

Evaluation of practical technologies for Per - and Polyfluoroalkyl Substance (PFAS) remediation in marine fish hatcheries

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Glossary/abbreviations

ACAAR	Australian Centre for Applied Aquaculture Research
DPIRD	Department of Primary Industries and Regional Development
FTSA	Fluorotelomer sulfonic acids
HRT	Hydraulic retention time
LOR	Limit of reporting
OCRA	Ozofractionatively Catalysed Reagent Addition
ORP	oxidation-reduction potential
PAHs	Polycyclic aromatic hydrocarbon
PFAS	Perfluoroalkyl Substance
PFOS	Perfluoro octane sulfonate
PFOA	Perfluoro octanoic acid
PFHpA	Perfluro heptanoic acid
PFHxS	Perfluoro hexane sulfonic acid
PFNA	Perfluoro nonanoic acid
PFSI	Port Stephens Fisheries Institute
PFUdA	Perfluoro undecanoic acid
TPHs	Total petroleum hydrocarbons
YTK	Yellowtail Kingfish

Executive Summary

Per- and poly-fluoroalkly substances (PFASs) are now emerging as pollutants with potentially catastrophic impact on aquaculture facilities. Two key research institutes, Port Stephens Fisheries Institute (PSFI) in NSW and Australian Centre for Applied Aquaculture Research (ACAAR) in Western Australia have discovered the presence of PFASs in their influent seawater sources and in their broodstock fish. PFASs are proven Endocrine Disrupting Chemicals of fish and can cause reduction in fecundity, and deformity, abnormal development and increased mortality of fish larvae. Both research institutes have observed impacts on larvae that are broadly consistent with those observed for PFASs in literature studies. As testing for PFASs continues we expect that the number of facilities affected in Australia, and indeed globally, may increase. Further, to assess impacts, PFASs must be introduced into experimental systems in a controlled fashion and therefore we must have the capacity to remove those pollutants before release of effluent water. To protect our facilities and permit PFASs impacts research there was a need to assess available treatment technologies for removal of PFASs in seawater.

There are currently several technologies available for PFASs remediation including, activated carbon, ion exchange, foam fractionation combined with ozone (i.e. ozofractionation) and specific filtration with adsorbent materials. These are variously suitable for freshwater applications. The two approaches showing the greatest promise for seawater, in which PFASs react differently to that observed in freshwater, are fractionation and adsorbent materials in specialised filters. These technologies exist in some form in many aquaculture systems and could be optimised for PFAS extraction.

Foam fractionation uses the surfactant nature of PFASs to cause them to agglomerate on the surface of bubbles sparged through the contaminated fluid. In "ozofractionation" investigated in this study the addition of ozone increases the effectiveness of the process, although care is needed that ozone levels are not greater than those likely to be acceptable for aquaculture. The filtration media RemBind[®]; developed by Ziltek Pty Ltd, is an adsorbent used for the remediation of contaminated soil and groundwater. The product binds permanently to contaminants preventing them from leaching and causing environmental harm. Since 2011, RemBind[®] has been used commercially to treat a wide variety of organic contaminants including PFASs, TPHs, PAHs, pesticides, herbicides and mercury. The product has been successfully applied in USA, Europe and Australia.

This project set out to:

1) Confirm the effectiveness of ozofractionation and adsorbent media (RemBind®) in the removal of PFAS from seawater,

2) Investigate the impacts of flow rate through fractionation chambers on PFAS removal

- 3) Test fractionation PFAS removal efficiency with and without ozone.
- 4) Test the PFAS load capacity and subsequent replacement frequency of RemBind®

Before commencing the trials, further information on the extent of PFA pollution was gathered at the PSFI and ACAAR.

At the PSFI, previous work in the estuary had quantified the levels of PFASs in seawater and key commercial fish species, so assessments focussed on PFASs levels in fish stocks held at the institute. Samples of Yellowtail Kingfish eggs, larvae, blood and gonad, and Mulloway liver were collected and tested for a suite of PFASs. Of the suite of analytes tested, PFOS (Perfluorooctane sulfonate) was detected in all samples except YTK larvae, and PFUdA

(Perfluoroundecanoic acid) was detected in the ovaries of YTK. PFOS concentrations in YTK eggs and blood were slightly higher than the LOR (limit of resolution), however, PFOS concentrations were found to be 10-fold and 17-fold higher than the LOR for mulloway liver and YTK ovary, respectively.

At the ACAAR, initial testing focused on the two bores that provide the facility seawater supply. Despite being very close together and drawing from a similar depth (~20 m), the levels of PFASs in Bore #1 (range 11.7 to 45.2 ng/L; average 26.1 ng/L) were consistently higher than Bore #2 (range 3.6 to 13.4 ng/L; average 6.1 ng/L). Up to nine PFAS analytes were detected in each bore, with PFOS being the dominant analyte and comprising up to half the total PFASs detected.

Two sets of PFASs remediation trials were undertaken in this project to assess the performance of foam fractionation and specific filtration media. An initial set of foam fractionation trials, with both air and ozone, were undertaken at a test facility at the University of Newcastle using PFAS "spiked" seawater collected from the PSFI. Based on these results, further evaluation of air foam fractionation technology was done at ACAAR. The evaluation of RemBind[®] filtration was also undertaken at ACAAR.

Trials at the two facilities demonstrated that commonly available foam fractionation systems, using either air or ozone could remove more than 90% of PFOS and PFOA in spiked or contaminated seawater, while producing a small volume of contaminated fractionate fluid. The research highlighted several variables affecting the efficiency of foam fractionation in PFAS removal, notably gas flow rates and vacuum pressures, water flow rates, hydraulic retention time and fractionate flow rates. These varied with the systems tested and will vary with other commercial units, however, some guidance can be gained for the operation of all systems from the results obtained in these trials.

