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Occurrence and source characterization of perfluorochemicals in an urban watershed

Viet Tung Nguyen [a,*], Martin Reinhard [b], Gin Yew-Hoong Karina [c]

[a] School of Civil and Environmental Engineering, N1, 50 Nanyang Avenue, Singapore 639798, Singapore
[b] Department of Civil and Environmental Engineering, Yang & Yamasaki Environment & Energy Building, 473 Via Ortega, Stanford University, Stanford, CA 94305, USA
[c] Division of Environmental Science and Engineering, Faculty of Engineering, National University of Singapore, 1 Engineering Drive 2, Blk E1A #02-19, Singapore 117576, Singapore

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ABSTRACT

Perfluorochemicals (PFCs) are used in numerous applications, mainly as surfactants, and occur ubiquitously in the environment as complex mixtures. This study was undertaken to characterize the occurrence and sources of commonly detected PFC compounds in surface waters of the Marina catchment, a watershed that drains an urbanized section of Singapore. Of the 19 target PFCs, 13 were detected with perfluorooctanoic acid (PFOA) (5–31 ng L^{-1}) and perfluorooctane sulfonate (PFOS) (1–156 ng L^{-1}) being the dominant components. Other compounds detected included perfluoroalkyl carboxylates (C7–C12) and perfluoroalkyl sulfonates (C6 and C8). Sulfonamide compounds detected 2-(N-ethyl-perfluorooctanesulfonamido) acetic acid (N-EtFOSAA), 2-(N-methylperfluorooctanesulfonamido) acetic acid (N-MeFOSAA), perfluorooctanesulfonamido acetic acid (FOSAA) and perfluorooctanesulfonamide (FOSA) were putative transformation products of N-EtFOSE and N-MeFOSE, the N-ethylated and N-methylated ethyl alcohol derivatives, respectively. Surface water concentrations were generally higher during dry weather than during storm water flow: the median concentrations of total PFCs in dry and wet weather were 57 and 138 ng L^{-1} compared to 42 and 79 ng L^{-1}, respectively, at Stamford and Alexandra canal, suggesting the presence of a continuous source(s) which is subject to dilution during storm events. In rain water, median concentrations were 6.4 ng L^{-1}, suggesting rain contributed from 12–25% to the total PFC load for non-point source sites. The longitudinal concentration profile along one of the canals revealed a point source of sulfonated PFCs (PFOS), believed to originate from aqueous film-forming foam (AFFF). Sources were characterized using principal component analysis (PCA) and by plotting PFHxS/PFOA against PFOS/PFOA. Typical surface waters exhibit PFOS/PFOA and PFHxS/PFOA ratios below 0.9 and 0.5, respectively. PCA plots reveal waters impacted by “non-typical” PFC sources in Alexandra canal.

1. Introduction

Perfluorochemical (PFCs) surfactants are persistent, bioaccumulative, toxic, and ubiquitous contaminants and concern about their occurrence in the environment has been increasing in recent years (OECD, 2006). PFCs exhibit unique chemical properties: they are oil and water repellent, making surface active, and chemically and thermally stable (Kissa, 1994). They have been detected in all environment samples (Giesy and Kannan, 2002), including air (Stock et al., 2004), surface waters (Murakami et al., 2008; Plumlee et al., 2008), drinking water (Skutlarek et al., 2006) wastewater (Sinclair and Kannan, 2006), rain waters (Kim and Kannan, 2007), groundwater (Schultz et al., 2004) and sediment (Higgins et al., 2005). PFCs have also been found to accumulate in biota, and mammals (Giesy and Kannan, 2002), including humans (Kannan et al., 2004; Hölzer et al., 2008).

Influx into the aquatic environment occurs via three routes: (1) release of volatile PFCs into the atmosphere (Dinglasan-Panlilio and Mabury, 2006), where they are photochemically oxidized (Ellis et al., 2004), and cycling back into the hydrosphere by atmospheric precipitation; (2) discharge by wastewater treatment plants (Yu et al., 2009); (3) discharge by urban runoff contaminated by non-point sources (Murakami et al., 2009; Zushi and Masunaga, 2009), and (4) seepage from disposal and spill sites in the groundwater (Moody and Field, 1999; Moody et al., 2003). Environmental PFC sources are generally difficult to characterize because perfluorinated compounds are used in a wide variety of products and applications, are dispersed across the globe and undergo complex transformation pathways (Giesy and Kannan, 2002; Prevedouros et al., 2006), but often leading to perfluorocarboxylic and perfluorosulfonic acids corresponding to the length of their precursors. Therefore, source identification is a challenging task. In some cases, this can be addressed by knowing specific local activities and composition of samples (Moody et al., 2002; Schultz et al., 2004). In other cases, the sources of PFCs can be traced by studying the

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* Corresponding author. Tel.: +65 6790 5948; fax: +65 6791 9394.
E-mail address: nguy0062@e.ntu.edu.sg (V.T. Nguyen).

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spatial distribution of concentrations and the ratio of different components, e.g. the PFOA/PFOS (Kim and Kannan, 2007) and PFHpA/PFOA ratios (Simcik and Dorweiler, 2005). In water contaminated by aqueous film-forming foam (AFFF), the PFOA/PFOS and PFOA/6:2FtS values were ∼0.001 and 0.009, respectively (Schultz et al., 2004). Other reported PFOA/PFOS ratios include: ∼2.5 and 4.4 for lake and storm runoff water, respectively (Kim and Kannan, 2007); 1.1–100 (Lien et al., 2008) and 0.1–7041 for urban river water (Saito et al., 2004); 0.2–3.1 for wastewater (Yu et al., 2009). Concentration ratios can also be used to evaluate compound transformation (So et al., 2007; Murakami et al., 2008) and PFCs sources (Murakami et al., 2008). The behaviour of individual compounds contained in complex mixtures, such as PCBs, can be investigated using principle component analysis (PCA) (Zitko, 1989) although various factors should be considered before a conclusion is made.

