

## Source analysis of perfluorocarboxylates in Tokyo Bay during dry weather and wet weather using sewage markers

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**Environmental context.** As perfluorocarboxylates can be carried by surface runoff to waters and cause adverse effects to aquatic organisms, we evaluated the contributions of wastewater and surface runoff to the concentrations of these compounds in Tokyo Bay during dry and wet weather. Sewage markers revealed that the surface runoff was a significant source of perfluorocarboxylates in the bay during wet weather. This finding leads to a greater understanding of sources and pathways of perfluorocarboxylates in waters.

**Abstract.** We investigated the occurrence of perfluorocarboxylates (PFCAs) in Tokyo Bay during dry and wet weather and evaluated the contributions of wastewater effluent, untreated wastewater, and surface runoff by using two sewage markers, caffeine and crotonamiton.  $\Sigma$ 8PFCAs ranged from 11 to 185 ng L<sup>-1</sup>. Perfluorononanoate (PFNA) was the major species, followed by perfluorooctanoate (PFOA) and perfluoroheptanoate (PFHpA). Principal component analysis followed by multiple linear regression revealed that the PFCAs were derived mainly from wastewater effluent during dry weather, and jointly from wastewater effluent (59%) and combined sewer overflow (41%) during wet weather. We used caffeine-to-crotonamiton ratios to evaluate the contributions of untreated wastewater and wastewater effluent. Estimated concentrations of wastewater-derived PFCAs were much lower than observed concentrations during wet weather, indicating the contribution of surface runoff to contamination. During a combined sewer overflow, surface runoff had a significant effect on contamination in the bay.

**Additional keywords:** combined sewer overflow (CSO), diffuse pollution, non-point source, perfluorinated surfactants (PFSs), perfluorochemicals (PFCs), pharmaceuticals and personal care products (PPCPs), wastewater tracer.

### Introduction

After 3M began manufacturing perfluorinated surfactants (PFSs), such as perfluorooctane sulfonate (PFOS; C<sub>8</sub>F<sub>17</sub>SO<sub>3</sub><sup>-</sup>) and perfluorooctanoate (PFOA; C<sub>7</sub>F<sub>15</sub>COO<sup>-</sup>), in the USA in the late 1940s, PFSs and their precursors have been widely used by various industries in products such as waxes, carpet cleaners, fire retardants, apparel, and fluoropolymer manufacture, owing to their water repellency and oil repellency.<sup>[1,2]</sup> PFSs are water soluble (e.g. potassium salt of PFOS, 570 mg L<sup>-1</sup> at 24–25°C; PFOA, 9500 mg L<sup>-1</sup> at 25°C),<sup>[3,4]</sup> bioaccumulative,<sup>[5,6]</sup> and environmentally persistent. Owing to these features, PFSs have been ubiquitously detected in surface water,<sup>[7–9]</sup> groundwater,<sup>[10]</sup> seawater,<sup>[11–14]</sup> drinking water,<sup>[15]</sup> aquatic organisms,<sup>[16,17]</sup> and humans.<sup>[18,19]</sup> As PFSs are suspected of being carcinogenic, of being chronic and reproductive toxicants, and of having adverse effects on humans and other animals,<sup>[20–22]</sup> concerns about PFSs are increasing. Thus, an understanding of the sources and pathways of PFSs to waters is required.

PFSs in waters derive from both direct and indirect sources.<sup>[1,7]</sup> Direct sources include the discharge of contaminated water such as untreated wastewater, wastewater effluent and

surface runoff.<sup>[7,8,23–25]</sup> Indirect sources are related to the formation of PFSs from precursors in the atmosphere.<sup>[26]</sup>

Past studies showed that wastewater effluent is an important source of PFSs in waters.<sup>[7,8,23,25]</sup> Loadings of PFSs in rivers during dry weather were comparable to those in effluent from upstream wastewater treatment plants.<sup>[23]</sup> Effluent from semiconductor factories and other manufacturers was the primary source of PFSs in downstream rivers in Taiwan.<sup>[25]</sup> Concentrations of PFOS, perfluoroheptanoate (PFHpA; C<sub>6</sub>F<sub>13</sub>COO<sup>-</sup>), and perfluorononanoate (PFNA; C<sub>8</sub>F<sub>17</sub>COO<sup>-</sup>) in Japanese rivers were strongly correlated with those of crotonamiton, a sewage marker, indicating that these pollutants were derived from wastewater effluent.<sup>[8]</sup>