Higher concentration factors of PFASs were achieved from foam fractionation when used in combination with ozone. The use of ozone in aquaculture systems does, however, require care. In these trials, the ORP levels within the fractionation chamber were controlled at high levels of around 750mV, which would be useful for extraction following deliberate introduction of PFASs for experimentation, regardless, the chambers can be run at various, stable, ORP levels. Further investigation of the necessity for high ORP pre-treatment of hatchery influent water compared to recirculation is warranted to avoid creating dangerous ORP levels within the recirculation systems of aquaculture facilities.

If experimentation is planned where PFASs are to be deliberately added to water to test aquatic impacts, modifications will be required. One approach would be to store and dispose of the contaminated fraction. It is, however, possible that the fraction could be further concentrated by additional fractionation stages or dehydrated to reduce volume before disposal for destruction.

The use of adsorbent media was also assessed in this project. RemBind 200[®] powder was shown to be capable of removing all PFAS analytes to below detectable limits when added to contaminated seawater. However, when used within a filter matrix, PFAS removal efficiency declined over time and lost efficiency too quickly to be considered a viable filtration media for commercial-scale hatchery operations. Regardless, adsorbent media may be useful for sequestration of PFASs from a fluid fractionate before disposal or it may be considerably more convenient for treating small volumes of PFAS contaminated seawater that could arise from experimental trials.

In conclusion, foam fractionation was found to be effective in removing significant quantities of PFASs from seawater. If not already found in many aquaculture facilities, foam fractionators are comparatively cheap, readily available and scalable. They are simple to use and install and they are adjustable to increase PFAS removal efficiency. Ozone is currently commonly used in aquaculture facilities to disinfect seawater, and it has been shown to offer advantages in PFAS removal. However, care is required in using ozone in aquaculture systems and further research is needed to safely optimise ozone use. This project has highlighted many of the variables to be considered when operating foam fractionators that could improve PFAS removal efficiency, but a larger longer term project would be required to fully evaluate their beneficial use.

Keywords: Poly-fluoroalklys, Per-fluoroalklys, PFAS, Seawater, Filtration, Fractionation, Hatchery

Introduction

Per-and polyfluorinated alkyl substances (PFASs) are a group of synthetic chemicals that have been extensively used since the 1950s as constituents in many household items and prevalent in firefighting foams. PFASs are currently an emerging environmental contaminant, meaning that their impacts of human health and ecological health are uncertain, but with increasing concern to the detrimental effects on developing children and animals. The two most well-known PFASs are perfluorooctane sulphonate (PFOS) and perfluorooctanoic acid (PFOA). Due to their widespread use, high solubility and chemical stability, PFASs persist in the environment and can be transported through surface water and groundwater. Moreover, their high bioaccumulation potential means they can move through the food chain through plants and animals. Per- and polyfluoroalklys (PFASs) are now emerging as pollutants with potentially detrimental impact on aquaculture facilities.

Two key research institutes, Port Stephens Fisheries Institute (PSFI) in NSW and Australian Centre for Applied Aquaculture Research (ACAAR) in WA have already demonstrated the presence of PFASs in marine fish broodstock and influent seawater sources used to culture a range of marine fish, molluscs and crustaceans. PFASs are proven Endocrine Disrupting Chemicals of fish and can cause a reduction in fecundity, and deformity, abnormal development and increased mortality of larvae. Both research Institutes have observed impacts on larvae that are consistent with those observed in literature studies. As testing for PFASs continues there is the expectation that the number of facilities affected in Australia, and indeed globally, will increase. To compound the challenge, our understanding of the impacts of PFASs on aquatic species is limited. To our knowledge, there are very few projects underway that are investigating the impacts of PFASs on Australian aquatic species, especially marine species.

In order to further assess impacts, PFASs must be introduced into experimental systems in a controlled fashion and to ensure environmental protection we must have the capacity to remove those pollutants before release of effluent water. To protect our facilities and permit PFASs impact research there is a need to rapidly assess available PFASs treatment technologies.

There are currently several technologies available for PFASs remediation including, activated carbon, ion exchange, ozofractionation and specific filtration. These are variously suitable for freshwater applications. The two approaches showing the greatest promise for seawater, in which PFASs react differently to that observed in freshwater, are ozofractionation and absorbent materials in specialised filters. These technologies exist in some form in many aquaculture systems and could be used more broadly or optimised for PFAS extraction.

Foam fractionation uses the surfactant nature of PFAS to cause them to agglomerate on the surface of bubbles sparged through the contaminated fluid. While foam fractionation alone is successful, the addition of ozone increases the effectiveness of the process (i.e. ozofractionation), although care is needed that ozone levels are not in excess of those likely to be acceptable for aquaculture. The filtration media RemBind[®]; developed by Ziltek Pty Ltd, is an adsorbent for the remediation of contaminated soil and groundwater. The product binds permanently to contaminants preventing them from leaching and causing environmental harm. Since 2011, RemBind[®] has been used commercially to treat a wide variety of organic contaminants including PFASs, Total Petroleum Hydrocarbons, Polycyclic Aromatic Hydrocarbons, pesticides, herbicides and mercury. The product has been successfully applied in USA, Europe and Australia.

This work tests the utility of these two systems in PFAS extraction from seawater and provides a report to industry on their efficacy that would facilitate their adoption where required.

Objectives

- Confirm the effectiveness of ozofractionation and adsorbent media in the removal of PFASs from seawater,
- Investigate the impacts of flow rate through fractionation chambers on PFAS removal,
- Test fractionation PFAS removal efficiency with and without ozone, and
- Test the PFAS load capacity and subsequent replacement frequency of RemBind®

Methods, Results & Discussion

Background PFASs

Both the Port Stephens Fisheries Institute (PSFI) in NSW and Australian Centre for Applied Aquaculture Research (ACAAR) in Western Australia are in regions affected by PFAS contamination. The PSFI is adjacent to and draws water from Tilligerry Creek Port Stephens, NSW, which has been exposed to contaminated surface and groundwater arising from a nearby regional airport and military base. The contamination has arisen from decades of use of firefighting foams containing PFASs up until the early 2000s. Surveys of oysters and commercial fish species in Port Stephens confirmed the presence of PFASs (Taylor and Johnson, 2016: O'Connor et al. 2018) and raised concerns for the health of captive fish stocks held at the institute.

