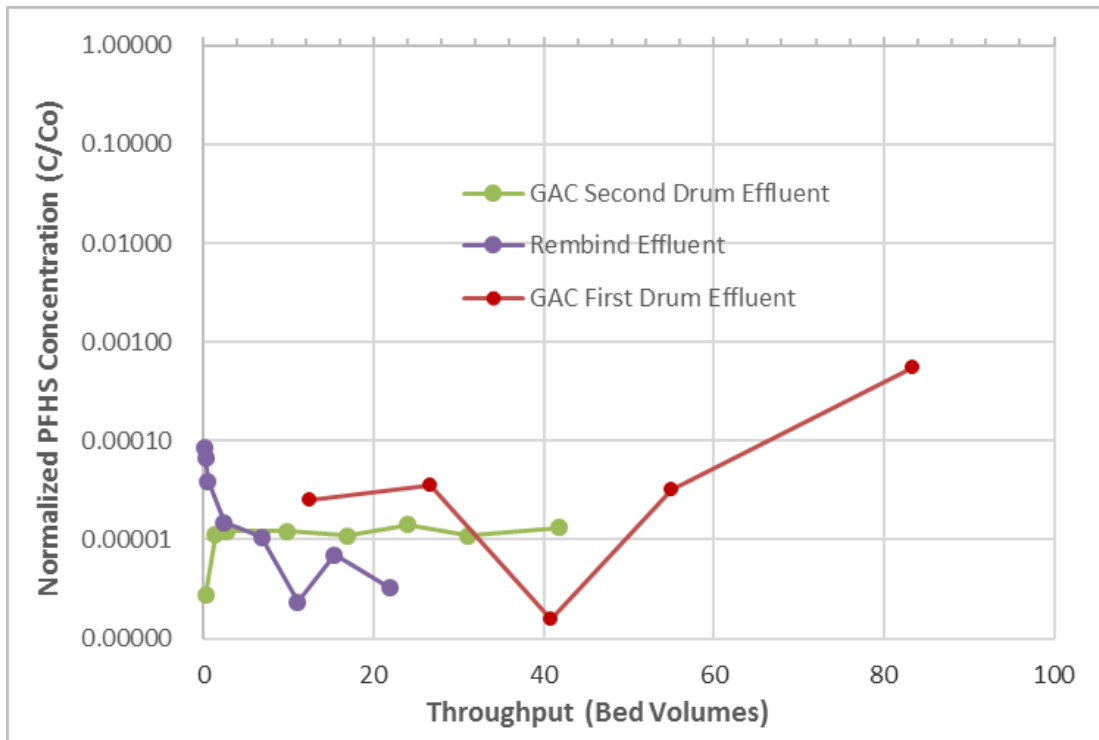


Figure 28. Normalized PFHS concentration change with increasing throughput (bed volumes).

Figure 29 shows the individual treatment system performance for PFHA. Figure 30 and Figure 31 show the normalized PFHA concentration plotted against the total volume treated and bed volumes treated. On average, the GAC media achieved a removal efficiency of 99.983%, and the RemBind™ (one drum) achieved 99.996% removal efficiency. Similar to the previous graphs, the upward trajectory of the GAC effluent from Drum 1 in may be an indicator that the GAC media is becoming spent.