PFSs are diffusely present in aerosols and street dust,<sup>[27,28]</sup> probably owing to the presence of PFSs and their precursors in waxes and windshield washer fluid, and of the atmospheric deposition of volatile precursors.<sup>[1,26,29]</sup> Consequently, PFSs are present in precipitation and surface runoff.<sup>[24,30,31]</sup> Surface runoff contributed to contamination by PFOA in urban lakes in the USA.<sup>[30]</sup> PFS fluxes in the Tsurumi and Hayabuchi rivers, Japan, were greater during wet weather than during dry

weather.<sup>[23,32]</sup> Unlike PFOS, PFOA concentrations in wastewater influent in Singapore during the wet season were not lower than those during the dry season, also suggesting that surface runoff contributed to contamination by PFOA.<sup>[33]</sup> Murakami et al. surveyed sources of perfluorocarboxylates (PFCAs) in groundwater in Tokyo using differences in PFS compositions among sources and suggested that surface runoff contributed to between 16 and 46% of PFCAs.<sup>[10]</sup> Consistent findings show that non-point sources play important roles in contamination by PFCAs, but not by perfluoroalkyl sulfonates (PFASs).<sup>[24,32,33]</sup> The entry of PFSs, especially PFCAs, from surface runoff into waters is a matter of concern.

We investigated the occurrence of PFCAs in Tokyo Bay during dry and wet weather. As a combined sewer overflow (CSO) can occur during wet weather, PFCAs might be derived from wastewater effluent, untreated wastewater, or surface runoff. So to evaluate the effect of a CSO, we used two pharmaceutical and personal care products (PPCPs), caffeine and crotamiton, as sewage markers. Caffeine is present at high concentrations in untreated wastewater, but >99% is typically removed during wastewater treatment.<sup>[34,35]</sup> Caffeine is therefore regarded as a labile marker and can be used as an indicator of a CSO.<sup>[36]</sup> In contrast, crotamiton is not well removed during conventional wastewater treatment processes and is therefore regarded as a conservative marker.<sup>[35,37]</sup> Combining these two sewage markers can identify the contribution of untreated wastewater to waters.<sup>[38]</sup> Using these sewage markers, we evaluated the contributions of PFCAs from wastewater effluent, untreated wastewater, and surface runoff to Tokyo Bay during wet weather. We studied eight PFCAs: PFHpA; PFOA; PFNA; perfluorodecanoate (PFDA; C<sub>9</sub>F<sub>19</sub>COO<sup>-</sup>); perfluoroundecanoate (PFUA; C<sub>10</sub>F<sub>21</sub>COO<sup>-</sup>); perfluorododecanoate (PFDoDA; C<sub>11</sub>F<sub>23</sub>COO<sup>-</sup>); perfluorotridecanoate (PFTTrDA; C<sub>12</sub>F<sub>25</sub>COO<sup>-</sup>); and perfluorotetradecanoate (PFTeDA; C<sub>13</sub>F<sub>27</sub>COO<sup>-</sup>).

## Experimental

### Sample collection

We collected grab water samples at several locations from the surface 30 cm of Tokyo Bay on 16 May, 15 October and 22 December 2009 in a stainless steel bucket (Fig. 1f). Sample IDs are the same as expressed in Environment of Tokyo (see <http://www.kankyo.metro.tokyo.jp/en/index.html>, accessed 19 April 2011), where St and Cn represent the samples from bay and canals respectively. As heavy rain (total 16 mm; maximum intensity 7.5 mm in 10 min) fell from 2000 to 2250 hours on 14 October, we regarded the samples collected on 15 October as wet-weather samples. As >8 days of dry weather preceded 16 May and 22 December, we regarded the samples collected on those dates as dry-weather samples. Water salinity was measured on site with an electrode. The samples were then transported to the laboratory and filtered through pre-baked glass fibre filters (Whatman GF/F, 0.7- $\mu$ m pore size). The samples for PPCP analysis were acidified with 4-M HCl to pH ~2. All samples were stored at 5°C before analysis. PFCAs were measured in the samples collected on all three dates. PPCPs were measured in the samples collected on 16 May and 15 October only.