Port Stephens Fisheries Institute

Prior to this study PFOA concentrations were analysed on 30/01/2018 in various tissues of Yellowtail Kingfish (YTK, *Seriola lalandi*) and Mulloway (*Argyrosomus japonicus*) which had been maintained for between 1 to 20 years in tanks filled with estuarine seawater at PSFI (Fielder and Heasman, 2011). The samples included: blood from a 1-year-old hatchery-reared YTK; tissue from the ovary of a wild-caught YTK which had been held at PSFI for >10 years; eggs and larvae produced from YTK broodstock which had been held at PSFI for > 10 years; and tissue from the ovary of a deceased Mulloway which had been held at PSFI for > 10 years; and tissue from the ovary of a deceased Mulloway which had been hatchery-reared and held at PSFI for ~20years. Of the suite of PFOA analytes tested, PFOS was detected in all samples except YTK larvae, and PFUdA was also detected in the ovary of YTK. Concentrations of all other PFOA (Perfluoro octanoic acid) analytes were below the Limit of Reporting (LOR; Table 1). PFOS concentrations in YTK eggs and blood were slightly higher than the LOR, however, PFOS concentrations were found to be 10-fold and 17-fold higher than the LOR for Mulloway liver and YTK ovary, respectively (Table 1).

		YTK eggs	YTK eggs	YTK	YTK ovary	YTK	Mulloway
		Tank1	Tank6	larvae	Tank1	blood	liver
	Limit of Reporting						
	(mg/kg)						
PFBuA (Perfluoro butanoic acid)	0.001	-	-	-	-	-	-
PFPeA (Perfluoro pentanoic acid)	0.0005	-	-	-	-	-	-
PFHxA (Perfluoro hexanoic acid)	0.0005	-	-	-	-	-	-
PFHpA (Perfluoro heptanoic acid)	0.0005	-	-	-	-	-	-
PFOA (Perfluoro octanoic acid)	0.0003	-	-	-	-	-	-
PFNA (Perfluoro nonanoic acid)	0.0005	-	-	-	-	-	-
PFDA (Perfluoro decanoic acid)	0.0005	-	-	-	-	-	-
PFUdA (Perfluoro undecanoic acid)	0.0005	-	-	-	0.00059	-	-
PFDoA (Perfluoro dodecanoic acid)	0.0005	-	-	-	-	-	-
PFBS (Perfluoro butane sulfonic acid)	0.0005	-	-	-	-	-	-
PFHxS (Perfluoro hexane sulfonic acid)	0.0005	-	-	-	-	-	-
PFOS (Perfluoro octane sulfonic acid)	0.0003	0.00033	0.00037	-	0.0052	0.00066	0.0031
6:2 FTS (C2H4-perfluorooctane sulfonate)	0.0005	-	-	-	-	-	-
8:2 FTS (C2H4-perfluorodecane sulfonate)	0.0005	-	-	-	-	-	-

Table 1. Concentrations of PFOA's in yellowtail kingfish (Seriola lalandi) eggs, larvae, blood and ovary, and Mulloway (Argyrosomus japonicus) liver.

Australian Centre for Applied Aquaculture Research

Prior to this study, PFASs levels in the two marine bores that supply ACAAR were sampled monthly between January and December 2018, along with the adjacent seawater. The concentration of the sum of all PFASs in each water source is shown in Figure . Of the 28 analytes tested (Table 5), up to nine were present in each water source (Table 1).

Despite being very close together and drawing from a similar depth (~20 m), the levels of PFASs in Bore #2 (range 3.6 to 13.4 ngL⁻¹; average 6.1 ngL⁻¹) were consistently lower than Bore #1 (range 11.7 to 45.2 ngL⁻¹; average 26.1 ngL⁻¹). Levels of PFASs in the adjacent seawater ranged from 0 to 13.8 ng/L, with an average value of 3.5 ngL⁻¹. The patterns in these data tend to suggest a greater hydraulic connection of Bore #2 with the ocean, with Bore #1 drawing off a groundwater stream with an unknown source of PFAS compounds. The most dominant compound in all three water sources is PFOS, which comprises approximately half of all the PFAS compounds (Table 2). The next most abundant compound in the two bores is PFHxS (Perfluoro hexane sulfonic acid, ~33%) while in the seawater it is PFHpA (Perfluoro hepatonic acid, 25%). This compound was only measured in Bore #1 at very low concentrations and never in Bore #2 (despite our hypothesis above that Bore #2 may have a greater connection to the ocean).



Figure 1: Concentrations of PFAs (*ngL*⁻¹: sum of all analytes) in Bore #1, Bore #2 and the adjacent seawater over a 12 month period.

Table 2:Composition of the various PFAS analytes as a % of all analytes in DPIRD bores
and adjacent seawater. Values are averages ± S.E. of the 12 monthly samples
shown in Figure 1.

	Bather's Beach	Bore 1	Bore 2
%PFBS	$0\pm0\%$	$1 \pm 0\%$	$0\pm0\%$
%PFPes	$0\pm0\%$	$3\pm0\%$	$0\pm0\%$
%PFHxS	$13 \pm 7\%$	$32\pm2\%$	$34 \pm 4\%$
%PFOS	$48\pm10\%$	$45\pm3\%$	$57 \pm 5\%$
%PFBA	$6\pm6\%$	$2\pm2\%$	$5\pm5\%$
%PFPeA	$3\pm2\%$	$4\pm0\%$	$1 \pm 1\%$
%PFHxA	$4\pm2\%$	$8\pm0\%$	$3 \pm 1\%$
%PFHpA	$25\pm7\%$	$1\pm0\%$	$0\pm0\%$
%PFOA	$1 \pm 1\%$	$3\pm0\%$	$0\pm0\%$

PFA Remediation Trials

Two sets of PFAS remediation trials were undertaken in this project to assess the performance of foam fractionation and specific filtration media. An initial set of fractionation trials were undertaken at a test facility at the University of Newcastle (UoN) using seawater collected from the PSFI. In the light of these trials, further evaluation of foam fractionation technology was undertaken at ACAAR.

