Occurrence, fate, and fluxes of perfluoroochemicals (PFCs) in an urban catchment: Marina Reservoir, Singapore

Viet Tung Nguyen, Karina Yew-Hoong Gin, Martin Reinhard and Changhui Liu

ABSTRACT

A study was carried out to characterize the occurrence, sources and sinks of perfluoroochemicals (PFCs) in the Marina Catchment and Reservoir, Singapore. Salinity depth profiles indicated the reservoir was stratified with lower layers consisting of sea water (salinity ranging from 32 to 35 g L⁻¹) and a brackish surface layer containing approximately 14–65% seawater. The PFC mixture detected in catchment waters contained perfluoroalkyl carboxylates (PFCAs), particularly perfluorooctanoate (PFOA), perfluorohexanoate (PFHpA), perfluorooctane sulfonate (PFOS) and PFC transformation products. PFC concentrations in storm runoff were generally higher than those in dry weather flow of canals and rivers. PFC concentration profiles measured during storm events indicated ‘first flush’ behavior, probably because storm water is leaching PFC compounds from non-point sources present in the catchment area. Storm runoff carries high concentrations of suspended solids (SS), which suggests that PFC transport is via SS. In Marina Bay, PFCs are deposited in the sediments along with the SS. In sediments, the total PFC concentration was 4,700 ng kg⁻¹, approximately 200 times higher than in the bottom water layers. Total perfluoroalkyl sulfonates (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 approximately 35 ± 12 kg y⁻¹. Contributions of SS, dry weather flow of river/canals, and rainfall were approximately 70, 25 and 5%, respectively. This information will be useful for improving strategies to protect the reservoir from PFC contamination.

Key words | fresh water, perfluoroochemicals, reservoir, runoff, sediment

INTRODUCTION

In an increasingly urban and densely populated world, the need to produce drinking water from local sources (ground-water, 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 perfluoroochemicals (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 & Kannan 2007; Piekartz et al. 2007) and wildlife (Houde et al. 2006a, b), streams (Murakami et al. 2008; Plumlee et al. 2008) and groundwater (Hoehn et al. 2007; Plumlee et al. 2008; Murakami et al. 2009). Recently, PFCs have been detected in canals and rivers that feed into the Marina Reservoir, Singapore (Nguyen et al. 2011).

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 sediments (Gurr & 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 & Masunaga 2009). Sorption of PFCs on sediments is affected by the sediment, especially organic carbon ($f_{oc}$ in %), 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, $K_d$.

$$K_d = \frac{C_s}{C_w}$$

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

$$K_{oc} = K_d \times \frac{100}{f_{oc}}$$

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 (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 to determine 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.

**METHODS**

**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 the city centre. Catchment flow drains into Marina Reservoir, a fresh water reservoir that was created by a gated 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 (Figure 1). Singapore’s river and canal system does not receive direct wastewater discharges, although input from leaking sewers cannot be excluded (Nguyen et al. 2011). During dry periods, the Barrage was opened at midnight; during rainy periods, it was opened when a predetermined water level was reached.

This study was conducted from December 2008, to February 2009, for reservoir sampling and December 2009, through April 2010, for catchment runoff, approximately 8–12 months after closing of the Barrage. Figure 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.

**Sampling**

Runoff samples were collected at CM1–CM3 (Figure 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.

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 to 7.2 m (Figure 2). River and canal water samples were collected at the sites indicated in Figure 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 24 h by multiprobes (Lake Diagnostic Systems, LDS, http://rtm.cwr.uwa.edu.au/olaris/index.php) that were placed at Kallang Basin and Marina Bay. The probe data were validated by a portable YSI probe (556, MPS, USA). Variations in the water parameters, including salinity, conductivity and temperature were insignificant during the 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 laboratory in an icebox 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.

Sample extraction and analysis

Methods for the analysis of PFCs in water (Plumlee et al. 2008; Nguyen et al. 2011) 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 a 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 (approximately 40 mL) were combined and concentrated with 200 mg C18 SPE cartridges (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 (6:2PfTS), 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 standards: [d₅]-N-EtFOSA (for analysis of N-MeFOSA and N-EtFOSA), [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).