### Analyses

Details of analyses of PFCAs are given in Murakami et al.<sup>[8]</sup> Briefly, <sup>13</sup>C-labelled PFOA and <sup>13</sup>C-labelled PFDA were spiked into the filtrates (1 L), and the samples were then passed through

Sep-Pak Plus tC18 cartridges (Waters) preconditioned with 20 mL of methanol and then 10 mL of distilled water. A flow rate of <10 mL min<sup>-1</sup> was maintained. The cartridges were washed with 7 mL of 30% (v/v) methanol in distilled water, and then 7 mL of 55% (v/v) methanol in distilled water that was acidified with 4-M HCl to pH 2.0–2.5. The target compounds were eluted with 20 mL of methanol. The eluate was concentrated to 0.5 or 1 mL, and PFCAs were analysed by liquid chromatography–tandem mass spectrometry (LC-MS/MS: Agilent 1100 and TSQ Quantum) with a Zorbax Rx-C8 column (4.6  $\times$  150 mm, 5  $\mu$ m, Agilent) in electrospray negative ionisation mode. Ions were monitored in selected reaction monitoring mode. PFHpA, PFOA, and PFNA were label-recovery corrected with <sup>13</sup>C-PFOA, as were PFDA and PFUA with <sup>13</sup>C-PFDA. PFDoDA, PFTTrDA, and PFTeDA were not label-recovery corrected.

Details of analyses of PPCPs are given in Nakada et al.<sup>[37,38]</sup> Briefly, acidified filtrates were neutralised with 4-M NaOH to pH 6–8. Crotamiton-d<sub>7</sub> and caffeine-d<sub>9</sub> were spiked into the neutralised filtrates (500 mL), and the samples were then passed through Oasis HLB cartridges (Waters) preconditioned with 10 mL of methanol and then 10 mL of distilled water. A flow rate of <10 mL min<sup>-1</sup> was maintained. The target compounds were eluted with 20 mL of methanol. The eluate was rotary-evaporated to dryness, redissolved in *n*-hexane, and then purified by 5% H<sub>2</sub>O-deactivated silica gel column chromatography. The column (1-cm internal diameter  $\times$  9 cm) was eluted with 20 mL of *n*-hexane/dichloromethane (DCM; 75:25, v/v), 40 mL of DCM, 30 mL of DCM/acetone (70:30, v/v), and 40 mL of DCM/acetone (50:50, v/v). The two DCM/acetone fractions were individually reduced in volume, supplemented with injection internal standards (anthracene-d<sub>10</sub>, benz[*a*]anthracene-d<sub>12</sub> in isooctane), and directly analysed by gas chromatography–mass spectrometry (GC-MS: Agilent, HP5973) with an HP-5MS capillary column (30 m  $\times$  0.25-mm internal diameter, Agilent) in selected-ion monitoring mode.