PSFI Foam Fractionation Trials

The University of Newcastle in collaboration with an industry partner, Evocra Pty Ltd, has developed a novel Ozofractionatively Catalysed Reagent Addition (OCRA) process to treat a variety of water contaminations, including PFASs, hydrocarbons and acid mine drainage. The OCRA process uses high concentrations of ozone to manage both the pH and the oxidation-reduction potential (ORP) of a solution in an efficient fractionation system. Contaminants are either removed via foam flotation (for all PFASs contaminants), oxidative and hydroxyl precipitation (for metals) and destruction by advanced oxidation processes (most hydrocarbon organics). For the trials reported, the process typically produces a PFAS rich foam fractionate concentration ranging between 1000-100,000 μ g/L, depending on the influent PFAS concentration and at fractionate volumes less than 1% of the influent flow rate.



PFOS/PFOA Spiking and sample preparation

All raw seawater used in the trials was collected from the seawater supply system at the PSFI and delivered to the Evocra Pty Ltd facility at the University of Newcastle, where the evaluations took

place. PFOS and PFOA standard solutions were created by diluting pure components in reverse osmosis water to concentrations of 0.4 g L^{-1} . Test spiking solutions were then prepared from the stock by further dilution to concentrations of 0.4 mg L^{-1} when required.

For the trials, 25 mL of each solution was added to 1000L of seawater to achieve concentrations of 10 ng L⁻¹ PFOS and 10 ng L⁻¹ PFOA, or 20 ng L⁻¹ total PFASs. These concentrations, although close to our LOR, were chosen based on PFAS levels found in seawater in Port Stephens (Taylor et al. 2017) and were similar to levels found in seawater at ACAAR (Figure 1). The seawater was then mixed with a pump for 24 h to ensure adequate mixing occurred. Before introduction to the fractionator, a sample of the spiked seawater was collected to confirm PFAS levels. A pump was used to deliver the seawater into the fractionation chamber at a rate of 100 Lh⁻¹. Pre-calibrated multi-meter probes capable of measuring pH, EC, DO and ORP were placed into the fractionation chamber and the chamber was half-filled with raw water



Figure 3. Foam fractionation unit at the University of Newcastle

Experimental procedure

Two sets of trials were undertaken in which either air or ozone was introduced to the foam fractionator at four different rates (Table 3). At the start of each trial a multi-meter (YSI Corp) and was turned on and data logging commenced. The recirculation pump to the foam fractionator was started and the gas supply (air or ozone) to the system was turned on.

When testing with ozone, the ozone generator was set at low voltage and then adjusted as required. Initially, the gas supply was set at the lowest of the rates that were to be tested (Table 4). Two types of venturi were used. The ozofractionation system used an Evocra proprietary venturi that produced a maximum gas flow of 23,105 mL min⁻¹. The air fractionation system used a Mazzei venturi that produced a maximum gas flow of 6,752 mL min⁻¹.

When using ozone, care was taken when adjusting the output voltage of the ozone generator to ensure an ORP of less than 750 mV was maintained to avoid the formation of hypobromous acid.

PFASs spiked seawater was then introduced to the chamber at a rate of 100 Lh⁻¹. Care was then taken to allow the chamber to run with continuous seawater feed for at 3 x the residence time before sampling. At a rate of 100 L h⁻¹, with a chamber volume of approximately 15 L, the residence time of the chamber was 9 minutes. Accordingly, the system was allowed to run with a continuous seawater feed for at least 30 mins before sampling occurred. At this time, samples of both chamber output water and fractionate were collected and stored for later analyses.

In each round of trials, the gas supply rate was then increased to the next test level (Table 3) and the system allowed to run for a further 30 mins before another set of samples was collected. This procedure was then repeated two further times to provide the four test flow rates. When using ozone, the output voltage of the ozone generator was adjusted to ensure an ORP of less than 750 mV was maintained (Fig 4).



Figure 4. YSI data log of ORP during the first fractionation trial

Data Analysis

Each data point is collected at a certain gas-flow rate. This gas flow-rate can be expressed as a gas flux where the gas flux is equal to the volumetric flow of gas divided by the chamber diameter. Similarly, the liquid flow-rate can be expressed as a liquid flux, where the liquid flux is equal to the volumetric flow of gas divided by the chamber diameter. The ratio of the gas flux to the liquid flux is the gas-liquid flux ratio.

Samples of raw water, output water and fractionate sent for PFAS analysis were used to calculate PFAS removal. Plotting PFAS removal against the gas-liquid flux ratio will give a curve demonstrating the required gas-liquid flux for the removal of PFASs. This curve allows determination of gas flow-rates for various liquid flows independent of fractionation chamber diameters. Fraction concentration factor is the simple calculation of fraction concentration over initial influent concentration and allows for a comparison of removal efficiency between the methods where the higher the concentration factor the higher the efficiency of process.

Results & Discussion

The concentrations of PFOS and PFOA in the spiked influent seawater, and in the effluent water at each flow rate for both ozone and air, are presented in Table 3. While there are challenges with PFAS levels close to the LOR, this data confirms the presence of PFASs in the seawater. In the case of PFOA in the seawater used for the ozone trail, the level is assumed to be close to 10 ng/L so that estimations of removal efficiency in the fractionate could be made. The concentrations of PFASs in the fractionate are presented in Table 4. Comparing these two tables, a gentle gas flow

of 1 - 4 L/min removes more than 90% of PFOA and PFOS compounds for both air and ozone (Table 4).

Table 3. PFOA and PFOS concentrations in the influent (spiked) and effluent water following air and ozone foam fractionation at various flow rates and vacuum pressures.

