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**OCCURRENCE AND PHOTOCHEMICAL FATE OF
PERFLUOROCHEMICALS IN A TROPICAL URBAN
WATERSHED**

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Abstract

The rapid development and urbanization have raised concern on water quality issues in cities worldwide. Urban water bodies receive discharges from point and non-point sources which may contain micro organic pollutants some of which are environmentally persistent and likely to cause harm to aquatic organisms as well as human health when they are present in drinking water. Singapore like many densely populated regions, relies on natural and constructed water catchments across the country which are potentially exposed to various contamination sources. The presence of emerging organic constituents and their potential impacts on ecosystem and human health is thus of concern and the public water management authorities.

The present study focuses on the occurrence and source characterization of a group of persistent organic contaminants, perfluorochemicals (PFCs), in a watershed that drains an urbanized section of Singapore. Samples were collected at five canals and rivers around the Marina catchment including dry weather surface water and storm runoff during rain events. Although there are no direct discharges of wastewater, 13 out of 19 target PFCs were detected in dry-weather surface water from the rivers and canals. Perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS) are dominant contaminants with concentrations ranging from 5-31 and 1-156 ngL⁻¹, respectively among other constituents including perfluoroalkyl carboxylates (PFCAs, C7-C12), perfluoroalkyl sulfonates (PFSAs, C6 and C8) and perfluoroalkyl sulfonamides (PFSAMs, C8). Results indicated that rain water may have contributed from 12-25% of the total PFC load for non-point source sites. The longitudinal concentration profile along one of the canals revealed a localized source of sulfonated PFCs (PFOS) believed to originate from aqueous film-forming foam (AFFF). Depth profiles of salinity indicated that the receiving water body, Marina reservoir, was stratified, with lower layers consisting of seawater and a brackish surface layer. Storm runoff carries high concentrations of suspended solids (SS), which suggests that PFC transport is via SS. In sediments, the total PFC concentration was 4700 ng kg⁻¹, approximately 200 times higher than in the bottom water layers including some undetectable PFCs in aqueous phase. Total PFSAs, particularly PFOS and 6:2 fluoro telomer sulfonate (6:2 FtS) were dominant PFCs in the sediments. PFC sorption by sediments varied with perfluorocarbon chain length, type of functional group and sediment characteristics. A first approximation analysis based on SS transport suggested that the

annual PFC input into the reservoir was $35 \pm 12 \text{ kg y}^{-1}$. Contributions of SS, dry weather flow of river/canals, and rainfall were approximately 70, 25 and 5%, respectively.

In sunlit environments, recalcitrant organic contaminants i.e. PFCs can be transformed to the more stable forms by indirect photolysis. Aqueous solutions of selected PFCs were individually irradiated by laboratory sunlight simulator in the presence of hydrogen peroxide (H_2O_2) as the source of photochemically produced hydroxyl radical ($\cdot\text{OH}$). Using competitive kinetics with 4-tert octyl phenol (OP) as the reference compound, this study predicted the bimolecular rates for the reactions between the $\cdot\text{OH}$ and N-ethyl perfluorooctane sulfonamidoethanol (N-EtFOSE), N-EtFOSAA, N-ethyl perfluorooctane sulfonamide (N-EtFOSA) and perfluorooctane sulfonamido acetic acid (FOSAA). Photodegradation rate of N-EtFOSE decreased in alkaline solution (pH 10) compared to neutral and acidic solutions (pH 1 to pH 8) by a factor of 4. Reaction rate constants of N-EtFOSA and FOSAA were observed to be affected by the activity of amidic protons and $\cdot\text{OH}$ reduction. In sunlit environments, PFCs could be transformed to more stable metabolites and products, i.e. 38% PFOA and 3% FOSA with a total of 58% of the fluorinated products unidentified.

The photochemical degradation of N-EtFOSE and OP under simulated sunlight was expanded in the presence of nitrate, nitrite, humic acid (HA), and active and inactive algae as photosensitizers occurring in surface water. Products formed included N-EtFOSAA, N-EtFOSA, PFOA, and PFOS. Because PFOS was not observed in reactions initiated by $\cdot\text{OH}$, it is assumed that other reaction pathways might involve in the transformations. In the presence of algae, N-EtFOSE and OP irradiation in simulated sunlight led to 40% and 90% transformation for 5 h, respectively compared to insignificant photodegradation in ultrapure water. In the presence of nitrate and nitrite, N-EtFOSE showed similar bimolecular reaction rates. In the presence of HA, concentration-dependent rates of N-EtFOSE degradation were higher at higher HA concentrations. Nitrite, nitrate and HA performed as photosensitizers which accelerated the light-induced photodegradation rates of N-EtFOSE. However, adding H_2O_2 into the aqueous samples containing these constituents did not seem to enhance the N-EtFOSE photodegradation rate. This indicates that those constituents could behave simultaneously as photosensitizers and scavengers for active species. The behaviours of these constituents would provide more understanding about the fate of PFCs in natural waters.

List of publications arising from the thesis

Journal articles:

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- 2- Xu, Y.; Nguyen, V. T.; Reinhard, M.; Gin, K. Y.-H., Photodegradation kinetics of octylphenol, 4-tert-octylphenoxy-acetic acid and Ibuprofen under simulated solar conditions. *Chemosphere*. **2011** (in press, [doi:10.1016/j.chemosphere.2011.06.069](https://doi.org/10.1016/j.chemosphere.2011.06.069)).
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Chapter 1 Introduction

1.1 Emerging organic contaminants in aquatic environments

Access to safe, clean drinking water is a critical issue that most cities face at a time of rapid population expansion and unpredictable climate change. In order to deal with the scarcity of fresh water, people have resorted to utilizing all available resources, including reclamation or augmentation of used water. At the same time, rapid economic development has led to the production of numerous anthropogenic chemicals, some of which are known to have significant impacts on human and ecosystem health. These chemicals are introduced daily into the environment by either industrial or domestic activities. Many of these substances are environmentally persistent, survive conventional treatment processes, and some potentially accumulate in the food chain. To date, there is still a huge knowledge gap on the environmental behavior and impacts of emerging organic contaminants on and humans.

In Singapore, water consumption has increased dramatically with the rise in population and development. An increasingly important supply of fresh water is rain and surface runoff collected in local reservoirs. Urban catchments have been designed to collect these fresh waters for further treatment into potable water. Therefore, preserving high water quality in urban catchments and reservoirs is important in order to reduce costs of treatment. Although in Singapore wastewater effluent is not directly discharged into the watershed, there is the potential of contamination by non-point sources, such as leakage of old domestic wastewater pipelines, urban land use activities, and atmospheric precipitation. Consequently, micropollutants can be introduced into the catchment system and end up in the reservoirs which will be used for drinking water. Many of these contaminants are classified as emerging organic contaminants (EOCs). EOCs are synthetic or naturally occurring organic chemicals which are not commonly regulated and monitored in the environment but have the potential to adversely affect humans and ecosystem health. For example, current list of EOCs includes endocrine disrupting chemicals and pharmaceuticals,

brominated flame retardants, drinking water disinfection by products, algal toxins, organotins, methyl tert-butyl ether (MTBE), chiral contaminants, new pesticides and pesticide transformation products, personal care products, plasticizers, surfactants, artificial sweeteners, sunscreen-UV filters, food additives, perchlorate, antimony, musk, benzotriazoles, dioxin, siloxane, naphthenic acids and nanomaterials. While the list is building up with new contaminants, perfluorochemicals (PFCs) were selected for the current study because they are potentially toxic even at low levels, extremely refractory, and ubiquitous in the environment. The occurrence and photochemical fate of PFCs were investigated in Marina Catchment, one of the largest urban watersheds in Singapore.

1.2 Perfluorochemicals in the environment

Perfluorochemicals are composed of a diverse class of chemicals that are constituents in a wide range of industrial and consumer products including fluoropolymers; liquid repellants for paper, packaging, textile, leather, and carpet goods, industrial surfactants, additives, coating, and aqueous film forming foams (AFFF) for fire fighting (Kissa, 1994). These substances are produced by two major processes: electrochemical fluorination (ECF) and telomerization. The first method generates two major products: perfluoroalkyl carbonyl fluoride and perfluoroalkyl sulfonyl fluoride intermediates (Schultz et al., 2003b). The second process for manufacturing PFCs, telomerization, which was developed by Du Pont (Lange, 2006) involves reacting pentafluoroiodoethane with tetrafluoroethylene oligomers to yield a mixture of perfluoroalkyl iodides. These straight, even chained perfluoroalkyl iodides are used to make a variety of telomer products, including telomer alcohols (FtOHs). Generally, PFCs in the environment are composed of C₄ to C₁₈ carbons in structure (Villagrasa et al., 2006), while C₄ to C₁₃ is the typical backbone for the ECF process, in which C₈ is the most abundant constituent (Schultz et al., 2003b). The structures of PFCs demonstrate high thermal and chemical stability, high polarity and non-biodegradability with the fully fluorinated alkyl chain. The combination with functional groups makes them versatile and commercially useful surfactants.

Since the 1940s, a huge amount of PFCs has been produced and discharged to the environment. With respect to perfluorooctanoate (PFOA) related compounds, from the year 1951-2004, about 4400-8000 tons of perfluoroalkyl carboxylates (PFCAs) were produced, of which 3200-7300 tons were emitted to the environment through various pathways. About 4650 tons of perfluorooctyl sulfonyl fluoride was produced in 2000 with an emission amount of about 3700 tons (Lange, 2006; Prevedouros et al., 2006). The contribution of PFCAs is approximately 65%, 23% and 12% in water, air and land, respectively (USEPA,

2002). In terms of application, Schultz et al. (2003) reported that of the 3 million kg of PFCs produced by 3M company, 41% was coated onto paper and packaging products, 37% was used in fabric, leather and carpet goods, 10% was used as ingredients in industrial surfactants, additives and coatings and 3% was used in AFFF (aqueous film forming foam) (Schultz et al., 2003b). Therefore, through both manufacture and product use, PFCs have been found to be widely distributed in environmental and human samples, especially PFOA and perfluorooctane sulfonate (PFOS) (Boulanger et al., 2004; Saito et al., 2004; So et al., 2004; Yamashita et al., 2004; Higgins et al., 2005; Loewen et al., 2005; Moriwaki et al., 2005; Yamashita et al., 2005; Skutlarek et al., 2006; Villagrasa et al., 2006; So et al., 2007; Loos et al., 2008; Murakami et al., 2009b; Yu et al., 2009; Zushi and Masunaga, 2009; Ahrens et al., 2010; Nguyen et al., 2011c).

Two major pathways of PFCs in the environment are hydrospheric and atmospheric transport. Neutral and volatile compounds such as fluorotelomer alcohols (FtOHs) and perfluoroalkyl sulfonamides (discussed as precursors) may have been released to the air from factories, consumer products, indoor air and have potential for long-range atmospheric transport. The ubiquitous presence of airborne precursors and their products, i.e. PFOA and PFOS, indicates that PFCs are commercial PFC products are breaking down and products are dispersed globally (Shoeib et al., 2004; Martin et al., 2005; D'Eon et al., 2006; Dinglasan-Panlilio and Mabury, 2006; Scott et al., 2006; Wallington et al., 2006; Jahnke et al., 2007b). The second pathway, i.e. via hydrospheric transport, have resulted in the spread of PFCs in wastewater treatment plant effluents (Sinclair and Kannan, 2006), rivers, canals, surface runoff, suspended particulate matter (So et al., 2007; Murakami et al., 2009b; Zushi and Masunaga, 2009; Ahrens et al., 2010; Nguyen et al., 2011c), aerosols (Prevedouros et al., 2006; McMurdo et al., 2008) and oceanic currents (So et al., 2004; Yamashita et al., 2005). This has led to their occurrence even in remote regions, such as the polar ice caps. Though PFOS and PFOA are recently no longer manufactured by major global producers, their widespread distribution in the environment, humans and wildlife is still a long term concern. In order to fully understand the significance of PFCs, it is important to investigate the occurrence and fate in the environment.

1.3 Research objectives and thesis structure

The target of this study is to quantify and characterize the aqueous occurrence and photochemical fate of PFCs. Therefore, overall research objectives are followings to achieve the goal:

1. Develop sensitive analytical methods for PFCs for environmental samples including water and sediment. Another direct injection method was also adapted and developed for photochemical kinetics study.
2. Monitor PFCs occurrence in local environment including surface water, rain water, and sediments.
3. Characterize the occurrence of PFCs to figure out possible contamination sources and estimate the total load to the water reservoir.
4. Investigate the photochemical kinetics of PFCs in aqueous phase and model the photochemical fate of PFC precursors and metabolites.
5. Investigate the influence of environmental components on the degradation of PFCs.

In detail, research targets are following:

Occurrence study were to

- 1) Quantify the occurrence of PFCs in Marina Catchment surface water for both dry weather samples and storm runoff.
- 2) Characterize contamination pattern of PFCs in the surface waters of Marina Catchment.
- 3) Evaluate the depth profile of PFCs in Marina Reservoir during the transition from an estuary to a reservoir.
- 4) Study PFC distribution in sediments.
- 5) Quantify partitioning of PFCs between the water and solids.

Photochemical fate study were to

- 1) Estimate the bimolecular reaction rate constants of perfluoroalkyl sulfonamides using competitive kinetics.
- 2) Develop kinetic models for the degradation of perfluoroalkyl sulfonamides by hydroxyl radical.
- 3) Evaluate the influence of sensitizers, including nitrate, nitrite, humic acid, on the photodegradation of N-ethyl perfluorooctane sulfonamidoethanol.
- 4) Study the biotic and abiotic degradation of green-blue algae for N-ethyl perfluorooctane sulfonamidoethanol.
- 5) Estimate bimolecular reaction rate constants for these constituents in the presence of reference compound.

Following the literature review, there remains a scarcity of data with respect to the occurrence and fate of PFCs in surface waters from tropical urban environments. This thesis presents a detailed study of the occurrence of PFCs in a highly urbanized catchment in Singapore, and an understanding of their photochemical transformations in the aquatic environment. The field survey results are presented in Chapter 3 in terms of occurrence data and characteristics of surface water and runoff from rivers and canals in the Marina Catchment. Point sources and non-point sources are characterized by PFC composition patterns and correlations between pairs of individual PFCs. The catchment waters feed into Marina Reservoir, which was created by the construction of a barrage across the mouth of Marina Bay. More detailed studies of the occurrence and fate of PFCs in the reservoir are presented in Chapter 3, including an evaluation of the effect of sediments as a major sink for PFCs. A first estimation of the PFC fluxes into the reservoir provides an approximately quantitative assessment of the significance of their impact in an urban reservoir.

Chapters 5 and 6 discuss the photochemistry of PFCs in aquatic systems which have $\cdot\text{OH}$ as the typical transient photooxidant (generated from H_2O_2). Chapter 5 focuses on the determination of phototransformation rates of various PFCs using a competitive reaction approach, as well as the influence of pH. Based on kinetic data, reaction model was developed to predict the fate of N-EtFOSE by radical hydroxyl radical degradation. Chapter 6 further investigates the photochemical fate of PFCs in the presence of various natural photosensitizers, such as NO_2^- , NO_3^- , humic acid and green algae.

The data presented in this thesis contribute to our understanding of the occurrence, fate, and transport of PFCs in a typical urban watershed, and be useful for regulatory authorities to evaluate the potential impacts of PFC contamination. In addition, this information will be useful for the development of pollution prevention and treatment strategies.

Chapter 2 Literature review

Among the most prominent emerging contaminants, PFCs are unusual compounds with both hydrophobic and hydrophilic properties and they contain one of the most stable chemical bond (C-F) known in the molecules. They are characterized by unique properties of environmental persistence, bioaccumulation and ubiquity as the results of human manufacture and use. PFCs appear to be potential health concerns including developmental toxicity, cancer and bioaccumulation. Release of PFCs into the environment can occur at any time in life cycle of the products containing PFCs from the fluorochemical synthesis, incorporating fluorochemicals into products, and during product distribution, usage and disposal (3M, 2000). They reach the aquatic environment by both direct discharges to rivers or via wastewater discharge to receiving water bodies and by precipitation of air mass containing volatile PFCs and their transformation products. In aquatic system, their polarity and mobility in water and solid phase allow them to enter the sea and penetrate to groundwater in conservative conditions (Schröder, 2003). Therefore, investigation on occurrence of PFCs in various media including water, soil, sediment, biota and air has been increasingly interested. Research gaps also consider the fate of PFCs such as loss processes and deposition, relationship between sources and environmental concentrations, solid-water, air-water partitioning, transport mechanisms and, biological and photochemical transformation mechanisms. Monitoring data from different areas, partitioning coefficients transport and transformation kinetic parameters collected would help to depict a comprehensive illustration of PFCs in the environment.

2.1 Occurrence of PFCs in biological samples and in humans

PFCs have been detected in benthic algae, zooplankton, mollusks, shrimp, star fish, crab, seal, mink, albatross, bald eagle, polar bear and humans worldwide (3M, 2000; Giesy and Kannan, 2002; OEDC, 2002; Schultz et al., 2003b). In biota, various levels of PFCs have been reported in organisms of aquatic food webs from the bottom of the food chain to top invertebrates. PFOS, in particular, was found to be dominant in fish samples from fresh

and sea water. The highest PFOS level of 3250 $\mu\text{g L}^{-1}$ in the liver of the carnivorous and bottom-feed fish was detected in Japan (Taniyasu et al., 2003). It was also detected in every investigated wildlife sample in the EU, and even in the Arctic with levels ranging from several ng L^{-1} to thousands ng L^{-1} (Lange, 2006). For example, PFOS was detected in polar bear liver tissues with levels more than 1000 ng g^{-1} wet weight along with increasing levels of PFCAs in recent years (Smithwick et al., 2006). Animals around army bases and industrial zones had higher chance for animals to be exposed to elevated concentrations of PFCs, especially PFOS. The highest level of PFOS were found in birds and mammals within industrialized and terrestrial areas, and the lowest levels were seen in samples from remote areas such as Antarctica, the Arctic and open oceans. Overall, while only several species of animals have been investigated, PFOS was found to be the dominant constituent in both aquatic and terrestrial animal organs. Obviously, the higher the animal is in the food chain, the more elevated concentration of PFCs detected (e.g. polar bear, the apex predator has significant exposure from PFCs) (Houde et al., 2006b).

Literature also shows that there is ubiquitous occurrence of PFOS and PFOA in human blood and biological samples. PFOS was found in all the serum purchased in the US (18 blood banks), EU and Asia (US EPA, 1999). The levels of blood PFOS in occupational and non-occupational exposure people were in ranges of several $\mu\text{g L}^{-1}$ to tens ppb, respectively (OECD, 2002). Typical concentrations of PFOA and PFOS in the serum of non-occupationally exposed humans are 3-35 and 7-82 $\mu\text{g L}^{-1}$, respectively (Hansen et al., 2001; Kannan et al., 2004). Studies show that people from remote, industrialized and urban areas are also exposed to PFCs in the same manner. Potential sources are not only from food and water but also from indoor dust, food packaging materials and consumer products (D'eon et al., 2009; Kärman et al., 2009; D'Hollander et al., 2010). Humans have much greater concentrations of PFOA (the dominant form seen in blood samples) than wildlife (Houde et al., 2006b). To date, there is no acute toxic effect from PFOS or PFOA on humans but a high risk of cancer (potentially bladder cancer) was observed in workers in related industries with least 5 years of employment. Research on mammals revealed that high dose of PFOS and PFOA could lead to mortality or various types of cancers and adverse effects (Lange, 2006). In addition, toxicity was also enhanced when PFCs were present in a mixture (Hu et al., 2003). Currently, the US EPA (2006) has put PFOA on the list of potential cancer chemicals. However, specific evidence of chronic or acute effects has not been reported (3M, 2000; OECD, 2002; 3M, 2003).

2.2 Occurrence of PFCs in aquatic environments

A compilation of PFC occurrence in aquatic systems is tabulated in Table 2.1. In most cases, PFC precursors and their derivatives occur ubiquitously in environmental samples, with a dominance of PFOS and PFOA. Low concentrations of PFCs in air or waters were normally observed in remote and rural areas in contrast to urban and industrial areas. Fluorochemical production facilities, wastewater treatment plants and fire drill sites presented as hot spots for PFCs with overwhelming levels (Hansen et al., 2002; Moody et al., 2002; Schultz et al., 2004; Rostkowski et al., 2006; Sinclair and Kannan, 2006). Wet transformation and deposition may contribute a significant flux of PFCs to the hydrosphere although concentrations in rain waters were normally small (Scott et al., 2006; Kim and Kannan, 2007; Nguyen et al., 2011c). Flows from rivers and streams were diluted and mixed with sea water and subsequently transported PFCs to oceans (So et al., 2004; Yamashita et al., 2004; Ju et al., 2008). Sediments have been suggested to act as major sinks for PFCs (Higgins et al., 2005; Nakata et al., 2006; Becker et al., 2008; Ahrens et al., 2009a; Ahrens et al., 2010). Ultimately, the widespread occurrence of PFCs in water bodies and their low removal efficiency in drinking water have led to the presence of PFCs in drinking waters (Harada et al., 2003; Skutlarek et al., 2006; Ericson et al., 2008; Takagi et al., 2008; Mak et al., 2009). These findings raise the concern that human health may become compromised by the ubiquitous occurrence of PFCs. Occurrence studies generally focused on water, sediment or various media. Followings are some relatively comprehensive occurrence studies.

Boulanger et al. (2005) estimated mass fluxes to Lake Ontario from the distribution of PFCs in dissolved phases (from water and wastewater discharges), air-water partition and gaseous particulate phase deposition. Authors proposed an adverse assumption about the negligible sorption capacity of PFCs on sediment and particle phase according to the best knowledge of the time (Boulanger et al., 2005a). Obviously, the importance of PFC partition on sediment and particulate has not been considered properly. Later on, Higgins et al. reported one of the first detailed sorption studies of PFCs on sediments associated with significant concentrations in San Francisco Bay sediment (Higgins et al., 2005; Higgins and Luthy, 2006).

Kim et al. (2007) reported a comprehensive occurrence study for perfluoroalkyl carboxylates in various matrixes (air, rain, snow, surface runoff water and lake water). The estimated mass balance to the local lake indicated that an unknown input pathway contributing a significant amount of PFCs were possibly existed (Kim and Kannan, 2007). This suggested the important of sorption of PFCs on solid and particulate phase.

Murakami et al. (2008) analyzed aqueous PFCs in 20 rivers and 5 wastewater effluents in Japan to characterize the source. Authors indicated non sewage point sources for PFC input to the water bodies (Murakami et al., 2008). Significant contributions of long carbon chain PFCs from street runoff to water environments suggested that sorption on particulate matters could be prominent process (Murakami et al., 2009b). The wide spread of PFCs was also detected in groundwater due to the seepage and soil infiltration from street runoff and wastewater. This study showed the importance of soil-water partitioning in removal of PFCs by infiltration and source characterization (Murakami et al., 2009a).

Ahren et al. (2009) reported partitioning behaviour of PFCs between pore water and sediment in Tokyo Bay and estimated fluxes of PFCs using dry sediment concentration multiplied by the density-corrected yearly sedimentation rate (Ahrens et al., 2009b). The study was expanded to partitioning behavior between water-suspended particulate matters in three depths of the water column and water-sediment (Ahrens et al., 2010).

In general, these studies focused on more than one type of sample matrix however, there were no study covered all environmental matrixes or missing important media. Furthermore, these studies were normally conducted in open water systems with various unknown inputs compared to a highly constructed catchment in this study. Therefore, contributions of environmental media to the terminal water body were not easy to estimate.

To date, no official regulation for PFOA and PFOS or PFCs in surface water has been issued by the U.S. EPA or other countries. However, guidelines for PFOS and PFOA have been recommended for water and drinking waters as follows:

- Proposed values of Dutch water quality objective are $5 \mu\text{g L}^{-1}$ and $3.8 \mu\text{g L}^{-1}$ for PFOS and PFOA, respectively (Hekster, 2002).
- $0.5 \mu\text{g L}^{-1}$ of PFOA is applied for site-specific drinking water (near DuPont facilities in Washington) (EPA, 2006).
- Maximum acceptable levels of PFOS and PFOA for drinking water are 0.3 and $10 \mu\text{g L}^{-1}$, respectively, by UK Health Protection Agency (HPA, 2006).
- German FEA (Federal Environment Agency) proposed total concentrations of PFOS and PFOA at $0.1 \mu\text{g L}^{-1}$ for drinking water (based on life exposure, expectancy risk $< 10^{-6}$) (TWK, 2007).
- New Jersey and Minnesota recommended 0.04 and $0.5 \mu\text{g L}^{-1}$ as limits of PFOA in drinking water, respectively (Renner, 2007).