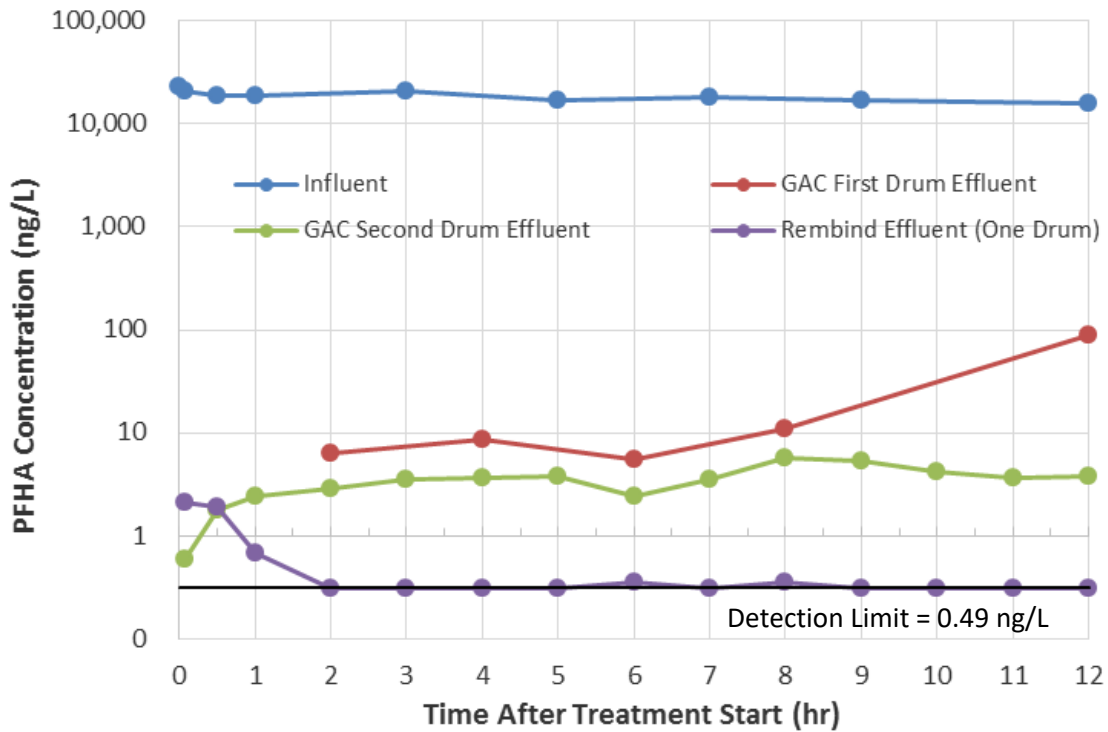


Figure 29. Removal of PFHA from lagoon water using GAC and Rembind media.

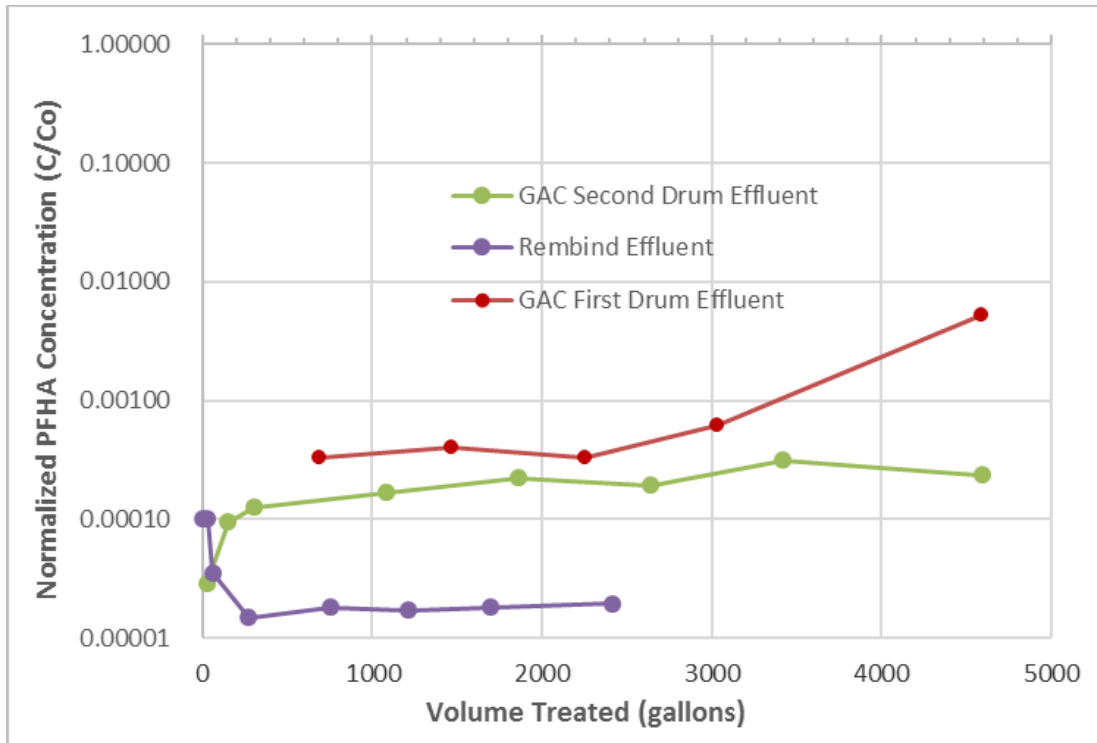


Figure 30. Normalized PFHA concentration change with increasing treated water volume.