	Vacuum, (mmHg)	Perfluorooctanoic acid (PFOA) μg/L	Perfluorooctanesulfonic acid (PFOS) μg/L
Raw seawater	-	< 0.01	< 0.01
Spiked Seawater (air trial)	-	<0.01*	0.02
Spiked seawater (ozone trial)	-	0.01	0.02
1161 (mL/min) Air	-295	< 0.01	< 0.01
1161 (mL/min) Ozone	-350	< 0.01	< 0.01
4013 (mL/min) Air	-65	< 0.01	< 0.01
4013 (mL/min) Ozone	-185	< 0.01	0.01
5213 (mL/min) Air	-25	< 0.01	< 0.01
5213 (mL/min) Ozone	-125	< 0.01	< 0.01
6752 (mL/min) Air	-5	< 0.01	0.02
23105 (mL/min) Ozone	50	< 0.01	< 0.01

*The spiked PFOA concentration in the ozone trial is assumed to be just below the LOR of 0.01 as the same volume of PFOA stock solution was added to the raw seawater sample as for the air seawater sample.

Analysis of the PFAS concentrations in the fractionate found several other PFAS analytes to be present (Table 4). This is thought to have arisen from challenges around the LOR of the analysis method for PFAS. Fractions will often produce levels above the LOR of the raw water as the fractions can concentrate the raw water contaminant concentration by as much as 3 orders of magnitude. Further, it is also possible that these analytes were present in the water from the PSFI and/or arose from the stock solutions that may have impurities in them that the fractions will reveal. Regardless, there was a significant reduction in removal efficiency as demonstrated by the concentration factor for both total PFASs and for both PFOS and PFOA as vacuum was decreased (Figures 5 & 6). All gas flow rates under vacuum of equal to or greater than 25 mmHg demonstrated some removal of PFOS and PFOA from solution. The two higher tested gas flows for air resulted a greatly reduced efficiency in the removal of PFOS. The high gas flow for ozone removed both PFOA and PFOS. Fraction concentration factor was seen to be significantly higher at the lower flow rates where the vacuum was higher.

Table 4. PFAS concentrations in the fractionate following air and ozone foam fractionation at various flow rates and vacuum pressures.

	Vacuum, (mmHg)	(8:2 FTSA) μg/L	(6:2 FTSA) μg/L	(PFHpA) µg/L	(PFHxA) µg/L	(PFNA) µg/L	(PFOA) µg/L	(PFHpS) µg/L	(PFHxS) µg/L	(PFOS) µg/L
1161 (mL/min) Air	-295	6.70	37.05	2.68	1.34	<0.45	14.73	<0.45	0.45	9.37
1161 (mL/min) Ozone	-350	3.95	19.74	<1.32	1.32	< 0.01	47.37	< 0.01	<1.32	18.42
4013 (mL/min) Air	-65	1.03	5.74	0.37	0.22	0.07	6.54	0.07	0.29	3.75
4013 (mL/min) Ozone	-185	0.18	2.14	0.09	0.09	< 0.01	3.26	< 0.01	0.09	1.43
5213 (mL/min) Air	-25	0.06	0.53	0.03	0.02	< 0.01	0.68	< 0.01	0.03	0.27
5213 (mL/min) Ozone	-125	0.23	2.85	0.12	0.23	< 0.01	4.30	0.01	0.12	1.22
6752 (mL/min) Air	-5	0.09	0.59	0.03	0.02	<0.01	0.85	0.01	0.03	0.57
23105 (mL/min) Ozone	50	0.02	0.21	< 0.01	< 0.01	< 0.01	0.10	< 0.01	< 0.01	0.08



Figure 5

Concentration factor for the sum of PFASs



Figure 6. Concentration factor for PFOA & PFOS

Comparison of PFAS fraction concentration between the two approaches found the use of ozone showed a slightly different PFAS speciation to air, indicating a higher removal efficiency for 8:2 FTSA, 6:2 FTSA groups and potential conversion of PFHpS and PFNA to other PFAS species, which may demonstrate known oxidation conversion of precursor compounds. The oxidation power of ozone can convert low level, undetectable precursors into measurable PFAS compounds.

ACAAR Foam Fractionation Trials

Based on the results obtained using foam fractionation at the PSFI, trials testing PFAS removal commenced at ACAAR using water from both Bore #1 and Bore #2 using conventional aquaculture foam fractionation with only air (not ozone). The first trials tested a relatively small foam fractionator (Aqua Medic Turboflotor 5000 Skimmer Twin; Figure 7) with a column volume of 57L. This foam fractionator is driven by two Aqua Medic Ocean Runner OR3500 pumps (max flow 3500 Lh⁻¹) and bubbles are created by venturis; one at each of the two pump suctions. Needle wheel pump impellers then create even smaller bubbles. Using a vacuum gauge, we estimated that the total airflow created by these two venturis was 6 L min⁻¹ (105 mL min⁻¹ L⁻¹ of column volume).

The EVOCRA trials described previously tested varying air flow rates on removal efficiency at a fixed HRT of 9 minutes; the fractionate flow rate was not recorded. The first two trials done at ACAAR investigated various fractionate flow rates and hydraulic retention times (HRT) using flow-through water from Bore #1 (high PFAS bore) at the fixed airflow rate of 6 L min⁻¹. The third trial investigated varying fractionate flow rates at a constant HRT of 10 minutes in Bore #2 (low PFAS bore), also with 6 L min⁻¹ of airflow.



Figure 7: Aqua Medic Turboflotor 5000 Skimmer Twin

In these trials:

Total flow
$$\left(\frac{l}{hr}\right) = Fractionate flow \left(\frac{l}{hr}\right) + Outlet flow \left(\frac{l}{hr}\right)$$

Fractionator retention time (minutes) = column volume(l)/flow $\left(\frac{l}{hr}\right) * 60$

Results of the first trial with Bore #1 (8) demonstrate an increasing removal efficiency with increasing fractionate flow rate, from 90% removal at a 1% fractionate flow rate (i.e. from Σ PFAS of 25 ngL⁻¹ to 2.5 ngL⁻¹), to 97% removal at a 22% fractionate flow rate (from Σ PFAS 25 ng/L to 0.8 ngL⁻¹). We hypothesised that the improved removal efficiency using a higher fractionate flow (i.e. wetter foam) is due to the reduction in collapsing bubbles which would re-release of PFOAs back into the water column. Whilst the wetter foam is more 'wasteful' of water, if water is not in short supply, then using a wetter foam is recommended although it must be considered that production of a wet foam may require downstream processing of this foam to further concentrate the contaminants.