Table 2.1. Compilation of PFC occurrences in environmental samples from literature and the current study

Sites	PFOA (ng L ⁻¹)	PFOS (ng L ⁻¹)	Other homologous and metabolites	Potential sources	References
Fresh surface and ground water					
Tennessee River, AL, USA	<25 at upstream <25-513 at downstream	17-53 upstream 30-140 downstream	n.a.	Fluorochemical factory	(Hansen <i>et al.</i> , 2002)
Etobicoke Creek (Toronto, Canada)	n.d.-33 (upstream) n.d.-10,600 (downstream)	n.d. (upstream) n.d.-995,000 (downstream)	PFHxS	Spill of AFFFs	(Moody <i>et al.</i> , 2002)
Groundwater (Wurtsmith, Michigan and Tyndall, Florida Air Force Bases)	3,000-6,570,000	4,000-2,300,000	PFBS, PFHxS, 6:2FtS, 8:2FtS, 10:2FtS	Fire training exercise, AFFFs	(Schultz <i>et al.</i> , 2004)
Great Lake water	17-50	21-70	PFOSA, N-EtFOSAA, PFOSulfinate		(Boulanger <i>et al.</i> , 2004)
Iowa city, USA, WWTP effluent and river	22 (effluent) 8.7 (river)	26 (effluent) 23 (river)	N-EtFOSAA	WWTP effluent	(Boulanger <i>et al.</i> , 2005b)
Surface water (Lake Superior, Minnesota, USA; Voyageurs National Park lakes, Canada)	0.1-0.7	n.d.-1.2	PFHxA, PFHpA, PFNA, PFDA	Atmospheric deposition	(Simcik and Dorweiler, 2005)
WWTP effluent in Austria	10-21	4.5-20	PFDS, PFHxA, PFHpA, PFNA, PFDA, PFUnA, PFDoA, FOSA, N-EtFOSA	Domestic wastewater	(González-Barreiro <i>et al.</i> , 2006)
WWTPs (New York, USA)	58-1,050	3-68	PFHxS, PFNA, PFDA, PFUnDA, 8:2FTCA, 8:2FTUCA	Domestic, industrial discharges	(Sinclair and Kannan, 2006)
Rhine river and tributaries	n.d.-48	n.d.-26	PFBS, PFHxS, PFBuA, PFPeA, PFHxA, PFHpA, PFNA	Surface runoff and wastewater discharge	(Skutlarek <i>et al.</i> , 2006)
Ruhr area	n.d.-3640	n.d.-193			
Lake at Albany New York	3.27-5.18	<LOQ-9.3	PFHpA, PFNA, PFDA, PFUnA, PFDoA, PFHxS, PFDS, FOSA, 6:2FtS, 8:2FtS	Wet precipitation, unknown sources	(Kim and Kannan, 2007)
Lake, streams in Shihwa, South Korea	0.9-62	2.2-651	PFBS, PFHxS, PFHxA, PFHpA, PFDA, FOSA	Industrial emission	(Rostkowski <i>et al.</i> , 2006)
Cape Fear Basin, North Carolina, USA	<LOQ-287	<LOQ-132	PFBS, PFHxS, PFHxA, PFHpA, PFNA, PFDA, PFUnA, PFDoA	Wastewater discharge on upstream	(Nakayama <i>et al.</i> , 2007)

Table 2.1 Compilation of PFC occurrences in environmental samples from literature and the current study (continued)

Surface water (Lake Maggiore, Italy) and tap water	1.8-2.9	7.2-8.6	PFNA, PFDA, PFUnA, PFDoA	Municipal, agricultural and industrial discharges	(Loos <i>et al.</i> , 2007)
	1.0-2.9	6.2-7.9			
River and wastewater water	7.85	1.75	PFBA, PFHpA, , PFNA, PFDA		(Zhao <i>et al.</i> , 2007)
Pearl and Yangtze River, China	0.85-13	0.9-99	PFBS, PFHxS PFOSA PFHxA, PFHpA, PFNA, PFDA, PFUnA, PFDoA, PFTA, PFHxDA, PFOcDA	Urbanized, industrial effluents, fluorochemical manufacturing facilities	(So <i>et al.</i> , 2007)
Rivers from Catalonia, Spain	0.22-24.9	<0.24-5.88	PFHxS, PFHpA, PFNA, PFDA, FOSA	Not mentioned	(Ericson <i>et al.</i> , 2008)
Tsurumi Basin, Japan	13.4-15.9	179.9	PFHxA, PFHpA, PFNA, PFDA	Domestic and industrial effluents	(Zushi <i>et al.</i> , 2008)
Rivers in Japan	0.91-192	<0.1-191	PFHpA, PFNA, PFDA, PFUnA, PFDoA, PFTA	Urban activities, sewage	(Murakami <i>et al.</i> , 2008)
Reclaimed water 4 WWTPs (CA, USA)	12-185	20-187	PFHxS, PFDS, PFHxA, PFHpA, PFNA, PFDA, 6:2 FtS, FOSA, N-EtFOSAA	Domestic, industrial effluents	(Plumlee <i>et al.</i> , 2008)
Marina watershed runoff, Singapore	7.2-38.2	4.5-139	PFHxS, 6:2FtS, PFHpA, PFNA, PFDA, PFUnA, PFDoA, FOSA, FOSAA,, N-MeFOSAA, N-EtFOSAA	Point and non-point sources	<i>This study</i>
Marina watershed streams, Singapore	5.4-30.6	2.1-156.2	PFHxS, 6:2FtS, PFHpA, PFNA, PFDA, PFUnA, N-MeFOSAA, N-EtFOSAA	Point and non-point sources	<i>This study</i>
Sea and oceanic surface water					
Coastal water Hong Kong, South China, South Korea	0.24-320 (SK)	0.09-730 (SK) 0.11-3.1 (HK)	PFHxA, PFHpA, PFNA, PFDA, PFOSA	Sea currents	(So <i>et al.</i> , 2004)
Sea and ocean water, Tokyo Bay-East Pacific Ocean	192.0-0.142	0.25-0.054	PFHxS, PFBS, PFNA		(Yamashita <i>et al.</i> , 2004)
Tokyo Bay	34.8-35.1	13.5-13.7	PFBS, PFHxS, PFBA, PFPeA, PFHxA, PFHpA, PFNA, PFDA, PFUnA, PFDoA, PFTA, PFHxDA, PFOcDA, FOSA, N-EtFOSA, 8:2, 10:1, 7:1FTOH, 8:2FTCA, 8:2FTUCA	Not mentioned	(Taniyasu <i>et al.</i> , 2005)
Tomakomai Bay, Japan	62.4-63.7	2250-2880			
Dalian coastal water, China	0.17-37.55	<LOQ-0.96	n.a.	Urban and industrial discharge	(Ju <i>et al.</i> , 2008)

Table 2.1. Compilation of PFC occurrences in environmental samples from literature and the current study (continued)

Rain and wet precipitation					
Rain water, Winnipeg, Canada	n.d.	0.59	6:2, 8:2, 10:2 FTCA; 6:2, 8:2, 10:2 FTUCA;	Atmospheric transformation and deposition	(Loewen <i>et al.</i> , 2005)
Rain water, urban and rural sites in USA and Canada	<0.1-98 (urban) <0.1-10 (rural)	n.a.	PFEtA, PFPrA, PFBuA, PFPeA, PFHxA, PFHpA, , PFNA, PTCAs, PTUCAs	Degradation from telomer alcohols	(Scott <i>et al.</i> , 2006)
Rain at urban area, Albany, NY	<LOQ-7.27	LOQ-1.51	PFHpA, PFNA, PFDA, PFUnA, PFDaA, PFHxS, PFDS, FOSA, 6:2FtS, 8:2FtS	Atmospheric oxidation and transport	(Kim and Kannan, 2007)
Marina Catchment, Singapore	0.6-1.3	1.1-7.9	PFHxS, 6:2FtS, PFHpA, PFNA, PFDA, PFUnA, PFDaA, FOSA, N-EtFOSAA	Not mentioned	<i>This study</i>
Tap and drinking water					
4 cities in Japan	n.a.	0.1-51	n.a.	Contaminated supply from Tama river	(Harada <i>et al.</i> , 2003)
Drinking water in Ruhr area	n.d.-519	n.d.-22	PFBS, PFHxS, PFBA, PFPeA, PFHxA, PFHpA, PFNA	Contaminated water supplies	(Skutlarek <i>et al.</i> , 2006)
Raw and treated tap water, Osaka, Japan	5.2-92 (raw) 2.3-84 (tap)	0.26-22 (raw) 0.16-22 (tap)	n.a.	Contaminated raw water, low removal efficiency	(Takagi <i>et al.</i> , 2008)
Tap water, Catalonia, Spain	0.32-6.28	0.39-0.87	PFHxS, PFHpA, PFNA	Contaminated river tributaries	(Ericson <i>et al.</i> , 2008)
Tap water in Asian, Europe and North America countries	0.18-78	0.61-11	n.a.	Not mentioned	(Mak <i>et al.</i> , 2009)
New Jersey public drinking water system	5-39	n.a.	n.a.	Impact from industrial areas	(Post <i>et al.</i> , 2009)

Table 2.1. Compilation of PFC occurrences in environmental samples from literature and the current study (continued)

Sediment and particulate					
Sediments and domestic sludge in San Francisco Bay, USA	n.d.-3.76 (ng g ⁻¹ dw)	n.d.-0.652 (ng g ⁻¹ dw)	N-MeFOSAA, N-EtFOSAA, PFNA, PFDA, PFUnA, PFDoA, PFTA	Municipal sewer discharge, WWTP effluent	(Higgins <i>et al.</i> , 2005)
Sediment from tidal flat, Ariake Sea, Japan	0.09-0.14	0.84-1.1	PFHxS, PFNA, FOSA	Not mentioned	(Nakata <i>et al.</i> , 2006)
Sediment from Tenjin river, Kyoto, Japan	1.3-3.9 (ng g ⁻¹ dw)	n.d.	n.d.	Industrial inputs	(Senthilkumar <i>et al.</i> , 2007)
Sediment in Roter Main river, Bayreuth, Germany	18-68 (ng g ⁻¹ dw)	72-210 (ng g ⁻¹ dw)	n.a.	WWTP discharge	(Becker <i>et al.</i> , 2008)
Sediment and suspended particulates (SPM) in Tokyo Bay, Japan	6.8 (ng g ⁻¹ dw, 0-3 cm sediment)	96 (ng g ⁻¹ dw, 0-3 cm sediment)	PFHxS, PFDS, PFNA, PFDA, PFUnA, PFDoA, PFTA, FOSA, N-EtFOSAA	Domestic, industrial, AFFF wastewater discharge	(Ahrens <i>et al.</i> , 2009a; Ahrens <i>et al.</i> , 2010)
Marina Reservoir, Singapore	1.8 (ng g ⁻¹ dw, max, SPM) 39-322 (ng g ⁻¹ dw)	7.2 (ng g ⁻¹ dw, max, SPM) 858-3570 (ng g ⁻¹ dw)	PFHxS, 6:2FtS, PFHpA, PFNA, PFDA, PFUnA, PFDoA, PFTA, FOSA, FOSAA, N-EtFOSA, N-MeFOSAA, N-EtFOSAA	Point sources and non point sources from the catchment	<i>This study</i>
Airborne					
Home dust in Japan	11-2500 (ng g ⁻¹ dw)	69-3,700 (ng g ⁻¹ dw)	Not measured	Wax coating agent, other consumer products	(Moriwaki <i>et al.</i> , 2003)
Indoor air	n.a.	n.a.	N-MeFOSE, N-EtFOSE, N-MeFOSEA	Indoor consumer products, particle-gas partitioning	(Shoeib <i>et al.</i> , 2004)
Rural and urban air in Northern Germany	n.a.	n.a.	N-MeFOSA, N-EtFOSA, N-MeFOSE N-EtFOSE, 4:2, 6:2, 8:2, 10:2 FTOH	Atmospheric degradation and transport	(Jahnke <i>et al.</i> , 2007a)
Arctic snow	0.0012-0.147	0.0026-0.086	PFNA, PFDA, PFUnA	Atmospheric oxidation of volatile precursors	(Young <i>et al.</i> , 2007)
Indoor, outdoor window film in urban and rural area, Ontario, Canada	7-5385 pg cm ⁻² (carpet) <0.1 pg cm ⁻² (film)	154-510 pg cm ⁻² (carpet) <0.1 pg cm ⁻² (film)	PFHxS, PFDS, PFHpA, PFNA, PFDA, PFUnA, PFDoA, PFTA, 6:2, 8:2, 10:2FTUCAs	Carpet installation, window film, wax application	(Gewurtz <i>et al.</i> , 2009)
Indoor dust, Stockholm, Sweden	93 (ng g ⁻¹ dw)	110 (ng g ⁻¹ dw)	n.a.	Consumer and applicant products	(Björklund <i>et al.</i> , 2009)

Table 2.1. Compilation of PFC occurrences in environmental samples from literature and the current study (continued)

Consumer products-linked to human exposure					
Consumer products i.e. carpet, textile	n.a.	n.a.	C6-C14 FTOHs, N-MeFOSE (0.04-3.8% residual fluoroalcohol mass applied)	Carpet treatment substances	(Dinglasan-Panlilio and Mabury, 2006)
Paper fiber products	n.a.	n.a.	4:2/6:2diPAP (34 ng g ⁻¹), 6:2/8:2diPAP (730-2200 ng g ⁻¹)	Fluorinated materials for product processing	(D'eon et al., 2009)
WWTP sludge	1.5 ng g ⁻¹	100 ng g ⁻¹	PFNA, PFDA, PFUnA		
Human sera	1,700	10,000	6:2diPAP (150-630 ng L ⁻¹), 8:2diPAP (140 ng L ⁻¹)		

* n.d. = not detected; n.a. = not analysed; dw = dry weight; WWTP = wastewater treatment plant; AFFF= aqueous film-forming foam.

Table 2.2. Abbreviation of PFCs

FOSA: Perfluorooctanesulfonamide, $C_8F_{17}SO_2NH_2$	PFDA: Perfluorodecanoic acid or perfluorodecanoate
FOSAA: Perfluorooctanesulfoamido acetic acid, $C_8F_{17}SO_2NHCH_2COOH$	PFUnA: Perfluoroundecanoic acid or perfluoroundecanoate
N-MeFOSAA: 2-(N-methyl perfluoro-1-octanesulfoamido) acetic acid, $C_8F_{17}SO_2N(CH_2CH_3)CH_2COOH$	PFDoA: Perfluorododecanoic acid or perfluorododecanoate
N-EtFOSAA: 2-(N-ethyl perfluoro-1-octanesulfoamido) acetic acid, $C_8F_{17}SO_2N(CH_2CH_3)CH_2COOH$	PFPHxDA: Perfluorohexadecanoic acid or perfluorohexadecanoate
N-EtFOSE: 2-(N-ethylperfluoro-1-octanesulfoamido)ethanol, $C_8F_{17}SO_2N(CH_2CH_3)CH_2CH_2OH$	PFOcDA: Perfluorooctadecanoic acid or perfluorooctadecanoate
N-MeFBSE: 2-(N-methylperfluoro-1-butan sulfoamido)ethanol, $C_4F_9SO_2N(CH_3)CH_2CH_2OH$	THPFOS: 1H,1H,2H,2H- perfluorooctanesulfonic acid, $C_8F_{13}H_4SOO^-$
N-MeFBSA: 2-(N-methylperfluoro-1-butan sulfoamide, $C_4F_9SO_2NH(CH_3)$	6:2 FTOH: 1H, 1H, 2H, 2H-perfluorooctanol, $C_6F_{13}CH_2CH_2OH$
N-MeFOSEA: N-ethylperfluoro-1-octanesulfoamidethyl acrylate	8:2 FTOH: 1H,1H, 2H, 2H-perfluorodecanol, $C_8F_{17}CH_2CH_2OH$
PFBS: Perfluorobutane sulfonic acid or perfluorobutane sulfonate	6:2 FtS: 6:2 telomer sulfonate
PFHxS: Perfluorohexanoic acid or perfluorohexane sulfonate	8:2 FtS: 8:2 telomer sulfonate
PFOS: Perfluorooctane sulfonic acid or perfluorooctane sulfonate	10:2 FtS: 10:2 telomer sulfonate
PFBA: Perfluorobutanoic acid or perfluorobutanoate	8:2FTCA: 2H, 2H-perfluorooctanoic acid, $C_6F_{13}CH_2CO_2H$
PFPeA: Perfluoropentanoic acid or perfluoropentanoate	10:2FTCA: 2H, 2H-perfluorododecanoic acid, $C_{10}F_{21}CH_2CO_2H$
PFHxA: Perfluorohexanoic acid or perfluorohexanoate	8:2FTUCA: 2H-perfluoro-2-decenoic acid, $C_8F_{16}CHCO_2H$
PFHpA: Perfluoroheptanoic acid or perfluoroheptanoate	10:2FTUCA: 2H-perfluoro-2-dodecenoic acid, $C_{10}F_{20}CHCO_2H$
PFOA: Perfluorooctanoic acid or perfluorooctanoate	4:2, 6:2, 8:2, 10:2diPAP: fluoroalkyl phosphoric acid diesters (equal carbon chain in diester)
PFNA: Perfluorononanoic acid or perfluorononanoate	4:2/6:2, 6:2/8:2diPAP: fluoroalkyl phosphoric acid diesters (2CF ₂ moieties different in carbon chain of diester)

2.3 Environmental fate of PFCs

Fate of PFCs in the environment is complicated because it is involved in multiple media interactions with solid, liquid, aerosol and biomass. Wastewater treatment plants (WWTPs) receive influxes of various contaminants from solid and liquid wastes. In the WWTP, volatile PFCs can be released to the atmosphere with up to 76% by air stripping (Rhoads et al., 2008). In aerobic mixed biomass conditions, volatile precursors were reported to be biodegradable to form shorter carbon chain PFCs and other metabolites (Dinglasan et al., 2004). In aerobic sludge, 13% of the PFC precursor (i.e. N-EtFOSE) can be biologically transformed to metabolites whereas 5% stays sorbed in the sludge (Rhoads et al., 2008). Another telomer precursor, 1H,1H,2H,2H-perfluorodecanol (8:2 telomer alcohol, 8:2 FtOH) could be degraded up to 35% after 28 days in aerobic activated sludge according to Wang et al., 2005 (Wang et al., 2005). In general, biological and physicochemical processes in WWTPs only provide incomplete removal of recalcitrant substances and their effluents release significant amounts of PFCs and metabolites to the environment (Boulanger et al., 2005b; Sinclair and Kannan, 2006).

As mentioned above, sediment and suspended particulate matter (SPM) are also important sinks for PFCs in the environment. Due to the affinity to the organic fraction, PFCs are strongly bound to the solid phase resulting in elevated contents. Concentrations and concentration ratios (sediment/water) of PFCs from the waters downstream of WWTPs were observed to be remarkably higher than those from upstream for both dissolved phase and sediments (Becker et al., 2008). Elevated levels of PFOA and PFOS were also detected in sediments from San Francisco Bay, USA ($< \text{LOD} - 1300 \text{ ng kg}^{-1} \text{ dw}$) (Higgins et al., 2005); the Tidal flat of Ariake Sea, Japan ($840\text{--}1100 \text{ ng kg}^{-1} \text{ dw}$) and rivers in Japan ($1300\text{--}3900 \text{ ng kg}^{-1} \text{ dw}$). Transport of PFCs from urban areas can be supplemented by runoff which carries SPM. Ahren et al., (2010) reported that 6400 to 15100 ng kg^{-1} dry weight of total PFCs were detected in SPM compared to 17 to 42 ng L^{-1} in the dissolved phase in Tokyo Bay (Ahrens et al., 2010). The partitioning behaviour of PFCs depends on many factors, e.g. organic and mineral content, pH, and chemistry of PFCs, etc. (Higgins and Luthy, 2006; Ahrens et al., 2010). However these correlations are not always applicable (Becker et al., 2008) and there is still insufficient data on PFCs in sediments and other solid phases to interpret their behavior.

The atmosphere-water interactions are complex manner. The non-volatile PFCs, such as PFOS and PFOA, are likely enriched in aerosols from the water body before being released into

the gas phase for transport. The partitioning factor between water phase and condensed aerosol ranges from 4 to 56 for fresh water to ocean water (McMurdo et al., 2008). This suggests that the water bodies are not the ultimate sink and aerosol enrichment should be considered for the mass balance evaluations of PFC fluxes into reservoirs.

Environmental monitoring data showed that volatile PFCs such as telomer alcohols and perfluoroalkyl sulfonamide alcohols with atmospheric lifetimes long enough to cause the regional distribution of various PFCs (Martin et al., 2002; Wallington et al., 2003; Stock et al., 2004). Atmospheric fluorotelomer alcohols can be degraded to yield perfluorocarboxylic acids (Wallington et al., 2003) and a 3D model indicated that 8:2 FtOH could be the source of globally transport of PFOA and other perfluorocarboxylic acids (Wallington et al., 2006). Gas phase OH radical oxidation of N-methyl perfluorobutane sulfonamidoethanol (N-MeFBSE) released longer lifetime dealkylation product (N-methyl perfluorobutane sulfonamide, N-MeFBSA), perfluorobutanoic acid (PFBA) and perfluorobutane sulfonic acid (PFBS) which were strong evidence for the ubiquitous distribution of perfluoroalkyl carboxylates and sulfonates in the environment (D'Eon et al., 2006). The atmospheric fate therefore results in ineligible contribution of PFCs to aquatic environment through wet precipitation (Scott et al., 2006; Kim and Kannan, 2007; Nguyen et al., 2011c).

2.4 Photochemical fate of PFCs

In general, the absorption of photon from light energy is the inception of photochemical processes. A photochemical reaction occurs when at least one component (S) in the system is able to absorb photon to raise orbital electron from the ground state to an excited state which is more reactive species (S*). Important photophysical processes that S* may undergo are tabulated in Table 2.3.

Table 2.3. General photophysical and photochemical reactions

Photophysical processes	
$S_0 + h\nu \rightarrow {}^1S^*$	Light absorption, excitation
${}^1S^* \rightarrow {}^3S^*$	Intersystem crossing
${}^1S^* \text{ or } {}^3S^* \rightarrow S_0$	Radiationless deactivation
${}^1S^* \rightarrow S_0^v + h\nu$	Fluorescence
${}^3S^* \rightarrow S_0^v + h\nu$	Phosphorescence

$^3S^* + P \rightarrow S_0 + ^3Ps^*$	Sensitization
$^3S^* + Q \rightarrow S_0 (+ Q^*)$	Quenching of S^* and (radiationless) deactivation of quenching agent
$Q^* \rightarrow Q$	
$^3S^* + O_2 \rightarrow S_0 + ^1O_2^*$	Formation of singlet oxygen
$^1O_2^* + Q \rightarrow O_2 + ^3Q$	Quenching of singlet oxygen and (radiationless) deactivation of quenching agent
$^3Q \rightarrow Q$	
Photochemical reactions	
$S^* \rightarrow \text{products or}$	Direct photolysis, may involve many steps and
$S^* + R \rightarrow \text{products}$	other ground state reactants
$^3S^* + HR \rightarrow SH^* + R^*$	Hydrogen transfer, leading to “photosensitized” oxidation of HR by free radical mechanism
$^1O_2 + R \rightarrow RO_2 \text{ or } R'O + R''O$	Addition of singlet oxygen to olefinic organic molecule
$^3S^* + O_2 \rightarrow S_{ox} + O_2^{\bullet -}$	Oxidation of light absorbing molecule and reduction of O_2 to superoxide ion
$^3S^* + R \rightarrow S + R^*$	Energy transfer from sensitizer to reactant,
$R^* \rightarrow \rightarrow \text{products}$	producing excited reactant state that subsequently forms product(s)

Table adapted from Brezonik (Brezonik, 1993).

S_0 -singlet state with electron spins paired in the ground state; 1S_1 , 1S_2 - excited singlet state due to absorption of a photon; S_0^v - vibrational or rotational excited level of lower excited state by internal conversion; $^3S^*$ - triple state due to intersystem crossing inverts the spin of an electron so that two electrons have parallel spins and the molecule has a net spin of 1.

It is well known that the end transformation products of PFCs, i.e. PFOA and PFOS, are particularly resistant to degradation processes in the environment. However, their precursors and other PFC intermediates have shown that they have the potential to be transformed in natural environments via photochemical processes. Hence, in this study, we focus on photolysis as a mechanism for degrading PFCs in surface waters.

Sunlight interact with photosensitizers both directly and indirectly and generate highly reactive oxygen species, such as singlet oxygen (1O_2 from DOM), superoxide anion ($O_2^{\bullet -}$, from photolysis of Fe complexes, deprotonation of hydroperoxyl), hydroperoxyl ($^{\bullet}OH_2$ from atmosphere, deprotonation of $O_2^{\bullet -}$), hydroxyl radical ($^{\bullet}OH$ from photolysis of hydroxo or Fe

complex or nitrite, nitrate, decomposition of ozone, hydrolysis of H_2O_2), H_2O_2 (photolysis of Fe complex, disproportion of $\cdot O_2^-$, exchange with atmosphere), organic peroxides ($ROO\cdot$ from photolysis of DOM) and solvated electrons (e_{sol}^- from photolysis of DOM) (Stumm and Morgan, 1981).

Radical production and scavenging by irradiated naturally-occurring constituents can be expressed in the following equations (Buxton et al., 1988; Mack and Bolton, 1999; Wang et al., 2007):

The $\cdot OH$ are scavenged by other constituents such as DOC and bicarbonate:

For compounds that absorb little or no sunlight undergo negligible biodegradation (e.g. PFCs), transformation via indirect photolysis (i.e. involving oxidation by transient photooxidants) is an important degradation pathway. In many freshwaters, $\cdot OH$ is one of the important transient photooxidants which is generated by various constituents upon absorption of sunlight (equation 2.1 to 2.4). $\cdot OH$ reacts with a number of compounds at nearly diffusion controlled-reaction rates by one of two major paths: (1) electrophilic addition to a double bond or an aromatic system; or (2) by abstraction of a hydrogen atom from a carbon atom (Schwarzenbach et al., 2003). In the case of PFCs, the second mechanism was observed to be more significant (Plumlee et al., 2009). A comparison of concentrations and reaction rates of various photo transients is tabulated in Table 2.4. The steady state concentration of $\cdot OH$ is generally lower than other reactive species due to their non-selectivity (Lam et al., 2003) and high rate of being consumed within a few microseconds by dissolved organic carbon (DOC), carbonate and other species in water (Zafiriou et al., 1984).

Among reactive species, $^1\text{O}_2$ is also one of very important constituents for aquatic photochemical processes. Being formed by the collision of ground state O_2 with excited triplet states of sensitizer molecules (Table 2.3), its energy level is only 96 kJ/mol above the ground state, which is much smaller than triplet state energies of other organic compounds. This results in efficient energy transfer to O_2 from triplet sensitizers, however, aquatic lifetime of $^1\text{O}_2$ is short (4×10^{-6} s) due to its dominant fate of quenching (Brezonik, 1993).

Table 2.4. Concentrations and rate constants with pollutants of reactive transients in natural surface waters (Mill et al., 1980; Lam et al., 2003; Schwarzenbach et al., 2003)

Species	Conc. (M)	Rate constant ($\text{M}^{-1} \text{s}^{-1}$)
$\cdot\text{OH}$	$10^{-14} - 10^{-18}$	$10^7, 5 \times 10^9 - 10^{10}$
$\text{ROO}\cdot$	$10^{-9}, 10^{-11}$	10^3
$\text{CO}_3^{\cdot-}$	$10^{-13} - 10^{-15}$	$10^6 - 10^7$
$^1\text{O}_2$	10^{-14}	10^7
H_2O_2	3×10^{-9}	-
DOM^3 (triplet excited state)	6×10^{-14}	-
$\text{e}^-_{(\text{aq})}$	10^{-17}	10^{10}

In general, the stable perfluoroalkyl chain is unlikely to be cleaved off by direct or indirect photolysis. In order to destroy the refractory molecules of PFCs, especially PFOS and PFOA and homologues, high energy and vigorous destruction methods are required. To date, no single physical or chemical technique is applicable for destroying these compounds generally, a combination of methods is more favorable. Current mineralization methods for these constituents were divided into three different groups: sonochemistry, photocatalysis and advanced oxidation (Hori et al., 2005; Moriwaki et al., 2005). Final products of these destruction methods are F^- and CO_2 . However, these are typically used for highly contaminated wastewaters, rather than for treatment of natural waters.

Aqueous $\cdot\text{OH}$ in an irradiated solution was generated according to Equation 2.4. The irradiated aqueous solution of 8:2 FtOH in the presence of H_2O_2 produced perfluoroalkyl carboxylic acids with 8:2 FTCA, 8:2 telomer aldehyde and PFOA as major products and 8:2 FTUCA and PFNA as minor products (Gauthier and Mabury, 2005). It was also reported that

the pseudo-first order rate constant of 8:2 FtOH could be promoted by nitrate and inhibited in the presence of humic acid. In natural lake water the half-life of 8:2 FtOH decreased by approximately 110 times compared to that in pure water (with addition of 10 mM H₂O₂) (Gauthier and Mabury, 2005). Hatfield (2001) reported that N-EtFOSE was oxidized by [•]OH (generated from H₂O₂ under simulated sunlight) to form N-EtFOSA, FOSA and PFOA (Hatfield, 2001). In a recent study, N-EtFOSE was observed to form N-EtFOSAA, N-EtFOSA, FOSAA, FOSA and PFOA under similar experimental conditions (Plumlee et al., 2009). The reaction pathway and mechanism were proposed based on the dependent irradiation of each metabolite under the same conditions with N-EtFOSE. Results indicated that [•]OH initiated reactions of N-EtFOSAA, N-EtFOSA and FOSAA to produce N-EtFOSA, FOSAA, FOSA and PFOA; FOSAA, FOSA and PFOA; and PFOA and FOSA, respectively. Atmospheric reaction between [•]OH and N-MeFBSE, an analogue of N-EtFOSE, revealed that the lifetime is about 2 days and the second order rate constant was determined at $(5.8 \pm 0.8) \times 10^{-12}$ molecule cm⁻¹ s⁻¹. N-MeFBSA, a homologous carbonyl compound, PFBS and homologous carboxylic acids were observed as degradation metabolites (D'Eon et al., 2006).

The common findings from irradiated aqueous solutions (Hatfield, 2001; Plumlee et al., 2009) are: 1) there is no PFOS formation in the [•]OH initiated oxidation of N-EtFOSE and its metabolites; 2) PFOA and FOSA are final products of the photodegradation reaction and resistant to [•]OH; and 3) there is significant appearance of unidentified intermediates and unknown pathways during the transformation of N-EtFOSE and its metabolites.

However, the reaction kinetics and metabolite production profiles which are important to predict the fate of PFCs in sunlit environments are not fully understood. The upper limit for bimolecular reaction rate constant of [•]OH and N-EtFOSAA was estimated to be $(1.7 \pm 0.7) \times 10^9$ M⁻¹ s⁻¹ due to the absence of reference compound in the irradiated solutions. Furthermore, the influence of other factors such as pH and naturally occurring constituents (e.g. NO₂⁻, NO₃⁻, DOC and algae) has not been assessed. These factors may contribute significant roles in degradation rates of PFCs (Gauthier and Mabury, 2005). The appearance of perfluoroalkyl sulfonate in atmospheric oxidation of N-MeFBSE suggests that different radicals may modify reaction pathways resulting in the production of different final products (D'Eon et al., 2006).

2.5 Analysis of PFCs

The major trend in analysis of emerging contaminants is using liquid and gas chromatography (LC and GC) coupled with mass spectrometry (MS) for quantification and identification. Recently, the use of liquid chromatography becomes more popular because of its flexibility in environmental sample analysis, particularly for non-volatile trace organics. Gas chromatography can be used to detect volatile species however derivatization required for non-volatile compounds seems to be complicated with non-reproducible reaction yields (De Voogt and Sáez, 2006). Compared to common LC, ultra performance LC using small diameter particles in stationary phase which allows high pressure can provide narrow peak and improve separation capacity in a shorter run. For detector, triple quadrupole mass spectrometer operating at selected reaction monitoring (SRM) or multiple reaction monitoring (MRM) modes has been employed widely in quantification of trace contaminants. With the development of instruments, the time-of-flight mass spectrometer has been reckoned as a state-of-the-art tool to identify unknown metabolites or transformation products which are highly polar, nonvolatile or high molecular weight and are not amenable to GC (Richardson and Ternes, 2011). Various ionization techniques can be used with LC-MS/MS for different compounds of interest such as atmospheric pressure photoionization (APPI) (for highly non polar compounds), electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI) (for nonpolar solvent), atmospheric pressure laser ionization (APLI) (for aromatic and polyaromatic compounds), desorption electrospray ionization (DESI) and matrix-assisted laser desorption/ionization (MALDI) (for biomolecules).

