

Accurately forecasting the extra treatment cost associated with removal of lesser regulated PFAS species in water.

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Abstract

Per-and poly-fluoroalkyl substances (PFAS) are a group of recalcitrant, man-made, fluorinated molecules. PFAS contamination is commonly associated with Aqueous Film Forming Foam (AFFF) manufacture and application. Since PFAS contamination was first discovered in water supplies, associated regulation has been constantly changing. Historically, the main molecules of concern were PFOS and PFOA, with PFHxS garnering more attention shortly after. It happens that these three molecules are considered long-chain PFAS molecules and as such are some of the easiest, and therefore cheapest, commonly encountered PFAS molecules to remove from water. However, there are thousands of other (some currently undetectable) PFAS molecules that exist, many of which are currently less or unregulated. Regulation will continue to change as more research is done on the toxicity of individual molecules and associated families. As a complication, poorly understood and modelled degradation pathways exist for PFAS, meaning water free of specific molecules at the time of discharge may, in future, have detections. Regulators perceive this risk differently, and as such, human health and environmental guidelines drastically differ across local, state, and national borders.

The global PFAS remediation market is estimated to be worth over \$80 billion over the next five years (EBJ, 2019), with the Australian Defence Force spending over \$505 million on their PFAS contamination response since 2015 (ADF, 2021). For the mining and infrastructure sectors, PFAS remediation is often triggered by new developments requiring environmental impact assessments or investigation into water reuse, discharge and dewatering activities. These sectors find themselves operating across multiple regulatory environments and, as a result, managing legacy PFAS contamination (usually a cocktail of both regulated and less/unregulated PFAS molecules) in significantly different ways. The risk associated with the discharge of water contaminated with less/unregulated variants is typically well quantified by legal and environmental departments, but to implement successful long-term PFAS remediation strategies management teams also need the extra cost to be quantified.

The most common technologies for ex-situ remediation of PFAS contaminated water is the use of both adsorptive filter media such as Granular Activated Carbon (GAC) and ion exchange (IX) media in a conventional water treatment plant (WTP). This research investigates long-term breakthrough trends for PFAS families and individual PFAS molecules at different stages of treatment within PFAS WTPs. Total Oxidizable Precursors (TOPA) and carboxylic acids families are the focus, with data sets gathered from two different industrial scale WTPs designed, built, and operating in Australia. Despite both WTPs utilising adsorptive media and IX media as the primary treatment technology, each WTP is significantly different (low vs high flowrate, heavy vs trace influent contamination). However, similar trends of breakthroughs and, therefore, cost increases to manage lesser/unregulated PFAS molecules can be seen.

The first case study is a historical fire training ground operational from 1973 to 2015, when it was closed for remediation. This site was typical of hotspot/source contamination, with surface water concentration levels ranging to as high as $600\mu\text{g/L}$ for sum of PFAS, and $685\mu\text{g/L}$ for TOPA. The historical use of old-age AFFFs resulted in the majority of the PFAS compounds being in the sulfonic acid family, with 50.88% being (n:2) fluorotelomer sulfonic acids, 32.54% being sulfonic acids, 16.57% being in the Carboxylic acid family, and only 0.01% being Sulfonamides. Despite the national guidelines only regulating PFOS, PFOA and PFHxS, the Environmental Protection Licence (EPL) issued by the Environmental Protection Authority (EPA) required the treated water to be below $0.002\mu\text{g/L}$ for all PFAS molecules and TOPA that can be determined in Australian National Association of Testing Authorities (NATA) accredited laboratories. The WTP for this project operated at a flow rate of 5.8L/s with a maximum instantaneous flow rate of 8L/s and treated around 80ML of contaminated surface water on-site over a 12-month period. A block flow diagram outlining the WTP process flow can be seen in *figure 01*.