Figure 8. Percentage (%) PFOAs removal (∑PFAS) vs fractionate flow rate (Lh⁻¹) at constant HRT of ~10 minutes (data labels show %fractionate rate) in Bore #1 with small foam fractionator

The second trial measured removal efficiency at different hydraulic retention times of 2, 6 and 10 minutes of Bore #1 water. The fractionate flow rate was fixed at ca. 20% (i.e. the optimum identified in the previous trial). This trial demonstrated a linear reduction in removal efficiency from 92% at a 10 min HRT to 86% at a 2 minute HRT (Figure 9). Whilst longer HRTs require larger foam fractionators to process the same flow of water, this can be justified by the improvement in removal efficiency.



Percentage (%) PFASs removal (\sum PFAS) vs hydraulic retention time (HRT) at 20% fractionate flow rate in Bore #1 with small foam fractionator.

The first trial described above with Bore #1 was repeated with Bore #2. The foam fractionator removed all PFASs to <LOR from this bore (from an inlet \sum PFAS of 7 ng L⁻¹), regardless of fractionate flow rate with a HRT of 10 minutes (Figure 10). Whilst it would have been beneficial to conduct a trial on Bore #2 water to determine if 100% removal efficiency could still be obtained at lower (faster) HRTs this was not done due to time constraints.

Figure 10: Percentage (%) PFOAs removal ($\sum PFAS$) vs fractionate flow rate (Lh⁻¹) at constant HRT of ~10 minutes (data labels show %fractionate rate) in Bore #2 (inlet concentration 7 ngL⁻¹)

As anticipated, PFOA analysis of the fractionate in these small fractionator trials revealed increases in PFOA concentrations that were inversely correlated with the fractionate flow rate (Figure 11). Interestingly, some additional PFOA compounds were detected in the fractionate that were not detected in the incoming water, due to them being concentrated in the foam to levels above the LOR. These compounds were PFNA, FOSA and 6:2 FTS.

Figure 11: Fold increase in the $\sum PFAS$ in the fractionate relative to the inlet $\sum PFAS$ concentration at various fractionate flow rates in the small fractionator trials.

Following these positive results obtained with the small foam fractionator, ACAAR trialled a commercial foam fractionator large enough to process all of the supply water to its 4 commercial recirculating broodstock tanks (40 Lmin⁻¹ per tank = 160 Lmin⁻¹ = 9.6 m³hour⁻¹) (Aquasonic PPS12N; Figure 2). This fractionator is 4.8 m tall and has a column volume of 2060 L. Bubbles are created via venturis (Mazzei injectors) on the discharge of 3 x Waterco Turboflo 150 pumps (max flow per pump 27 m³hr⁻¹).

Figure 2: Aquasonic PPS12N foam fractionator.

Based on the plumbing layout in the DPRID hatchery, PFAS removal by this large foam fractionator was tested only in Bore #1 (high PFAS bore). Due to inlet plumbing restrictions, a wide range of HRTs could not be tested and HRT values ranged from 10 to 14 minutes. Removal rate was again positively correlated with HRT (Figure 3) and >90% removal was achieved at all HRTs tested.

Figure 3: Percentage (%) PFASs removed ($\sum PFAS$) vs hydraulic retention time (HRT) at fractionate flow rates indicated in data labels in Bore #1 with large foam fractionator.

The correlation between fractionate flow rate and removal efficiency for this data set was poor ($R^2 = 0.18$)(Figure 4). This may be the result of the relatively tight range of fractionate flow rates tested (10% to 20% in this trial compared with 1% to 22% in the small fractionator trial). It is noteworthy, however, that 90% removal was achieved in the small fractionator trial at a 1% fractionate flow and therefore this large foam fractionator trial could be repeated with much lower fractionate flow rates and we aim to conduct this trial. Further studies with the large fractionator will include testing of total gas pressure to ensure the very deep column does not induce nitrogen supersaturation.

Comparing the performance of the small and large foam fractionators is difficult given the significant differences in their design and operation. Measurement of key variables such as bubble size and bubble retention time are not possible, however we believe the bubbles in the smaller foam fractionator are smaller which would improve their removal capacity due to being more stable and having a greater surface area to volume ratio (Pagureva et al. 2016).

We are also currently investigating options to changing the plumbing in the DPIRD hatchery to supply broodstock tanks with water from Bore #2. This plumbing change will enable us to confirm whether we can achieve 100% removal of PFOAs using this large foam fractionator, (as was achieved with the small foam fractionator) and to deliver the lowest possible concentration of PFOS into the broodstock tanks.

Figure 4: Percentage (%) PFOAs removal (\sum PFAS) vs fractionate flow rate (L/h) at HRT of 10 – 14 minutes (data labels show %fractionate rate) in Bore #1 (inlet concentration 25 ng/L)

Ziltek RemBind[®]

The filtration media RemBind[®]; developed by Ziltek Pty Ltd, is an adsorbent for the remediation of contaminated soil and groundwater. The product binds permanently to contaminants preventing them from leaching and causing environmental harm. Since 2011, RemBind[®] has been used commercially to treat a wide variety of organic contaminants including PFASs, TPH, PAH, pesticides, herbicides and mercury. The product has been successfully applied in USA, Europe and Australia.

<u>Trial 1</u>

DPIRD's investigations into the use of RemBind[®] for PFAS removal started by testing its removal capacity in static water.