Samples were analyzed by liquid chromatography-tandem mass spectrometry (Shimadzu LC-10 AD, Singapore; API3000 AB Sciei, USA). Sample extracts were injected on to a C18 column (3.5 μm pore size,
RESULTS AND DISCUSSION

Distribution of PFCs and impact of seawater in Marina Reservoir

PFC concentrations and product distribution in the top layer (Figure 3) are consistent with the surface water concentrations determined previously (Nguyen et al. 2011). The major PFC fraction consisted of total perfluoroalkyl carboxylates (PFCAs) (16–74 ng L$^{-1}$) followed by total perfluoroalkyl sulfonates (PFSAs) (6–28 ng L$^{-1}$) and metabolites (1–5 ng L$^{-1}$) (Figure 4). In catchment waters, the previously reported concentration ranges of these fractions were similar (Nguyen et al. 2011). The most abundant species were PFOA, PFOS and PFHpA with concentrations ranging from 8 to 37, 6 to 20 and 4 to 28 ng L$^{-1}$, respectively (data not shown).

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 (data not shown).

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 (32–36 g L$^{-1}$) (Figure 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 Figure 3 were $36.8 \pm 2.9$, to $26.6 \pm 3.6$, $20.3 \pm 3.1$ and $17.8 \pm 2.7$ ng L$^{-1}$, respectively. Higher total PFC concentrations from 8 to 37, 6 to 20 and 4 to 28 ng L$^{-1}$, respectively (data not shown).

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![Figure 3](https://iwaponline.com/wst/article-pdf/66/11/2439/441028/2439.pdf)

Figure 3 | Depth profiles of average total PFCs concentrations and salinity in Marina Reservoir at S1–S4. Values represent the average of six sampling events and the standard deviation (n = 6).
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–S4 decreased with depth, as indicated in Figure 4(c).

**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 (Figure 4(a)). The PFC composition during the rain event stayed relatively constant at all sites with some notable exceptions of dominant PFOS at site CM3 (Figure 5). The highest total PFCs concentrations were observed in CM3 (Figure 4(a)) perhaps a point source released PFSA (Nguyen et al. 2014). Samples collected during rain events showed first flush behavior: 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 min (until the third composite sample), suggesting that the point source releasing PFSAs was located at some distance from the storm water sampler.

The average concentration ratios of 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.

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

Table 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 PFSAs, five PFCAs with chain lengths ranging from C₆ to C₁₃ (except C₉), and three metabolites (N-EtFOSA, N-MeFOSAA, N-EtFOSAA). Concentrations of total PFCs, PFSAs, metabolites, N-EtFOSA and PFOS in Marina Bay sediments (Table 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. 2011). The reasons for this...

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**Figure 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).
Figure 5 | Vertical composition of PFCs in Marina Reservoir and PFC concentration profile in runoff during a rain event. T1–T6 represent composite samples obtained at 40 min intervals, from 40 min (T1) to 240 min (T6).

Table 1 | Mean concentrations with standard deviation of PFCs in sediment and comparison of log $K_d$ and log $K_{oc}$ of this study with literature values