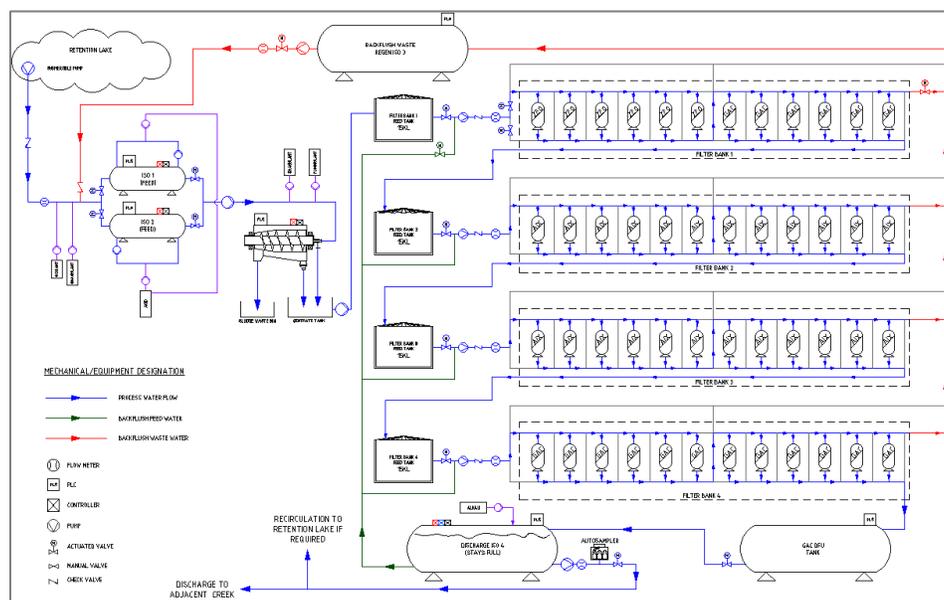
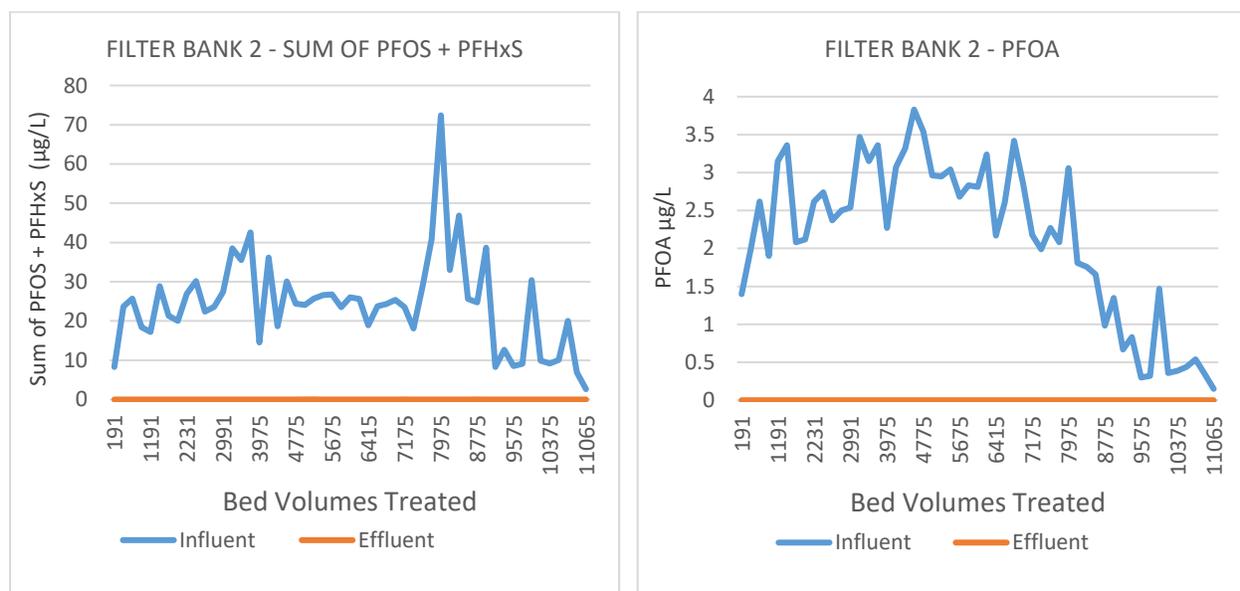


Figure 1 – Block Flow Diagram of the Case Study 01 Water Treatment Plant

The regulated PFAS molecules (PFOA, PFHxS and PFOS) at this site were removed entirely from the process water after filter bank 02, as seen below in *graph 01*. If this site was regulated in accordance with the national guidelines, we could remove every treatment stage after filter bank 02 and could most likely replace four (4) of the AIX filters in filter bank 02 with Granular Activated Carbon (GAC), which is a significantly cheaper adsorptive media. This simplification of the process flow would result in cost saving of over \$460,000.00 in initial procurement alone for this project. To compare the cost of design, procurement, installation, commissioning, operation, maintenance and then demob post completion of the project, the cost of this project was \$0.054/L of water treated. Whereas the cost to treat to only the regulated PFAS compounds would only be \$0.045/L of water treated.