Analytical methods for PFCs have been reported in many studies (Prevedouros et al., 2006; Villagrasa et al., 2006). For PFCs analysis, GC can be used to detect neutral and volatile species such as sulfonamides and telomer alcohols (Shoeib et al., 2004; Jahnke et al., 2007a). However, the LC electrospray ionization (ESI) couple with tandem MS is widely applied for most environmental samples with simplicity and providing low detection limits and reliable performances (Boulanger et al., 2004; Saito et al., 2004; Yamashita et al., 2004; Higgins et al., 2005; Loewen et al., 2005; González-Barreiro et al., 2006; Skutlarek et al., 2006; Loos et al., 2007; Murakami et al., 2008; Plumlee et al., 2008; Zushi and Masunaga, 2009; Ahrens et al., 2010; Nguyen et al., 2011c). To extract and concentrate environmental samples, solid phase extraction (SPE) remains one of the most popular techniques employed for trace organics and

also PFCs (Richardson and Ternes, 2011). To minimize the matrix effects such as ion suppression or enhancement from environmental samples, isotopically labeled compounds (deuterated or ^{13}C -labeled or ^{18}O labeled) have been increasingly used as internal or surrogate standards in quantification.

The analytical work may have its inherent troubles such as the lack of authentic standards for surrogates or internal standards (Hansen et al., 2001; Villagrasa et al., 2006); procedural and instrumental background contamination in which laboratory sources are not well characterized (Schultz et al., 2003a; Villagrasa et al., 2006). Typical contamination (PFOA, PFOS) were detected in procedural blanks at levels of ng L^{-1} in the final extracts (Taniyasu et al., 2005).

In order to minimize various sorts of contamination, Yamashita et al. 2004 examined the source of blank contamination at different steps including sample collection, extraction and treatment of samples (Yamashita et al., 2004). Authors suggested that Oasis® HLB (C18) was 10 times better than Sep-Pak® (C18) cartridge for SPE with lower levels of fluorinated contaminants. In the later investigation, Milli-Q water was observed to be less contaminated than HPLC-graded water; polypropylene (PP) was better than polyethylene (PE) materials for sampling, storage (Yamashita et al., 2005).

In another approach, PFOS and PFOA in deionized water were able to be eliminated by Presep-C Agri® cartridges (220mg) (Saito et al., 2004); and washing the sampling tool, bottle, cartridge, and filter with methanol rather than Milli-Q water prior to sampling, extraction and filtration were strongly recommended (Villagrasa et al., 2006). In addition, all PP lab-wares instead of glass wares should be used to avoid analytes sticking on glass surface, vial caps using PP (So et al., 2007).

Higgins et al. (2006) and Washington et al. (2007) analyzed PFCs in sediments and soils, respectively (Higgins et al., 2005; Washington et al., 2007). Higgins applied the same sample treatment method in sewage sludge as in sediments but achieved more sensitivity (Higgins et al., 2005). The procedure employed a solvent mixture of 90:10 (v/v) methanol and 1% acetic acid in Milli-Q water then C18 Sep Pak cartridges for cleaning up. In addition, the problem of coextracted matrix compounds from soil and sediment may cause disturbing quantitative determination. However, other studies showed the significant effectiveness of C 18

HLB cartridges in cleaning up and concentration of samples (Yamashita et al., 2004). New fluorinated reverse phase material for LC column may solve the matrix trouble in sediment analysis of PFCs. The analytes will retain stronger by C8 columns than by the C18 or phenyl columns, especially by ESI in the negative ionization mode (Villagrasa et al., 2006). Regarding to mobile phase, mixtures of acetonitrile-water and methanol-water often modified with ammonium acetate to improve LC separation and mass spectrometry sensitivity. Inoue et al. (2004) investigated the effect of the mobile phase ammonium acetate concentration of 1mM provided peak maximum responses with PFOS, PFOA and PFOSA (Inoue et al., 2004).

From the reviewed literature, HLB cartridges and PP lab wares were used and fluorinated materials were avoided in this study to improve the detection performance.

Chapter 3 Occurrence and source characterization of perfluorochemicals in Marina Catchment

3.1 Introduction

Perfluorochemicals (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 them surface active, chemically and thermally stable (Kissa, 1994). They have been detected in all environmental 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), groundwaters (Schultz et al., 2004) and sediments (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) urban runoff contaminated by non-point sources (Murakami et al., 2009b; Zushi and Masunaga, 2009), and (4) seepage from disposal and spill sites in 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. They are dispersed across the globe and undergo complex transformation pathways (Giesy and Kannan, 2002; Prevedouros et al., 2006), 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 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 PFC 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 leaking sewers can 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 consume 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 $0.04 \text{ } \mu\text{g L}^{-1}$ PFOA (NJ-Guidance, 2005) and for sum of PFOA plus PFOS of $0.1 \text{ } \mu\text{g L}^{-1}$ (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. 3.1). The Marina catchment covers approximately $1/6$ of Singapore ($10,000 \text{ ha}$), 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.

3.2 Experimental Section

3.2.1 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. 3.1. 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).

3.2.2 Sampling

Surface water samples were collected under dry weather conditions ("dry-samples") (June 2008-March 2009) and under rainy conditions when the flow consisted predominantly of storm runoff ("wet-samples") (November 2009-April 2010). The Alexandra canal was sampled at seven sites (AX1-AX7) 600-800 m apart during the period February to April 2009 (Fig. 3.1). The canal collects surface and groundwater that exfiltrates from surrounding soil. Dry-samples were collected in dry and clear weather condition, approximately 10-20 cm below the water surface. Physical parameters i.e. total dissolved solids (TDS), pH, and temperature were measured on site using a water quality monitoring probe (YSI 556 MPS, USA).

Fig. 3.1 Sampling map of the Marina catchment. Four point stars and dots depict sampling locations in the five streams across the catchment and along Alexandra canal, respectively.

Wet-samples were collected at the Alexandra and Stamford sampling sites during rain events using rain-activated automated samplers approximately 20 cm below the surface at exactly the same sites. Rainwater was collected from an open field at Nanyang Technological University (NTU) about 10 min after the onset of the rain event (approx. 1 h duration). All samples were contained in polypropylene bottles (Nalgene, Rochester, USA) which were kept in an ice box and stored in a cool room at 4 °C in the dark until analysis.

3.2.3 Extraction and analysis

Water samples (500 ml) were filtered using cellulose acetate 0.45 μm -membrane (Advantec MFS, Inc, CA, USA) prior to solid phase extraction (SPE), passed through a HLB[®] C18 cartridge (6 cc, Waters Corp, MA, USA) which was preferable for extraction of PFCs

(Yamashita et al., 2004). The loaded cartridge mounted in a SPE manifold was eluted three times by gravity drip with 2 mL methanol into 15 mL PP centrifuge test tubes (Greiner, Germany). Extracts were concentrated by a gentle nitrogen gas stream (99.99%, Soxal, Singapore) and reconstituted with methanol. Contact with glassware and Teflon surfaces was avoided to minimize sorptive losses and contamination.

Samples were analysed by liquid chromatography-tandem mass spectrometry (LC: Shimadzu LC-10 AD; MS/MS: API3000 AB Sciex, Toronto, Canada). Prior to injection, 100 μ L of internal standard solution containing 6ppb of [d_9]-*N*-EtFOSE, [$^{13}C_2$] PFNA, [d_5] *N*-EtFOSA, [d_5] *N*-EtFOSAA, [$^{13}C_2$] PFDA, [$^{13}C_2$] PFOS and [$^{13}C_2$] PFOA (Wellington Laboratories, ON, Canada) was added. 20 μ L of aliquot was then injected into C18 column (3.5 μ m, 40 mm $\times$ 2.1 mm ID, Higgins Analytical, CA, USA). In Milli-Q water, recovery rates ranged from 85-120%, except for FOSA, which was 52.4% (see Fig. A1, Appendix A). In surface water samples, the mean recoveries ranged from $53.2 \pm 3.9\%$ for PFUnA (95% confidence limit) to $104.8 \pm 7.7\%$ except for PFDoA and FOSA, which were $36.6 \pm 3.8\%$ and $46.8 \pm 3.3\%$, respectively. The results presented in this chapter was not corrected with the recovery since dominant PFCs showed good recoveries while those with low recoveries were normally detected at insignificant concentrations. Furthermore, periodical recovery test during monitoring period (approximately every 2 months) showed acceptable data ($\sim 75\%$) for these compounds. Details of the sample collection, analytical procedure, blank and recovery test are described in the supplementary information (Appendix A).

3.3 Results and discussion

3.3.1 Composition and spatial distribution of PFCs

Median PFC concentrations determined in dry, wet weather and rain samples are summarized in Table 3.1. Of the 19 targeted PFCs (see Table A1, Appendix A), 13 were detected. PFHxS, PFOS, PFOA, PFNA, PFDA, PFUnA were detected at all sites under both dry- and wet-weather conditions; FOSA, N-MeFOSAA and PFUnA were detected only in dry-samples. Table 2.1 also presents higher concentrations of PFCs in dry-samples compared to wet-samples in Alexandra and Stamford sites. Median total concentrations were 57 and 138 ng L^{-1} compared to 42 and 79 ng L^{-1} for dry and wet samples, respectively. This suggests the presence of a continuous source(s) which is subject to dilution during storm events.

In rain water, the median total PFC concentration was 6.4 ng L^{-1} (Table 3.1), consistent with concentrations measured in north Germany, Europe and on the North American Continent (Prevedouros et al., 2006; Scott et al., 2006; Dreyer et al., 2010). For example, the total concentration of 17 PFCs in northern Germany in rain samples ranged from $2\text{--}49 \text{ ng L}^{-1}$ (Dreyer et al., 2010) compared to $5\text{--}12 \text{ ng L}^{-1}$ for the 13 PFCs in this study. The PFC concentration in rain water was approximately 25% of the lowest median concentration observed in Kallang River. The air-born PFCs were also found to contribute significantly to the surface water environment, which in turn depended on air mass history and meteorological conditions (Liu et al., 2009; Dreyer et al., 2010).

Total concentrations and distribution of PFCs in dry and wet-samples are shown in Figs. 3.2 and 3.3. Total PFC concentrations were highest at Alexandra canal (157 ng L^{-1}) and ranged relatively narrowly (from 27 to 59 ng L^{-1}) at the other sites. In addition, most of the individual PFCs were also highest at the Alexandra canal sites. Compared to the other sites, compounds including PFOS, PFHxS, 6:2FtS and PFOA occurred at relatively high concentrations with maximum concentrations reaching 156 , 68 , 36 and 31 ng L^{-1} , respectively (Table 3.1). The high concentrations in Alexandra canal (three times higher than at the other sites) were considered to be attributed to a localized source(s) since the horizontal transect showed high inputs of PFCs (especially PFOS and PFHxS) at mid-stream locations.

A comparison of total dissolved solids (TDS) and PFC concentrations (Fig. 3.2a) suggests that PFC concentrations were lowered by seawater intrusion, as is evident at the Stamford and Rochor canal, Geylang and Kallang River sites. In seawater surrounding Singapore, the reported PFOA and PFOS concentrations are below 1 ng L^{-1} (Yamashita et al., 2005) and approximate 1 ng L^{-1} (unpublished data). The Alexandra canal site exhibited unique characteristics of TDS and PFCs, in that both TDS and PFCs were elevated compared to the other sites.

Fig. 3.2b depicts the composition of total perfluoroalkyl carboxylates, sulfonates and metabolites. Patterns were similar (i.e., high in perfluoroalkyl carboxylates) at all sites except in the Alexandra canal, an observation that is consistent with Japanese data of urban runoff where the median ratio of PFOA/PFOS was 9 (Murakami et al., 2009b) and 4 for river water (Murakami et al., 2008) compared to 5 from our study. Furthermore, median concentrations of PFOA and PFOS were 9 and 92 ; 3 and 64 ; and 5 and 25 ng L^{-1} for runoff, river water and this study, respectively. In general, PFOA constituted a higher proportion of total measured PFCs

(25-33%) compared to PFOS (12-22%) based on data collected from Geylang, Kallang, Rochor and Stamford waters, i.e. the carboxylates dominate over sulfonates. Concentrations of PFOA and PFOS and the sum of PFOA and PFOS at these 4 sites could meet the recommended levels for drinking waters in Germany (TWK, 2007), New Jersey (NJ-Guidance, 2005) and avian wildlife protection (Rostkowski et al., 2006), respectively (see Table 3.1 and Fig. A5, Appendix A). However, corresponding values for the Alexander Canal (except for PFOA) were unable to meet these standards.

Fig. 3.2 Average total PFC concentrations at sites corresponding to TDS (a-Total PFCs vs. TDS, b-Composition of PFCs). Error bar represents standard deviations (n=12 and 24 for dry and wet-sample, respectively; n=6 for TDS).

Table 3.1. PFC concentrations (median and range, ng L⁻¹) under dry and wet conditions in Marina Catchment

Site		PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	Total Carboxylates	PFHxS	PFOS	6:2FtS	Total Sulfonates	FOSA	FOSAA	N-Me- FOSAA	N-Et- FOSAA	Total Metabolites	Total PFCs
Geylang River-dry	Median	1.9	10.9	2.8	2.84	0.9	0.6	18.4	2.6	7.9	1.2	10.4	0.24	0.3	0.8	1.7	2.9	32.7
	Range	<0.7-1.9	6.0-16.3	1.5-4.9	1.7-6.8	0.7-1.3	ND-0.7	11.1-30.0	1.2-5.0	1.3-12.5	0.7-4.3	6.2-16.1	0.19-0.32	0.3-0.4	0.4-1.3	1.3-3.1	2.0-4.9	20.1-47.5
Kallang River-dry	Median	-	7.1	2.3	2.4	0.8	-	13.9	2.7	5.7	1.2	11.1	0.20	-	0.6	1.4	2.2	25.6
	Range	<0.7-1.5	5.4-7.1	1.3-3.7	1.3-3.9	0.4-1.0	ND-0.6	9.7-18.4	1.7-13.5	1.3-6.4	0.8-4.3	4.2-19.4	0.14-0.32	ND- <0.2	0.3-0.9	1.1-1.7	1.9-2.8	17.6-35.7
Rochor Canal-dry	Median	7.2	16.5	4.5	7.3	1.3	0.4	32.2	3.1	7.0	1.0	10.3	0.26	-	1.3	2.4	4.2	47.5
	Range	ND-7.2	12.7-19.9	3.4-6.7	4.7-10.4	0.9-2.5	<0.4-1.0	29.5-38.4	1.5-6.1	2.1-7.0	<0.4-1.5	2.1-12.7	0.14-0.83	ND-0.3	1.1-2.2	2.0-2.7	3.9-4.4	37.8-52.3
Stamford Canal-dry	Median	8.9	16.4	3.3	3.8	1.2	0.2	31.8	7.3	7.56	0.8	16.2	0.28	-	0.9	4.0	5.5	56.8
	Range	<0.7-12.4	13.9-20.7	2.3-4.9	2.4-6.3	0.6-2.0	0.1-0.9	26.1-40.7	2.7-9.5	4.7-32.5	0.7-8.5	10.7-40.7	0.21-0.74	ND-0.2	0.56-3.1	2.8-5.0	4.3-7.5	48.3-75.6
Alexandra Canal-dry	Median	10.7	19.2	5.9	7.0	1.9	0.8	37.9	39.5	28.0	7.8	89.6	0.31	1.0	0.9	5.1	8.4	138.1
	Range	<0.7-14.4	16.2-30.6	4.0-9.0	4.0-9.3	0.7-3.6	<0.4-1.0	35.5-57.3	17.7-67.8	9.7-156.2	0.9-35.9	37.8- 194.0	0.19-3.15	ND-1.8	0.5-3.2	4.5-14.7	5.6-15.7	96.9- 235.7
Stamford Canal-wet	Median	4.2	12.7	4.8	3.3	0.6	-	26.4	1.6	8.4	0.7	10.8	-	-	1.0	2.8	3.8	41.8
	Range	<0.7-8.8	7.8-27.9	1.4-78.3	0.7-28.2	<0.2-3.1	<0.4	17.8- 119.2	<0.4-3.4	4.5-20.8	<0.4-2.2	6.2-23.1	ND	ND	0.5-4.0	0.3-11.0	1.0-15	30.8- 143.9
Alexandra Canal-wet	Median	3.2	9.2	1.6	1.6	0.4	-	15.7	19.5	40.1	2.3	60	-	-	0.9	2.2	3.0	79.1
	Range	2.0-10.5	7.2-38.2	0.9-9.5	0.9-10.9	0.2-1.6	<0.4	12.8-67.4	9.7-73.0	22.0- 139.0	1.0-11.1	33.2- 223.2	ND	ND	0.5-3.4	0.8-7.6	1.5-11.0	49.7- 301.5
Rain water ⁺	Median	0.4	1.0	0.4	0.4	0.4	0.1	2.8	1.1	1.6	-	2.9	0.04	-	-	0.7	0.8	6.4
	Range	<0.7-0.8	0.6-1.3	<0.4-0.9	<0.4-0.8	0.4-0.9	0.1-0.4	1.9-4.9	ND-1.7	1.1-7.9	<0.4	1.0-7.9	0.03-0.05	-	-	0.4-1.0	0.2-1.0	5.2-11.5

Surface water: sampled August 2008

Storm runoff and rain water: sampled from Jan 2010-March 2010, n = 24; *ND: not detected

3.3.2 PFC profile in Alexandra canal

The longitudinal profile of Alexandra canal is shown in Fig. 3.3. At AX1, the total concentration of PFCs was 90 ng L^{-1} , comparable to that at other surface water sites, and the PFOA content was relatively high. In contrast, at the downstream sites, PFOS and PFHxS concentrations dominated and reached a maximum of 1478 and 252 ng L^{-1} at AX4, respectively, suggesting impact of an AFFF source (Schultz et al., 2004). Total PFCs were observed to be the highest at 1848 ng L^{-1} which also indicates a possible localized or point source in the vicinity. Two fire stations, located about 300m and 500m from sites AX4 and AX5 respectively, are thought to be the likely sources of AFFF although the spillage discharge patterns were unidentified. Downstream of AX4, the PFC concentration diminished, suggesting dilution with intruding Marina Bay water (Fig. 3.3). In addition, the occurrence of PFOA and PFOS along the Alexandra Canal failed to meet recommended values for drinking water, avian and aquatic chronic protection (Fig. 3.4) (NJ-Guidance, 2005; Rostkowski et al., 2006; TWK, 2007).

3.3.3 Correlation among PFCs

Correlation among various PFCs in dry and wet-samples were evaluated by performing a Spearman rank correlation analysis (statistic analysis performed by Microsoft Excel version 2007, see Table A2, Appendix A). Results were similar to those reported by others (So et al., 2007): perfluoroalkyl carboxylates/perfluoroalkyl carboxylates correlation coefficients are relatively high in dry-samples (average 0.63) whereas the correlations between carboxylates/carboxylates and most sulfonates/sulfonates are lower (0.41) and negative in wet-samples. The correlation between PFOA and PFOS was relatively high (0.72), similar to observations for treated wastewater (Loganathan et al., 2007). Significant log-linear relationship between PFC species was also observed in dry-samples (see Table A3, Appendix A). This prominent relationship together with dominant compositions of carboxylate species (except for Alexandra site) in dry-samples implied that carboxylates and sulfonates migrated to surface water from different but common sources including wastewater. In addition, the significant correlation between PFOS/PFHxS (0.89) and PFOS/6:2FtS (0.83) in wet-samples (at Alexandra and Stamford) compared to that in the dry-samples (4 sites, except Alexandra) indicates that surface runoff may carry sulfonates to these particular streams (Table A2, Appendix A).

Fig. 3.3 Longitudinal profile of PFCs in Alexandra Canal, 24th March 2009 (a-TDS longitudinal profile, b-PFC longitudinal profile).

Fig. 3.4 a-Concentrations of PFOA+PFOS along Alexandra Canal and German precautionary level for drinking water (100 ng L⁻¹) (TWK, 2007); b-Concentration of PFOS along Alexandra Canal against New Jersey recommended level for drinking water (40 ng L⁻¹) (NJ-Guidance, 2005); avian wildlife precautionary level (50 ng L⁻¹) and aquatic chronic level (1200 ng L⁻¹) (Rostkowski et al., 2006).

3.3.4 Pattern analysis of PFC composition

To compare the PFC composition with literature data, the PFHxS/PFOA ratios were plotted against the corresponding PFOS/PFOA ratio (Fig. 3.5). With the exception of Alexandra site, the surface water samples plotted within the quadrant 0 to 1. Dilution with water practically free of PFCs (i.e., seawater) does not affect ratios and similar input pattern results in tight clusters (Fig. 3.5a). Fig. 3.5b shows that most literature data falls within the range of ratios found in Singapore surface waters, i.e., PFHxS/PFOA <0.5 and PFOS/PFOA <0.9. Exceptions are *m*, *n*, *f*, *k* and the Alexandra canal samples where these ratios are significantly higher. Sites *m* and *n* represent surface water from lake Shihwa (South Korea) and its tributaries, which are impacted by manufacturing sectors such as electrical, electronic and petrochemical industries (Rostkowski et al., 2006) while *f* and *k* may have received urban runoff and wastewater (Plumlee et al., 2008; Zushi and Masunaga, 2009), respectively. The two groundwater samples (*TAFB*, *AFB*) are relatively low in PFOS perhaps because PFOS has stronger sorption characteristics than PFHxS (Higgins and Luthy, 2006) and was removed. Typical surface waters including our catchment waters (except for Alexandra canal) usually group in the region where PFOS/PFOA- PFHxS/PFOA is less than 2.

The ratios of dry-samples from AX1 at Alexandra canal are typical for surface waters whereas the mid stream locations (AX2 and AX3 and AX5 and AX6) fall far outside that range. Significant linear regression of these data points was observed in high correlation coefficient ($r^2 = 0.8$) suggesting that the source water which was most concentrated in PFCs at AX4 (Fig. 3.5b), is diluted at the downstream sites i.e., AX5, AX6 and AX7. Fig. 3.5c shows data from Asia, Europe and US plotted together with the Marina catchment data. In most cases, the PFHxS/PFOA and PFOS/PFOA ratios are relatively low (<0.2 and <0.9, respectively). The trend from lower to higher PFOS/PFOA ratios appears to correlate with higher urbanization levels. The PFHpA/PFOA ratio can be used to differentiate waters from urban and remote areas (see Fig. A3, Appendix A) because direct input of PFOA in the former is believed to be a major source compared to the latter (Kim and Kannan, 2007).

The PFC data set was subjected to principal component analysis (performed by PASW Statistics version 18) to evaluate the compositional similarities of the PFC mixtures in the Marina catchment waters (see Fig. A4, Appendix A). The data dimensionality is reduced by performing a covariance analysis between factors. There are nine factors were used to for covariance analysis i.e. N-EtFOSAA, PFDA, PFNA, PFUnA, FOSA, N-MeFOSAA, PFOS,

PFOA and PFHxS. The eigenvector and eigenvalues relevant to the data in the covariance matrix were then estimated as the preferential direction for the data set with 42 values larger than 0.3 which present highly substantial correlation (see Table A4). The Kaiser-Meyer-Olkin measure of sampling adequacy was determined at 0.8 which exceeds the minimum requirement of 0.5 and the Bartlett's test of sphericity satisfies the requirement (< 0.001) (Table A5). The output from eigenvalues showed 2 components greater than 1 which were later extracted by latent root criterion and able to explain 65.1% of the total variance (Table A6). Component matrix showed high load of 7 PFCs except PFOS and PFHxS on the component 1 whereas only relative load of PFHxS on component 2. The scatter plot was created from the regression factor scores. From this plot, it is evident that the Geylang, Kallang, Stamford, and Rochor site samples cluster close to each other whereas the downstream Alexandra canal samples fall outside that cluster, consistent with the data shown in Fig. 3.5a. Concentrations for five out of six Alexandra samples were significantly larger than average (Fig. A4, Appendix A). In contrast, concentrations of Geylang and Kallang samples were lower than average whereas Stamford and Rochor samples gathered at the centre of the plot. It suggests that Marina catchment surface water without point-source input is mostly characterized by perfluoroalkyl carboxylates (except PFOA) while the input emphasized on PFOA, perfluoroalkyl sulfonates and perfluoroalkyl substituted sulfonamides. This type of analysis may be useful to differentiate sources of PFCs in urban surface water with multiple inputs.

Fig. 3.5 Ratio correlation and characteristic distribution of different surface waters. a-Marina catchment water. b, c-Ratio correlation of median values of Marina catchment and Alexandra canal water plotted together with Asia, Europe and US water.

3.4 Conclusions

In tributaries of Marina Bay, Singapore, two distinct patterns of perfluorochemical contamination were detected: (i) waters dominated by perfluoroalkyl carboxylic acids and (ii) waters dominated by perfluoroalkyl sulfonates. PFOA and PFOS and PFHxS were the major components of perfluorinated carboxylates and sulfonates, respectively. From transect data collected along the Alexander Canal, a localized source of AFFF (aqueous film forming foam) input was detected based on the sulfonate pattern, presumably from nearby fire stations.

The PFOS/PFOA and the PFHxS/PFOA ratios were used to compare compositional changes in different surface waters. The perfluoroalkyl carboxylate pattern was similar to those observed in surface waters impacted by urbanization elsewhere. Similar to sites in Japan, the occurrence of PFCs in Singapore surface water lies in the mid-range of the PFOS/PFOA scale, but is relatively high on the PFHxS/PFOA scale. In Singapore, PFCs are mainly attributed to non-point sources such as roads, pavements, built structures, street litter and leaking sewer pipes.

The PFC concentrations in the tributaries of Marina reservoir are below the precautionary level specified by the German Drinking Water Commission for total PFOA and PFOS ($0.1 \mu\text{g L}^{-1}$), the New Jersey limit ($0.04 \mu\text{g L}^{-1}$ for PFOA), and the avian wildlife value limit ($0.05 \mu\text{g L}^{-1}$ for PFOS) (Rostkowski et al., 2006; Plumlee et al., 2008) in all cases except for the Alexandra Canal. However, these values are close to threshold levels and could rise as urbanization increases.

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Chapter 4 Occurrence, fate and fluxes of perfluorochemicals (PFCs) in Marina Reservoir

4.1 Introduction

In an increasingly urban and densely populated world, the need to produce drinking water from local sources (groundwater, runoff and urban surface waters) is becoming increasingly urgent. Urban water resources are vulnerable to pollution from a wide range of human activities. Pollutants may originate from point sources, such as leaking sewer lines, chemical spills, leaking chemical storage facilities, or from diffuse sources, such as painted buildings, road surfaces or littered consumer products (WHO, 2004). A growing concern is the ubiquitous environmental occurrence of PFCs, which are toxic, bioaccumulative and extremely persistent (OECD, 2006). PFCs have been detected in sediments (Higgins et al., 2005; Becker et al., 2008; Ahrens et al., 2010), air (Kim and Kannan, 2007; Piekarz et al., 2007) and wildlife (Houde et al., 2006a; Houde et al., 2006b), streams (Murakami et al., 2008; Plumlee et al., 2008) and groundwater (Hoehn et al., 2007; Plumlee et al., 2008; Murakami et al., 2009a). Recently, PFCs have been detected in canals and rivers that feed into the Marina Reservoir, Singapore (Nguyen et al., 2011c).

Managing water quality of urban reservoirs requires that contaminant sources are characterized and their transport and fate in the reservoir are understood. Contaminant attenuation may occur naturally by volatilization, abiotic or biological transformation, and sorption onto particulate matter and burial in the sediments (Gurr and Reinhard, 2006). During rain events, PFC loads in urban rivers increase because surface runoff contains higher levels of PFCs, most of which are sorbed onto suspended solids (SS) (Lam, 2008; Zushi and Masunaga, 2009). Sorption of PFCs on sediments is affected by the sediment (especially organic carbon (f_{oc}) and compound properties (chain length, functional groups), and water

chemistry (pH) (Higgins et al., 2005; Ahrens et al., 2010). Sorption can be evaluated in terms of partition coefficients, K_d ,

$$K_d = C_s / C_w \quad (4.1)$$

Assuming that organic carbon is the dominant sorbing phase, the K_d can be normalized with respect to the sediment carbon content as follows:

$$K_{oc} = K_d \times 100 / f_{oc} \quad (4.2)$$

where C_s , C_w are concentrations of PFCs in sediment, ng kg^{-1} dry weight (dw) and bottom layer water, ng L^{-1} , respectively. The K_{oc} value indicates the affinity of solutes for the sediment organic matter (expressed as organic carbon). Equation 4.2 is applicable for organic compounds that have a high affinity for organic matter, such as PFCs. The K_{oc} typically increases with the length of the perfluorinated carbon chain carboxylates (Higgins et al., 2005; Ahrens et al., 2010). The goal of this study was study the occurrence and fate of PFCs in the Marina Catchment and to estimate the PFC mass that is transported into the reservoir from runoff, dry weather flow, and rainfall.