Although Singapore collects wastewater in centralized treatment facilities, there is concern that contaminants from leaky sewers seep into surface waters. The release of PFCs-containing wastewater into surface waters is a potential concern (Plumlee et al., 2008). For trophic level IV avian species (wildlife that consumes organisms in equilibrium with the concentrations in water), the calculated safe water concentration for PFOS is 50 ng L^{-1} (Rostkowski et al., 2006). To our knowledge, there are no regulatory limits for PFCs in drinking water except for the state of New Jersey and the German Drinking Water Commission, which have recommended levels for PFOA of 0.04 μg L^{-1} PFOA (NJ-Guidance, 2005) and for total of PFOA plus PFOS of 0.1 μg L^{-1} (TWK, 2007), respectively.

The purpose of this study was to characterize the distribution and sources of PFC in surface waters of the Marina catchment, the largest and most heavily urbanized watershed in Singapore (Fig. 1). The Marina catchment covers approximately 1/6 of Singapore (10 000 ha), encompassing its most highly developed section with a population of approximately one million. Water quality issues are critical because runoff collected by the Marina catchment water will be sourced to augment the city's water supply. In this study, the concentrations of 19 different PFCs were determined in the five major tributaries of the Marina catchment under wet-weather (storm) and dry-weather conditions. The baseline data collected will serve as a reference for further studies on the occurrence, fate and control of PFCs in a tropical and highly urbanized environment.

2. Experimental section

2.1. Study area

The Marina reservoir was formed by the closure of a tidal barrage constructed at the mouth of Marina Bay in April 2009. The barrage was constructed to convert the estuary into a freshwater reservoir and also to prevent upstream flooding through the operation of tidal gates. From April 2009 onwards, the reservoir has been undergoing a transition from saline to freshwater conditions. The Marina reservoir receives water from five major tributaries, i.e. the Alexandra (upstream of the Singapore River), Stamford, Rochor canals, Kallang and Geylang Rivers which contribute about 20.3%, 9.8%, 7.6%, 49.1% and 9.3% water to the reservoir, respectively (Chua, 2010). A map of the Marina catchment and sampling locations are depicted in Fig. 1. Sampling sites were selected to characterize the inputs into the Marina reservoir. The data reported here were collected before the actual closure of the barrage (April 2009).

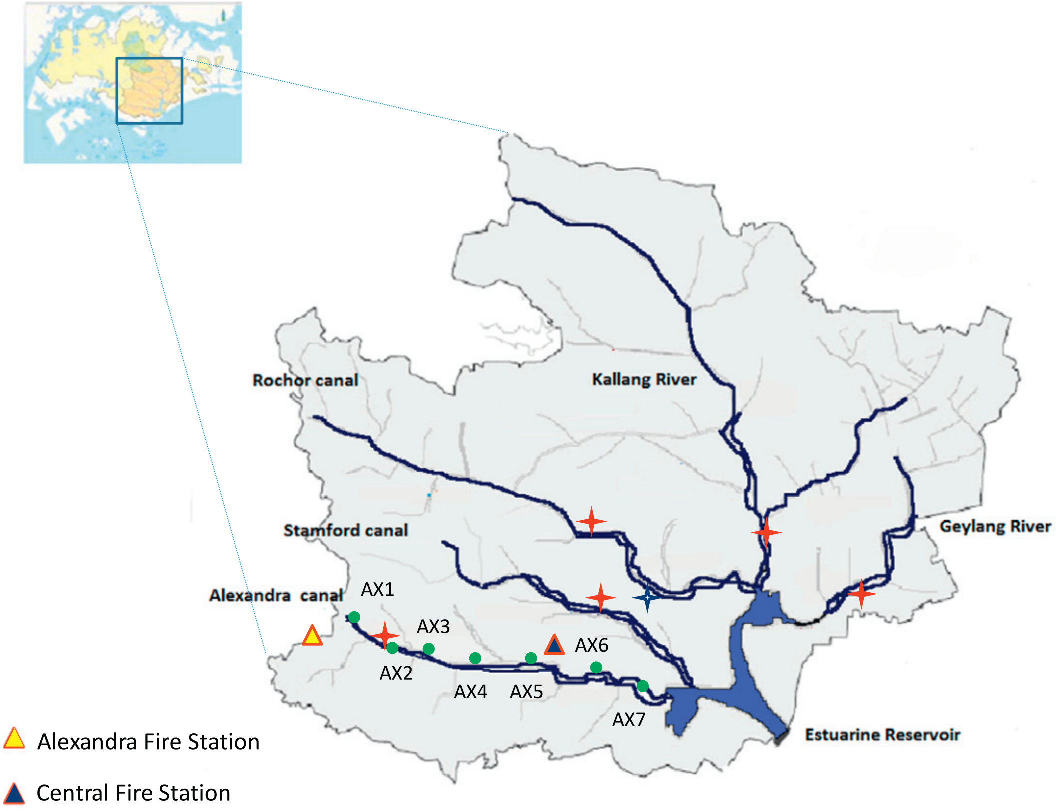

Fig. 1. Sampling map of the Marina catchment. Four point stars and dots depict sampling locations of the five streams across the catchment and along Alexandra canal, respectively.