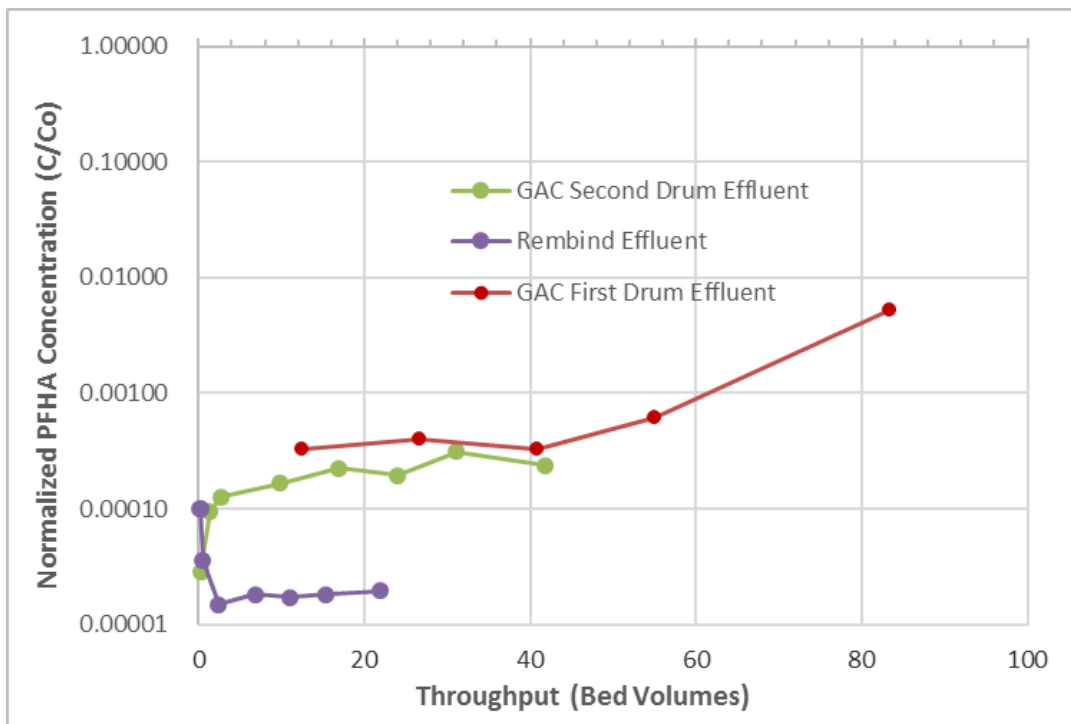


Figure 31. Normalized PFHA concentration change with increasing throughput (bed volumes).

Figure 32 shows the individual treatment system performance for PFOS. Figure 33 and Figure 34 show the normalized PFOS concentration plotted against the total volume treated and bed volumes treated. On average, the GAC media achieved a removal efficiency of 99.986%, and the RemBind™ (one drum) achieved 99.991% removal efficiency. Unlike the shorter chain compounds, there is no noticeable upward trajectory of the GAC effluent from Drum 1.