4.2 Experimental Section

4.2.1 The hydrological status of the Marina Reservoir

Marina Catchment covers approximately one sixth (10,000 ha) of Singapore's land area and includes a major section of down town. Catchment flow drains into Marina Reservoir, a fresh water reservoir that was created by a dam (Marina Barrage) built across the mouth of Marina Bay. The barrage has been in operation since April 2009. The main inflows into Marina Reservoir are Singapore River, Stamford Canal, Rochor Canal, Kallang River and Geylang River (Fig. 4.1). Singapore's river and canal system does not receive direct wastewater discharges, although input from leaking sewers cannot be excluded (Nguyen et al., 2011c). During dry periods, the Barrage was opened at midnight; during rainy periods, it was opened when a preset water level was reached.

Fig. 4.1 Location of sampling sites in Marina Watershed and Reservoir. Depth profiles were obtained at sites indicated S1–S4. Runoff samples were collected at CM1–CM3.

This study was conducted from December 2008, to February 2009, for reservoir sampling and December 2009, through April 2010, for catchment runoff, approximately 8 to 12 months after closing of the Barrage. Fig. 2 shows the vertical profiles of salinity, pH and temperature. Salinity profiles indicate that the bottom layer (L3, L4) was still seawater. The surface (L1) and middle (L2) layers contain approximately 86% and 50% fresh water, respectively. More information about the sampling sites can be found in Appendix B.

4.2.2 Sampling

Runoff samples were collected at CM1–CM3 (Fig. 4.1) using an autosampler (ISCO model 6712). The sampler was automatically triggered by rainfall. Water samples (500 mL) were pumped into 24 polypropylene (PP) bottles. The first sample was collected after 5 min activation and the time series of

samples were obtained every 10 min, as detailed previously by Nguyen et al., 2011. Four consecutive samples were combined and a total of six composite samples were analyzed.

Fig. 4.2 Depth profiles of temperature, pH and salinity in Marina Reservoir. Data shown represents the average of data collected at S1 to S4 collected in December, 2008-March, 2009. Error bars represent standard deviation (n=12 to 18). L1 indicates the surface layer, L2 the transition layer, and L3 and L4 the bottom layers at S4 and S3, respectively.

Grab samples were collected at discrete depths using a Niskin water sampler (KC-Denmark, Model 1010, Silkeborg, Denmark). Water from four depths was collected at each site as follows: the top sample from 10 cm below the surface; the other three depths at 30%, 70% and 90% of the total depth, which ranged from 4.9-7.2 m (Fig. 4.2). River and canal water samples were collected at the sites indicated in Fig. 4.1. S1, S2 and S3 were selected to characterize the input from the Singapore River-Stamford Canal (Marina Bay), Geylang-Kallang River-Rochor Canal (Kallang Basin) and the Barrage zone, respectively. S4 was sampled to observe the mixing between the Marina and Kallang Basins. Transects across S2 and S3 were developed by sampling two additional sites (S3-a, S3-b, S2-a and S2-b) across the width of the reservoir. Coordinates of all sites were recorded using a portable GPS device. Physical parameters, including salinity, conductivity and temperature were monitored continuously for 24h by multiprobes (Lake Diagnostic Systems, LDS, <http://rtm.cwr.uwa.edu.au/olaris/index.php>) that were placed at Kallang Basin and Marina Bay (which sites). The probe data was validated by a portable YSI probe (556, MPS, USA). Variations in the water depth were insignificant during sampling period.

Water samples were transferred from the PVC Niskin sample bottles into 500 mL screw cap narrow mouth PP bottles (Nalgene, Rochester, NY, USA). Samples were transported to the lab in an ice box and stored in a cold room at 4 °C in the dark until analysis.

Sediments were collected at site S4 using a sediment core sampler (Kajak-Brinkhurst, Denmark) that was equipped with a stainless steel barrel and slicer. The sediment cores were sliced into a PP tube inside the sampler and then transported to the laboratory. Only the inner portion of the core (0-10 cm from top) was analyzed.

4.2.3 Sample extraction and analysis

Methods for the analysis of PFCs in water (Plumlee et al., 2008; Nguyen et al., 2011c) and in sediments (Higgins et al., 2005) were reported previously. Water samples were filtered using cellulose acetate (0.45 µm pore size) membranes and solid-phase extracted (SPE) using HLB[®] C18 sorbent (Waters Corp, MA, USA). PFCs were eluted three times with 2 mL methanol. The extract was dried with pure nitrogen gas (99.99%, Soxal, Singapore) and reconstituted in methanol before analysis. Sediments were freeze dried and ground with mortar and pestle. Subsamples (1 g) were extracted after repeated washing with acetic acid and solvent extracted with 90:10 v/v methanol containing 1% acetic acid in Milli-Q water. Vortexing, sonication (at 60 °C) and centrifugation were performed at each washing and extraction step. Decanted aliquots (approx. 40 mL) were combined and concentrated with 200 mg C18 SPE cartridge (Supelco, Sigma-Aldrich, USA). SPE-cartridges were preconditioned with 10 mL methanol followed by 10 mL of 1% aqueous acetic acid (Sigma-Aldrich, Germany). Aliquots of the extracts were loaded at a flow rate of 2 mL min⁻¹, cartridges were washed with 10 mL Milli-Q water and dried by connecting to an aspirator vacuum for 2 h. PFCs were eluted with 6 mL methanol into a 15 mL PP centrifuge test tube (Greiner, Germany) and concentrated to about 2 mL by a gentle stream of nitrogen gas (99.99%, Soxal, Singapore). Aliquots were transferred to 10 mL glass vials and combined with 800 µL rinsing methanol before adding 1.2 mL of 0.01% aqueous ammonium hydroxide solution (Sigma-Aldrich, Germany).

A mixture of 6 ng of each internal standard was added into the final extracts, which were kept at 4 °C until analysis. All PFC standards and internal standards were purchased from Wellington Laboratories (Guelph, ON, Canada), i.e. perfluorohexane sulfonate (PFHxS), perfluorooctane sulfonate (PFOS), 6:2 fluoro telomer sulfonate (6:2FtS), perfluorohexanoate (PFHpA), perfluorooctanoate (PFOA), perfluorononanoate (PFNA), perfluorodecanoate (PFDA), perfluoroundecanoate (PFUnA), perfluorododecanoate (PFDoA), perfluorotridecanoate (PFTA), perfluoro-1-octanesulfonamide (FOSA), N-ethylperfluoro-1-octanesulfonamide (N-EtFOSA), perfluoro-1-octanesulfonamidoacetate (FOSAA),

N-methylperfluoro-1-octanesulfonamido-acetate (N-MeFOSAA) and N-ethylperfluoro-1-octanesulfonamidoacetate (N-EtFOSAA). Isotopic PFCs were used for internal standard: [d₉]-N-EtFOSE (for analysis of N-MeFOSE and N-EtFOSE), [¹³C₂] PFNA (for PFNA), [d₅] N-EtFOSA (for N-EtFOSA and FOSA), [d₅] N-EtFOSAA (for N-EtFOSAA, N-MeFOSAA and FOSAA), [¹³C₂] PFDA (for PFDA, PFUnA, PFDaA), [¹³C₂] PFOS (for PFHxS, PFOS) and [¹³C₂] PFOA (for PFHpA and PFOA).

Samples were analyzed by liquid chromatography-tandem mass spectrometry (Shimadzu LC-10 AD, Singapore; API3000 AB Sciex, USA). Sample extracts were injected on to a C18 column (3.5 µm pore size, 40 mm × 2.1 mm ID, Higgins Analytical, USA) with a gradient mobile phase scheme of methanol/water-ammonium acetate. Since the analytical method in chapter 3 for water samples was used for reservoir water, method recovery test showed similar results. For sediment analysis, good recovery percentages were observed for most of detected PFCs except two sulfonamides and C6 sulfonate (N-EtFOSA, FOSA and PFHxS for 24%, 40% and 180%, respectively). These neutral sulfonamides were probably lost during SPE clean up, extraction in acidic solution. Ion enhancement and suppression could contribute to those compounds without isotopically mass labeled standards (FOSA and PFHxS). Since the variation of recovery percentages was large and PFC distribution in sediments was ununiformed, analytical data were only corrected with concentration and dilution factors. More information about recovery rates of can be found in Appendix A and B.

4.3 Results and discussion

4.3.1 Distribution of PFCs and impact of seawater in Marina Reservoir

PFC concentrations and product distribution in the top layer (Fig. 4.3) are consistent with the surface water concentrations determined previously (Nguyen et al., 2011c). The major PFC fraction consisted of total perfluoroalkyl carboxylates (PFCAs) (16-74 ng L⁻¹) followed by total perfluoroalkyl sulfonates (PFSA) (6-28 ng L⁻¹) and metabolites (1-5 ng L⁻¹) (Fig. 4.4). In catchment waters, the previously reported concentration ranges of these fractions were similar (Nguyen et al., 2011c). The most abundant species were perfluorooctanoate (PFOA), perfluorooctane sulfonate (PFOS) and perfluorohexanoate (PFHpA) with concentrations ranging from 8-37, 6-20 and 4-28 ng L⁻¹, respectively (Table B4, Appendix B).

Fig. 4.3 Depth profiles of average total PFCs concentrations and salinity in Marina Reservoir at S1 through S4. Values represent the average of six sampling events and the standard deviation ($n = 6$).

The transect profiles of S1 and S3 (*a* and *b*) indicated total PFCs concentrations were highest in the middle. For PFCAs, mid-stream samples were 1.9 to 2.3 times higher than samples from the adjacent sides, indicating incomplete lateral mixing of the reservoir surface layer (Table B4, Appendix B).

The salinity depth-profiles at the four sites (S1-S4) were similar with salinities lowest at the surface, ranging from 5 to 21 g L⁻¹ and highest at the bottom (32 to 36 g L⁻¹) (Fig. 4.3). The total PFCs concentrations showed the opposite trend with average concentrations highest in the surface layer (L1) (57 ng L⁻¹) and lowest (29 ng L⁻¹) in the bottom layers (L3 and L4). The PFCA decreased with depth in all cases. On average, the total PFCA concentrations in L1, L2, L3 and L4 (obtained by averaging concentrations from S1, S2, S3 and S4) shown in Fig. 3.3 were 36.8 ± 2.9 , to 26.6 ± 3.6 , 20.3 ± 3.1 and 17.8 ± 2.7 ng L⁻¹, respectively. Higher total PFC concentrations in the surface and transition layers were consistent with the runoff content in these layers. The vertical distribution of total PFCAs, total PFSAs

and total metabolites at S1 to S4 decreased with depth, as indicated in Fig. 4.4c. A typical depth profile of PFCs and salinity can be found in Fig. B3, Appendix B.

Fig. 4.4 Total PFCs in runoff (a), runoff time profile (b) and vertical profile of total perfluorinated carboxylates, sulfonates, and metabolites, fractions in Marina Reservoir (c) (average value, error bar represents standard deviation, $n = 24, 8$ and 6 for a, b and c , respectively).

4.3.2 PFC content in storm runoff

The average total PFCs concentration and standard deviation in the tributaries CM1, CM2 and CM3 were 64 ± 19 , 65 ± 27 and 92 ± 35 ng L⁻¹, respectively (Fig. 4.4a). The PFC composition during the rain event stayed relatively constant at all sites with some notable exceptions of dominant PFOS at site CM3 (Fig. 4.5). The highest total PFCs concentrations were observed in CM3 (Fig. 4.4a) perhaps because of contributions from a point source that released PFSA (Nguyen et al., 2011c). Samples collected during rain events showed first flush behaviour: PFC concentrations were highest in the first

samples taken and then decreased thereafter. In CM1 and CM2, concentrations of total PFCs in the first flush samples were as high as 100 ng L⁻¹ and the composition was dominated by PFCAs. In contrast, the PFC composition in the first flush samples of CM3 was dominated by PFSAs. In CM3, the PFSA concentration maximum was delayed for 160 minutes (until the third composite sample), suggesting that the source releasing PFSAs was located at some distance from the storm water sampler.

Fig. 4.5 Vertical composition of PFCs in Marina Reservoir and PFC concentration profile in runoff during a rain event. T1 to T6 represent composite samples obtained 40 min intervals, from 40 min (T1) to 240 min (T3).

The average concentration ratios of perfluorooctanoate to perfluorooctane sulfonate (PFOA/PFOS) observed at CM1, CM2, and CM3 were 2.0, 4.8 and 0.3, respectively. In Marina Reservoir, this ratio was approximately 2 at all depths, suggesting that the freshwater that blends with the seawater is well mixed.

4.3.3 Occurrence of PFCs in sediments and partition coefficients of PFCs between dissolved phase and sediment

Table 4.1 shows the occurrence data of PFCs in sediment collected in the top layer (1-10 cm) at site S4. Eleven PFCs were detected, including three PFSA, five PFCAs with chain-lengths ranging from C₈-C₁₃ (except C₉), and three metabolites (N-EtFOSA, N-MeFOSAA, N-EtFOSAA). Concentrations of total PFCs, PFSA, metabolites, N-EtFOSAA and PFOS in Marina Bay sediments (Table 4.1) were higher than in San Francisco Bay (Higgins & Luthy, 2006) and in Tokyo Bay (Ahrens et al., 2010). The concentrations of PFTA and N-EtFOSA were relatively high considering that these compounds were not detected in Marina Catchment waters (Nguyen et al., 2011c). The reasons for this apparent anomaly are not known. Perhaps, the detection limit for these compounds in water was too high or these compounds were formed in the sediment. Conversely, PFNA and FOSA were prevalent in the water column but were not detected in the sediment samples, an observation that was made previously with San Francisco Bay sediment (Higgins et al., 2005). The PFSA were the predominant PFC fraction with PFOS, 6:2FtS and PFHxS contributing 35.2%, 15.5% and 10.5%, respectively. Higher-weight molecules, such as N-EtFOSAA (MW=585 g mol⁻¹) and N-MeFOSAA (MW=571 g mol⁻¹) were relatively concentrated (14.1 and 7.9%, respectively), as was observed previously in Tokyo Bay sediments (Ahrens et al., 2010).

Organic content measurements of Marina Bay sediment were not available. Instead, the value of 1.05% measured by Nayar et al., 2007 in sediments outside the Marina Barrage was used. Data reported by others indicate that the f_{oc} in sediments can vary widely: Higgins & Luthy, 2006 measured f_{oc} ranging from 0.56 to 9.7% in San Francisco Bay and Ahrens et al., 2010 report 1.5 to 10.6% Tokyo Bay. The K_{oc} values shown in Table 3.1 are comparatively high, likely because the f_{oc} value used as an estimate is low. In spite of this uncertainty, the data allows a qualitative evaluation of the influence of structure on sorption by soil organic carbon: sorption increases with the length of the perfluorinated carbon chain, sulfonated PFCs sorbed more strongly than their carboxylated analogues, and substitution of hydrogen with fluorine lowers sorption. The latter is evident from comparing the K_{oc} value of PFOS with that of 6:2FtS.

4.3.4 Estimation for PFC load to the reservoir

The PFC input into the Marina reservoir was estimated based on the following assumptions: (i) the concentration of total PFCs in rain water was 6 ng L⁻¹, as reported earlier (Nguyen et al., 2011c); (ii) all rainfall in the catchment drains as runoff into the reservoir; (iii) the input of suspended solids (SS) from the total catchment area was proportional to the input from the sub-catchments evaluated by Lam (Lam, 2008); (iv) PFCs adsorbed to SS were in equilibrium with aqueous PFCs; and (v) the K_d values

estimated for sediments were applicable to SS transported into Marina Bay. Hydrological data were taken from Ng, who reports an average annual rainfall of 2.80 cm (Ng., 2009). Using these assumptions, the estimated total PFC annual input into Marina Reservoir was $35 \pm 12 \text{ kg y}^{-1}$ with most (70%) transported by SS. Dry weather flow contributed approximately 25% and rainwater, 5%.

Table 4.1. Mean concentrations of PFCs in sediment and comparison of log K_d and K_{oc} of this study with literature values.

PFCs	Mean (STD)	Range	Contribution	Log K_d	Log K_{oc}	Log K_d	Log K_{oc}	Log K_{oc}
	(ng kg ⁻¹ dw)	(ng L ⁻¹ dw)	to total (average %)	This study (cm ³ g ⁻¹) ^a	This study (cm ³ g ⁻¹) ^a	Ahrens et al. (2010) (cm ³ g ⁻¹) ^b	Ahrens et al. (2010) (cm ³ g ⁻¹) ^b	Luthy & Higgins 2006 (cm ³ g ⁻¹) ^c
PFHxS	636 ± 143	483-803	10.5	2.5 ± 0.2	4.5 ± 0.2	1.8 ± 0.1	3.6 ± 0.1	
PFOS	2126 ± 1059	858-3570	35.2	2.5 ± 0.3	4.5 ± 0.3	2.1 ± 0.1	3.8 ± 0.1	2.57 ± 0.13
6:2FtS	938 ± 471	605-1271	15.5	2.8 ± 0.3	4.8 ± 0.3	n.a.	n.a.	n.a.
ΣPFSA s	2996 ± 1546	1341-4978	-	2.5 ± 0.2	4.5 ± 0.2	n.a.	n.a.	n.a.
PFHpA	<0.2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
PFOA	197 ± 105	39-322	3.3	1.3 ± 0.4	3.3 ± 0.3	0.04 ± 0.03	1.8 ± 0.1	2.1
PFNA	<0.4	n.a.	n.a.	n.a.	n.a.	0.6 ± 0.1	2.4 ± 0.1	2.4 ± 0.1
PFDA	55 ± 13	40-64	0.9	1.2 ± 0.4	3.4 ± 0.4	1.8 ± 0.1	3.6 ± 0.3	2.7 ± 0.1
PFUnA	214 ± 131	75-383	3.5	2.2 ± 0.5	4.2 ± 0.5	3.0 ± 0.1	4.8 ± 0.2	3.3 ± 0.1
PFDoA	156 ± 99	28-397	2.6	2.4 ± 0.2	4.4 ± 0.2	n.a.	n.a.	n.a.
PFTA	168 ± 55	118-227	2.8	n.a.	n.a.	n.a.	n.a.	n.a.
ΣPFCA s	645 ± 149	396-841	-	1.5 ± 0.1	3.4 ± 0.1	n.a.	n.a.	n.a.
FOSA	nd	n.a.	n.a.	n.a.	n.a.	2.5 ± 0.2	4.3 ± 0.2	
N-EtFOSA	476 ± 146	282-638	7.9	n.a.	n.a.	n.a.	n.a.	n.a.
N-MeFOSAA	223 ± 42	160-261	3.7	2.6 ± 0.2	4.6 ± 0.2	n.a.	n.a.	3.1 ± 0.2
N-EtFOSAA	849 ± 59	781-886	14.1	2.8 ± 0.3	4.8 ± 0.3	3.0 ± 0.1	4.8 ± 0.1	3.2 ± 0.2
ΣMetabolites	1086 ± 440	540-1524	-	2.8 ± 0.2	4.8 ± 0.2	n.a.	n.a.	n.a.
ΣPFC s	4700 ± 1116	3546-6325	-	2.1 ± 0.1	4.1 ± 0.1	n.a.	n.a.	n.a.

^an = 6; n.a. = not available; ^b(Ahrens et al., 2010); ^c(Higgins and Luthy, 2006).

4.4 Conclusions

Marina Reservoir is in the early stages of conversion to a freshwater reservoir. The depth profiles showed the reservoir is vertically stratified with surface layers containing approximately 86% freshwater and bottom layers 98% seawater. Surface layers contain higher PFC concentrations than the bottom layers. Approximately 70% of fresh water input originates from runoff, 25% from dry weather flow and 5% from rain, respectively.

The input of PFC in the reservoir originates primarily from runoff. The composition of PFCs in runoff and reservoir water was similar to storm runoff. The PFC content in Marina Reservoir sediments was higher compared to those measured elsewhere (San Francisco and Tokyo Bay). Sedimentation was the major sink for PFCs, as expected. Sorption of PFCs was strongest for PFCs with long carbon chains and bulky functional groups. The estimated annual PFC input into the reservoir was $35 \pm 12 \text{ kg y}^{-1}$.

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Chapter 5 Reaction rates of substituted perfluorooctane sulfonamides with photochemically produced hydroxyl radical in aqueous solution

5.1 Introduction

The ubiquitous occurrence of perfluorochemicals (PFCs) in surface waters is a growing ecotoxicological concern (Tomy et al., 2004; Verreault et al., 2005; Houde et al., 2006b; Kelly et al., 2009) and a water supply issue (Harada et al., 2003; Loos et al., 2007; Ericson et al., 2009; Mak et al., 2009). PFCs are widely used as surfactants, fire fighting chemicals, coatings, and oil and water repellents (Schultz et al., 2003b). The non-fluorinated moiety of PFC derivatives can be transformed biologically by activated sludge (Rhoads et al., 2008) and by photolytically produced hydroxyl radicals, $\cdot\text{OH}$ (Plumlee et al., 2009) producing a variety of products. In the environment, perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) generally predominate except where point sources release specific PFC products (Martin et al., 2002; Yamashita et al., 2005; Scott et al., 2006; Skutlarek et al., 2006; Plumlee et al., 2008). PFCs in surface water bodies may originate from wastewater effluents (Prevedouros et al., 2006; D'eon et al., 2009), urban runoff (Murakami et al., 2009b; Zushi and Masunaga, 2009; Nguyen et al., 2011c), rain (Simcik and Dorweiler, 2005; Kim and Kannan, 2007; Nguyen et al., 2011c) or from point-sources, such as spills and fire fighting training sites (Moody and Field, 1999; Moody et al., 2002; Nguyen et al., 2011c).

Most perfluorooctane sulfonamide compounds detected in the environment do not absorb within the spectral range of sunlight (λ 290 – 800 nm) (Plumlee et al., 2009) and therefore do not react by direct photolysis. In sunlit surface water, photolysis, may occur indirectly via photosensitizers, such as dissolved organic matter (DOM), NO_2^- , NO_3^- , Br^- , CO_3^{2-} (Zafiriou et al., 1984) and algae (Zepp and Schlotzhauer, 1983). By absorbing light, sensitizers produce extremely low concentrations of highly reactive species, such as singlet oxygen ($^1\text{O}_2$), hydroxyl radical ($^{\bullet}\text{OH}$), triplet excited state DOM (^3DOM), alkylperoxy radicals and others (Zepp and Schlotzhauer, 1983; Zafiriou et al., 1984). Steady state (SS) concentrations of these phototransients depend on the type of species and water quality. For example, $^{\bullet}\text{OH}$, one of the most important and least selective phototransients occurs at SS concentrations of 10^{-18} to 10^{-14} M (Mill et al., 1980; Buxton et al., 1988; Lam et al., 2003). Attacks by $^{\bullet}\text{OH}$ on C-H and unsaturated C-C bonds are nearly diffusion controlled ($10^{-10} \text{ M}^{-1} \text{ s}^{-1}$) and transformations of typical contaminants under environmental conditions can be significant (Mill et al., 1980; Chiron et al., 2009).

Sensitized transformations of PFCs under surface water conditions are relatively poorly understood. Attack by $^{\bullet}\text{OH}$ transforms N-ethyl perfluorooctane sulfonamidoethanol (N-EtFOSE) into PFOA and FOSA via a pathway that includes the transient formation of N-EtFOSAA, N-EtFOSA, and FOSAA (Hatfield, 2001; Plumlee et al., 2009). The rate constants, k , for the reaction between N-EtFOSAA and $^{\bullet}\text{OH}$ was estimated to be at most $(1.7 \pm 0.7) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (corresponding to a half-life of 0.47 d at a $[^{\bullet}\text{OH}]_{\text{ss}}$ of 10^{-14} M). The goal of this study was to determine k for the reaction between $^{\bullet}\text{OH}$ and N-EtFOSE and the reaction intermediates, to model the transformation pathway, and to evaluate the mass of unknown fluorinated compounds formed. 4-tert octyl phenol (OP) which bimolecular rate constant estimated in our previous study was used as competitor in the irradiation experiment (Xu et al., 2011c). Rate constants were measured over a range of pH values to study the potential influence of amide group ionization (Rayne and Forest, 2009). These data will aid in the development of models that predict the photochemical fate of these compounds in the environment and help explain the observed product distribution under environmental conditions.

5.2 Experimental section

5.2.1 Irradiation Experiments

An Atlas Suntest CPS+ sunlight simulator (Chicago, IL, USA) equipped with a 1500 W xenon arc lamp, a glass filter to block wavelengths below 290 nm, and a temperature-controlled water bath was used to perform irradiation experiments, as described previously (Plumlee et al., 2009). Factory calibration confirmed light intensity and stability. Sample preparation and irradiation were described previously (Plumlee et al., 2009). Briefly, *N*-EtFOSE, *N*-EtFOSAA, *N*-EtFOSA, FOSAA, FOSA and PFOA were irradiated individually at initial concentrations ranging from 5-10 $\mu\text{g L}^{-1}$. Aqueous reaction mixtures were prepared by adding appropriate aliquots of OP and PFC stock solutions in methanol into a 1 L volumetric flask. After evaporating the methanol under a nitrogen gas stream (99.99%, Soxal, Singapore), 1 L of water (Milli-Q, Barnstead, Iowa, USA) was added. Quartz test tubes were fill avoiding headspace and placed horizontally in the constant temperature ($25 \pm 2^\circ\text{C}$) water bath. Quartz bottles were sacrificed for sampling every 15 min. Absorbance spectra for PFCs in methanol and the irradiance of the simulator have been reported previously (Plumlee et al., 2009).

Controls included samples exposed to simulated sunlight without added H_2O_2 and samples with H_2O_2 added and darkened with aluminum foil (dark controls). Reaction mixtures were quenched by transfer into 50 mL polypropylene centrifuge test tubes (Greiner, Germany) containing 5 mL methanol (MeOH, Optima grade, Fisher Scientific; Pittsburgh, PA, USA). Quartz bottles were washed methanol (3x), which was added to the sample. Then the methanol content in the sample was adjusted to 40%, which was analyzed as described in section B1, Appendix B and elsewhere (Rhoads et al., 2008; Plumlee et al., 2009). To evaluate the effect of pH on reaction rates, reaction solutions were adjusted to pH 1, 3, 6, 8, and 11 using dilute sodium hydroxide or trifluoroacetic acid (Sigma Aldrich, Germany). The pH was measured using a pH electrode (Thermo Electron Orion, 920A, Sigma Aldrich, Singapore).

5.2.2 Analytical Method

The analytical method used was adopted from Plumlee et al. (Plumlee et al., 2008; Plumlee et al., 2009). Standards and internal standard of PFCs and their impurities were described in Rhoads et al. 2008 (Rhoads et al., 2008). For instance, *N*-EtFOSE (97.7%), *N*-EtFOSAA (54%), *N*-EtFOSA (95%), FOSAA (99.6%) were provided by 3M Co. (St. Paul, MN); PFOS (98%), PFOA (98%) and was purchased from Fluka through Sigma-Aldrich (St.

Louis, MO) and Aldrich Chemical Co. (Milwaukee, WI), respectively. All internal standards such as [d9]*N*-EtFOSE, [d5]*N*-EtFOSAA, [d5]*N*-EtFOSA, [¹³C₂]PFOA and [¹³C₂]PFOS were purchased from Wellington Laboratories (ON, Canada). In brief, voltages and gas flows were optimized for optimal intensities; electron ionization spray source was set at 425 °C. Pure nitrogen was used for nebulizer, curtain and collision gas were set at 4, 6 and 12 respectively; the drying gas flow was 8 L min⁻¹. The ion spray voltage was at - 4500 V and dwelling time was adjusted to 100 ms. OP was combined with the available PFC detection method so that all compounds would be detected in one run.