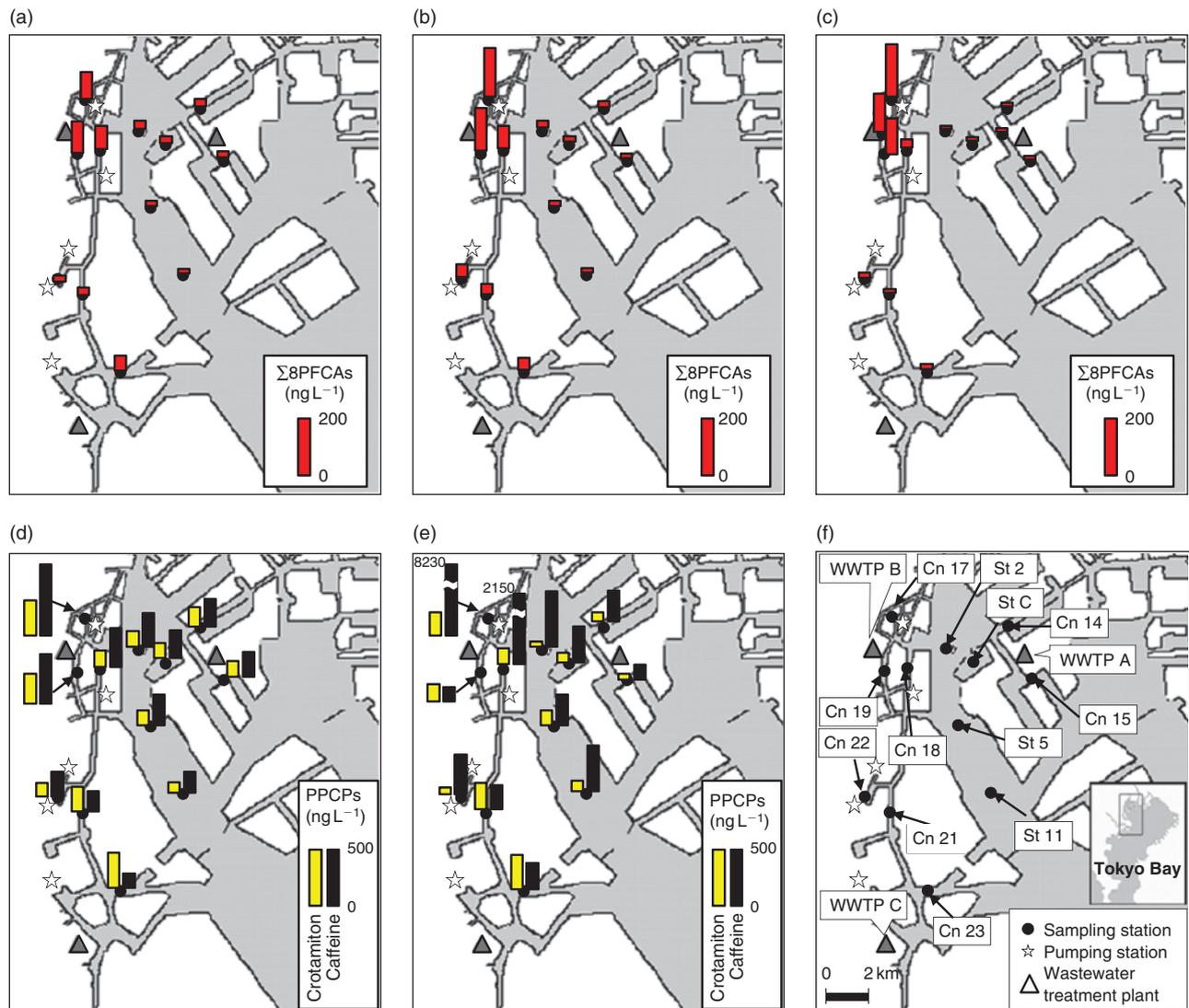
The reproducibility and recovery rates were confirmed by using secondary effluent from a wastewater treatment plant (Table A1 of the Accessory publication, see [http://www.publish.csiro.au/?act=view\\_file&file\\_id=EN10130\\_AC.pdf](http://www.publish.csiro.au/?act=view_file&file_id=EN10130_AC.pdf)). The relative standard deviation (RSD) was  $\leq$ 21% for all PFCAs ( $n = 3$ ) and  $\leq$ 4% for PPCPs ( $n = 4$ ). We spiked each PFCA and PPCP standard into the filtrate of each wastewater sample to confirm the recovery rates. Recovery rates ( $n = 4$ ) ranged from 85 to 114%.

## Results and discussion

### Occurrence of PFCAs and PPCPs during dry and wet weather

$\sum$ 8PFCAs ranged from 11 to 185 ng L<sup>-1</sup> (Fig. 1a–c). The distributions of PFCAs were similar between the two dry-weather periods (Fig. 1a, c). PFCAs were heavily contaminated at the stations near WWTP B (Cn 17, 18, 19). This result is consistent with previous findings that wastewater effluent is a major source of PFCAs.<sup>[8,23]</sup> PFCA concentrations during the wet-weather period were comparable to those during the two dry-weather periods. During dry weather, PFHpA represented 11% of  $\sum$ 8PFCAs (arithmetic mean composition), PFOA 23%, PFNA 51%, PFDA 3.5%, PFUA 6.3%, PFDoDA 2.4%, PFTTrDA 2.9%, and PFTeDA 0.1%. During wet weather, PFHpA represented 7% of  $\sum$ 8PFCAs, PFOA 24%, PFNA 59%, PFDA 3.3%, PFUA 5.3%, and PFDoDA 1.4%. Neither PFTTrDA nor PFTeDA was detected during wet weather. During both