Six x 500 mL samples from DPRID's Bore #1 (high PFAS bore) were collected on the 17th December 2018 into glass beakers. RemBind 200[®] powder was added to these water samples at three inclusion rates, 0% (i.e. control), 0.1% and 1% w/v, with each inclusion rate tested in duplicate. A magnetic stirrer bar was added to each beaker and the samples stirred for 1 hour. Samples were then filtered through 40 μ m GFC filter papers and collected into PFOA sample bottles. Samples were sent to ALS for PFAS super trace analysis.

The results of this trial are detailed in Table 5 and demonstrate that the RemBind 200[®] powder removed all PFAS analytes to below detectable limits at 1% addition. The addition of 0.1% RemBind[®] removed all PFASs to below detectable limits in one replicate. In the second replicate PFOS and PFHxS (i.e. the most abundant compounds) were still detected, albeit at very low levels and with >90% reduction relative to the control.

<u>Trial 2</u>

Following the positive results obtained in Trial 1, Trial 2 was designed to test the removal capacity of Ziltek's Aquagate (matrix) + RemBind[®] in a small-scale, flow-through system designed to replicate the conditions of a largescale filter capable of removing PFASs from hatchery intake water. Aquagate + RemBind[®] is the aforementioned RemBind 200[®] powder adhered to a solid matrix thereby allowing the RemBind[®] to be housed in a filter. The system designed and built for this purpose by DPIRD is shown in Figure 12.

Table 5:

PFOA analytes in ACAAR Bore #1 samples treated with RemBind 200[®] powder at two inclusion levels.

	Control (0% inclusion)		Rembir	nd 0.1%	Rembind 1%	
	Rep 1	Rep 2	Rep 1	Rep 2	Rep 1	Rep 2
– Perfluoroalkyl Sulfonic Acids						<u> </u>
Perfluorobutane sulfonic acid (PFBS)	0.0019	0.0018	<0.0005	<0.0005	<0.0005	<0.0005
Perfluoropentane sulfonic acid (PFPeS)	0.0013	0.0014	<0.0005	<0.0005	<0.0005	<0.0005
Perfluorohexane sulfonic acid (PFHxS)	0.0181	0.0195	0.0011	<0.0005	<0.0005	<0.0005
Perfluoroheptane sulfonic acid (PFHpS)	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Perfluorooctane sulfonic acid (PFOS)	0.0118	0.0112	0.0005	<0.0003	<0.0003	<0.0003
Perfluorodecane sulfonic acid (PFDS)	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Perfluoroalkyl Carboxylic Acids						
Perfluorobutanoic acid (PFBA)	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Perfluoropentanoic acid (PFPeA)	0.0020	0.0023	<0.0005	<0.0005	<0.0005	<0.0005
Perfluorohexanoic acid (PFHxA)	0.0044	0.0045	<0.0005	<0.0005	<0.0005	<0.0005
Perfluoroheptanoic acid (PFHpA)	0.0012	0.0012	<0.0005	<0.0005	<0.0005	<0.0005
Perfluorooctanoic acid (PFOA)	0.0013	0.0012	<0.0005	<0.0005	<0.0005	<0.0005
Perfluorononanoic acid (PFNA)	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Perfluorodecanoic acid (PFDA)	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Perfluoroundecanoic acid (PFUnDA)	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Perfluorododecanoic acid (PFDoDA)	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Perfluorotridecanoic acid (PFTrDA)	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Perfluorotetradecanoic acid (PFTeDA)	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Perfluoroalkyl Sulfonamides						
Perfluorooctane sulfonamide (FOSA)	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
N-Methyl perfluorooctane sulfonamide (MeFOSA)	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
N-Ethyl perfluorooctane sulfonamide (EtFOSA)	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
N-Methyl perfluorooctane sulfonamidoethanol (MeFOSE)	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
N-Ethyl perfluorooctane sulfonamidoethanol (EtFOSE)	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
N-Methyl perfluorooctane sulfonamidoacetic acid (MeFO	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
N-Ethyl perfluorooctane sulfonamidoacetic acid (EtFOSA	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
(n:2) Fluorotelomer Sulfonic Acids						
4:2 Fluorotelomer sulfonic acid (4:2 FTS)	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
6:2 Fluorotelomer sulfonic acid (6:2 FTS)	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
8:2 Fluorotelomer sulfonic acid (8:2 FTS)	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
10:2 Fluorotelomer sulfonic acid (10:2 FTS)	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
PFAS Sums						
Sum of PFAS	0.0420	0.0431	0.0016	< 0.0003	< 0.0003	<0.0003
Sum of PFHxS and PFOS	0.0299	0.0307	0.0016	<0.0003	< 0.0003	<0.0003
Sum of PFAS	0.0407	0.0417	0.0016	<0.0003	<0.0003	<0.0003

Figure 12: Experimental system for testing PFOA removal efficiency of Aquagate[®] + RemBind[®] housed in cartridge filters

Water was pre-filtered with a 1 µm cartridge in an FSI X100 filter housing. It then upwelled through two x 4" canister filter housings, each containing 3 kg of Aguagate + REMBind. The outlet flow rate on each canister was controlled by a needle valve (Genebre 2225) and the flow rate and total flow was measured using a Meister DHGF-2 impeller flow meter and RedLion CUB5 electronic counter. Flow rates for the two filters were set at 50 and 300 mLmin⁻¹ to provide hydraulic retention times of 30 minutes and 10 minutes, respectively as recommended by Ziltek. Once a week for 11 weeks, water was sampled from the common inlet of the two filters (i.e. untreated Bore #1 water) and the outlet of each filter. Samples were analysed by ALS for the 28 analytes detailed in Table 5. 14 shows the sum of all PFOA compounds in the inlet and outlet flows over time and 15 shows the % removal of all PFAS compounds at the two flow rates relative to the inlet water concentration on that day. The Bore #1 inlet concentrations ranged from 19.2 ng/L to 34.6 ng/L with an average of $27.2 \pm 1.1 \text{ ng/L}$ (S.E., n = 11), similar to the concentrations measured in the year prior (Figure). Removal efficiency was always greater in the low flow canister. After 1 week, removal efficiency in the low and high flow filters were 100% and 90%, respectively. However, there was a trend of declining removal efficiency over time recorded, with the low flow and high flow filters removing 36% and 16% of all PFASs, respectively, at week 11 (Figure 14).