For PFC analysis, 800 µL of a 60/40 aqueous sample:methanol mixture were transferred to autosampler vials containing 200 µL aqueous 0.01% ammonium hydroxide (Sigma Aldrich, Steinheim, Germany). Prior to injection, 100 µL of a 3 ng L⁻¹ internal standard mixture containing [d9]*N*-EtFOSE (for analysis of *N*-EtFOSE and OP), [d5]*N*-EtFOSAA (for analysis of *N*-EtFOSAA and FOSAA), [d5]*N*-EtFOSA (for *N*-EtFOSA and FOSA), [¹³C₂]PFOA (for PFOA) and [¹³C₂]PFOS (for PFOS analysis) in methanol were added to the vial to a total volume of 1100 µL. The aliquot was then vibrated and placed in a 4 °C autosampler rack. Samples were injected directly into liquid chromatography (LC) (liquid chromatography, Shimadzu Asia Pacific Pte. Ltd., Singapore) coupled to a tandem-mass spectrometer (MS/MS) (AP 3000, Applied Biosystems, MDS Sciex, Toronto, Canada). Aqueous solutions and methanol were degassed and delivered at a total flow rate of 0.25 mL min⁻¹.

A large volume of 490 µL of sample was injected into a C18 column (3.5 µm pore size, 40 mm × 2.1 mm ID, Higgins Analytical, CA, USA) with the following chromatography program: methanol started from 35% to 100% at 7.5 min, held at 100% to 10 min then returned to 35% for 15 min at a total flow rate of 0.25 mL min⁻¹ with 2 mM ammonium acetate as the inorganic mobile phase. Good recovery rates for target compounds (*N*-EtFOSE, *N*-EtFOSAA, *N*-EtFOSA, FOSAA, FOSA, PFOA and PFOS) from periodical tests were typically around 100% ranging from 90-120% except for *N*-EtFOSA at 55% (Fig. C14, Appendix C). The correction to recovery rates therefore was not carried out either with the consideration that correction variation might fall in the range of analytical variation. Fig. C14 (Appendix C) showed results from one of recovery tests with low *N*-EtFOSA recovery however it was improved in other periodical recovery test (one every two months).

5.2.3 Competitive kinetics of PFCs and OP with $\cdot\text{OH}$

OP was used as reference compound for competitive kinetics evaluations as described previously (Mazellier and Leverd, 2003; Xu et al., 2011c). Mazellier et al. (2003) reported k_{OP} of $(6.4 \pm 0.5) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ using H_2O_2 (Mazellier and Leverd, 2003), $14 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ using ozonation (Graham et al., 2007), $(20 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ using radiolysis (Bledzka et al., 2010). Reported rates range for different alkylphenols range from $11 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for *o*-cresol to $19 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for 4-*tert*-butylphenol (Buxton et al., 1988). Using ibuprofen as the reference, we obtained $(11 \pm 0.5) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Xu et al., 2011c). The latter value was used for competitive rate calculations because OP degradation data obtained here were consistent with the data obtained previously. The average of the four published rate constants for OP is $(11.28 \pm 2.15) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The k_{PFC} rate constant data obtained in this study are shown in the Appendix C. Initial rate constants were determined in short-term (<3 h) experiments with N-EtFOSE and the three intermediates, N-EtFOSAA, N-EtFOSA, FOSAA, as the parent compounds. Short-term data were used to determine bimolecular rate constants and to develop kinetic rate laws and long-term (32 h) data were used to validate kinetic models. Rate laws were evaluated using COMSOL Multiphysics Software version 4.1 equipped with the Chemical Engineering module (COMSOL, Burlington, MA).

5.3 Results and discussion

5.3.1 The pathway and rate laws of N-EtFOSE degradation by $\cdot\text{OH}$.

The reaction scheme shown in Fig. 5.1 was obtained by combining the results of short-term (<5 h) experiments with N-EtFOSE and the three intermediates that were detected, N-EtFOSAA, N-EtFOSA, FOSAA. All data were collected at pH 6. The rate laws that correspond to the pathways shown in Fig. 5.1 are shown in Table 5.1. Rate constants evaluated from short-term experiments were modeled as consecutive and/or parallel first-order reactions. Kinetic data are shown in Figs C1 through C8 and in Tables 5.2, 5.3. The reaction system shown in Table 5.1 was modeled using COMSOL Multiphysics Software version 4.1 equipped with the Chemical Engineering module. $[\cdot\text{OH}]_{ss}$ in the reaction solutions was calculated from the experimental pseudo-first order disappearance rate constant of OP as $5.5 \times 10^{-14} \text{ M}$. This value exceeds environmental values by approximately a factor of 10 to 10^4 . As expected, the rate constant determined for N-EtFOSAA, $(0.68 \pm 0.05) \times 10^{-9} \text{ M}^{-1} \text{ s}^{-1}$ (Table 5.2), was below the previously reported upper limit (Plumlee et al., 2009). For all PFCs, the measured rate constants

ranged narrowly from $(1.05 \pm 0.12) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for N-EtFOSE to $(0.53 \pm 0.12) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for FOSAA, and were approximately an order of magnitude below the diffusion-controlled limit (approximately $10^{10} \text{ M}^{-1} \text{ s}^{-1}$).

Fig. 5.1 Reaction scheme for the transformation of N-EtFOSE by $\cdot\text{OH}$. Reactions labelled with an X form unknown products.

Table 5.1. Rate laws of substrate removals and product formation for the reactions shown in

Fig. 5.1.

Removal	
A	$-\frac{d[A]}{dt} = (k_{AB} + k_{AC} + k_{AD} + k_{AE} + k_{AF} + k_{AX})[A][\bullet OH]$
B	$-\frac{d[B]}{dt} = (k_{BC} + k_{BD} + k_{BE} + k_{BF} + k_{BX})[B][\bullet OH]$
C	$-\frac{d[C]}{dt} = (k_{CD} + k_{CE} + k_{CF} + k_{CX})[C][\bullet OH]$
D	$-\frac{d[D]}{dt} = (k_{DE} + k_{DF} + k_{DX})[D][\bullet OH]$
Formation	
B	$\frac{d[B]}{dt} = k_{AB}[A][\bullet OH]$
BX	$\frac{d[BX]}{dt} = k_{BX}[A][\bullet OH]$
C	$\frac{d[C]}{dt} = k_{AC}[A][\bullet OH] + k_{BC}[B][\bullet OH]$
CX	$\frac{d[CX]}{dt} = k_{CX}[C][\bullet OH]$
D	$\frac{d[D]}{dt} = k_{AD}[A][\bullet OH] + k_{BD}[B][\bullet OH] + k_{CD}[C][\bullet OH]$
DX	$\frac{d[DX]}{dt} = k_{DX}[D]$
E	$\frac{d[E]}{dt} = k_{AE}[A][\bullet OH] + k_{BE}[B][\bullet OH] + k_{CE}[C][\bullet OH] + k_{DE}[D][\bullet OH]$
F	$\frac{d[F]}{dt} = k_{AF}[A][\bullet OH] + k_{BF}[B][\bullet OH] + k_{CF}[C][\bullet OH] + k_{DF}[D][\bullet OH]$

Table 5.2. Pseudo first-order decay rate constants of OP and PFC and the bimolecular rate constants for the reaction between PFCs with $\cdot\text{OH}$ at pH 6 obtained using competitive kinetics with OP as the reference compound ^a.

Compound	pKa ^c	OP decay (h ⁻¹) ^b	PFC decay (h ⁻¹) ^b	Rate constant $\times 10^9$ (M ⁻¹ s ⁻¹)	Half-life (h) (95% confidence interval)	Half-life (d) where [$\cdot\text{OH}$]=10 ⁻¹⁸ M ^d
N-EtFOSE*	-	2.20 $\pm$ 0.08	0.21 $\pm$ 0.02	1.05 $\pm$ 0.12	3.3 (3.0, 3.6)	7.64 $\times$ 10 ³
N-EtFOSAA	3.9	2.76 $\pm$ 0.13	0.17 $\pm$ 0.01	0.68 $\pm$ 0.05	4.1 (3.9, 4.3)	1.18 $\times$ 10 ⁴
N-EtFOSA	9.0	1.77 $\pm$ 0.07	0.11 $\pm$ 0.01	0.68 $\pm$ 0.07	6.3 (5.8, 6.9)	1.18 $\times$ 10 ⁴
FOSAA	3.9	3.09 $\pm$ 0.09	0.15 $\pm$ 0.01	0.53 $\pm$ 0.05	4.6 (4.3, 5.0)	1.51 $\times$ 10 ⁴
OP	10.4					

^a $k_{\text{OP}} = (11 \pm 0.5) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

^b n=3, mean $\pm$ standard error (n=4).

^c pKa values were estimated using SPARC (Rayne and Forest, 2009)

^d half-life estimated from PFC decay rates (with relevant environmental concentration of $\cdot\text{OH}$)

Table 5.3. Rate constants for the PFCs transformation reactions shown in Fig. 5.1 obtained at pH 6 ^a.

PFCs	Abbrev.	Constant	Rate constant ^b × 10 ⁹ (M ⁻¹ s ⁻¹)	Yield (%)
N-EtFOSE	A	Degradation	(1.05 ± 0.12)	
→N-EtFOSAA	A→B	k _{AB}	(0.13 ± 0.05)	12.4
→N-EtFOSA	A→C	k _{AC}	(0.14 ± 0.04)	13.3
→FOSAA	A→D	k _{AD}	(0.02 ± 0.01)	1.9
→FOSA	A→E	k _{AE}	(0.01 ± 0.01)	1.0
→PFOA	A→F	k _{AF}	(0.31 ± 0.19)	29.5
→unknown	A→AX	k _{AX}	(0.49 ± 0.35)	46.7
N-EtFOSAA	B	Degradation	(0.68 ± 0.07)	
→N-EtFOSA	B→C	k _{BC}	(0.03 ± 0.01)	4.4
→FOSAA	B→D	k _{BD}	(0.01)	1.0
→FOSA	B→E	k _{BE}	(0.01 ± 0.01)	1.5
→PFOA	B→F	k _{BF}	(0.15 ± 0.13)	21.2
→unknown	B→BX	k _{BX}	(0.45 ± 0.16)	66.2
N-EtFOSA	C	Degradation	(0.68 ± 0.07)	
→FOSAA	C→D	k _{CD}	n.d. ^c	0.1
→FOSA	C→E	k _{CE}	(0.1 ± 0.07)	14.7
→PFOA	C→F	k _{CF}	(0.35 ± 0.09)	52.0
→unknown	C→CX	k _{CX}	(0.27 ± 0.12)	37.9
FOSAA	D	Degradation	(0.53 ± 0.05)	
→FOSA	D→E	k _{DE}	(0.25 ± 0.07)	47.2
→PFOA	D→F	k _{DF}	(0.02 ± 0.01)	3.8
→unknown	D→DX	k _{DX}	(0.25 ± 0.07)	47.2

^a The yield was estimated using data that was collected for the first 3 h of irradiation.

^b (x ± y) represent mean ± standard deviation, n=5-10.

^c n.d : not formed at quantifiable levels.

Long-term experiments (32 h) were conducted to validate the kinetic data and modeling. N-EtFOSE disappearance and product formation data and modeling results are shown in Fig. 5.2. The transient appearance of the measured intermediates is evident in Figs 5.2b and 5.2d. N-EtFOSE formed two transient intermediates N-EtFOSAA and N-EtFOSA and two stable products, FOSA and PFOA. FOSAA was detected only at trace levels (see Figs 5.2b and 5.2d) and PFOS was not observed, as reported in our previous study (Plumlee et al., 2009). To examine whether first order rate constants were dependent on the initial concentrations, experiments with N-EtFOSE at 10 µg L⁻¹ were carried out (Table C1). At 10 µg L⁻¹, the

disappearance rates stayed constant (data not shown) but the appearance rate constants tended to be higher (in the case of N-EtFOSA appearance by nearly a factor of two). When investigated individually, N-EtFOSAA and N-EtFOSA produced FOSAA (Table C1) with yields of 0.2% and 0.1%, respectively.

Fig. C9 indicates the disappearance and product formation of N-EtFOSE, N-EtFOSAA, and N-EtFOSA for the long-term experiments. Also shown is the sum of the measured compounds (parent plus intermediates and products = “total”). The fraction of unknown products formed was calculated from the difference to $C/C_0 = 1$. Product yields and the formation of unknowns depended on the parent compound. N-EtFOSE and N-EtFOSA produced only 25% and 20% unknowns, respectively, whereas for N-EtFOSAA, unknowns constituted approximately 80% of the total products formed. Fig. C10 indicates that the fraction of unknown products increased in the order N-EtFOSA, FOSAA, N-EtFOSE and N-EtFOSAA. Modeling indicated that reaction of N-EtFOSE yielded 45.5%, 7.3%, 4.5%, and 0% of AX, BX, CX and DX, respectively, totaling 57%. Once the intermediates are transformed, PFOA and FOSA reach a stable value, indicating that there are no precursors for PFOA and FOSA in the pool of unknown products. In the reaction with N-EtFOSE, the amount of unknowns were approximately 25 to 30% suggesting that the yield may depend on the presence of co-solutes, perhaps because of enhanced coupling. The first-order rate of N-EtFOSE transformation decreased after 22 h likely because by then a substantial fraction of H_2O_2 had decayed and the decrease of $[^{\bullet}OH]_{ss}$ became significant.

Model calculations with data comparison are shown for N-EtFOSAA, N-EtFOSA and FOSAA in Figs. C11 C12 and C13 (no data available), respectively. N-EtFOSA appears as a minor intermediate with a maximum concentration of 1.7% in the transformation of N-EtFOSAA (Figs C11a and C11b). For N-EtFOSA and FOSAA (Figs C12 and C13), intermediates are not predicted. FOSAA was not detected except occasionally as an unquantifiable trace (Fig. C9).

The reaction scheme shown in Fig. 5.1 and in Table 5.3 indicate that direct pathways contribute 29.5% to PFOA formation and only 1.0% to FOSA formation. The relative yields of N-EtFOSAA and N-EtFOSA are 12.4% and 13.3%, respectively, and these react to PFOA with yields of 21% and 52%, respectively. This indicates that cleaving off the sulfonate group is the preferred pathway. FOSAA reacted by dealkylation to FOSA and by deamination to PFOA with yields of 47% and 3.8%, respectively.

Fig. 5.2 Reaction profiles of N-EtFOSE reaction and product formation. Left: a and b: experimental data (for conditions see text, initial concentration $5 \mu\text{g L}^{-1}$). Right: c and d: model output using COMSOL (version 4.1), kinetic parameter input from Table 5.3, initial concentration $5 \mu\text{g L}^{-1}$, estimated $[\cdot\text{OH}]_{\text{ss}} = 5.5 \times 10^{-14} \text{ M}$. For b and d the y scale is 10 times enlarged. N-EtFOSE half-life/complete degradation is 2 h/32 h and 2.4 h/22 h for experiment result (a) and model output (c), respectively. Transient intermediates maximized after 7.7 h (experimental) and 5.8 h (modelling data).

5.3.2 Dependence of rate constant on pH

Table 5.4 summarizes the rate constants obtained for N-EtFOSE at different pH values. For N-EtFOSE, rate constants in the range of pH 1 to 8 varied relatively little. The pooled average was $0.86 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, relatively close to the rate constants measured under the same conditions in Singapore surface water (Alexandra Canal) (Xu et al., 2011c) but only about 42% compared to clean water (pH 1 to 8). The bimolecular rate of N-EtFOSE in surface water was slightly lower than in clean water suggesting that the water matrix has minimal effect on radical initiated reaction. The value measured at pH 10 was approximately 4 times faster but a significant pH trend could not be discerned. For N-EtFOSA and FOSAA, rate constants were determined at pH 6, 8 and 10 (Table 5.5). Rate constants varied by a factor of 2 to 4 with highest values at pH 8. Based on modeling, it was previously suggested that the pK_a of the primary and secondary amidic protons of N-EtFOSAA, N-EtFOSA and FOSAA are sufficiently low ($\text{pK}_a = 3.9$ to 9.0) to affect speciation within the pH of interest (Rayne and Forest, 2009). However, the data obtained here do not show a pronounced pH effect, because either the estimated pK_a values are inaccurate or the influence of speciation on the rate constants is weak.

Table 5.4. Photodegradation rate of N-EtFOSE in various pH solutions and in surface water background (mean $\pm$ standard deviation, n=3 runs, *n=2 runs)

	Decay rate constant (h^{-1})		Transformation rate constant
	OP	N-EtFOSE	$\times 10^9 (\text{M}^{-1} \text{ s}^{-1})$
pH 1-8	2.81 ± 0.29	0.22 ± 0.03	0.86 ± 0.15
pH 10	1.66 ± 0.08	0.03 ± 0.01	0.23 ± 0.04
Surface water (pH 8)*	1.17 ± 0.13	0.18 ± 0.01	0.61 ± 0.06

Table 5.5. Transformation rate constants of OP, N-EtFOSA and FOSAA at pH 6, 8 and 10 ^a.

	N-EtFOSA (h^{-1})	OP (h^{-1})	$k_{\text{N-EtFOSA}}$ ($\text{M}^{-1} \text{ s}^{-1}$)	FOSAA (h^{-1})	OP (h^{-1})	k_{FOSAA} ($\text{M}^{-1} \text{ s}^{-1}$)
pH 6^b	0.11 ± 0.01	1.77 ± 0.07	$(0.68 \pm 0.07) \times 10^9$	0.15 ± 0.01	3.09 ± 0.09	$(0.53 \pm 0.05) \times 10^9$
pH 8^c	0.22 ± 0.02	1.61 ± 0.06	$(1.54 \pm 0.14) \times 10^9$	0.41 ± 0.06	2.1 ± 0.09	$(2.15 \pm 0.34) \times 10^9$
pH 10^d	0.13 ± 0.02	1.88 ± 0.11	$(0.74 \pm 0.10) \times 10^9$	0.18 ± 0.01	2.59 ± 0.17	$(0.76 \pm 0.07) \times 10^9$

^a Values represent mean $\pm$ standard deviation, ^b n = 4, ^c n = 3.

5.3.3 Environmental implications

Under environmental conditions, $[\cdot\text{OH}]_{\text{ss}}$ concentrations are expected to range widely, from 10^{-18} M to 10^{-14} M (Lam et al., 2003). In this range, the half-life of N-EtFOSE is expected to range from 21 years to approximately 1 day. The bimolecular rates of the substituted perfluoroalkyl sulfonamides measured here range from $0.53 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ to $1.05 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and are generally lower (by as much as 16 times) than those reported for herbicides (Armbrust, 2000), sulfa drugs (Boreen et al., 2005), and chlorinated phenols (Tang and Huang, 1996). Hence, substituted perfluoroalkyl sulfonamides are more stable against radical attack than other commonly found micropollutants. For N-EtFOSE to be completely (99%) converted into FOSA, PFOA, and unknowns by environmental $\cdot\text{OH}$ would take 159 years at 10^{-18} M but only 5 days at 10^{-14} M.

It is interesting to compare the product distribution of OH-initiated and biological transformation of N-EtFOSE. In biological transformation studies, N-EtFOSAA accumulated to relatively high concentrations and only 7% reacted to PFOS. Interestingly, PFOA formation was not observed [10]. Biological transformation first oxidizes the alcohol group of N-EtFOSE to the carboxylic acid and dealkylates the amid group before cleaving S-N bond and forming PFOS. Hence, the most significant difference between OH-initiated and biological transformation in water appears to be that the former produces perfluoroalkanoic acids and perfluoroalkane sulfonamids whereas the latter produces only perfluoroactane sulfonates. By contrast in the gas phase, N-Methyl perfluorobutane sulfonamidoethanol reacted with $\cdot\text{OH}$ to both perfluoroalkanoic acid and perfluorobutane sulfonate whereas the perfluorobutane sulfonamide was not observed (D'Eon et al., 2006). These observations suggest that the presence of water prevents cleavage of the S-N bond by $\cdot\text{OH}$.

The disappearance rates of the perfluoroalkyl substituted sulfonamides decrease in the order N-EtFOSE > N-EtFOSAA > N-EtFOSA > FOSAA which agree with the reported decrease of the ethanol, alkane and acetic acid substituents (Dorfman and Adams, 1973). The disappearance rates of N-EtFOSAA and N-EtFOSA are nearly identical but the respective yields of PFOA were 21% and 52%, respectively. This indicates that the N-substituents influence the rate of OH-initiated C-S bond cleavage. FOSAA react slowly via C-S cleavage forming only 4% PFOA and for FOSA C-S cleavage was observed, suggesting that electron donating substituents on the amidic nitrogen promote C-S cleavage.

Results obtained here indicate significant production of photochemically stable FOSA during aqueous indirect photochemical transformation. By contrast, field observations indicate that FOSA is typically present only at very small concentrations (Nguyen et al., 2011c). A possible explanation for this discrepancy is that indirect phototransformation is insignificant or that FOSA is biologically transformed

into PFOS. In sediments of a Singapore reservoir, the molar ratio of N-EtFOSA/N-EtFOSAA was 0.7, a value that is close to the ratio predicted by the model (0.8) for the transformation of N-EtFOSE by hydroxyl radical. There is insufficient data to assess the contribution of various transformation pathways to explain the observed PFC distributions in different environmental compartments.

5.4 Conclusions

The rate constants, k , for the bimolecular reaction of photochemically produced $\cdot\text{OH}$ and N-EtFOSE, N-EtFOSAA, N-EtFOSA and FOSAA were determined using competitive kinetics with OP as the reference compound. The measured constants for N-EtFOSE, N-EtFOSAA, N-EtFOSA and FOSAA were $(1.05 \pm 0.12) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, $(0.68 \pm 0.05) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, $(0.68 \pm 0.05) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $(0.53 \pm 0.05) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, respectively. For N-EtFOSE, k decreased in alkaline solution (pH 10) compared to neutral and acidic solutions (pH 1 to pH 8) by a factor of 4 and by factor of 7 with OP exclusion. The dependence of k on pH was relatively small: for N-EtFOSA and FOSAA, k was approximately 2 to 3 times higher at pH 8 than at pH 6 and 10. Modeling and mass balance evaluation of N-EtFOSE in batch experiments predicts that photodegradation of N-EtFOSE yields 38% perfluorooctanoate (PFOA), 3% perfluorooctane sulfonamide (FOSA), and 58% unknown products, the transient concentrations of N-EtFOSAA and N-EtFOSA are nearly equal with a molar concentration ratio of approximately 0.8. These compounds reach a peak concentration of 6% of the initial N-EtFOSE concentration. We propose that characteristic ratios of PFC degradation products might be diagnostic for $\cdot\text{OH}$ initiated degradation processes.

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Chapter 6 Influence of algae and other natural photosensitizers on the indirect photolysis of N-ethyl perfluorooctane sulfonamidoethanol (N-EtFOSE) and 4-tert-octyl phenol (OP)

6.1 Introduction

Because cities such as Singapore are increasingly relying on runoff from urban catchments to augment water supplies, occurrence and fate of emerging contaminants, such as perfluorochemicals (PFCs) and alkylphenol ethoxylates (APEOs) in surface water need to be understood (Xu et al., 2011b). Photochemical transformation is one of several processes that can naturally attenuate organic contaminants in surface waters (Gurr and Reinhard, 2006). Photodegradation can occur either through direct interaction with sunlight, indirectly through reactions with reactive intermediates that are produced through the interaction of light with photosensitizers often occurring in surface water, or a combination of both. Common photosensitizers include nitrate, nitrite (Zepp et al., 1987; Mack and Bolton, 1999), dissolved organic matters (DOM), humic acid (HA) (Kotzias et al., 1986), and algae (Wang et al., 2007). Under the irradiation of light, photosensitizers produce highly reactive intermediates (phototransients), most importantly hydroxyl radicals ($\cdot\text{OH}$), alkylperoxy ($\text{RO}_2\cdot$) and singlet oxygen ($^1\text{O}_2$) (Mill et al., 1980) and triplet excited state DOM ($^3\text{DOM}^*$) (Zepp and Cline, 1977; Zepp et al., 1981; Vione et al., 2006; Xu et al., 2011a). Different compounds can present different behaviours to these active species. Significant role of $\cdot\text{OH}$ was reported by Lam et al., (2003) whereas DOM can also strongly contribute to the fate of pharmaceuticals (Boreen et al., 2005). Recent finding showed that $^3\text{DOM}^*$ can result in 48-74% disappearance of amoxicillin (Xu et al., 2011a). In another example, isoxazole group quickly reacted with $^1\text{O}_2$ while thiadiazole showed little reactivity toward this reactive species (Boreen et al., 2004).

Active agents such as $\cdot\text{OH}$ and $^1\text{O}_2$ produced from algal exudates and pigments are thought to be the major photochemical components which react with the contaminant. Intracellular components could also be released to the surrounding environment when algae are irradiated (Herth, 1979). $\cdot\text{OH}$ presents non-selective behaviour and aims to alpha carbon whereas $^1\text{O}_2$ targets to electron rich centres such as double bonds, lone pair electrons etc. of the contaminants. Hydrogen abstraction and oxygen addition are normally conducted with these active reagents (Grossweiner) (<http://www.photobiology.com/educational/len2/singox.html>). Hence, PFC precursors and metabolites with moieties such as substituted sulfonamide, saturated and unsaturated hydrocarbon are assumed to be susceptible to these active species. Algae have been reported to be capable of accelerating the sunlight induced transformation of some organic contaminants (Zepp and Schlottzhauer, 1983), where they are able to produce up to 5 μM and 75 μM of $\cdot\text{OH}$ and $^1\text{O}_2$, respectively, in the first 4 h of irradiation (Wang et al., 2007).

In term of algal biotransformation, microalgae *Chlorella vulgaris* showed high ability to degrade more than 80% nonyl phenol which associated with photosynthetic and metabolic activities in a recent study (Gao et al., 2011). Lei et al. (2007) reported that up to 78% PAHs (pyrene and fluoranthene) were removed by algal species after 7 days in culture medium (Lei et al., 2007) and the composition and cell wall structure were important for the bio sorption (Lei et al., 2002). Micro algal cell wall was reported to be able to provide various binding sites to aqueous contaminants and the binding capacity could be improved in dead cell preparation (Avery et al., 1998). Algal cells were denatured and inactivated by heat-killing but more photosensitive to pesticides than the live algae (Wang et al., 2007). For instance, dead phytoplankton cells showed more photosensitizing activities on the phytol side chain of chlorophylls (Rontani et al., 1996). In general, the removal of contaminants by algae involves both abiotic and biotic processes where the former was dominant in the initial period (Lei et al., 2002).

It has been reported that atrazine degradation was enhanced three fold in the presence of HA in aqueous phase (Minero et al., 1992). For $\lambda > 280 \text{ nm}$, two primary pathways have been proposed for nitrate photolysis (equation 6.1, 6.2).

Self-quenching effects and recombination can occur during nitrate photolysis:

Nitrite photolysis occurs for $200\text{ nm} < \lambda < 400\text{ nm}$ (equation 6.5) (Buxton et al., 1988; Warneck and Wurzinger, 1988; Mack and Bolton, 1999):

Nitrite, DOM and bicarbonate also behave as radical scavengers:

Gauthier and Mabury, (2005) reported that nitrate can promote the decay rate of aqueous 8:2 telomer alcohol (8:2FtOH) whereas humic acid inhibited the reaction by scavenging radicals (Gauthier and Mabury, 2005).

In this study, the photochemical degradation of N-ethyl perfluorooctane sulfonamidoethanol (N-EtFOSE, one of the precursors of PFCs) and 4-tert octylphenol (OP), a degradation product of alkylphenol ethoxylates), were investigated in the presence of an aqueous suspension of blue-green algae collected from a local reservoir in Singapore. The influence of active and inactive algae in both irradiated and non-irradiated conditions was studied. In addition, bimolecular reaction rates of N-EtFOSE and the roles of natural constituents such as nitrite, nitrate and HA were also considered and examined individually as photosensitizer. Finally, in order to assess the influence of different background scenarios on the $\cdot OH$ -initiated oxidation of N-EtFOSE, hydrogen peroxide (H_2O_2) was added to solutions for the irradiation experiment. The results obtained from the laboratory simulated conditions provide useful information on the kinetics of contaminant fate for extrapolation to natural environmental conditions.

6.2 Materials and Methods

6.2.1 Preparation of reaction mixtures

6.2.1.1 Algae suspensions

Table 6.1 summarizes the solution compositions and the experimental design. Cyanobacteria isolated from Kranji reservoir, Singapore, were cultured in the medium used for isolation of toxic strains of *Anabaena flos-aquae* (MLA) until the stationary phase was reached. The algae were harvested and washed 3 times with ultra-pure water to remove the medium. Aqueous solutions of N-EtFOSE and OP were prepared by adding 250 μL and 50 μL of methanolic stock solutions of N-EtFOSE (20.44 mg L^{-1}) and OP

(200 mg L⁻¹) to a 1 L flask, respectively, and evaporating the solvent to dryness by nitrogen gas purging. Appropriate amounts of Milli-Q water were added to obtain concentrations of 5 and 10 µg L⁻¹ of N-EtFOSE and OP solutions (solution A) respectively, for studying photoreactions. For experiments with live cells, washed algae were mixed with aqueous N-EtFOSE to obtain a concentration of 387 µg L⁻¹ of cell (solution LA). For experiments with dead cells, washed algae were heat-killed in a 55 °C-water bath for 30 min. The dead algae were then mixed with solution A to obtain the same conditions as LA (solution DA). Solutions A, LA and DA were added to quartz tubes and capped avoiding headspace.