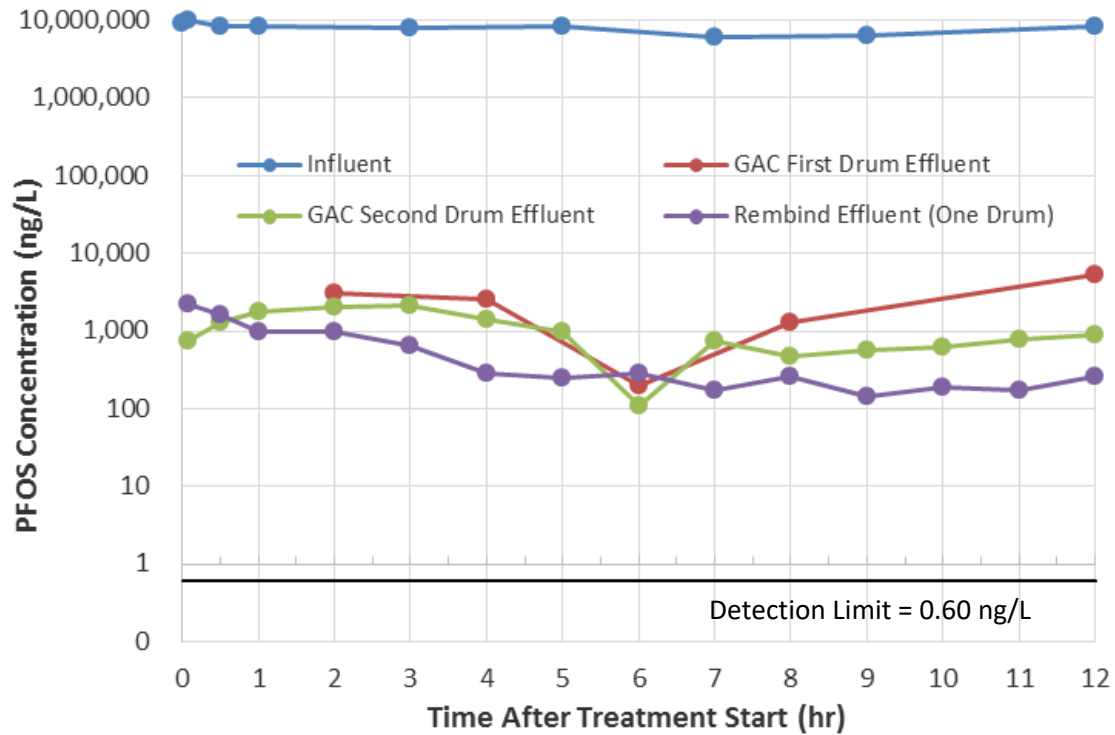


Figure 32. Removal of PFOS from lagoon water using GAC and Rembind media.

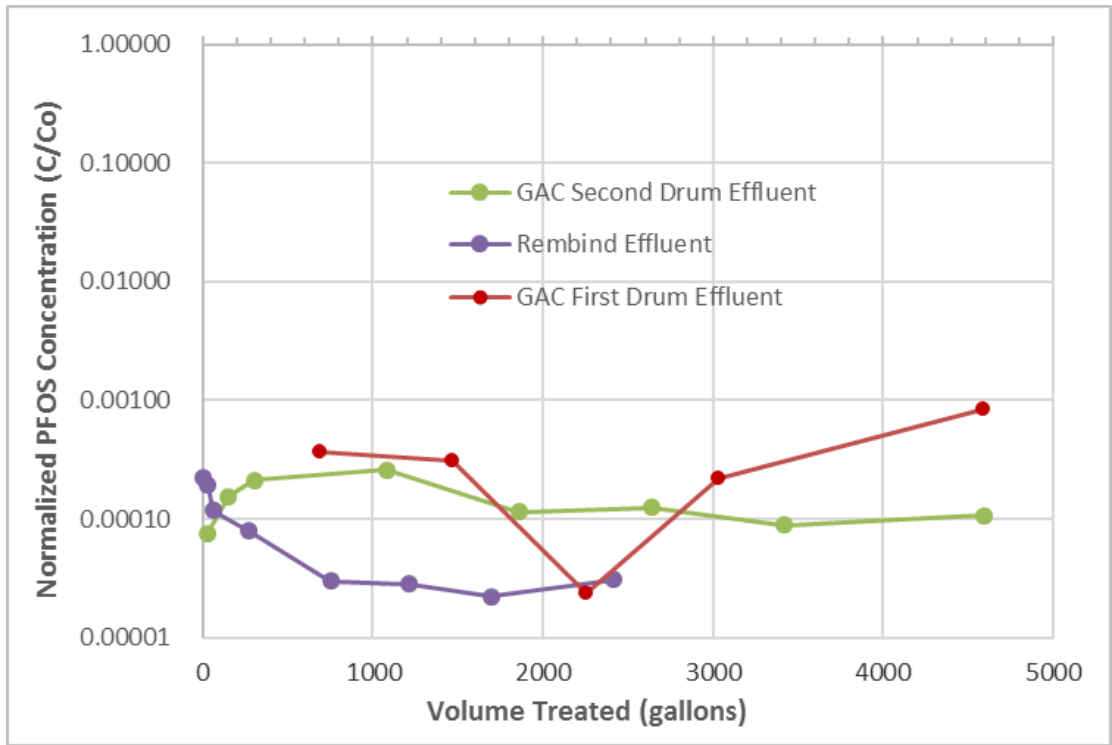


Figure 33. Normalized PFOS concentration change with increasing treated water volume.