The GAC from filter bank 01 was replaced after 8,000 bed volumes (BV) of water was treated (as can be seen from the drop in influent concentration to filter bank 02 below) and the IX media in filter bank 02 was showing evidence of dumping short chain carboxylic acids after 11,000 BV. Assuming 65% recovery of IX media capacity after caustic brine regeneration and two successful regenerations before requiring new IX media, if this project was to continue long-term (1,000ML) the cost for each system would be adjusted to \$0.0365/L for the treatment of regulated PFAS compounds, and \$0.0378/L for the treatment of full-suite PFAS and TOPA compounds. Showing a much lower disparity than the short-term treatment costs.



Graph 1 – Sum of PFOS & PFHxS, and PFOA from filter bank 02

The second case study is a mine site located in Australia with no evidence of source contamination with only low-level PFAS concentrations present in surface water runoff. However, due to the site residing in a drinking water catchment, the WTP was required to remove PFAS contamination down to below super ultra-trace (SUT) levels (below 0.0002µg/L) for all 28 PFAS compounds. This criterion guarantees

adherence to the 99th percentile level of ecological protection under the Australian and New Zealand Environment and Conservation Council (ANZECC) guidelines for discharge to the environment. The WTP operates at a flow rate of 20L/s with a maximum instantaneous flow rate of 29L/s and has currently treated 355ML of contaminated surface water over the last 16 months. A block flow diagram outlining the WTP process flow can be seen in *figure 02*.

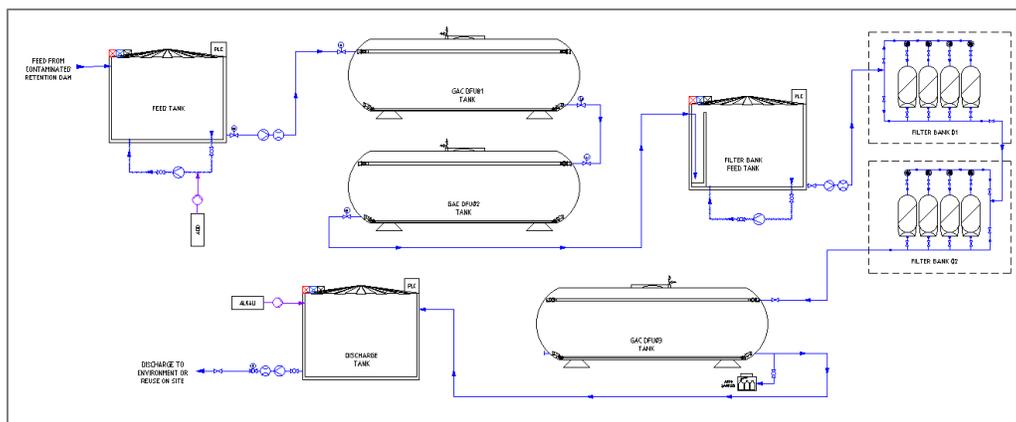


Figure 2 – Block Flow Diagram of the Case Study 02 Water Treatment Plant

The sum of PFAS influent concentration for this project is quite low, with an average concentration of 0.36 μ g/L. However, the distribution of PFAS compounds makes the treatment much more complex, with 43.20% of the PFAS compounds being in the Carboxylic acid family, 56.37% being (n:2) fluorotelomer sulfonic acids, and 0.43% being sulfonic acids. In addition, with the majority of the carboxylic acids present having 7 carbons or less (98.49% of Carboxylic acids present), the removal of these short-chain compounds down to a SUT via GAC adsorption alone would be incredibly difficult even with large volumes of media.

Results show that regulated PFAS molecules at this site are removed to below SUT levels after filter bank 01. However, the majority of these compounds are removed in earlier stages, with 88% of the removal occurring in the DFU01 and DFU02. At the time this paper was written, filter bank 01 hadn't discharged any regulated PFAS molecules after 355ML of treatment. However, unregulated molecules started to break through filter bank 01 after 140ML of treatment and from filter bank 02 after 270ML, with the WTP currently offline for the replacement of all filter media in order to continue treating all PFAS down to SUT.

If this project only required treatment of regulated compounds to super ultra-trace levels, not only could we remove every treatment stage after filter bank 01 but we wouldn't need to replace any media, or at least not the AIX resin, for roughly another 50-70ML. The simplification of the process alone would result in a cost-saving of over \$327,00.00 in initial procurement. The overall cost of this project so far has been \$0.008/L of water treated compared to \$0.007/L to treat only the regulated compounds down to SUT. Comparing treatment models with long-term treatment (1,000ML) the costs would be adjusted to \$0.0078/L for the treatment of full-suite PFAS and \$0.0061/L for the treatment of regulated compounds.