6.2.1.2 Nitrate, nitrite and HA solutions

Solutions for the indirect photolysis experiments of N-EtFOSE in the presence of nitrate and nitrite were prepared as follows: appropriate volumes of methanol in stock solutions of N-EtFOSE and OP were spiked into 1 L volumetric flask, the solvent was evaporated and substrates were dissolved in 1 L Milli-Q water. A subsample of 500 ml containing only N-EtFOSE was set aside as a control (Ctr). The remainder was amended with nitrite, nitrate, or HA (Sigma-Aldrich, Germany) to obtain final concentrations of 10 mg L⁻¹ for nitrate and nitrate and 1 and 5 mg L⁻¹ for HA. The amended solutions were divided into two samples and studied pairwise, one under experimental conditions (Exp, light-exposed) and the other in the dark (DCtr, dark).

To investigate the influence of nitrite, nitrate, and HA on the [•]OH initiated reaction, solutions containing 10 or 100 µg L⁻¹ nitrite or nitrate and 1-5 µg L⁻¹ HA were prepared. An appropriate amount of hydrogen peroxide (H₂O₂ approx. 30%, Sigma Aldrich, Germany) was spiked into DCtr and Exp samples to obtain a 10 mM solution. The composition of all samples can be found in Table 6.1.

6.2.2 Irradiation experiments

Solutions were poured into 25 mL quartz test tubes and capped without headspace. The quartz test tubes were placed horizontally in a circulating water bath (25 ± 2 °C) of a solar simulator (equipped with 1500 W Xe-lamp, CPS+, Atlas, USA) operated under 765 W m⁻² light intensity for simulating solar noon time irradiation. Samples were sacrificed, mixed with methanol and centrifuged (16,000 rpm in 20 min) before analysis.

6.2.3 Analytical method

The analytical method has been described in detail previously (Plumlee et al., 2009; Nguyen et al., 2011a) and in section 5.2.2 of Chapter 5. Similarly, the large volume injection method was used for irradiated samples. Recovery tests were also carried out for target compounds. N-EtFOSE (97.7%), N-ethyl perfluorooctane sulfonamido acetate (N-EtFOSAA, 54%), N-ethyl perfluorooctane sulfonamide (N-

EtFOSA, 95%), perfluorooctane sulfonamido acetate (FOSAA, 99.6%) were provided by 3M Co. (St. Paul, MN); perfluorooctane sulfonate (PFOS, 98%), perfluorooctanoate (PFOA, 98%) and was purchased from Fluka through Sigma-Aldrich (St. Louis, MO) and Aldrich Chemical Co. (Milwaukee, WI), respectively. All internal standards such as [d9]N-EtFOSE, [d5]N-EtFOSAA, [d5]N-EtFOSA, [¹³C₂]PFOA and [¹³C₂]PFOS were purchased from Wellington Laboratories (ON, Canada).

A large volume of 490 µL of sample was injected into a C18 column (3.5 µm pore size, 40 mm × 2.1 mm ID, Higgins Analytical, CA, USA) with the following chromatography program: methanol started from 35% to 100% at 7.5 min, held at 100% to 10 min then returned to 35% for 15 min at a total flow rate of 0.25 mL min⁻¹ with 2 mM ammonium acetate as the inorganic mobile phase. Samples were injected directly into liquid chromatography (LC) (liquid chromatography, Shimadzu Asia Pacific Pte. Ltd., Singapore) coupled to a tandem-mass spectrometer (MS/MS) (AP 3000, Applied Biosystems, MDS Sciex, Toronto, Canada). Aqueous solutions and methanol were degassed and delivered at a total flow rate of 0.25 mL min⁻¹.

6.3 Results and discussion

6.3.1 Degradation in algae suspension

Both live and dead algae promoted the transformation of N-EtFOSE transformation whereas the transformation in water (Ctr or A) was insignificant (Fig. 6.1). In the irradiated solution LA, N-EtFOSE was degraded substantially, up to 35-40%, after 5 h of exposure under sunlight, while the removal in the irradiated control samples were insignificant as expected (only less than 5% degradation was observed in the control samples, in the range of error). Significant mass change was observed in the first 6 h, relatively stable trend (5-10% reduction) remained in the next 20 h (Fig. 6.1c). Approximately 15-20% N-EtFOSE decline under dark conditions in the presence of live and dead algae suspension likely due to sorption since no significant product appearance was observed. The similarity between live and dead algae suspension in irradiated and dark conditions (Figs. 6.1a and 6.1b) suggests that there was no substrate metabolism or bioaccumulation under these conditions. This result agrees with the finding that the amount of pyrene removed by algal species was similar to both live and death cell or slightly higher in death cells (Lei et al., 2002). In term of sorption, the cell surface charge was unchanged by heat-killing (reported for pesticides) (Mac Rae, 1985) which could also explain for the same degree of removal of N-EtFOSE. In both cases of irradiated live and dead cells, initial removal rate constants were approximately 5.7 min⁻¹ (corresponding to a half-life of 7.2 h, Fig. 6.1 and Table 6.1) revealing no sign of biodegradation, which agrees with the finding for aniline presented by Wang et al. (2007). The relatively higher decay constant and relative yields

of products in dead cell condition also suggests that more lysed cell can improve the degradation of contaminant (Table 6.1).

Five metabolites were detected (Fig. 6.2), N-EtFOSAA, N-EtFOSA, PFOA, and trace quantities perfluorooctane sulfonate (PFOS) and FOSA. Only the first three PFCs were observed in the first 5 h irradiation (Fig. 6.2a) whereas PFOS and FOSA appeared only after 5 h (Fig. 6.2b). In contrast to the reaction profile of N-EtFOSE described in the chapter 5, appearance rates of N-EtFOSAA and N-EtFOSA were faster than that of PFOA. The mass of these two perfluoroalkyl substituted sulfonamides were also larger than that of PFOA after long term irradiation of 20 h (Fig. 6.2b). The trend of product appearance suggested that N-EtFOSAA, N-EtFOSA and PFOA were produced directly from N-EtFOSE in parallel (Fig. 6.2a) while PFOS and FOSA could be products of stepwise reactions in addition to the direct pathway.

The formation of PFOS (relative yield from 0.2-0.8%, Table 6.1) is noteworthy because this compound was not formed in $\cdot\text{OH}$ -initiated transformations (Plumlee et al., 2009; Nguyen et al., 2011a). A possible explanation is the reaction is initiated by $^1\text{O}_2$, which may occur at 15 times higher concentrations than $\cdot\text{OH}$ in algae suspensions (Wang et al., 2007). However, the concentration of $^1\text{O}_2$ was not measured in this study and there was no obvious evidence. Another possible explanation was derived based on mechanisms proposed by other researchers for solution phase for organosulfur compounds (Larson and Weber, 2000) and atmospheric conditions for $\cdot\text{OH}$ (D'Eon et al., 2006). In this case, $\cdot\text{OH}$ or some reactive species in aqueous solution behaves such as $\cdot\text{OH}$ in atmospheric phase. The sulfur atom in N-EtFOSE is attacked by $\cdot\text{OH}$ in aqueous phase to create a peroxy intermediate. Oxidation of the sulfur atom may occur spontaneously with elimination of the ethyl aminoethanol moiety in the presence of dissolved oxygen (oxygen addition). To date, this product profile was one of the most comprehensive set with the appearance of N-EtFOSAA, N-EtFOSA, FOSA, PFOS and PFOA whereas FOSAA could be observed at detection limit levels. The product composition was different from the aqueous aerobic transformation of N-EtFOSE where PFOA was not produced (Rhoads et al., 2008); atmospheric photooxidation with no appearance of N-EtFOSAA, PFOA and FOSA (D'Eon et al., 2006); aqueous $\cdot\text{OH}$ initiated phototransformation produced no PFOS (Plumlee et al., 2009; Nguyen et al., 2011a). The minimal appearance of PFOS suggests that $\cdot\text{OH}$ could be a dominant species for transformation pathway of N-EtFOSE and the appearance of other reactive species in the presence of photosensitizing algae was possible.

Figs. 6.3a and 6.3b show that the photochemical degradation of OP was significantly promoted in both live and dead cell suspensions with approximately 80% removal after 4 h compared to the control (Fig. 6.4c), at similar degradation constant of 20 min^{-1} or half-life of 2.1 h (Table 6.1). The decay rates of OP in both cases were faster than that of N-EtFOSE by a factor of 4 compared to 10 for photooxidation by $\cdot\text{OH}$

mentioned in chapter 5 (Table 5.2). The dead algae showed relatively faster degradation which agrees with previous common findings (Lei et al., 2002; Wang et al., 2007) (Fig. 6.3c). Once again, there is no sign of biotransformation for OP in the first 5 h and the degradation was accounted for the photochemical process in addition of sorption. In general, aqueous algal suspensions were likely to enhance the photochemical degradation of N-EtFOSE and OP following an assumed bimolecular reaction for which the second order reaction rate can be determined (Table 6.1).

Fig. 6.1 Fluorine content of measurable compounds in irradiated N-EtFOSE solutions containing live and dead algae cells. F/F_0 is calculated from the mass of fluorine contained measurable compounds: N-EtFOSE, N-EtFOSAA, N-EtFOSA, FOSA, PFOA and PFOS; error bar represents standard deviation ($n = 2-3$). Ctr: light-exposed solution A; DCtr-live cells: dark-exposed solution B; Exp-live cells: irradiated solution B; DCtr-dead cell: dark-exposed solution DA; Exp-dead cells: irradiated solution DA.

Fig. 6.2 Appearance of metabolites during irradiation of N-EtFOSE in live cell suspension. Conversion is calculated by mass of molar fluorine, F/F_0 . a: Short term; b: Long term. Error bar shows standard deviation ($n = 2-3$)

Fig. 6.3 Transformation of OP in presence of algae suspension (error bar represents standard deviation, $n=2-3$). Ctr: light-exposed solution A; DCtr-live cells: solution LA with no light exposure; Exp-live cells: light-exposed solution LA; DCtr-dead cell: solution DA with no light exposure; Exp-dead cells: light-exposed solution DA.

Table 6.1. Influence of various photosensitizers on degradation of PFCs and OP

Sample	Sensitizer (S1) mg L ⁻¹	H ₂ O ₂ (S2) mM	PFC decay k ^d (min ⁻¹)	k ^d _{S1} -k ^d _{LCtr}	k ^d _{S1+S2} - (k ^d _{LCtr} + k ^d _{S1})	Y ^a _{M1} N- EtFOSAA %	Y ^a _{M2} N- EtFOSA %	Y ^a _{M3} FOSA %	Y ^a _{M4} PFOA %	Y ^a _{M5} PFOS %	OP decay k ^{OP} (min ⁻¹)	k ^{OP} _{S1} - k ^{OP} _{LCtr} (min ⁻¹)	k ^{OP} _{S1+S2} - (k ^{OP} _{LCtr} + k ^{OP} _{S1}) (min ⁻¹)	Rate constants ×10 ⁹ M ⁻¹ s ⁻¹	F/F ₀ ⁺⁺ %
Nitrate influence	Nitrate														
*LCtr-A (L)	0	0	0.40±0.01	0	-	-	-	-	-	-	0.5±0.1	0	-	-	97
DCtr-NO ₃ ⁻ (D)	10	0	n.a.	-	-	-	-	-	-	-	n.a.	n.a.	-	-	-
Exp-NO ₃ ⁻ (L)	10	0	0.6±0.1	0.24±0.06	-	2.1±0.4	7.1±0.9	1.8±0.2	32.6±3.2	11.1±1.3	8.4±0.6	7.86±0.6	-	0.94±0.01	76
DCtr-H ₂ O ₂ -NO ₃ ⁻ (D)	10, 100	10	n.a.	-	-	-	-	-	-	-	n.a.	n.a.	-	-	-
Exp-H ₂ O ₂ -NO ₃ ⁻ 10 (L)	10	10	6.6±1.2	6.24 ±1.2	5.6±1.2	9.9±1.0	7.3±0.4	0.2±0.03	32.6±1.4	2.2±0.8	96.6±7.8	96.1±7.8	87.8±7.8	1.0±0.2	46
Exp-H ₂ O ₂ -NO ₃ ⁻ 100 (L)	100	10	6.0±1.2	5.64±1.2	5.0±1.2	10.6±5.0	9.4±4.4	-	30.3±14.2	-	91.2±7.2	90.7±7.2	82.3±7.2	0.7±0.2	70
Nitrite influence	Nitrite														
DCtr-NO ₂ ⁻ (D)	10	0	n.a.	-	-	-	-	-	-	-	n.a.	n.a.	-	-	-
Exp-NO ₂ ⁻ (L)	10	0	0.84±0.6	0.48±0.6	-	3.4±1.0	8.3±1.0	1.8±0.3	42.7±4.6	0.3±0.1	9.6±1.2	9.1±1.2	-	0.96±0.02	87
DCtr-H ₂ O ₂ -NO ₂ ⁻ (D)	10, 100	10	n.a.	-	-	-	-	-	-	-	n.a.	n.a.	-	-	-
Exp-H ₂ O ₂ -NO ₂ ⁻ 10 (L)	10	10	4.2±1.2	3.84±1.2	3.0±1.2	7.4±1.0	4.6±0.6	-	22.5±3.0	-	24.6±3.6	24.1±3.6	14.5±3.6	1.9±1.0	45
Exp-H ₂ O ₂ -NO ₂ ⁻ 100 (L)	100	10	4.2±0.6	3.84±0.6	3.0±0.6	14.3±2.3	11.6±1.9	-	33.9±5.6	-	28.2±1.8	27.7±1.8	18.1±2.2	1.6±0.3	80

Table 6.1 (cont.) Influence of various photosensitizers on degradation of PFCs and OP

	Sensitiser (S1) mg L ⁻¹	H ₂ O ₂ (S2) mM	PFC decay k _d (min ⁻¹)	k ^d _{S1} -k ^d _{LCtr}	k ^d _{S1+S2} - (k ^d _{LCtr} + k ^d _{S1})	Y ^a _{M1} N- EtFOSAA %	Y ^a _{M2} N- EtFOSA %	Y ^a _{M3} FOSA %	Y ^a _{M4} PFOA %	Y ^a _{M5} PFOS %	OP decay k ^{OP} (min ⁻¹)	k ^{OP} _{S1} - k ^{OP} _{LCtr} (min ⁻¹)	k ^{OP} _{S1+S2} - (k ^{OP} _{LCtr} + k ^{OP} _{S1}) (min ⁻¹)	Rate constants ×10 ⁹ M ⁻¹ s ⁻¹	F/F ₀ ⁺⁺ %
HA influence	HA														
*Ctr-HA1 (L)	1	0	0.2±0.2	0	-	-	-	-	-	-	4.8±1.2	4.3±1.2	-	0.5±0.5	-
Ctr-HA5 (L)	5	0	4.8±0.6	4.4±0.6	-	3.5±0.8	0.8±0.2	-	1.9±0.5	-	11.4±2.4	10.9±2.4	-	5.0±1.2	-
*DCtr-HA (D)	1, 5	0	n.a.	-	-	-	-	-	-	-	n.a.	n.a.	-	-	-
DCtr-H ₂ O ₂ -HA (D)	1, 5	10	n.a.	-	-	-	-	-	-	-	n.a.	n.a.	-	-	-
Exp- H ₂ O ₂ -HA1 (L)	1	10	10.2±0.6	9.8±0.6	9.84±0.6	20.3±3.1	7.7±1.2	0.5±1.1	37.7±4.9	0.2±0.1	91.8±7.2	91.3±7.2	87.0±7.3	1.2± 0.1	60
Exp- H ₂ O ₂ -HA5 (L)	5	10	12.0±0.6	11.6±0.6	11.6±0.6	14.4±2.4	6.1±0.6	0.4±0.1	35.6±4.0	0.2±0.05	109.2±19.8	108.7±19.8	97.8±19.9	1.2±0.2	54
	OP µg L⁻¹														
Exp-OP50 (L)	50	10	12.6±1.2	12.2±1.2	0	8.4±0.53	4.7±0.3	0.3±0.02	22.1±1.4	n.a.	132.6±6.0	132.1±6	-	1.1±0.1	53
Exp-Op100 (L)	100	10	15.0±1.8	14.6±1.8	2.4±2.2	4.7±0.13	4.2±0.2	0.6±0.04	14.0±0.3	n.a.	152.4±9.0	151.9±9	-	1.1±0.2	54
Exp-surface ⁺ (L)	10	10	10.8±0.6	10.4±0.6	-1.8±1.3	17.2±2.9	6.0±1.0	-	19.4±3.3	-	70.2±7.8	69.7±7.8	-	0.6±0.6	80 ⁺
Exp-Milli-Q ⁺⁺⁺ (L)	10	10	12.6±1.2	12.2±1.2	-	12.4	13.3	0.1	29.5	-	132.0±4.8	131.5±4.8	-	1.1±0.1	70
Algae influence	Algae (cell mL⁻¹)														
DCtr-LA (D)	387	0	n.a.	-	-	-	-	-	-	-	n.a.	n.a.	-	-	-
Exp-LA (L)	387	0	5.4±0.1	5.0±0.1	-	1.0±0.3	1.45±0.2	0.1±0.02	0.8±0.1	0.15±0.04	19.8 ± 1.8	19.3±1.8	-	3.09± 0.1	72
DCtr-DA (D)	387	0	n.a.	-	-	-	-	-	-	-	n.a.	n.a.	-	-	-
Exp-DA (L)	0	0	6.0±0.6	5.6±0.6	-	2.9±0.9	2.4±0.7	0.4±0.2	3.4±1.1	0.8±0.3	19.8±2.4	19.3±2.4	-	3.1±0.1	71

⁺ After 4h photolysis in filtered surface water solution (n=2).

⁺⁺ Mass balance after 24h irradiation, based on mass loss of molar fluorine (F/F_0).

⁺⁺⁺ From our previous photochemical degradation study (n=3-4) (Nguyen et al., 2011a).

*LCtr, DCtr, Exp: Light control, dark control, experiment sample, respectively.

L and D stand for light and dark exposure, respectively. n.a.: not applicable or not quantifiable.

6.3.2 Nitrate and nitrite induced photodegradation of N-EtFOSE and OP

Nitrate and nitrite enhanced the photodegradation of N-EtFOSE and OP by simulated sunlight (Figs. 6.4). Their degradation kinetics compared to control sample can be found in Figs. D1a (nitrite), D1b (OP) and D2a (nitrate), D2b (OP). In the absence nitrate and nitrite, N-EtFOSE and OP were degraded with half-lives of 116 h and 77 h, respectively (Fig. 6.4a). Direct photolysis of OP may lead to the formation of the 4-tert-octylphenoxy radical ($\text{OP}^\bullet$) and other radical intermediates (Mazellier, 2003), which may act as photosensitizers in the indirect phototransformation of N-EtFOSE in the absence of other dominant active reagents. However, with minor initial concentration of OP ($10 \mu\text{g L}^{-1}$), this was unlikely to occur but the activity of impurities might cause the slightly decline of N-EtFOSE. The fact that the same intermediates (N-EtFOSAA, N-EtFOSA) and products formed (PFOA) as in H_2O_2 sensitized reactions (Plumlee et al., 2009; Nguyen et al., 2011a) implied that the transformation was initiated by a radical attack in both cases under these conditions (Fig. D2a).

The transformation efficiency of OP and N-EtFOSE in aqueous nitrite solution was higher than that occurred in nitrate solution. Degradation constants normalized to nitrite and nitrate molar concentrations were 2.2 and 1.5, respectively (Table 6.1, Figs. D1 and D2). The reported $\text{OH}^\bullet$ quantum yield (ϕ_{OH}) at wavelengths between 300-350 nm for nitrate and nitrite is relatively similar (1.5 and 1.3%, respectively), which may explain this observation (Mack and Bolton, 1999).

When N-EtFOSE was irradiated for 96 h in the presence of nitrite and nitrate, 18-32% of the initial N-EtFOSE was converted into N-EtFOSAA, N-EtFOSA, FOSA, PFOA and PFOS or 54.7% of the converted N-EtFOSE (Figs. 6.4a and 5.4b). The relative yields of products were higher in nitrite compared to nitrate solution with the largest yield of PFOA (43%). However, nitrate solution yielded more PFOS with remarkable 11% compared to 0.3% in the more reactive nitrite solution (Table 6.1).

Approximately 1-5% of PFOS by total initial mass or 0.3-11.1% of the converted N-EtFOSE were observed in irradiated aqueous nitrite and nitrate solutions (Figs. 6.4b and 6.4c) which were likely due to different pathways under the plausible presence of several reactive species (i.e. $\text{NO}^\bullet$, $\text{NO}_2^\bullet$ and $\text{O}^\bullet$) however $\text{OH}^\bullet$ is thought to be the dominant species. Compared to the rate of degradation occurred in algae suspensions, the decay rate constants of N-EtFOSE and OP induced by nitrate and nitrite were slower by a factor of 8 and 2.2, respectively. The conclusion one would draw from this comparison is that nitrate and nitrite may only be involved to a minimal degree.

When H_2O_2 was added into the solution, increasing the nitrate concentrations from 10 to 100 mg L^{-1} did not lead to an increase of transformation rates of N-EtFOSE and OP (Figs. D3a and D3b). The involvement of H_2O_2 promoted the degradation of both compounds by about 26 times (Exp- NO_3^- compared to Exp- H_2O_2 - NO_3^- 10 or 100) whereas nitrate exhibited slower reaction by a factor of 2 compared to that in nitrate-free solution (Exp- H_2O_2 - NO_3^- 10 or 100 compared to Exp-Milli-Q) (see Table 6.1). The recombination of $\cdot\text{OH}$ and $\text{NO}_2\cdot$ to produce peroxyxynitrite anion (ONOO^-) (equation 6.3) or self-quenching (equation 6.4) during the photolysis of nitrate in Milli-Q solution could explain the experimental results (Mack and Bolton, 1999).

In a similar manner to nitrate, insignificant decay constants were observed with different concentrations of nitrite. Rates were accelerated about 3 and 5 times by H_2O_2 (compared to Exp- NO_2^-) but were decreased about 5 and 3 times by nitrite for OP and N-EtFOSE (compared to Exp-Milli-Q), respectively (Table 6.1).

Irradiated nitrate solution formed all five monitored products whereas nitrite solution did not form FOSA and PFOS. PFOA was the dominant species in both cases but at lower yield for nitrite. It suggested that nitrite was likely the stronger inhibitor for $\cdot\text{OH}$ compared to nitrate.

In contrast to our previous study (Xu et al., 2011c), degradation rates for OP in the presence of nitrite were much slower compared to nitrate in the current study. H_2O_2 is considered as the major source of radicals compared to those generated from other photosensitizers in the water matrix. Therefore, aromatic nitritation or nitration was unlikely but instead, hydrogen abstraction by $\cdot\text{OH}$ was likely to have occurred. Furthermore, although both nitrate and nitrite gave similar $\phi_{\cdot\text{OH}}$, the rate for nitrite combining with $\cdot\text{OH}$ (equation 6.6) is about 8 times faster than the rate of $\cdot\text{OH}$ recombining with $\text{NO}_2\cdot$ (Mack and Bolton, 1999). This could explain the slower degradation rates of OP and N-EtFOSE in the solution with nitrite (Table 6.1).

Fig. 6.4 Transformation of N-EtFOSE in a- Milli-Q water; b- 10 mg L⁻¹ aqueous nitrite solution; c- 10 mg L⁻¹ aqueous nitrate solution. Conversion is calculated by mass of molar fluorine (F/F₀).

6.3.3 Influence of different aqueous matrices in the $\cdot\text{OH}$ initiated photodegradation of N-EtFOSE and OP

6.3.3.1 Influence of HA

In order to test the influence of matrices on photochemical degradation of PFCs, rate constants were determined with (i) HA as the photosensitizers and (ii) H_2O_2 as the $\cdot\text{OH}$ source at two different HA concentrations (Table 6.1).

When HA was added in the solution to serve as a photosensitizer, no degradation of N-EtFOSE was observed in 1 mg L^{-1} HA solution whereas 5 mg L^{-1} HA showed approximately 20 times faster than that occurred at 1 mg L^{-1} or light control (Fig. D4a). OP decay rate was also enhanced in higher HA concentration by a factor of 2.5 (Table 6.1). This could be explained by activities of $\cdot\text{OH}$ and other reactive species generated from the commercial HA at visible wavelengths or minor solvated electron generated in oxygenated solution (near UV wavelength) or excited triplet states of HA in the solution (Canonica et al., 1995; Aguer and Richard, 1996).

When H_2O_2 was added as a $\cdot\text{OH}$ source, HA inhibited the reaction compared to the case of no addition while the dark control showed insignificant degradation (Fig. D3). The degradation rate in the 5 mg L^{-1} HA working solution (Exp-HA 5) was only 2 times faster than that in the dark control solution (Ctr-HA 5) whereas a rate difference by a factor of 47 was obtained for the 1 mg L^{-1} HA solution (Table 6.1). A plausible explanation is that HA, although being a light attenuator, can also play a dual role in irradiated waters as both source and sink for $\cdot\text{OH}$, $^1\text{O}_2$ and $\text{ROO}\cdot$ (Lam et al., 2003) and the quenching effect increases with a higher content of dissolved organic matter (Haag and Hoigne, 1985). With the major source of $\cdot\text{OH}$ being H_2O_2 , HA may act as a radical scavenger thereby slowing N-EtFOSE degradation. The same effect was observed with OP whereby the degradation rates decreased from a factor of 18 to 10 at 1 and 5 mg L^{-1} HA, respectively (Fig. D4b).

Product formation in the presence of only HA is shown in Table 6.1 with minimal relative yields of N-EtFOSAA, N-EtFOSA and PFOA which were not formed in pure water. With the addition of H_2O_2 , the transformation patterns shown in Figs. D5a and D5b which were similar to the case of being without HA (Exp-Milli-Q, Table 6.1).

The similar rates from the two concentrations of HA likely resulted in the relatively similar pattern of metabolite appearance with PFOA as a dominant species as well as minimal fraction of PFOS (Figs. D5a and D5b, Table 6.1).

6.3.3.2 Influence of OP concentration

Minimal change was observed for photochemical degradation of OP and N-EtFOSE when exposed to elevated concentrations of OP. These rate constants were slightly increased with higher OP concentration and are comparable to our previous study with $10 \mu\text{g L}^{-1}$ OP in the Milli-Q water solution (Nguyen et al., 2011a). However, the results are contrary to another study in which OP removal rate decreased with increasing initial OP concentration which was irradiated by a solar UV simulator (290-400 nm) (Neamtu and Frimmel, 2006).

Local surface water characteristics and degradation rates were also studied based on the estimated steady state concentration of radical, $[\cdot\text{OH}]_{\text{ss}} = 5.03 \times 10^{-15} \text{ M}$, as reported in our previous study (Xu et al., 2011c). The control sample of this test indicated insignificant degradation of N-EtFOSE after 6 h irradiation. Against this background, the light induced photolysis of N-EtFOSE and OP with the introduction of H_2O_2 produced results in the range between pure and mixed solution matrices (Table 6.1). The results imply that natural waters contain both photosensitizers and scavengers where active species are continuously being produced and quenched.

6.3.4 Competitive kinetics of N-EtFOSE

The calculation of bimolecular reaction rates for N-EtFOSE under varying conditions was conducted according to competitive kinetics estimation in a previous study (Nguyen et al., 2011a), where a reference rate of OP, $k_{\text{OP}} = 11 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ was adopted (Xu et al., 2011c). Photosensitizing constituents were assumed to produce single active species which reacted and resulted in the disappearance of N-EtFOSE and OP. The results are tabulated in Table 6.1 along with the mass balance estimation based on fluoride mass (F/F_0) of measured PFCs. The case of Milli-Q water alone (Ctr) was not calculated because OP was directly photolyzed and then triggered interaction with N-EtFOSE which is not a steady state reaction. In general, the bimolecular rate constants for the different scenarios containing H_2O_2 , $(1.15 \pm 0.38) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, was relatively similar to Milli-Q water. This indicates that H_2O_2 performed as a dominant source of $\cdot\text{OH}$ in these reactions and the interference of solution matrix was considered minimal.