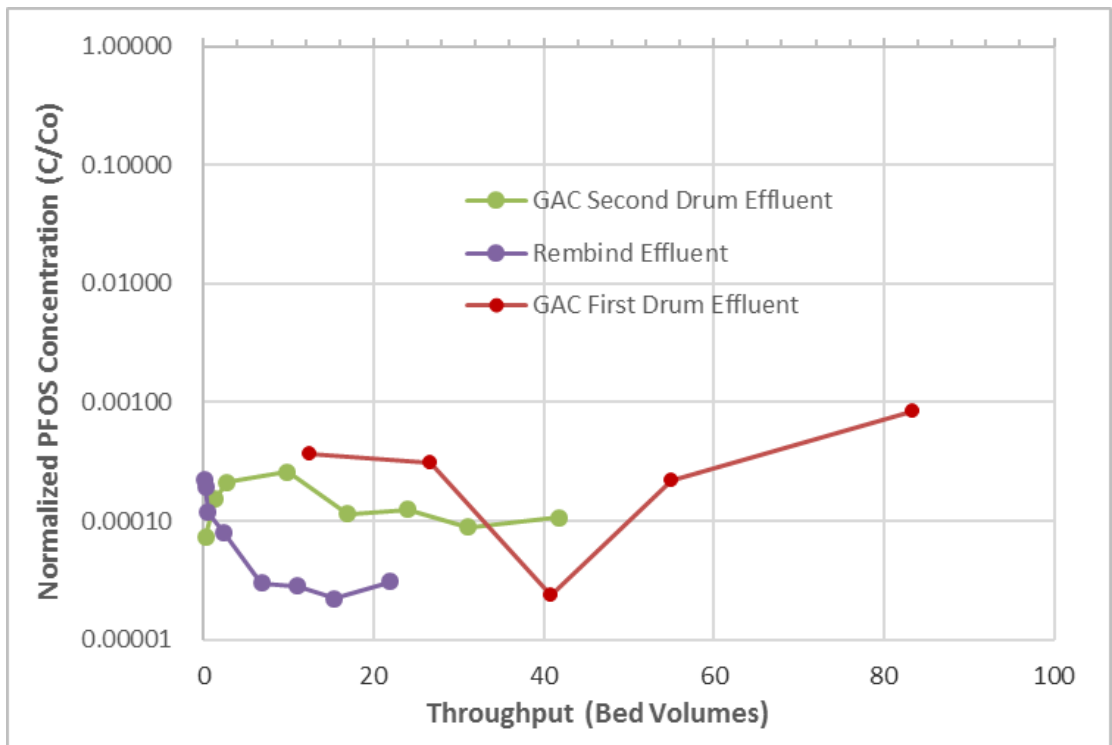


Figure 34. Normalized PFOS concentration change with increasing throughput (bed volumes).

Figure 35 shows the individual treatment system performance for PFOA. Figure 36 and Figure 37 show the normalized PFOA concentration plotted against the total volume treated and bed volumes treated. On average, the GAC media achieved a removal efficiency of 99.997%, and the RemBind™ (one drum) achieved 99.996% removal efficiency. Similar to the previous graphs (other than PFOS), the upward trajectory of the GAC effluent from Drum 1 in may be an indicator that the GAC media is becoming spent.