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**Fig. 1.** Spatial distributions of PFCAs and PPCPs in Tokyo Bay: (a) PFCAs on 16 May (dry weather); (b) PFCAs on 15 October (wet weather); (c) PFCAs on 22 December (dry weather); (d) PPCPs on 16 May (dry weather); (e) PPCPs on 15 October (wet weather); and (f) sampling locations. Wastewater treatment plant (WWTP) A services a separate sewer system, and WWTPs B and C service combined systems.

dry and wet weather, PFNA was greatest, followed by PFOA and PFHpA. The heavy contamination by PFNA was probably related to primary manufacturing of ammonium perfluorooctanoate in Japan.<sup>[8]</sup> The ratio of short-chain to long-chain PFCAs (i.e. (PFHpA + PFOA + PFNA)/(PFDA + PFUA + PFDoDA + PFTrDA + PFTeDA)) was significantly higher during wet weather than dry weather (paired *t*-test:  $P < 0.05$ ), indicating that there were differences in sources or behaviour (e.g. partition to solids) of PFCAs between dry and wet weather.

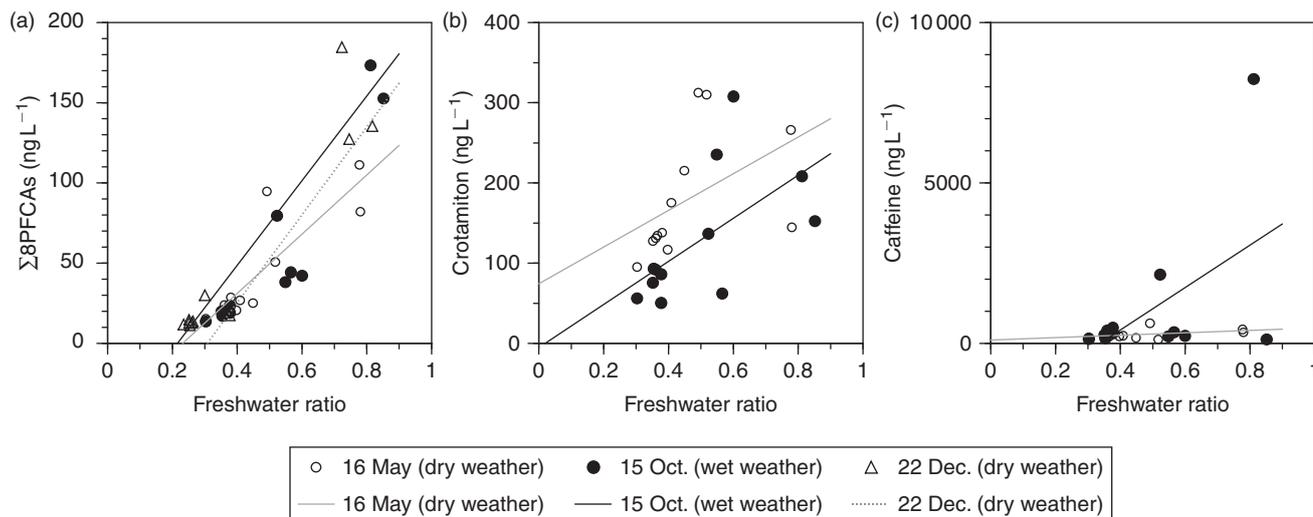
Of the PPCPs, caffeine was detected at high concentrations at stations Cn 17 and 18, near pumping stations, during wet weather, approximately one order of magnitude higher than during dry weather (Fig. 1d, e), indicating a CSO during the wet weather.

Chemical concentrations in the bay are largely affected by the tides. Therefore, to correct for the effects of the tides, we investigated the relationships between chemical concentrations and freshwater ratios, defined as:

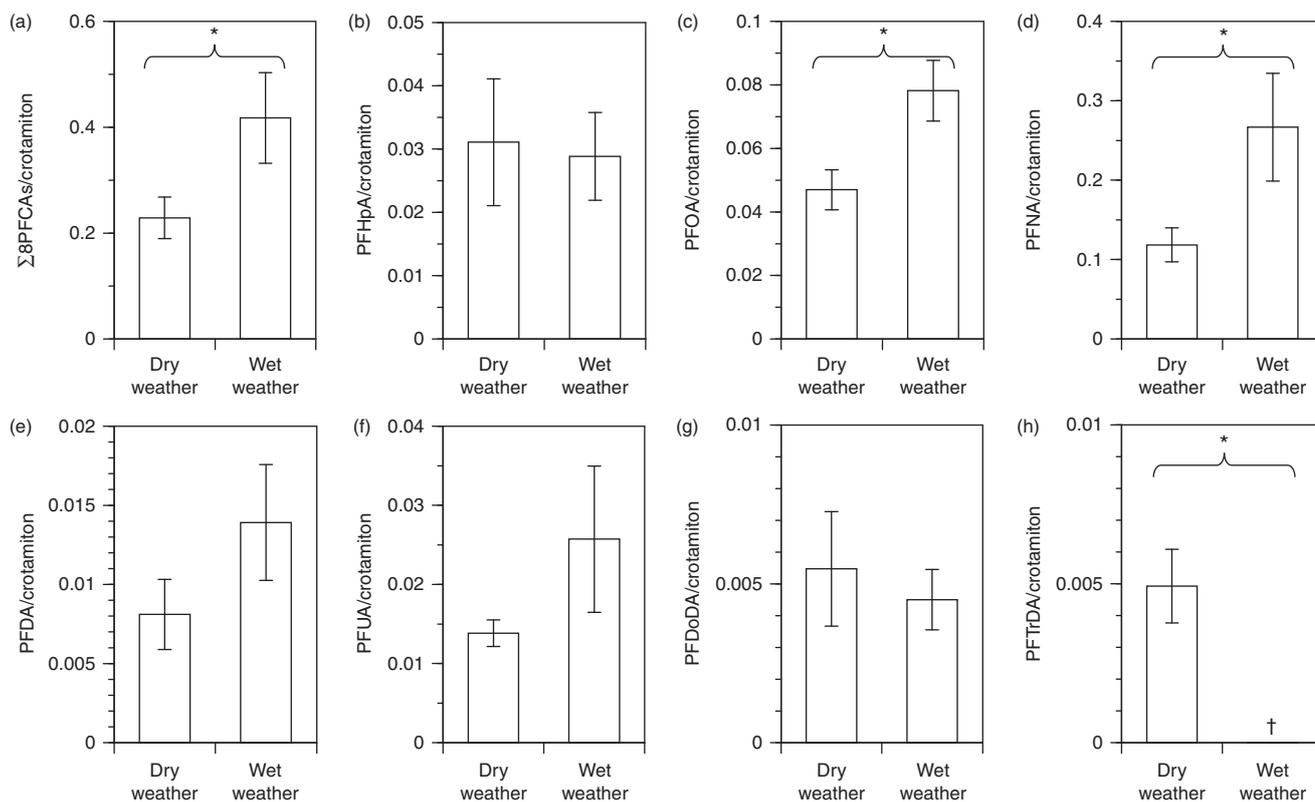
$$\text{Freshwater ratio} = 1 - \text{Salinity}_{\text{sample}} / \text{Salinity}_{\text{sea}} \quad (1)$$

where  $\text{Salinity}_{\text{sea}}$  is Pacific Ocean salinity (35‰).<sup>[12]</sup>

There was a significant relationship between  $\Sigma 8\text{PFCAs}$  concentration and freshwater ratio (dry weather,  $n = 24$ ;  $R^2 = 0.80$ ,  $P < 0.001$ ; Fig. 2a), indicating that the PFCAs were derived from freshwater inputs into the bay and that PFCA concentrations in the bay depended on dilution by seawater. This is consistent with a previous finding that PFOS and PFOA concentrations were correlated with freshwater ratios in Tokyo Bay.<sup>[12]</sup> Ratios of crotamiton concentrations to freshwater ratios were significantly lower during wet weather (arithmetic mean  $\pm$  standard error:  $253 \pm 33 \text{ ng L}^{-1}$ ) than during dry weather ( $395 \pm 26 \text{ ng L}^{-1}$ ; paired *t*-test,  $P = 0.001$ ). This difference indicates that crotamiton was diluted by surface runoff during wet weather. In comparison, the caffeine/freshwater ratios during wet weather ( $1730 \pm 820 \text{ ng L}^{-1}$ ) tended to be higher than those during dry weather ( $625 \pm 74 \text{ ng L}^{-1}$ ), reflecting the effect of untreated wastewater via a CSO. There were no large differences in the  $\Sigma 8\text{PFCAs}$ /freshwater ratios among the three dates (16 May,  $85 \pm 14 \text{ ng L}^{-1}$ ; 15 October,  $90 \pm 17 \text{ ng L}^{-1}$ ; 22 December,  $92 \pm 20 \text{ ng L}^{-1}$ ), showing that PFCA concentrations were not decreased during wet weather despite the entry of surface runoff into the bay. Unlike