On the other hand, the presence of common environmental constituents (i.e. nitrate, nitrite, HA and algae) promoted N-EtFOSE and OP degradation, particularly in algae suspension with rates ca. 3 times faster than for H_2O_2 induced photooxidation (Table 6.1). HA solution showed potential as a radical-rich photosensitizer but its behavior with concentration changes is still inconclusive (Garbin et al., 2007). Xu et al. (2010) reported that the degradation of OP and OP1EC was promoted about 3 times when HA was increased from 5 to 50 mg L^{-1}

whereas ibuprofen was slowed down by a factor of 7 from 25 to 50 mg L⁻¹ HA (Xu et al., 2011c).

6.3.5 Environmental implications

Data obtained from bench-scale experiments showed that constituents such as nitrate, nitrite, HA and algae suspension promoted the photooxidation of N-EtFOSE and OP. Exudates from algae and the sorption effect could accelerate the bimolecular reaction rate by generating radicals, exceeding the upper limit of $1.7 \pm 0.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ measured in a previous study (Plumlee et al., 2009).

Brownish or black water with humic substances can be expected to be a good sink for recalcitrant pollutants as well. However, the dual role of humic substances as source and sink still needs further study with suitable radical scavengers before a conclusion can be made.

On the other hand, in sunlit environments and in the presence of other naturally occurring constituents, the transformation processes are likely to be slower due to various inhibiting factors, e.g. turbidity, scavengers, reduced solar intensity, etc. For example, insignificant degradation of N-EtFOSE was observed after 12 h irradiation (data not shown) compared to a half-life of 24 h for acetochlor with the estimated concentrations of steady-state $\cdot\text{OH}$ from 1.4 to $5.4 \times 10^{-15} \text{ M}^{-1} \text{ s}^{-1}$ and $10^{-15} \text{ M}^{-1} \text{ s}^{-1}$, for local surface waters and Blue Earth River, Minnesota (Brezonik and Fulkerson-Brekken, 1998; Xu et al., 2011c), respectively. Perhaps, the water properties might have been changed by the filtration process and the conditions of the laboratory test tube experiment.

There are many other environmental factors which are known to affect the light-induced photolysis of pollutants. Pollutant concentration can be enriched by sorption on suspended matter and be more photoreactive than the dissolved phase (Zepp et al., 1977; Miller and Zepp, 1979a). Clay surfaces provide significant roles in the light induced production of $\cdot\text{OH}$ (Katagi, 1993). Although light attenuation may occur, scattered light can enhance photolysis rate in some suspended clay materials (Miller and Zepp, 1979b). With this in mind, PFCs with high affinity to suspended matter and sediment (Higgins et al., 2005; Ahrens et al., 2010; Nguyen et al., 2011b) could undergo indirect photolysis as a significant pathway for transformation.

The interface between air and water is able to perform as a concentration compartment for pollutants, e.g. PFCs (McMurdo et al., 2008; Renner, 2008) and is particularly receptive to short-lived oxidants and radicals from the atmosphere. This creates a surface film in which

transformation and transport processes are likely to occur simultaneously (Zafiriou et al., 1984). Therefore, at the very top layer or in the aerosol of sunlit surface water, chemical photodegradation rates of semi-volatile or volatile PFC precursors such as N-EtFOSE are expected to be significantly enhanced.

6.4 Conclusions

This study focuses on the influence of environment constituents on the light-induced photochemical degradation of N-EtFOSE and OP. Ubiquitous constituents in surface water i.e. nitrate, nitrite, HA and algae, perform as potential photosensitisers producing reactive species and radicals for the indirect photolysis of micro-pollutants. Under irradiated conditions, the transformation of N-EtFOSE and OP was accelerated in the presence of these constituents following pseudo-first order kinetics. They also showed inhibiting behaviour or self-quenching effects in solutions containing other dominant sources of radicals (i.e. H_2O_2) or with elevated concentrations of matrix constituents. Therefore, insignificant effects of the solution matrix on photooxidation bimolecular rates were observed from the experimental data. The average rate constants obtained in the solution matrix was $(1.15 \pm 0.38) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ which is approximately 2 times faster than the case of when the local waters was used as background. However, aqueous algae suspension and humic acid exhibited faster degradation rates of N-EtFOSE by a factor of 3 to 5 compared to pure water spiked with H_2O_2 , respectively. The appearance of various metabolites and end-products such as PFOA, FOSA, PFOS suggests that a complex transformation mechanism associated with different reactive reagents ($\cdot\text{OH}$, $^1\text{O}_2$, $\text{ROO}\cdot$ etc.) may be occurring in natural sunlit waters.

Publication Information

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Chapter 7 Conclusions and Recommendations

This research has identified and quantified the occurrence and fate of perfluorochemicals in an urban watershed of Singapore, a city situated in the tropical climate zone. Occurrence studies included PFC profile in surface waters, storm runoff, reservoir waters and sediment. Fate studies focused on the photochemical transformation of N-EtFOSE in the aquatic environment and the uptake of PFCs by blue green algae.

7.1 Findings:

7.1.1 Occurrence study of perfluorochemicals in urban catchment.

1. The occurrence data showed that all 13 out of 19 target PFCs were present in water and runoff feeding into the Marina Reservoir and the Marina Reservoir water. PFOA and PFOS were two major constituents with concentrations ranging from 5 to 31 ng L⁻¹ and 1 to 156 ng L⁻¹, respectively. The perfluoroalkyl carboxylates were more dominant over perfluoroalkyl sulfonates except in Alexandra Canal samples, where a point source released aqueous film forming foam (AFFF) chemicals. Trace levels of perfluoroalkyl sulfonamides detected implied putative transformation of PFC precursors in aqueous environment. Rain water was observed to contribute up to 25% into total PFC load of non-point source sites. The contamination pattern is similar to that reported for other urbanized locations.
2. The salinity depth profile in the Marina Reservoir showed distinct stratification with the bottom layer consisting of sea water, and the brackish top layer consisting of mainly of runoff and rainwater (fresh water), and a mixed transition zone. These data indicate the PFC concentrations that can be expected in the reservoir once displacement of seawater by runoff will be complete. The total PFC concentration measured in sediment from the

top layer was approximately 4700 ng kg^{-1} , indicating that Marina Reservoir sediment acts as a sink for PFCs. Sorption increased with perfluoroalkyl chain-length and with sulfonate and sulfonamide substituted groups. The estimated annual PFC load to Marina Reservoir was $35 \pm 12 \text{ kg y}^{-1}$.

7.1.2 Photochemical fate study

1. N-EtFOSE can be degraded by photochemically produced $\cdot\text{OH}$ forming N-EtFOSAA, N-EtFOSA and FOSAA as transient intermediates and PFOA and FOSA as final products. Bimolecular rate constants, k , of N-EtFOSE and its intermediates, N-EtFOSAA, N-EtFOSA and FOSAA ranged from $(0.53 \pm 0.05) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for FOSAA to $(1.05 \pm 0.12) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for N-EtFOSE which were relatively insensitive to pH. Model output revealed that the relative yield of unknown products can reach up to 57% and the minimum half-life is approximately 21 years for typical aquatic environment.
2. Naturally occurring sensitizers, such as nitrate, nitrite, humic acid and algae (including their lyses) promote the photodegradation of N-EtFOSE and OP. Formation of PFOS with the highest relative yields of 11% suggests that the contribution of various active species and other transformation pathways occurred. However, these photosensitizers behave as partial inhibitors in the presence of other constituents. Unidentified fluorinated species were observed to be attributed to significant portion throughout irradiation experiments.

7.2 Recommendations for future works:

7.2.1 Occurrence study

This study was limited to a highly urbanized catchment therefore data should be collected in other catchments and reservoirs which are categorized by protected (pristine, no input i.e. Upper Pierce, Mac Ritchie), unprotected (with agricultural discharge i.e. Kranji, industrial area i.e. Pandan) and proposed (mixed between industrial, residential, commercial zone i.e. Bedok) catchments. These catchments are then classified upon impacts by different commercial, industrial activities or wastewater. Comparing contamination patterns obtained from these areas would reveal source characteristics. Furthermore, other compounds such as fecal sterols, artificial sweeteners (acesulfame, saccharin, sucralose and cyclamate), ethylenediamine tetraacetic acid (EDTA) etc. should be included in the list of target chemicals for origin tracers.

Despite the large number of studies on PFC occurrence has been increasing, there are little knowledge about the possible branched PFC congeners. Houde et al., 2008 showed exceeded branched PFOS over linear PFOS in fresh lake water. This suggested that branched isomers may be more prevalent than linear counterparts in natural waters. They could be a good marker for source characterization. Moreover, some more PFC biotransformation intermediates i.e. perfluorooctane sulfinic acid (PFOSI) should be monitored in dissolved and non-dissolved phases in order to know if microbial process occur.

With the properties of typical surfactants, the partition of PFCs in different phases should be emphasized. As the elevated concentrations in sediment, suspended particulate matters are thought to be the transition phase for PFCs in aqueous phase before sedimentation. It is important because the contribution of these matters is significant for places with high annual rainfall. In addition, the atmospheric distribution data of PFCs would be necessary for the estimation of total load of contaminants. It is also useful if inventory information about PFC compositions used in consumer products is studied. The non-point source contamination from leakage, washout from consumer products, indoor dust, is significant for urbanized areas where industrial and domestic discharges are separated from watersheds.

Our understanding of biological effects, including bioaccumulation and toxicity, is inadequate to assess the significance of emerging contaminants occurring in natural waters. This information is needed for decision making in establishing protective thresholds. Finally, given that PFC contamination is a global issue due to long-range transport, a shared and updatable

occurrence database should be established and accessible for reference and monitoring purposes.

7.2.2 Fate study

In order to obtain comprehensive understanding about the transformation pathways of PFCs in hydroxyl radical mediated indirect photolysis, the characterization of unidentified species is essential. Limited understandings of PFC transformation mechanisms requires additional list of target PFCs including fluorinated dimers, polymers, complexes and volatile PFCs with novel analytical methods. At least, a mineralization method needs to be developed for fluoride so that the mass balance of the transformation products can be evaluated.

Given that microcontaminants are attenuated in sunlit aquatic environment, the photochemical fates are promising eco-friendly approach compared to other treatment methods due to the “reusable reactive species” initiated from naturally occurred constituents. Active species mediated photodegradation of PFC in sunlit aqueous algae was preliminarily studied as presented in Chapter 5.

However, more works are necessary to obtain more comprehensive understanding about the transformation mechanism: (i) Identify active radicals attending to the abiotic degradation of PFCs since different “active species” may lead to different pathways and products. (ii) The algal biotic transformation under stressed environment is still a gap. Different types of algae would behave differently to microcontaminants in the solution. (iii) Products yielded from the algal biotic transformation. For biotic processes including microbial transformation, enantiomer homologous (especially α -branched) would be a good biomarker for the exposure of PFCs. The study of unidentified PFCs mentioned above may be also applicable for this case.

There is little understanding about the physicochemical properties of PFCs which results in difficulty for predicting their environmental behaviors. To date, some parameters such as pK_a , K_{ow} have been estimated for few PFCs using modeling tools which are uneasy to validate. Therefore, experiments focus on environmental behaviors would be useful to achieve precise prediction of PFC property.

The current bench-scale study has provided kinetic information of batch experiment and in pure solutions. Naturally simulated system which makes use of natural sunlight irradiation and continuous flows of real environment matrix would be able to obtain better kinetics parameters. With this system, various factors governing the photochemical process will be

investigated. The analytical, representative availability and inertness also need to consider for selection of reference compounds.

Since there is still knowledge gap about the microbial transformation of PFC precursors such as N-EtFOSE, FtOHs and fluoroalkyl phosphoric acid diesters in sediment, microcosm studies would be expanded on topics such as sorption, biotransformation and air-liquid equilibrium. The transformation mechanism could provide useful information for interpreting the fates of PFCs in organisms exposed to contaminated environments.

On top of many possible treatment methods for PFCs (i.e. evaporation, extraction, thermal destruction, advanced oxidation, reduction, catalytic or non-catalytic photochemistry, sonochemistry and biodegradation) with the feasibility under debating, phytoremediation is suggested for the natural reclamation of surface water contaminated with PFCs. This should be the good fit because the system can include different attenuation and burial processes such as photochemical and microbial degradation, sorption and sedimentation, and aquatic plant intake. Another advantage is that low-level contamination of the effluent can minimize startup and acclimation run. The system provides environmental friendly approach: no emission and low consumption; and green landscape would be a good choice for management strategy.

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Appendix A

A.1 Flow and sampling conditions

During storms, when the tributaries collect runoff, as well as water exfiltrating from soils; the flow is in the direction of the bay (Chua, 2010). Direct wastewater discharge does not occur although the possibility of illegal waste discharges from individuals and local businesses to storm drains cannot be excluded. During dry weather, flows were slow and either outward or inward depending on the tide (Chua, 2010). The flow inward was saline water from Marina Bay. During the 4h prior and after sampling, flow rates changed directions, ranging from -0.3 (inflow) to 0.3 m³ s⁻¹ (outflow) (Geylang), -40 to 20 m³ s⁻¹ (Kallang), -0.41 to 0.22 m³ s⁻¹ (Rochor), -0.35 to 0.22 m³ s⁻¹ (Stamford) and -8.0 to 2.5 m³ s⁻¹ (Alexandra), respectively. Dry samples were collected approximately 10-20 cm below the water surface using a stainless steel bucket. Water from the bucket was transferred to 500 mL screw cap narrow mouth PP bottles (Nalgene, Rochester, USA), which were kept in an ice box and stored in a cool room at 4 °C in the dark until analysis.

Sites for wet sampling were within 5 m radius from the dry weather sampling location. Wet samples were collected every 10 min, approximately 500 mL runoff was pumped into one of 24 polypropylene (PP) bottles (500 mL/one bottle) using an autosampler (ISCO model 6712). Samples were transported to the laboratory within 4 h after the rain event. Four consecutive autosampler bottles were combined and 1 L of the composite was set aside in a PP bottle and stored at 4 °C until processing. PFC concentrations in storm weather samples remained stable during the 4 h sampling period (data not shown), as was observed previously with medium chain length PFCs (Zushi and Masunaga, 2009).

A.2 Material and analytical method

A.2.1 Solid phase extraction

Water samples (500 mL) were filtered using cellulose acetate 0.45 µm-membrane (47 mm diameter, Advantec MFS, Inc, CA, USA) prior to solid phase extraction (SPE), passed through a HLB[®] C18 cartridge (6 cc, 150 g packing material, Waters Corp, MA, USA) which was preferable for extraction of PFCs (Yamashita et al., 2004). Cartridges were conditioned with 5 mL methanol and 5 mL Milli-Q water (Barnstead, Iowa, USA). Cartridges were avoided

from drying during sample loading. After loading the samples, cartridges were washed with 5 mL Milli-Q water and dried for 1 h under vacuum.

The loaded cartridge was eluted 3 times by gravity drip with 2 mL methanol into 15 mL PP centrifuge test tubes (Greiner, Frickenhausen, Germany) mounted in a SPE manifold (Supelco, Visiprep™). Extracts were concentrated by a gentle nitrogen gas stream (99.99%, Soxal, Singapore) to approximately 1 mL and reconstituted to 2 mL with methanol. Contact with glassware and Teflon surfaces was avoided to minimize losses due to sorption and contamination.

A.2.2 Instrumental analyses

The target compounds, abbreviations, and the detection limits are listed in Table A1. For PFC analysis, 1 mL of extract was transferred to autosampler vials. Using small volume injection (20 µL), samples were analyzed by liquid chromatography-tandem mass spectrometry (LC: Shimadzu LC-10 AD; MS/MS: API3000 AB Sciex, Toronto, Canada). Prior to injection, 100 µL of internal standard solution containing 6 ppb of [d₉]-*N*-EtFOSE (for analysis of *N*-MeFOSE and *N*-EtFOSE), [¹³C₂] PFNA (for PFNA), [d₅] *N*-EtFOSA (for *N*-EtFOSA and FOSA), [d₅] *N*-EtFOSAA (for *N*-EtFOSAA, *N*-MeFOSAA and FOSAA), [¹³C₂] PFDA (for PFDA, PFUnA, PFDoA), [¹³C₂] PFOS (for PFHxS, PFOS) and [¹³C₂] PFOA (for PFHpA and PFOA) were added. All PFC standards and internal standards were purchased from Wellington Laboratories (Guelph, ON, Canada). Instrumental details, chromatography conditions, and multiple-reaction monitoring (MRM) parameters have been described elsewhere (Higgins et al., 2005; Plumlee et al., 2008; Rhoads et al., 2008). To lower detection limits, the method was modified as follows: volume injection of 20 µL into C18 column (3.5 µm pore size, 40 mm × 2.1 mm ID, Higgins Analytical, CA, USA) with the following chromatography program: methanol increased from 35% to 100% over 0 to 7.5 min, held at 100% to 10 min, then returned to 35% until 15 min at a flow rate of 0.25 mL min⁻¹ with aqueous 2 mM ammonium acetate as the second mobile phase.

A.2.3 Recovery test and blanks

Representative water samples (500 mL) were spiked with 10ng each of target PFCs and analyzed using the standard protocol. Blank samples consisted of Milli-Q water and spiked Milli-Q water. Method recoveries were calculated by analyzing 4 to 6 spiked real dry-weather water samples. In Milli-Q water, recovery rates ranged from 85-120%, except for FOSA, which was 52.4% (Fig. A1). In surface water samples, the mean recoveries ranged from 53.2 ± 3.9% for PFUnA (95% confidence limit) to 104.8 ± 7.7% except for PFDoA and FOSA, which were

36.6 $\pm$ 3.8% and 46.8 $\pm$ 3.3%, respectively. The losses were thought to occur during the filtration process where long-chain PFCs such as PFDoA (each CF₂ contributes 0.5-0.6 log unit to measured sorption coefficient) and FOSA can be strongly sorbed to particulate matters (Higgins and Luthy, 2006). Furthermore, ion suppression by co-elution might contribute to the losses. Ion enhancement is believed to account for the high apparent recovery of 8:2FtS (113.4 $\pm$ 1.5%) (Plumlee et al., 2008). Reported data were not corrected for recovery.

A.2.4 Quantitation of PFCs

PFCs were quantified using an external calibration curve with internal standards, as described above. Concentrations from 0.0009 to 50 $\mu\text{g L}^{-1}$ in 23 increments were prepared for calibration; 9-14 points (from 0.05 to 9.09 $\mu\text{g L}^{-1}$) were usually used for quantitation. Considering dilution, the internal standard concentration corresponded to 0.273 $\mu\text{g L}^{-1}$ for each species of PFCs. Calibration curves were acquired for every batch of samples; linearity correlation coefficients (r) were > 0.99 .

Blanks (500 mL of Milli-Q water) were analyzed in triplicate using the same procedure (including filtration). The triplicate blank test was carried out every month in Milli-Q water and in solvent (methanol) blanks, where PFC concentrations were below the instrument detection limit (from 15-100 ng L⁻¹). The limit of quantitation (LOQ) of each compound was the lowest concentration in the calibration curve with a signal to noise ratio (S/N) larger than 3, corresponding to an accuracy of 70-130%. The criteria were previously described elsewhere (Higgins et al., 2005; Plumlee et al., 2008).

Table A1. Abbreviations and limit of quantitation of PFCs

PFCs	LOQ (ng/l)	PFCs	LOQ (ng/l)
PFOA: Perfluorooctanoic acid, C ₇ F ₁₅ COOH	0.1	N-MeFOSAA: N-methyl-perfluoro-1-octane-sulfonamidoacetic acid, C ₈ F ₁₇ SO ₂ N(CH ₃)(CH ₃ COOH)	0.2
PFHxA: Perfluorohexanoic acid, C ₅ F ₁₁ COOH	-	N-EtFOSAA: N-ethyl-perfluoro-1-octane-sulfonamidoacetic acid, C ₈ F ₁₇ SO ₂ N(C ₂ H ₅)(CH ₃ COOH)	0.4
PFHpA: Perfluoroheptanoic acid, C ₆ F ₁₃ COOH	0.7	N-MeFOSE: 2-(N-methylperfluoro-1-octanesulfoamido) ethanol, C ₈ F ₁₇ SO ₂ N(CH ₃)(C ₂ H ₄ OH)	0.1
PFNA: Perfluorononanoic acid, C ₈ F ₁₇ COOH	0.4	N-EtFOSE: 2-(N-ethylperfluoro-1-octanesulfoamido) ethanol, C ₈ F ₁₇ SO ₂ N(C ₂ H ₅)(C ₂ H ₄ OH)	0.1
PFDA: Perfluorodecanoic acid, C ₉ F ₁₉ COOH	0.4	[¹³ C ₂] PFOS: Perfluoro-1-[1,2,3,4- ¹³ C ₄]-octanesulfonate	-
PFUnA: Perfluoroundecanoic acid, C ₁₀ F ₂₁ COOH	0.2	[¹³ C ₂] PFOA: Perfluoro-1-[1,2,3,4- ¹³ C ₄]-octanoic acid	-
PFDoA: Perfluorododecanoic acid, C ₁₁ F ₂₃ COOH	0.4	[¹³ C ₂] PFNA: Perfluoro-1-[1,2,3,4- ¹³ C ₄]-nonanoic acid	-
PFHxS: Perfluorohexanesulfonate, C ₆ F ₁₃ SO ₃ ⁻	0.4	[¹³ C ₂] PFDA: Perfluoro-1-[1,2,3,4- ¹³ C ₄]-decanoic acid	-
PFOS: Perfluorooctanesulfonate, C ₈ F ₁₇ SO ₃ ⁻	0.4	[D ₅] N-EtFOSA: N-ethyl-d ₅ -perfluoro-1-octanesulfonamide	-
FOSA: Perfluoro-1-octanesulfonamide, C ₈ F ₁₇ SO ₂ NH ₂	0.03	[D ₉] N-EtFOSE: 2-(N-deuterioethylperfluoro-1-octanesulfoamido)-1,1,2,2-tetradeuterioethanol	-
PFBS: Perfluorobutane sulfonate, C ₄ F ₉ SO ₃ ⁻	0.8		
N-EtFOSA: N-ethylperfluoro-1-octanesulfonamide, C ₈ F ₁₇ SO ₂ NH(C ₂ H ₅)	0.1		

Table A2. Correlation coefficient of Spearman rank correlation analysis of PFC species

PFCs	Dry weather (n=30)		Storm runoff (n=48)	
	Spearman's rho	P value *	Spearman's rho	P value *
PFOA-PFOS	0.719	<0.0001	-0.345	0.016
PFOA-PFHxS	0.557	0.0013	-0.298	0.039
PFOA-6:2FtS	0.271	0.1474	-0.298	0.039
PFOA-PFHpA	0.608	0.0004	0.411	0.004
PFOA-PFNA	0.634	0.0002	0.601	<0.0001
PFOA-PFDA	0.649	0.0001	0.496	0.0003
PFOA-PFUnA	0.411	0.0241	0.105	0.476
PFOA-FOSA	0.268	0.1522	-	-
PFOA-N-MeFOSAA	0.461	0.0104	0.26	0.075
PFOA-N-EtFOSAA	0.861	<0.0001	0.098	0.051
PFOS-PFHxS	0.633	0.0002	0.878	<0.0001
PFOS-6:2FtS	0.164	0.3851	0.831	<0.0001
PFOS-PFHpA	0.599	0.0005	-0.279	0.055
PFOS-PFNA	0.441	0.0146	-0.531	0.0001
PFOS-PFDA	0.442	0.0145	-0.461	0.0009
PFOS-PFUnA	0.337	0.0683	-0.144	0.329
PFOS-FOSA	0.261	0.163	-	-
PFOS-N-MeFOSAA	0.138	0.4679	-0.05	0.734
PFOS-N-EtFOSAA	0.687	<0.0001	-0.03	0.841
PFNA-PFHxS	0.405	0.0266	-0.511	
PFNA-6:2FtS	0.333	0.0718	-0.442	0.002
PFNA-PFHpA	0.553	0.0015	0.291	0.045
PFNA-PFDA	0.874	<0.0001	0.78	<0.0001
PFNA-PFUnA	0.618	0.0003	0.357	0.013
PFNA-N-MeFOSAA	0.668	<0.0001	0.441	0.0017

PFNA-N-EtFOSAA	0.629	0.0002	0.217	0.138
PFDA-PFHxS	0.363	0.0485	-0.483	0.0005
PFDA-PFUnA	0.774	<0.0001	0.453	0.0012
PFDA-N-MeFOSAA	0.752	<0.0001	0.457	0.001
PFDA-N-EtFOSAA	0.533	0.0024	0.298	0.04
PFUnA-N-MeFOSAA	0.61	0.0004	0.585	<0.0001
PFUnA-N-EtFOSAA	0.325	0.08	0.411	0.004
				s
N-EtFOSAA-PFHxS	0.655	<0.0001	-0.142	0.335
N-MeFOSAA-N-EtFOSAA	0.368	0.0452	0.709	<0.0001
Total PFCs-TDS	-0.544	0.013		
Total PFCs-salinity	-0.551	0.011		

* Correlation is significant at the 0.05 level.

Table A3. Linear regression between log concentrations of PFCs

Log[A] – log[B]	S	R	P value
PFOA-PFHxS	1.607	0.548	0.0011
PFOA-PFOS	1.38	0.607	0.0004
PFOA-PFNA	0.764	0.679	< 0.0001
PFOA-PFDA	0.879	0.698	< 0.0001
PFOA-N-MeFOSAA	0.661	0.533	0.0024
PFOA-N-EtFOSAA	1.123	0.786	< 0.0001
PFNA-PFHxS	1.132	0.477	0.0116
PFNA-PFDA	0.967	0.845	< 0.0001
PFOS-PFNA	0.233	0.481	0.0071
PFOS-N-EtFOSAA	0.424	0.674	< 0.0001
PFOS-PFHxS	0.844	0.734	< 0.0001
PFHxS-N-EtFOSAA	0.4	0.742	< 0.0001

S- value of trend line slope, *R*- relative correlation coefficient, *P*- probability of zero slope occurs

Fig. A1 Method recovery efficiency. Error bars represent standard deviation with n=6 (real sample) and n=4 (Milli-Q water)

Fig. A2 Average relative abundance of PFCs: for Alexandra and Stamford Canal dry and wet samples were analyzed

Fig. A3 Ratio of PFHpA/PFOA in surface and rain water (only NTU and Albany³) from different areas. ¹So *et al.*, 2007, ²Simcik *et al.*, 2005, ³Kim *et al.*, 2007, ⁴Murakami *et al.*, 2008,

⁵Murakami et al., 2009 (Simcik and Dorweiler, 2005; Kim and Kannan, 2007; So et al., 2007; Murakami et al., 2008; Murakami et al., 2009a)

Table A4. The correlation matrix of 9 PFCs used in PCA

Correlation Matrix ^a										
		N-EtFOSAA	PFDA	PFNA	PFUnA	FOSA	NMeFOSAA	PFOA	PFOS	PFHxS
Correlation	N-EtFOSAA	1.000	.321	.408	.262	.442	.179	.633	.363	-.222
	PFDA	.321	1.000	.814	.750	.336	.578	.648	.279	.084
	PFNA	.408	.814	1.000	.807	.348	.627	.684	.228	-.110
	PFUnA	.262	.750	.807	1.000	.311	.690	.461	.140	.031
	FOSA	.442	.336	.348	.311	1.000	.296	.553	.305	-.107
	NMeFOSAA	.179	.578	.627	.690	.296	1.000	.387	-.022	-.060
	PFOA	.633	.648	.684	.461	.553	.387	1.000	.480	-.314
	PFOS	.363	.279	.228	.140	.305	-.022	.480	1.000	-.143
	PFHxS	-.222	.084	-.110	.031	-.107	-.060	-.314	-.143	1.000
Sig. (1-tailed)	N-EtFOSAA		.045	.014	.085	.008	.177	.000	.027	.123
	PFDA		.045	.000	.000	.038	.001	.000	.071	.332
	PFNA		.014	.000	.000	.032	.000	.000	.117	.284
	PFUnA		.085	.000	.000	.050	.000	.006	.235	.437
	FOSA		.008	.038	.032	.050	.059	.001	.054	.290
	NMeFOSAA		.177	.001	.000	.059		.019	.456	.378
	PFOA		.000	.000	.006	.001	.019		.004	.049
	PFOS		.027	.071	.117	.054	.456	.004		.230
	PFHxS		.123	.332	.284	.437	.378	.049	.230	

a. Determinant = .005

Table A5. Kaiser-Meyer-Olkin measure of sampling adequacy and Bartlett's test

KMO and Bartlett's Test		
Kaiser-Meyer-Olkin Measure of Sampling Adequacy.		.796
Bartlett's Test of Sphericity	Approx. Chi-Square	128.822
	df	36
	Sig.	.000

Table A6. Eigenvalues and total variance explanation

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	4.257	47.301	47.301	4.257	47.301	47.301
2	1.601	17.784	65.085	1.601	17.784	65.085
3	.943	10.479	75.564			
4	.719	7.991	83.555			
5	.557	6.193	89.747			
6	.374	4.156	93.904			
7	.279	3.098	97.002			
8	.148	1.649	98.651			
9	.121	1.349	100.000			

Extraction Method: Principal Component Analysis.