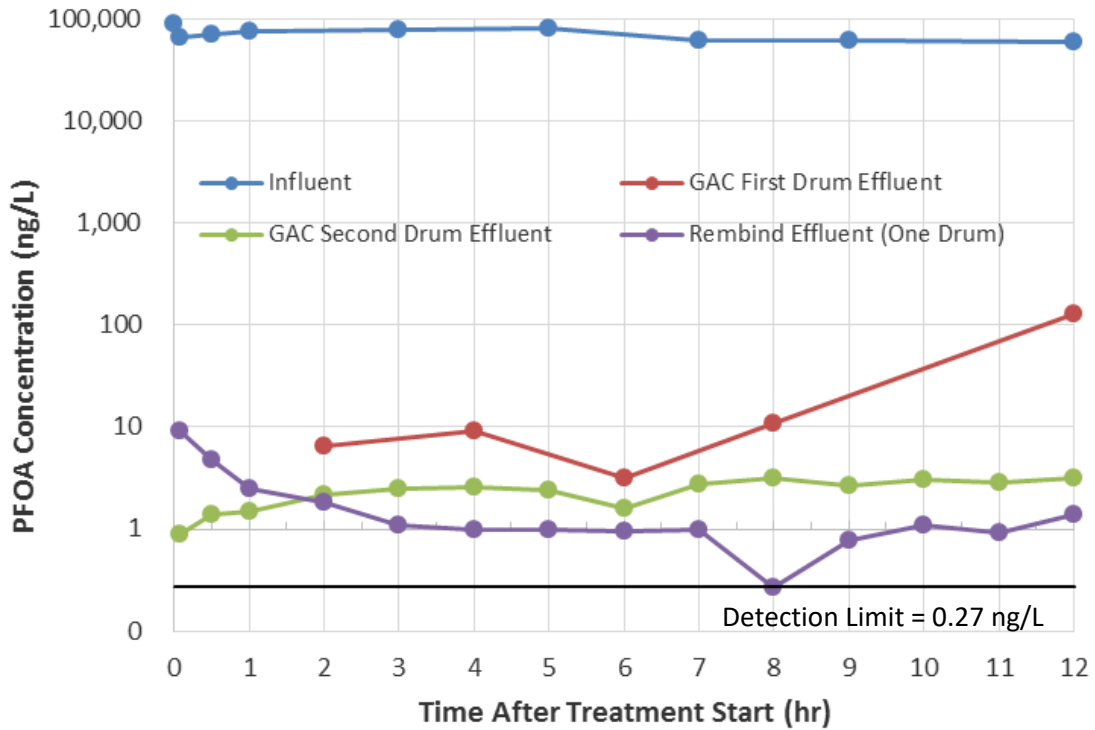


Figure 35. Removal of PFOA from lagoon water using GAC and Rembind media.