**Fig. 2.** Relationship between chemicals and freshwater ratio: (a)  $\Sigma 8$ PFCAAs on 16 May (dry weather),  $R^2 = 0.75$ ,  $P < 0.001$ , 15 October (wet weather),  $R^2 = 0.90$ ,  $P < 0.001$ , and 22 December (dry weather),  $R^2 = 0.85$ ,  $P < 0.001$ ; (b) crotamiton on 16 May (dry weather),  $R^2 = 0.22$ ,  $P = 0.12$ , 15 October (wet weather),  $R^2 = 0.36$ ,  $P < 0.05$ ; and (c) caffeine on 16 May (dry weather),  $R^2 = 0.19$ ,  $P = 0.16$ ; 15 October (wet weather),  $R^2 = 0.27$ ,  $P = 0.08$ .



**Fig. 3.** Comparison of PFCA/crotamiton between dry weather (16 May) and wet weather (15 October): (a)  $\Sigma 8$ PFCAAs/crotamiton; (b) PFHpA/crotamiton; (c) PFOA/crotamiton; (d) PFNA/crotamiton; (e) PFDA/crotamiton; (f) PFUA/crotamiton; (g) PFDoDA/crotamiton; and (h) PFTrDA/crotamiton. Error bars show standard errors. \*,  $P < 0.05$ ; †, PFTrDA/crotamiton  $< 0.002$ .

caffeine, PFCA concentrations in wastewater influent were lower than those in wastewater effluent, possibly because of biodegradation of their precursors.<sup>[8,39]</sup> Therefore, the entry of untreated wastewater via a CSO into the bay did not contribute to the increase of PFCA concentrations in the bay. Thus, surface runoff had a non-negligible effect on PFCA in the bay during wet weather.

Although crotamiton comes mainly from wastewater,<sup>[37,38]</sup> PFCAAs come from both wastewater and surface runoff.<sup>[7,8,23–25]</sup> Therefore, we compared the ratios of PFCAAs to crotamiton between dry weather (16 May) and wet weather (15 October) to evaluate the effect of surface runoff (Fig. 3). PFTrDA/crotamiton is not shown because PFTrDA was not detected on either date. Ratios during dry weather in the bay were comparable to

**Table 1. Principal component loadings for PFCAs and PPCPs**

	Principal component 1	Principal component 2
PFHpA	0.83	0.06
PFOA	0.97	0.00
PFNA	0.83	0.43
PFDA	0.81	0.25
PFUA	0.83	0.22
PFDODA	0.79	-0.53
PFTTrDA	0.55	-0.73
Crotamiton	0.60	-0.42
Caffeine	0.43	0.64
Engenvalue	5.1	1.7
Cumulative	57%	76%

those in wastewater effluent (e.g. PFOA/crotamiton during dry weather in the bay,  $0.047 \pm 0.006$ ; in wastewater effluent,  $0.064 \pm 0.032$ ),<sup>[8]</sup> indicating again that PFCAs during dry weather were mainly derived from wastewater effluent. This is consistent with the previous findings.<sup>[8,23]</sup>  $\sum 8$ PFCAs/crotamiton during wet weather was significantly higher than that during dry weather (paired *t*-test:  $P < 0.05$ , see Fig. 3a). PFOA/crotamiton and PFNA/crotamiton were each significantly higher during wet weather than during dry weather (paired *t*-test:  $P < 0.05$ , see Fig. 3c, d). This difference indicates that not only wastewater effluent but also other additional sources contributed these chemicals during wet weather. In contrast, PFTTrDA/crotamiton during wet weather was lower than that during dry weather. Owing to wash-off of surface deposits and suspension of sediments and sewer pipe deposits, suspended solids concentrations are typically higher during CSO events than during dry weather. Long-chain PFCAs are preferentially partitioned to solids.<sup>[14,40]</sup> The decrease of PFTTrDA/crotamiton during wet weather may be attributed to its preferential partitioning to solids.

