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Removal of PFOS, PFOA and other perfluoroalkyl acids at water reclamation plants in South East Queensland Australia

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ABSTRACT

This paper examines the fate of perfluorinated sulfonates (PFSAs) and carboxylic acids (PFCAs) in two water reclamation plants in Australia. Both facilities take treated water directly from WWTPs and treat it further to produce high quality recycled water. The first plant utilizes adsorption and filtration methods alongside ozonation, whilst the second uses membrane processes and advanced oxidation to produce purified recycled water. At both facilities perfluorooctane sulfonate (PFOS), perfluorohexane sulfonate (PFHxS), perfluorohexanoic acid (PFHxA) and perfluorooctanoic acid (PFOA) were the most frequently detected PFCs. Concentrations of PFOS and PFOA in influent (WWTP effluent) ranged up to 3.7 and 16 ng L^{-1} respectively, and were reduced to 0.7 and 12 ng L^{-1} in the finished water of the ozonation plant. Throughout this facility, concentrations of most of the detected perfluoroalkyl compounds (PFCs) remained relatively unchanged with each successive treatment step. PFOS was an exception to this, with some removal following coagulation and dissolved air flotation/sand filtration (DAFF). At the second plant, influent concentrations of PFOS and PFOA ranged up to 39 and 29 ng L^{-1}. All PFCs present were removed from the finished water by reverse osmosis (RO) to concentrations below detection and reporting limits (0.4–1.5 ng L^{-1}). At both plants the observed concentrations were in the low parts per trillion range, well below provisional health based drinking water guidelines suggested for PFOS and PFOA.

1. Introduction

1.1. Perfluorinated alkyl compounds

Perfluorinated alkyl compounds (PFCs) have received increasing attention in recent years as environmental contaminants due to their consistent detection in various environmental matrices (Giesy and Kannan, 2002), and their adverse effects in animal toxicity studies (Kennedy et al., 2004; Lau et al., 2007). The two groups given the most scrutiny to date have been the perfluoroalkyl sulfonates (PFSAs) ($C_nF_{2n+1}SO_3^-$) and the perfluorocarboxylic acids (PFCAs) ($C_nF_{2n+1}COOH$), and in particular the eight carbon members of these groups; perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA). These compounds have been produced commercially since the 1950s and used in a variety of consumer and industrial applications, including oil and water repellent surface coatings for packaging and textiles, surfactants, and aqueous fire-fighting foams (Prevedouros et al., 2006; Paul et al., 2009).

In 2009 PFOS was added to the Stockholm Convention for Persistent Organic Pollutants (Stockholm Convention, 2010). Production of PFOS and similar perfluorooctyl products was phased out in the USA and Europe 2000–2002 (OECD, 2002), however ongoing production continues elsewhere (Wang et al., 2009). Perfluorooctanoic acid and its salts continue to be used as processing agents in the manufacture of fluoropolymers but efforts have been made in conjunction with eight major PFOA manufacturers to reduce emissions from fluoropolymer manufacturing facilities by 95% of 2000 levels by 2010. A complete phase-out is sought by 2015 (USEPA, 2009).

In Australia there is no record of PFCA or PFSA manufacture and importation and use has been discouraged by the National Industrial Chemical Notification and Assessment Scheme (NICNAS, 2007, 2008). Despite this, there is potentially still a large stockpile of PFC containing products in inventories and personal ownership in Australia (e.g. PFC treated carpets). Additionally a large range of

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products may contain PFCAs and PFSAs as residual impurities from their manufacture (Washington et al., 2009), others still may contain compounds which may degrade to form these in the environment or metabolically (Vestergren et al., 2008). Pooled serum data from the general Australian population showed mean concentrations of PFOS and PFOA at 15 and 6.4 ng mL^{-1} respectively (Toms et al., 2009), comparable to those observed internationally (e.g. Calafat et al., 2007). Pharmacokinetic modeling of these concentrations has suggested that Australians are exposed to approximately 100 ± 37 and 54 ± 15 ng d^{-1} PFOS and PFOA respectively (Thompson et al., 2010), with currently no data describing the specific pathways responsible for these estimated intakes.

Studies of PFCs in primary and secondary wastewater treatment have shown them to be inefficiently removed (Sinclair and Kannan, 2006; Loganathan et al., 2007), and in some cases increasing in effluent relative to influent (Schultz et al., 2006; Sinclair and Kannan, 2006). Consequently, WWTP discharges have been shown to be point sources of these compounds to the aquatic environment. The limited efficiency of secondary water treatment technologies has meant that PFCs have been detected in finished tap water from various countries at parts per trillion ranges, often at concentrations similar to those in the source waters (Mak et al., 2009; Quinones and Snyder, 2009). Some success has been reported utilizing activated carbon for removal (e.g. Ochoa-Herrera and Sierra-Alvarez, 2008), but there are factors such as contact time and adsorption capacity which need to be considered in adopting this method. In studies on more advanced water treatment processes, a number of novel destruction techniques have been shown to be successful, such as sonochemical degradation (Cheng et al., 2008) and oxidation with persulfate radicals (Hori et al., 2005). Laboratory studies of rejection across nanofiltration and reverse osmosis membranes have demonstrated up to 99.9% removal of most PFCs studied (Tang et al., 2006; Steinle-Darling and Reinhard, 2008). Although there is information available on the response of PFCs to specific treatment processes, relatively little has been published on the fate of PFCs in actual full scale reclamation plants under operational conditions.