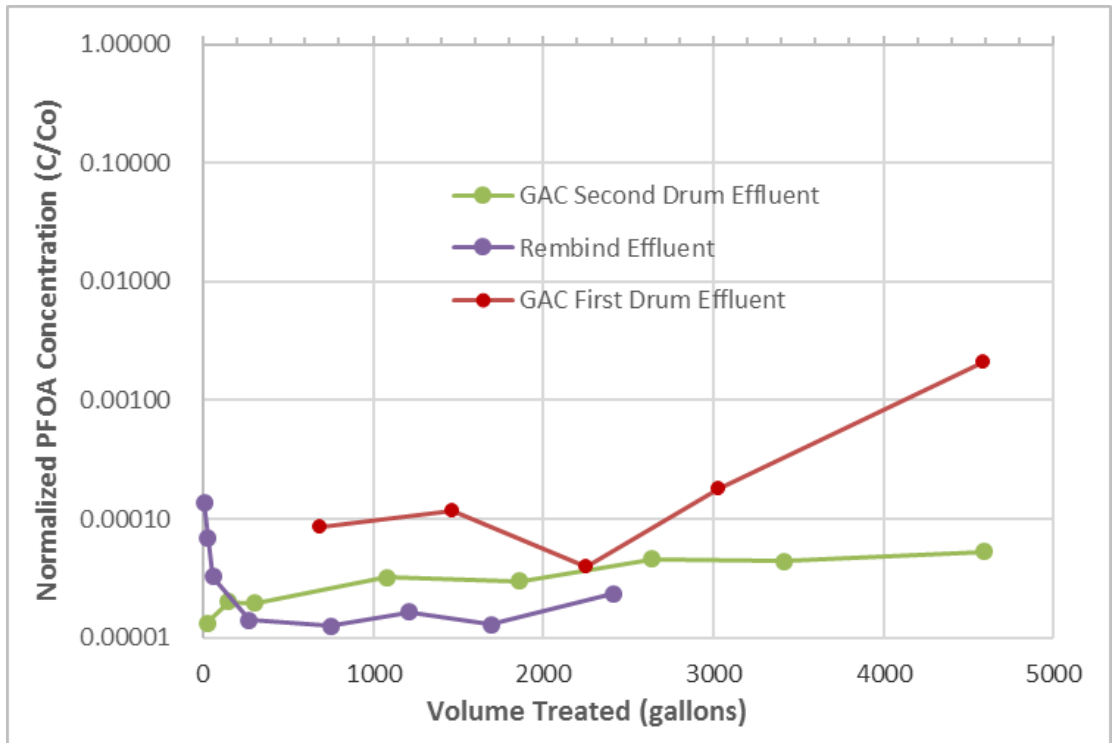


Figure 36. Normalized PFOA concentration change with increasing treated water volume.

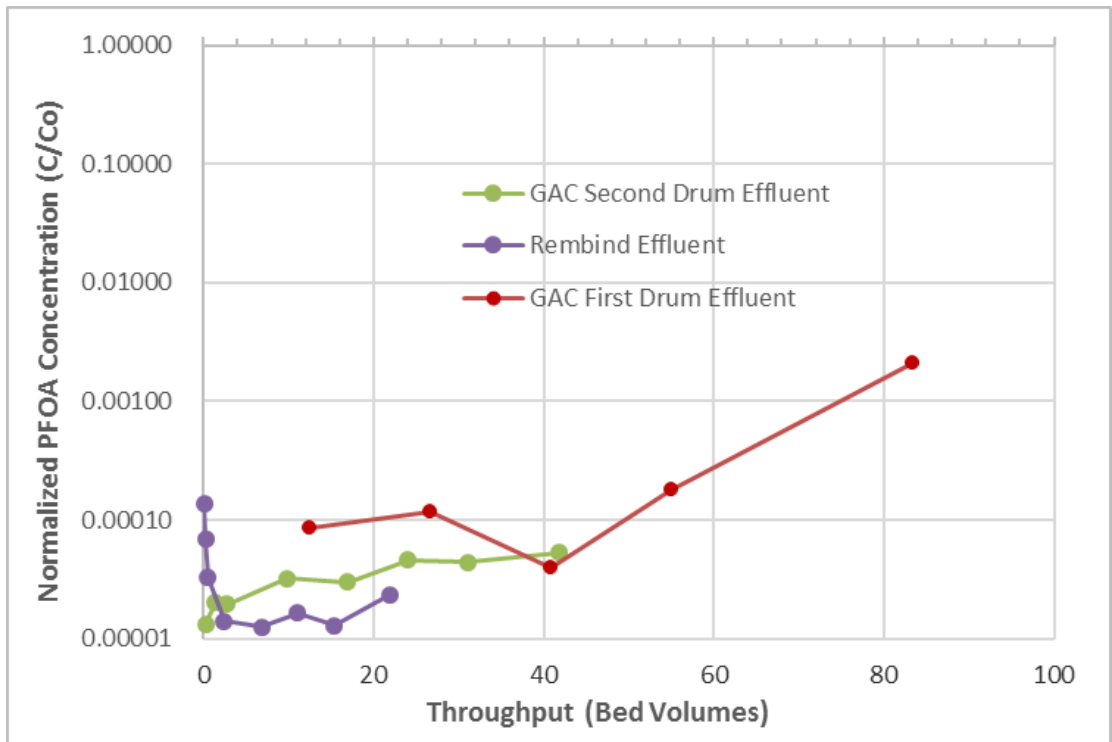


Figure 37. Normalized PFOA concentration change with increasing throughput (bed volumes).

4.0 Conclusions and Observations

Based on the data presented in Section 3, the following general conclusion can be drawn from the AFFF treatment experiments. Also presented below are some observations that may be relevant to field-treatment of AFFF-contaminated water at specific sites:

- The study results show that both GAC and RemBind™ are capable of removing various short-and-long chain PFAS with an efficiency greater than 99.9%, on average, over a 12-hour period when the lagoon water is spiked with firefighting levels of AFFF. The removal of shorter chains PFAS is of particular importance because newer AFFF products are formulated to eliminate longer chain PFAS. This suggests that water contaminated with newer AFFF formulations can also be treated with these adsorbents, although this should be experimentally verified, especially for each site-specific water, which may contain substances that interfere and may compete with PFAS adsorption.
- GAC media can accommodate a higher flowrate than the RemBind™ media. Up to 6.5 gpm was achieved in two drums of GAC in series. A total flow of 4 gpm was achieved through two modified RemBind™ drums (Rembind media mix with 50% sand by volume) operated in parallel with 2 gpm per drum. This impacts the configuration of a RemBind™ based treatment system, if this adsorbent is chosen based on site-specific needs.
- The RemBind™ media needs to be mixed with significant amount of sand to achieve operational flows in the field, as needed in this study. Also, the low flow through and high pressure drop across the RemBind™ media drum could be too significant for the RemBind™ drums to be operated in series without an intermediate pump and storage mechanism. This could also impact design of a RemBind™ based treatment system, along with requiring on-site availability of suitable sand or other material to mix with the media.
- For some PFAS, the data suggests that the first GAC drum in series (drum 1) was losing its adsorptive capacity, and breakthrough of PFAS was occurring. However, breakthrough was not observed in the second drum in series. Because such variations could impact utilization of the drums (with specific bed volumes), this observation merits further investigation to evaluate the number of drums needed to achieve the same treatment goals described in this study, at a specific site. Additionally, the water quality and the organic content of each water may impact the breakthrough.

In summary, should AFFF contaminate a water body after the response to a fire, the data show that either GAC or RemBind™ could be used to adsorb most of the PFAS before disposal of the treated water, e.g., in a sewer or by other means. (*Note: it is important to ensure discharge of treated water conforms to local regulation and requirements of the wastewater authorities at a particular discharge site.*) Despite similar performance at removing contaminants, from an implementation standpoint, these findings also indicate that the GAC could be used as received, while the RemBind™ needs to be mixed with sand, which is a time consuming process when performed manually.

5.0 References

- American Public Health Association. (1999). Method 2130: Turbidity. Standard Methods for the Examination of Water and Wastewater, 20th ed. Washington, DC: American Public Health Association,
- Calgon. (2015). Data Sheet for Filtrasorb® 600 Granular Activated Carbon (DS-FILTRA60015-EIN-E1), Moon Township, PA: Calgon Carbon Corporation.
- Extech. (2016). Extech Instruments Model 407229 pH meter User's Manual. Nashua, NH: Extech Instruments.
<http://www.extech.com/display/?id=14215>, accessed 05/31/2017.
- Hach Company. (2014a). Method 8000: Chemical Oxygen Demand.
<https://www.hach.com/asset-get.download.jsa?id=7639983816>, accessed 05/31/2007.
- Hach Company. (2014b). Method 10102: Free Chlorine. <https://www.hach.com/asset-get.download-en.jsa?code=55578>, accessed 05/31/2017.
- Potter, BB and Wimsatt, JC. (2005) Method 415.3. Measurement of Total Organic Carbon, Dissolved Organic Carbon, and Specific UV absorbance at 254 nm in Source Water and Drinking Water. Washington, DC: U.S. Environmental Protection Agency.
https://cfpub.epa.gov/si/si_public_record_report.cfm?dirEntryId=103917, accessed 05/31/2017.
- Shoemaker JA, Grimmett PE and Boutin BK. (2009) Method 537. Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS), Version 1.1. Cincinnati, OH: U.S. Environmental Protection Agency.
https://cfpub.epa.gov/si/si_public_record_report.cfm?dirEntryId=198984&simpleSearch=1&searchAll=EPA%2F600%2FR-08%2F092, accessed 05/31/2017.
- Thermo Scientific. (2014). Thermo Scientific Orion Versa Star User's Manual. Waltham, MA: Thermo Fisher Scientific Corporation.
<https://www.thermofisher.com/order/catalog/product/VSTAR90>, accessed 05/31/2017
- USEPA. (2016). Drinking Water Health Advisories for PFOA and PFOS.
<https://www.epa.gov/ground-water-and-drinking-water/drinking-water-health-advisories-pfoa-and-pfos>, accessed 05/31/2017.
- Ziltek. (2014). RemBind™ Product Overview. Immobilising Soil Contaminants. Z070-02 04/14. Thebarton, Australia: Ziltek corporation.



PRESORTED STANDARD
POSTAGE & FEES PAID
EPA
PERMIT NO. G-35

Office of Research and Development (8101R)
Washington, DC 20460

Official Business
Penalty for Private Use
\$300