Fig. A4 Principal component analysis plot of dry weather samples collected from Aug 2008 to Mar 2009

Fig. A5 A-Concentrations of PFOA+PFOS in Marina Catchment and precautionary levels in German drinking water (100 ng L⁻¹) (TWK, 2007); B-Concentration of PFOS in Marina Catchment and avian wildlife precautionary level (50 ng L⁻¹) (Rostkowski et al., 2006).

Fig. A6 Total PFC concentration in Marina watershed after the Barrage closure. MC1-Geylang River; MC2-Kallang River; MC3-Rochor Canal; MC4-Stamford Canal; MC5-Alexandra Canal (error bars represent standard deviation, n=3)

Fig. A7 Occurrence of PFOA and PFOS in surface waters in Singapore and other locations (1- So et al., 2007; 2-Skutlarek et al., 2006; 3-Simcik et al., 2005; Morikami et al., 2009).

Fig. A8 PFC profile in Alexandra Canal connected to Singapore River 1st April 09

Appendix B

Table B1. Depth of sampling points in Marina Barrage

Site	S1	S2	S3	S4
Depth (m)				
Surface (L1)	0.1	0.1	0.1	0.1
Middle (L2)	2.5-2.7	2.8-3.4	2.9-3.4	2.3-2.5
Sub-bottom (L3)	3.5-3.7	3.9-4.7	4.1-4.7	3.3-3.5
Bottom (L4)	4.5-4.8	5.0-6.0	5.2-6.1	4.2-4.4
Total depth	5.1-5.4	5.6-6.7	6.0-6.7	4.7-5.2

Table B2. Ratios of seawater dilution in different depths

Ratio	Site	Carboxylates	Sulfonates	Metabolites	Average $\pm$ stddev
L1/L2	S1	1.3	1.5	1.5	1.4 ± 0.1
	S2	1.8	1.5	1.4	1.5 ± 0.2
	S3	1.4	1.3	1.5	1.4 ± 0.1
	S4	1.1	1.3	0.7	1.0 ± 0.3
L2/L3	S1	1.3	1.1	1.6	1.3 ± 0.2
	S2	0.9	1.1	1.4	1.2 ± 0.2
	S3	1.5	1.4	1.8	1.6 ± 0.2
	S4	1.6	1.1	2.4	1.7 ± 0.3
L3/L4	S1	1.0	0.9	0.6	0.8 ± 0.2
	S2	1.2	1.2	0.7	1.0 ± 0.3
	S3	1.2	1.2	0.7	1.0 ± 0.3
	S4	1.1	1.3	0.7	1.0 ± 0.3

Table B3. Recovery test for sediment analysis (n =9)

	PFOS	PFOA	PFHxS	6-2FtS	PFNA	PFDA	PFUnA	PFDoA	PTA	N-EtFOSAA	N-MeFOSAA	FOSAA	N-EtFOSA
Recovery rate %	108.5	117.8	179.5	142	100.8	105	84	121.3	-	70.8	72.8	40	24
Standard deviation	10.3	4.5	59.3	-	25.8	16.3	16.4	11.9	-	15.6	10.9	6.7	5.7

Table B4. Average concentrations and standard deviations (n=6) of PFC compounds in the Marina Reservoir at sampling points S1, S2, 2a, 2b, 3, 3a, 3b, and 4.

Site	Depth	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDaA	Carboxylates Total	PFHxS	PFOS	6:2FtS	Sulfonates Total	FOSA	FOSAA	N-Me- FOSAA	N-Et- FOSAA	Metabolites Total	Total PFCs
S1	L1	10.1	20.1	4.7	7.7	0.8	0.6	47.7	3.2	9.7	2.1	13.3	0.3	<0.2	0.9	2.0	2.5	52.1
		(5.4-11.9)	(9.1-25.5)	(2.1-9.8)	(1.5-13.2)	(0.4-1.1)	(0.4-0.8)	(19-56)	(2.8-6.4)	(6.8-15.5)	(0.9-3.0)	(11-24)	(0.2-0.3)	-	(0.7-1)	(0.5-2.3)	(1.5-3.6)	(42-66)
	L2	7.3	14.2	3.0	4.1	0.9	0.5	26.1	2.7	8.0	1.8	12.4	0.2	<0.2	0.5	1.3	1.7	39.2
		(<0.7-9)	(6.5-21.7)	(nd-8.2)	(0.9-9.0)	(nd-1.9)	(<0.4-0.8)	(12-48)	(<0.4-2.6)	(5.5-11.9)	(0.7-3.6)	(8-17)	(0.1-0.3)	-	(<0.2-0.6)	(<0.4-1.8)	(1-3)	(23-67)
	L3	5.6	11.5	2.9	2.9	0.7	0.6	21.8	2.2	5.7	1.2	10.2	0.1	<0.2	0.5	1.1	1.6	28.1
		(<0.7-7.6)	(6.0-15.3)	(1.1-4.4)	(<0.4-6.3)	(nd-1.6)	(<0.4-0.7)	(11-35)	(<0.4-2.7)	(3.4-7.9)	(0.5-2.7)	(5-11)	(0.1-0.2)	-	(<0.2-0.5)	(<0.4-1.7)	(<0.1-1.9)	(21-48)
	L4	5.0	10.4	0.7	4.4	0.7	0.5	21.7	2.1	6.4	1.6	9.3	0.2	nd	0.5	1.0	1.7	30.1
		(1.8-10.9)	(3.2-16.2)	(<0.4-1.9)	(1.6-6.7)	(<0.2-0.9)	(<0.2-1.0)	(9-36)	(<0.4-2.7)	(4.4-7.1)	(<0.4-2.1)	(7-11)	(0.1-0.4)	-	(<0.2-0.7)	(0.7-0.3)	(1-4)	(20-48)
S2	L1	12.0	21.5	5.1	7.7	1.2	0.9	57.4	3.7	10.2	7.7	14.4	0.3	<0.2	0.7	1.8	3.2	74.9
		(5-28)	(8.4-34.7)	(1.9-11.9)	(1.3-8.3)	(0.6-1.6)	(0.5-1.3)	(17-71)	(3.4-4.2)	(9-17)	(1.3-8.3)	(12-24)	(0.2-0.4)	-	(<0.2-1)	(0.5-2.7)	(1-4)	(34-87)
	L2	6.7	12.6	0.7	6.4	1.1	0.7	25.8	2.1	6.8	1.3	11.0	0.2	<0.2	0.6	1.5	2.2	38.3
		(<0.7-7.6)	(6.5-20.9)	(nd-0.8)	(<0.4-7.6)	(nd-2.6)	(nd-0.8)	(11-43)	(<0.4-3.1)	(6.2-8.7)	(0.9-2.5)	(9-13)	(0.2-0.3)	-	(0.4-0.8)	(<0.4-2.6)	(1-4)	(21-58)
	L3	7.1	13.9	5.3	5.9	1.2	0.6	35.2	2.1	7.0	1.9	10.5	0.2	<0.2	0.5	1.2	1.7	45.0
		(<0.7-8.5)	(6.2-20.6)	(1.1-5.4)	(1.1-8.8)	(0.4-2.1)	(<0.4-0.9)	(12-43)	(0.4-2.6)	(5.7-8.3)	(<0.4-2.4)	(8-12)	(0.1-0.2)	-	(<0.2-0.6)	(<0.4-2.6)	(<0.1-3.4)	(22-53)
	L4	5.1	11.7	2.6	4.6	0.6	0.5	25.7	2.0	5.3	1.7	7.5	0.1	<0.2	0.5	1.3	1.7	34.5
		(<0.7-13.5)	(4.4-13.7)	(1.1-5.6)	(0.8-5.7)	(0.4-1.5)	(0.4-1.1)	(10-36)	(<0.4-2.3)	(3.8-7.2)	(<0.4-2.5)	(7.1-10.9)	(0.1-0.2)	-	(<0.2-0.6)	(0.9-3.9)	(0.7-4.4)	(18-45)

S3	L1	9.1 (5-13)	15.7 (8.6-28.9)	5.0 (2.0-6.7)	7.4 (2.1-10.8)	1.0 (0.6-1.8)	0.7 (0.4-17.2)	53.6 (19-58)	3.3 (2.9-5.9)	11.6 (6.4-20.3)	7.4 (0.4-10.8)	17.1 (6-28)	0.3 (0.2-1.3)	<0.2 -	0.7 (0.5-0.8)	2.0 (0.7-4.2)	2.8 (1.3-5.3)	63.3 (40-81)
	L2	6.8 (<0.7-8.4)	15.6 (8.4-21.7)	2.4 (<0.4-5.9)	6.3 (1.4-8.9)	1.7 (nd-2.1)	1.1 (<0.4-1.2)	30.5 (15-48)	2.8 (<0.4-2.3)	9.0 (6.5-12.0)	1.4 (<0.4-3.3)	14.2 (8-17)	0.2 (0.1-0.5)	<0.2 -	0.5 (nd-0.7)	1.6 (<0.4-2.6)	1.5 (1.5-3.5)	39.3 (32-67)
	L3	3.3 (<0.7-7.7)	8.4 (4.4-15.8)	1.6 (1.1-5.8)	3.9 (<0.4-6.4)	1.3 (nd-1.7)	0.5 (<0.4-1.1)	17.8 (7-37)	1.7 (<0.4-2.2)	3.9 (2.2-6.6)	1.1 (0.4-2.6)	6.2 (4.0-11)	0.2 (0.1-0.2)	<0.2 -	0.4 (<0.4-0.5)	0.7 (<0.4-2.1)	0.8 (<0.2-2.8)	22.5 (14-51)
	L4	2.7 (<0.7-7.4)	5.7 (2.2-15.4)	1.8 (1.0-5.1)	2.6 (1.0-7.1)	1.1 (<0.2-1.5)	0.8 (nd-1.2)	13.0 (4-38)	2.3 (<0.4-2.5)	4.3 (2.3-12.9)	0.8 (<0.4-2.3)	4.3 (3-17)	0.2 (0.1-0.2)	<0.2 -	0.4 (<0.2-0.4)	1.6 (<0.4-4.1)	1.0 (0.2-4.2)	24.2 (9-50)
S4	L1	10.0 (4.1-15.7)	22.0 (7.9-36.5)	4.7 (1.9-7.8)	5.4 (1.9-10.3)	1.0 (0.5-1.9)	0.4 (<0.4-1.9)	38.6 (16-74)	3.9 (2.4-5.5)	13.0 (6.0-19.2)	1.4 (0.7-2.5)	18.8 (9-26)	0.3 (0.1-0.4)	<0.2 -	0.7 (<0.2-0.9)	1.6 (0.9-2.3)	2.2 (1.7-2.7)	55.0 (45-95)
	L2	10.4 (<0.7-12)	17.9 (7.6-27.2)	4.4 (1.5-7.5)	5.4 (1.2-8.8)	1.0 (nd-1.9)	1.0 (<0.4-1.2)	36.7 (16-54)	2.7 (2.2-4.1)	7.7 (7.4-13.6)	1.4 (0.9-2.9)	12.6 (11-19)	0.2 (0.1-0.2)	<0.2 -	0.8 (<0.4-0.8)	2.4 (0.4-5.0)	3.6 (0.6-5.6)	52.3 (35-72)
	L3	4.0 (<0.7-8.9)	8.7 (5.7-19.0)	2.3 (1.2-5.5)	3.1 (<0.4-7.1)	0.5 (<0.2-2.0)	0.8 (<0.4-0.8)	16.2 (11-43)	2.4 (<0.4-2.9)	7.9 (3.2-11.9)	1.1 (0.5-3.9)	11.3 (5-20)	0.1 (0.1-0.3)	<0.2 -	0.5 (<0.3-0.6)	1.1 (0.4-2.0)	1.3 (<0.1-2.9)	26.1 (21-66)
	L4	3.4 (<0.7-6.9)	7.6 (4.3-18.2)	1.9 (1.3-4.4)	2.5 (1.1-7.9)	0.5 (<0.2-2.0)	0.9 (<0.4-1.1)	14.9 (9-40)	2.1 (1.0-2.6)	6.7 (3.2-9.2)	1.4 (0.5-2.3)	1.8 (1.1-3.5)	0.2 (0.1-0.4)	<0.2 -	0.5 (<0.2-0.8)	0.9 (0.7-2.5)	1.8 (1.1-3.5)	25.6 (19-57)
S1-a	L1	11 (<0.7-11)	12 (12-30)	4 (4-5)	8 (8-10)	1 (1-2)	0.7 (0.7-1.2)	25 (24-58)	2 (2-3)	8 (8-12)	1.2 (1.2)	12 (12-17)	0.2 (0.2-0.3)	<0.2 -	0.9 (0.5-0.9)	2.7 (2-3)	3.8 (3-4)	40.2 (40-78)
	L1	10 (<0.7-11)	14 (14-29)	4 (4-5)	4 (4-10)	1 (1)	0.6 (<0.4-1)	24 (24-56)	2 (2-3)	8 (8-10)	2 (1-2)	13 (12-13)	0.3 (0.3)	<0.2 -	1 (1)	3 (2-3)	5 (3-5)	42.2 (42-71)
S3-a	L1	11	13	4	4	0.5	0.7	22	4	13	2	19	0.3	<0.2	0.7	3	4	44.3

		(<0.7-11)	(13-28)	(4-6)	(4-11)	(0.5-1.3)	(nd-1)	(22-57)	(3-4)	(10-13)	(1-2)	(14-19)	(0.2-0.3)	-	(0.4-0.7)	(3)	(3-4)	(44-74)
S3-b	L1	10	17	4	4	1	1	24	4	11	2	17	0.3	<0.2	0.7	1.4	2.4	44
		(<0.7-10)	(17-26)	(4-6)	(4-9)	(1)	(nd-1)	(245-53)	(3-4)	(9-11)	(1-2)	(13-17)	(0.2-0.3)	-	(0.4-0.7)	(1.4-3)	(2-3)	(44-69)
LOQ		0.7	0.1	0.4	0.4	0.2	0.4		0.4	0.4	0.4		0.03	0.2	0.2	0.4		

L1-L4 represent different depths from top to bottom layer (n = 6 at each point).

Fig. B1 Vertical profile of PFCs in Marina Reservoir (average value, error bar represents standard deviation, $n = 6$)

Fig. B2 Trend of PFCs in storm runoff (average value, error bar represents standard deviation, $n = 24$ for total PFCs, $n = 8$ for CM1-CM3)

Fig. B3 Depth profile of PFCs and salinity in Marina Reservoir (29th December 2008) for 4 sampling sites, S1 to S4.

Fig. B4 Ratio of PFOA/PFOS (95% confidence interval) from Marina Catchment surface water, runoff and WWTP.

Appendix C

B.1 Analytical protocol for large volume injection

Sample Collection and Preparation

1. Collect water samples in 10 mL polypropylene falcon tubes, (replicates and extra for spike recovery test). Fill exactly to 6 mL mark by decanting extra water.
Example: Named A – C. Also prepare blanks same way using Milli-Q water (Named “MQ”)
2. One tube (or replicate tubes) from each sample (and MQ water) is spiked to ~100 ng/L PFC using PFC stock solution for the method recovery test.
 - a. Could do this for every sample, or just for every “type” of sample e.g. surface, ground water, wastewater
 - b. For spiking into 6 mL sample, spike 20 uL of the 50 ppb PFC stock using micropipette to achieve 166.7 ng/L. Mix.
3. Add methanol to each tube to the 10 mL mark (mix, check level) so that the solution is 40/60 MeOH/sample.
4. Carry out sample preparation*:
 - a. Transfer 2mL to a 2mL plastic centrifuge tube using micropipette.
 - b. Centrifuge for 30 min at 18,000 RCF.*could split into replicates of each tube
5. Carry out sample transfer to glass vials, prepare MS samples (matrix spike), and prepare MSR samples (matrix spike reference):
 - a. If performing MS for every sample, obtain 2 glass vials (non-teflon caps) for every centrifuge tube. One will be spiked, one will not be spiked. If performing MS for fewer samples, obtain a 2nd glass vial for those samples only. Also obtain 3 more glass vials for the triplicate MSRs.
 - b. To the vials which are not spiked: Add 200 uL of 70/30 MeOH/0.01% NH₄OH
 - c. To the spiked vials *and* to the 3 MSR vials, add 200 uL of PFC-containing 70/30 MeOH/0.01% NH₄OH such that the concentration is 2-3 times the highest expected concentration
 - i. The highest expected concentration is that in the MR vials (spiked at 166.7 ng/L which dilutes to 100 ng/L). Adding 200 uL of a 500ng/L PFCs stock (in 70/30) results in 100 ng/L in vial (not including the 100 ng/L, thus total is 200 ng/L).
 - d. Add 800 uL of the centrifuged sample supernatant (*or* 800 uL of MQ water to the MSR samples).
 - e. Add 100 uL of internal standard, mix.

*IS should be enough for the whole batch and it must come from same solution for every sample and standard.

*The total volume of standard (1100 uL) is enough for up to two 490 uL injections.

Table C1. Production rate constants of metabolites from photolysis of various PFCs at pH 6 (estimated from plots of C/C_0 versus time, value in bracket represents linear coefficient) (n=4). * FOSAA did not appear significantly in the first stage (2 h) of irradiation. Values were obtained by pooling data of long-term observation.

PFCs	$R_{N-EtFOSAA}$	$R_{N-EtFOSA}$	* R_{FOSAA}	R_{FOSA}	R_{PFOA}
N-EtFOSE					
10 $\mu\text{g L}^{-1}$	0.82 ± 0.08 (0.96)	0.96 ± 0.06 (0.98)	-	0.08 ± 0.02 (0.81)	3.69 ± 0.19 (0.99)
5 $\mu\text{g L}^{-1}$	0.68 ± 0.09 (0.82)	0.51 ± 0.04 (0.92)	-	0.07 ± 0.01 (0.9)	1.9 ± 0.17 (0.89)
N-EtFOSAA		0.29 ± 0.02 (0.88)	0.06 ± 0.005 (0.87)	-	1.8 ± 0.08 (0.94)
N-EtFOSA			0.044 ± 0.026	1.37 ± 0.05 (0.97)	4.83 ± 0.15
FOSAA			-	4.55 ± 0.19 (0.96)	0.23 ± 0.01 (0.94)

Table C2. Production rate constants of PFC metabolites from N-EtFOSE degradation at different pH (estimated from plots of C/C_0 versus time, value in bracket represents linear coefficient)

pH	$R_{N-EtFOSAA} (\text{h}^{-1})$	$R_{N-EtFOSA} (\text{h}^{-1})$	$R_{FOSA} (\text{h}^{-1})$	$R_{PFOA} (\text{h}^{-1})$
pH 1	1.09 ± 0.11 (0.88)	1.46 ± 0.06 (0.97)	0.04 ± 0.02 (0.4)	5.9 ± 0.22 (0.98)
pH 3	0.77 ± 0.05 (0.95)	0.77 ± 0.04 (0.97)	0.07 ± 0.01 (0.91)	3.46 ± 0.22 (0.94)
pH 6	0.68 ± 0.09 (0.82)	0.51 ± 0.04 (0.92)	0.07 ± 0.01 (0.9)	1.9 ± 0.17 (0.89)
pH 8	0.53 ± 0.07 (0.8)	1.49 ± 0.06 (0.98)	-	1.44 ± 0.013 (0.9)
pH 10	0.67 ± 0.08 (0.83)	1.51 ± 0.05 (0.99)	-	1.71 ± 0.22 (0.8)
Surface water (pH 8)	3.55 ± 0.12 (0.99)	1.24 ± 0.06 (0.99)	-	3.99 ± 0.2 (0.99)

Fig. C1 Disappearance of N-EtFOSE in irradiated H_2O_2 . Mid-line represents the first-order model fit. Outer and inner borders represent 95% prediction and 95% confidence bands, respectively.

Fig. C2 PFC production from N-EtFOSE irradiation. a-N-EtFOSAA; b-N-EtFOSA; c-FOSA; d-PFOA. Outer and inner borders represent 95% prediction and 95% confidence bands, respectively. Mid line represents linear regression curve.

Fig. C3 First order kinetics of irradiated N-EtFOSAA in presence of H₂O₂. Outer and inner borders represent 95% prediction and 95% confidence bands, respectively. Mid-line represents linear regression curve.

Fig. C4 PFC production from N-EtFOSAA irradiation. a) N-EtFOSA; b) FOSA; c) PFOA. Outer and inner borders represent 95% prediction and 95% confidence bands, respectively. Mid-line represents linear regression curve.

Fig. C5 First order kinetics of irradiated N-EtFOSA in presence of H₂O₂. Outer and inner borders represent 95% prediction and 95% confidence bands, respectively. Mid-line represents linear regression curve.

Fig. C6 PFC production from N-EtFOSA irradiation. a) FOSA; b) PFOA.

Fig. C7 First order kinetics of irradiated FOSAA in presence of H_2O_2 . Outer and inner borders represent 95% prediction and 95% confidence bands, respectively. Mid-line represents linear regression curve.

Fig. C8 PFOA and FOSA production from FOSAA irradiation. a) FOSA; b) PFOA. Outer and inner borders represent 95% prediction and 95% confidence bands, respectively. Mid-line represents linear regression curve.

Fig. C9 Disappearance, product formation and total compound concentrations of a) N-EtFOSE, b) N-EtFOSAA and c) N-EtFOSA. Initial concentrations of N-EtFOSE, N-EtFOSAA and N-EtFOSA were $5 \mu\text{g L}^{-1}$. The “total” was calculated as the sum of the analyzed PFC compounds. Concentration of H_2O_2 was 10 mM in all cases. Irradiation intensity was 765 W m^{-2} .

Fig. C10 The sum of parent compounds and known products over time observed in short-term irradiation experiments. a) N-EtFOSE and N-EtFOSA; b) N-EtFOSAA and FOSAA. Initial concentrations of N-EtFOSE, N-EtFOSAA, N-EtFOSA and FOSAA were $5 \mu\text{g L}^{-1}$. Concentration of H_2O_2 was 10 mM in all cases. Irradiation intensity was 765 W m^{-2} .

Fig. C11 Indirect photoreaction profile of N-EtFOSAA in the presence of H_2O_2 . a- Irradiation data, b- Enlarged scale of a, c- Model profile, d- Enlarged scale of c. Conditions: Initial concentration of N-EtFOSAA = 5ppb, $[H_2O_2]=10\text{mM}$, $[^{\bullet}\text{OH}]_{ss}=5.5\times 10^{-14}\text{M}$, irradiation intensity = 765 W m^{-2} .

Fig. C12 Indirect photoreaction profile of N-EtFOSA in the presence of H_2O_2 . a- Irradiation data, b- Enlarged scale of a, c- Model profile, d- Enlarged scale of c. Conditions: Initial concentration of N-EtFOSA = 5ppb, $[\text{H}_2\text{O}_2]=10\text{mM}$, $[\cdot\text{OH}]_{\text{ss}}=5.5\times 10^{-14}\text{M}$, irradiation intensity = 765 W m^{-2} .

Fig. C13 Model profile of FOSAA. Conditions: Initial concentration of N-EtFOSA = 5ppb, $[\cdot\text{OH}]_{\text{ss}}=5.5\times 10^{-14}\text{M}$,

Fig. C14 Recovery test for large volume injection method according to section A, Appendix C. Y-axis represents % recovery rate; X-axis represents PFCs with matrix recovery test (red color) and method recovery test (dark blue), n = 8-10.

B.2 Competitive kinetics of PFCs and OP with $\cdot\text{OH}$

OP was used as reference compound for competitive kinetics evaluations as described previously (Mazellier, 2003), (Xu et al., 2011c). The rates of PFC and OP disappearances via reaction with $\cdot\text{OH}$ were calculated as follows:

$$-\frac{d[\text{OP}]}{dt} = k_{\text{OP}}[\text{OP}][\cdot\text{OH}]_{ss} \quad (\text{C.1})$$

$$-\frac{d[\text{PFC}]}{dt} = k_{\text{PFC}}[\text{PFC}][\cdot\text{OH}]_{ss} \quad (\text{C.2})$$

Where k_{OP} and k_{PFC} is second order rate constant of OP and target PFC with steady state $[\cdot\text{OH}]_{ss}$, respectively; $[\text{OP}]_{0,t}$ and $[\text{PFC}]_{0,t}$ are concentration of OP and PFC at time zero and t , respectively.

By integration and transformation:

$$\ln \frac{[OP]_t}{[OP]_0} \times \frac{1}{k_{OP}} = \ln \frac{[PFC]_t}{[PFC]_0} \times \frac{1}{k_{PFC}} \quad (C.3)$$

Therefore,

$$k_{PFC} = \frac{\ln \frac{[PFC]_t}{[PFC]_0}}{\ln \frac{[OP]_t}{[OP]_0}} k_{OP} \quad (C.4)$$

Mazellier et al. reported a value for $k_{OP} = (6.4 \pm 0.5) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Mazellier, 2003) which was validated in our previous paper of $(11 \pm 0.5) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Xu et al., 2011c). k_{PFC} were evaluated according to equation C.4 using our reported data.

Parallel step reaction (Helfferich, 2004):

In a network of irreversible parallel first order steps, fractional distance from complete conversion at any conversion level is the same for all participants. The process rate $-r_x$, is proportional to the fractional distance x . The characteristic rate coefficient is the sum of the rate coefficients of all steps.

The reaction rate is described as followings:

$$\frac{dx}{dt} = -kx \quad (1)$$

After integration:

$$\ln x = -kt \quad (2)$$

Where x can be expressed in terms of any participant (A is initial compound, P, Q are products and so on):

$$x = \frac{C_A}{C_A^0} = 1 - \frac{C_P}{C_P^\infty} = \frac{C_Q}{C_Q^\infty} \quad (3)$$

The coefficients k_{AP} , k_{AQ} can be calculated from:

$$k_{AP} = \frac{C_P^\infty}{C_A^0} k, k_{AQ} = \frac{C_Q^\infty}{C_A^0} k \quad (4)$$

Where k can be obtained from slope of equation (2). Alternatively, individual coefficients can be calculated from data on incremental conversions:

$$k_{AP} = \frac{k \Delta C_P}{(-\Delta C_A)}, k_{AQ} = \frac{k \Delta C_Q}{(-\Delta C_A)} \quad (5)$$

Appendix D

Fig. D1 Photodegradation of N-EtFOSE and OP in 10 mg L⁻¹ aqueous nitrite solution: a- 5 µg L⁻¹ N-EtFOSE, b- 10 µg L⁻¹ OP.

Fig. D2 Photodegradation of N-EtFOSE and OP in 10 mg L⁻¹ aqueous nitrate solution: a- 5 µg L⁻¹ N-EtFOSE, b- 10 µg L⁻¹ OP.

Fig. D3 Photochemical degradation in solution containing HA and in the presence of H₂O₂: a- 5μg L⁻¹N-EtFOSE; b- 10 μg L⁻¹ OP; SE: standard error of linear regression slope.

Fig. D4 Photochemical degradation in solution containing HA and in the presence of 10 mM H₂O₂:(a) 5 μg L⁻¹N-EtFOSE; (b) 10 μg L⁻¹ OP; SE: standard error of linear regression slope. The light control sample in pure water showed decline of N-EtFOSE and OP.

Fig. D5 The appearance of PFC metabolites during photochemical degradation of N-EtFOSE in the presence of H_2O_2 : a- in 1 mg L⁻¹ HA solution; b- in 5 mg L⁻¹ HA solution. Conversion was calculated based on the mass of molar fluorine, F/F_0 (%).

Fig. D6 Photodegradation of N-EtFOSE and OP in the presence of H₂O₂: a- in 10 mg L⁻¹ nitrate solution; b- in 100 mg L⁻¹ nitrate solution.

Fig. D7 The appearance of PFC metabolites during photochemical degradation of N-EtFOSE in the presence of H₂O₂. a- in 10 mg L⁻¹ nitrate solution; b- in 100 mg L⁻¹ nitrate solution.

Fig. D8 Photodegradation of N-EtFOSE and OP in the presence of H₂O₂: a- in 10 mg L⁻¹ nitrite solution; b- in 100 mg L⁻¹ nitrite solution.

Fig. D9 The appearance of PFC metabolites during photochemical degradation of N-EtFOSE in the presence of H₂O₂: a- in 10 mg L⁻¹ nitrite solution; b- in 100 mg L⁻¹ nitrite solution.