In South East Queensland, a generally dry climate and increasing demands on water resources has prompted the construction of several advanced water treatment facilities. The aim of these facilities is to reclaim treated wastewater by further treatment, producing purified water of a high quality standard for use in industrial and commercial processes. This helps mitigate the environmental impacts associated with discharge of WWTP effluent, and also provides potential resources to supplement potable supplies if necessary in the future. This study aims to assess the effectiveness of two water reclamation plants using different types of advanced treatment approaches with regards to PFC removal under normal operating conditions. The PFCs studied were the C_4–C_{18} PFCAs, and the C_4, C_6, C_8 and C_{10} PFSAs.

1.2. Water reclamation plants

The two plants studied use contrasting methods, but share the aim of producing high quality purified recycled water. Schematics of both facilities, detailing the sequence of treatment steps are provided as Fig. 1 (Plant A) and Fig. 2 (Plant B). Plant A takes secondary effluent from a single WWTP, designed to service up to 40 000 EP (equivalent persons), as its influent. It produces up to 8 ML d^{-1} of recycled water for industry consumers and for public irrigation and non-potable household usage (toilets, irrigation) in a dual reticulation system. It is not used to supplement potable supplies at present, but was designed to meet potable standards. Treatment consists of de-nitrification, several stages of ozonation, coagulation/flocculation, dissolved air flotation and sand filtration (DAFF) and biologically activated carbon filtration (see Fig. 1).

At the time of sampling Plant B received effluent from 4 WWTPs, each taking predominantly residential sewage and designed to serve 30 000–185 000 EP. The plant has a 66 ML d^{-1} production capacity, and at sampling was producing approximately 40 ML d^{-1} purified water. Treatment at Plant B consists of coagulation/flocculation and sedimentation, then ultra-filtration (UF), reverse osmosis (RO), advanced oxidation (H_2O_2 + UV) and final stabilization and disinfection (see Fig. 2). The finished reclaimed water is piped to industry users including two power stations, which use it as process water. Plant B is also designed to provide water to a nearby dam for indirect potable reuse, if dam levels drop below 40%. The reverse osmosis concentrate (ROC) or brine is further treated to remove nutrients before being discharged into a nearby river. Generally at Plant B contaminants removed by RO are concentrated almost 7-fold, with typically 85% of water permeating the membrane and 15% going to ROC.

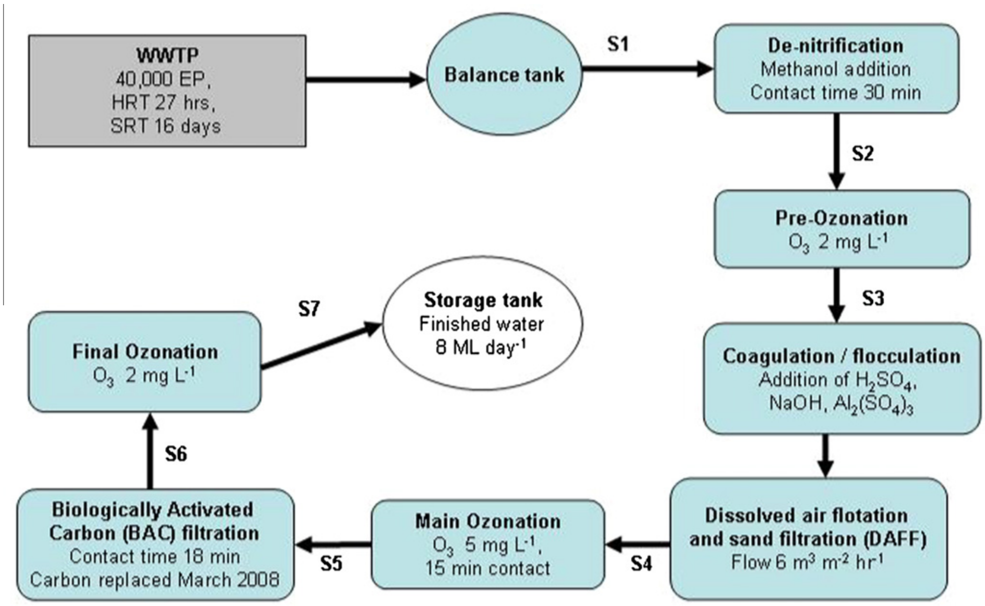

Fig. 1. Schematic of Plant A, with sampling points marked S1–S7. Note: SRT = sludge residence time, HRT = hydraulic residence time, EP = equivalent persons.