<table>
<thead>
<tr>
<th>PFCs</th>
<th>Mean (STD) (ng kg$^{-1}$ dw)</th>
<th>Range (ng kg$^{-1}$ dw)</th>
<th>Contribution to total (average %)</th>
<th>Log $K_d$ This study (cm$^3$ g$^{-1}$)</th>
<th>Log $K_{oc}$ This study (cm$^3$ g$^{-1}$)</th>
<th>Log $K_d$ Ahrens et al. (2010) (cm$^3$ g$^{-1}$)</th>
<th>Log $K_{oc}$ Ahrens et al. (2010) (cm$^3$ g$^{-1}$)</th>
<th>Log $K_{oc}$ Higgins &amp; Luthy (2006) (cm$^3$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFHxS</td>
<td>636 ± 145</td>
<td>483–803</td>
<td>10.5</td>
<td>2.5 ± 0.2</td>
<td>4.5 ± 0.2</td>
<td>1.8 ± 0.1</td>
<td>3.6 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>PFOS</td>
<td>2,126 ± 1,059</td>
<td>858–3,570</td>
<td>35.2</td>
<td>2.5 ± 0.3</td>
<td>4.5 ± 0.3</td>
<td>2.1 ± 0.1</td>
<td>3.8 ± 0.1</td>
<td>2.57 ± 0.13</td>
</tr>
<tr>
<td>6:2F8S</td>
<td>938 ± 471</td>
<td>605–1,271</td>
<td>15.5</td>
<td>2.8 ± 0.3</td>
<td>4.8 ± 0.3</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>2PFSAs</td>
<td>2,996 ± 1,546</td>
<td>1,341–4,978</td>
<td>–</td>
<td>2.5 ± 0.2</td>
<td>4.5 ± 0.2</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>PFHpA</td>
<td>&lt;0.2</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>PFOA</td>
<td>197 ± 105</td>
<td>39–322</td>
<td>3.3</td>
<td>1.3 ± 0.4</td>
<td>3.3 ± 0.3</td>
<td>0.04 ± 0.03</td>
<td>1.8 ± 0.1</td>
<td>2.1</td>
</tr>
<tr>
<td>PFNA</td>
<td>&lt;0.4</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>2.4 ± 0.1</td>
</tr>
<tr>
<td>PFDA</td>
<td>55 ± 13</td>
<td>40–64</td>
<td>0.9</td>
<td>1.2 ± 0.4</td>
<td>3.4 ± 0.4</td>
<td>1.8 ± 0.1</td>
<td>3.6 ± 0.3</td>
<td>2.7 ± 0.1</td>
</tr>
<tr>
<td>PFUnA</td>
<td>214 ± 131</td>
<td>75–383</td>
<td>3.5</td>
<td>2.2 ± 0.5</td>
<td>4.2 ± 0.5</td>
<td>3.0 ± 0.1</td>
<td>4.8 ± 0.2</td>
<td>3.3 ± 0.1</td>
</tr>
<tr>
<td>PFDoA</td>
<td>156 ± 99</td>
<td>28–397</td>
<td>2.6</td>
<td>2.4 ± 0.2</td>
<td>4.4 ± 0.2</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>PFTA</td>
<td>168 ± 55</td>
<td>118–227</td>
<td>2.8</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>2PFCAs</td>
<td>645 ± 149</td>
<td>396–841</td>
<td>–</td>
<td>1.5 ± 0.1</td>
<td>3.4 ± 0.1</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>FOSA</td>
<td>nd</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>2.5 ± 0.2</td>
<td>4.3 ± 0.2</td>
</tr>
<tr>
<td>N-EtFOSA</td>
<td>476 ± 146</td>
<td>282–638</td>
<td>7.9</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>N-MeFOSAA</td>
<td>223 ± 42</td>
<td>160–261</td>
<td>3.7</td>
<td>2.6 ± 0.2</td>
<td>4.6 ± 0.2</td>
<td>n.a.</td>
<td>n.a.</td>
<td>3.1 ± 0.2</td>
</tr>
<tr>
<td>N-EtFOSAA</td>
<td>849 ± 59</td>
<td>781–886</td>
<td>14.1</td>
<td>2.8 ± 0.3</td>
<td>4.8 ± 0.3</td>
<td>3.0 ± 0.1</td>
<td>4.8 ± 0.1</td>
<td>3.2 ± 0.2</td>
</tr>
<tr>
<td>2Metabolites</td>
<td>1,086 ± 440</td>
<td>540–1,524</td>
<td>–</td>
<td>2.8 ± 0.2</td>
<td>4.8 ± 0.2</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>2PFCs</td>
<td>4,700 ± 1,116</td>
<td>3,546–6,325</td>
<td>–</td>
<td>2.1 ± 0.1</td>
<td>4.1 ± 0.1</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

*a*- n; n.a. – not available.
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 PFSAs were the predominant PFC fraction with PFOS, 6:2FtS and PFHxS contributing 35.2, 15.5 and 10.5%, respectively. Higher-weight compounds, 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 $K_{oc}$ 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 1.5–10.6% in Tokyo Bay. The $K_{oc}$ values shown in Table 1 are comparatively high, likely because the $f_{oc}$ value used as an estimate is low. In spite of this uncertainty, the data allow 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.

**Estimation for PFC load to the reservoir**

The PFC input into the Marina reservoir was estimated based on the following assumptions: (1) the concentration of total PFCs in rain water was 6 ng L⁻¹, as reported earlier (Nguyen et al. 2011); (2) all rainfall in the catchment drains as runoff into the reservoir; (3) the input of SS from the total catchment area was proportional to the input from the sub-catchments evaluated by Lam (Lam 2008); (4) PFCs adsorbed to SS were in equilibrium with aqueous PFCs; and (5) 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 approximately 35 ± 12 kg y⁻¹ with most (70%) transported by SS. Dry weather flow contributed approximately 25% and rainwater, 5%.

**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 up to 86% freshwater with large variance and bottom layers sustainably 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 composition of PFCs in runoff and reservoir water was similar to storm runoff. The PFC content in Marina Reservoir sediments was higher compared with 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 approximately 35 ± 12 kg y⁻¹.

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