Therefore, despite being highly effective at removing PFOA compounds from static water, the Aquagate + RemBind filter media lost efficiency too quickly to be considered a viable filtration media for commercial-scale hatchery operations. Furthermore, the slow hydraulic retention time required for high removal efficiency would necessitate a very large filter to process commercial quantities of hatchery water. Frequent replenishment of large quantities of filter media would be required to maintain low levels of PFOAs in the outlet water and this would be costly and labour intensive.

Figure 13: $\sum PFAS (ng/L)$ in Bore #1 and in the outlet of Aquagate[®] + RemBind[®] filters at two flow rates.

Figure 14: Percentage (%) PFASs removal (∑PFAS) over time by Aquagate[®] + RemBind[®] filters at two flow rates relative to the inlet concentration (Bore #1)

Conclusions and Recommendations

Ideally, PFAS remediation technology for aquaculture should be simple to adapt, easy to operate and should avoid recurring costs. Our trials at two facilities demonstrated that commonly available foam fractionation systems, using either air or ozone could remove more than 90% of PFOS and PFOA in "spiked" or contaminated seawater, while producing a small volume of contaminated fractionate fluid. Many aquaculture facilities already have foam fractionation systems and may already unknowingly be benefitting from contaminant removal. Regardless the systems are readily available, simple to install and scalable to meet water treatment needs.

The research highlighted several variables affecting the efficiency of foam fractionation in PFAS removal, notably gas flow rates and vacuum pressures, water flow rates, hydraulic retention time and fractionate flow rates. These varied with the systems tested here and will vary with other commercial units. However, some guidance can be gained for the operation of all systems from the results obtained in these trials. Nonetheless, further work beyond the scope of this brief study could be undertaken to more clearly define the impacts of each of these variables.

Two gas sources were tested for fractionation, ozone and air. While both were effective, higher concentration factors were achieved with ozone and its efficiency is known to increase with increasing contamination. Ozone may also be beneficial where certain forms of contamination occur. In recirculating systems using feeds high in lipid, foam formation can be impeded. Ozone can degrade the lipids to maintain system performance. The use of ozone in aquaculture systems does, however, require care. In these trials, the ORP levels within the ozofractionation chamber were controlled at around 750mV. Further investigation of the necessary ORP for pre-treatment of hatchery influent water compared to recirculation ozofractionation is warranted to avoid creating dangerous residual ozone levels within the recirculation systems of the aquacultural facilities.

The use of adsorbent media was also assessed in this project. RemBind 200[®] powder was shown to be capable of removing all PFAS analytes to below detectable limits when added to contaminated seawater. However, when used within a filter matrix, PFAS removal efficiency declined over time and lost efficiency too quickly to be considered a viable filtration media for commercial-scale hatchery operations.

At both the PSFI and ACAAR, the water treatment process currently returns the fractions to the source (marine), which may not be an issue for uncontaminated water. However, if experimentation is planned where PFASs are to be added to water to test aquatic impacts, modifications will be required. One approach would be to store and dispose of the contaminated fraction, but volumes could be high, and disposal could be costly. It is possible that the fraction could be further concentrated by additional fractionation stages or dehydrated to reduce volume before disposal for destruction. Depending on the concentration present in the fractions secondary reconcentration followed by sequestration into media and safe disposal may be viable. Adsorbent media such as RemBind 200[®] may be useful for sequestration of PFASs from a fluid fractionate before disposal or it may be considerably more convenient for treating small volumes of PFAS contaminated seawater that could arise from experimental trials. Further work would be needed at individual sites to investigate this option.

Implications

These trials have allowed the PSFI and ACAAR to respond to an immediate threat to their ongoing operations. Critically it has provided both institutions with a means of protecting their broodstock fish populations that are used to support industry development. Many of these fish are highly valued as they can be difficult to acquire and can take years to acclimate to capture. Some stock has been genotyped and others are the early generations for selective breeding programs.

Beyond providing the basis for numerous ongoing research programs (including current or proposed FRDC projects), fish stocks held at both institutions feed industry development, with commercial quantities of YTK and Mulloway fingerlings having been supplied to farms. Significant quantities of fingerlings have also been supplied to recreational restocking programs.

Although this study was low-cost and brief and has highlighted a range of variables for further assessment, it does offer a simple, practical approach to the problem of PFAS contamination for the aquaculture industry. As the list of contaminated sites grows and the public becomes increasingly aware of the dangers of PFASs, more industry participants will be required to respond to threat to either protect their stock or protect against the perception that their stock have been contaminated.

Extension and Adoption

The outcomes of this research were directly applicable at both the ACAAR and the PSFI and changes have been made to the water treatment facilities at both locations.

Based on the results of these trials, ACAAR have made the decision to implement large scale foam fractionation over physical adsorption media on the inlet water to their broodstock systems. Foam fractionation was very easy to install and integrate with the current hatchery systems. There are no ongoing maintenance costs associated with foam fractionation and the operating costs associated with the pumps driving the venturis are minimal. The costs associated with the installation of the foam fractionation were therefore highly favourable against the alternative methods of physical adsorption media, which would have required many filter vessels, pre-filtration to prevent blockage of the media and regular replacement of the media.

At the PSFI, seawater supplies to the site for aquaculture purposes are being consolidated to one location on-site, where foam fractionation can be applied to all incoming estuarine seawater supplies.

The NSW Aquaculture Research Advisory Committee have been regularly informed of project progress. To ensure broader extension, all aquaculture permit holders in NSW are to be advised of the outcomes of the report via coverage in the NSW Aquaculture newsletter and all hatcheries and marine farms in Western Australia will be similarly advised.

Upon approval of this Final Report, the authors will ensure direct distribution to all participants in the Yellowtail Kingfish industry.

The leads in this project are currently working toward peer-reviewed publication of the outcomes of this short study and are looking for opportunities to present the work at an appropriate national/international conference.

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