#### Source apportionment of PFCAs by principal component analysis followed by multiple linear regression

To analyse the sources of PFCAs, we performed principal component analysis (PCA) followed by multiple linear regression using Excel Statistics 2008 software (Social Survey Research Information Co., Ltd). This technique is often used to apportion the sources of air pollutants such as polycyclic aromatic hydrocarbons.<sup>[41,42]</sup> The purpose of PCA is to represent the total variability of the original data in a minimum number of principal components (PCs). We used concentrations of seven PFCAs (except PFTeDA) and two PPCPs as the original dataset. PFTeDA was not detected on either 16 May or 15 October. PCA was performed to extract the PCs with an eigenvalue  $> 1$ . Together, PCs 1 and 2 were responsible for 76% of the total variance (Table 1). PC1 had high loadings on all PFCAs and crotamiton, whereas PC2 had a high loading on caffeine and low loadings on PFDODA and PFTTrDA. PC1 can be regarded as an indicator of wastewater effluent, which contain high levels of all PFCAs and crotamiton.<sup>[8,37]</sup> In contrast, PC2 can be regarded as an indicator of a CSO, because caffeine is present mainly in a CSO.<sup>[36]</sup> The low loadings on PFDODA and PFTTrDA in PC2 can be explained by preferential partitioning to solids during the CSO event, as described above. The PC2 scores during wet weather were significantly higher than those during dry weather (paired *t*-test:  $P < 0.05$ ), supporting the idea that PC2 indicates a CSO (Fig. A1).

The contribution of each source group to PFCAs in the waters was then quantitatively assessed by multiple linear regression. The analysis treated the  $\sum 7$ PFCa concentration in the samples as the criterion variable and the PC scores as the explanatory variables. Stepwise regression was used to add or remove explanatory variables ( $F_{in} = F_{out} = 2.0$ ). Multiple linear regressions were performed separately for the dry-weather and the wet-weather data:

Dry weather (16 May):

$$\sum 7\text{PFCa concentration} = 13.0 \times (\text{PC1 score}) + 38.7 \quad (R^2 = 0.94) \quad (2)$$

Wet weather (15 October):

$$\sum 7\text{PFCa concentration} = 17.7 \times (\text{PC1 score}) + 12.1 \times (\text{PC2 score}) + 48.2 \quad (R^2 = 0.96) \quad (3)$$

The selection of the PC1 score alone as the explanatory variable for dry weather indicates that the major source of PFCAs during dry weather was wastewater effluent alone. The selection of both PCs for wet weather indicates that the water samples were polluted by both wastewater effluent and a CSO. The average contribution of each source in wet weather was estimated from the ratio of each regression coefficient (PC1 or PC2) to the sum of regression coefficients: wastewater effluent contributed 59% ( $17.7/(17.7 + 12.1)$ ) and CSO 41% ( $12.1/(17.7 + 12.1)$ ). Thus, CSOs are a pathway to seawater contamination by PFCAs.

#### Source analyses of PFCAs by using caffeine/crotamiton ratios

PFCAs during a CSO can originate from both untreated wastewater and surface runoff, because both include PFCAs.<sup>[24]</sup> However, PCA followed by multiple linear regression using only two events could not discriminate between these sources. To evaluate the contributions from wastewater effluent, untreated wastewater, and surface runoff to PFCAs in the bay, we calculated caffeine/crotamiton ratios in the bay water samples, wastewater influent, and effluent.

First, we evaluated the contribution of untreated wastewater volume to total wastewater (untreated wastewater + wastewater effluent) volume, assuming that the crotamiton concentration is not changed during wastewater treatment and that both crotamiton and caffeine come from wastewater alone:

$$\text{caffeine/crotamiton}_{\text{sample}} = \text{caffeine/crotamiton}_{\text{wwi}} \times X + \text{caffeine/crotamiton}_{\text{wwe}} \times (1 - X) \quad (4)$$

where caffeine/crotamiton<sub>wwi</sub> is the ratio in wastewater influent (wwi) (30.6 in Japan),<sup>[35]</sup> caffeine/crotamiton<sub>wwe</sub> is the ratio in wastewater effluent (wwe) (0.03 in Japan),<sup>[35]</sup> and *X* is the fraction of untreated wastewater volume to total wastewater volume.

The caffeine/crotamiton ratios in the bay, especially at stations near pumping stations (Cn 17 and 18), during wet weather were higher than those during dry weather (Fig. 4). Untreated wastewater accounted for  $\sim 100\%$  of the total wastewater volume at Cn 17 and 51% at Cn 18.

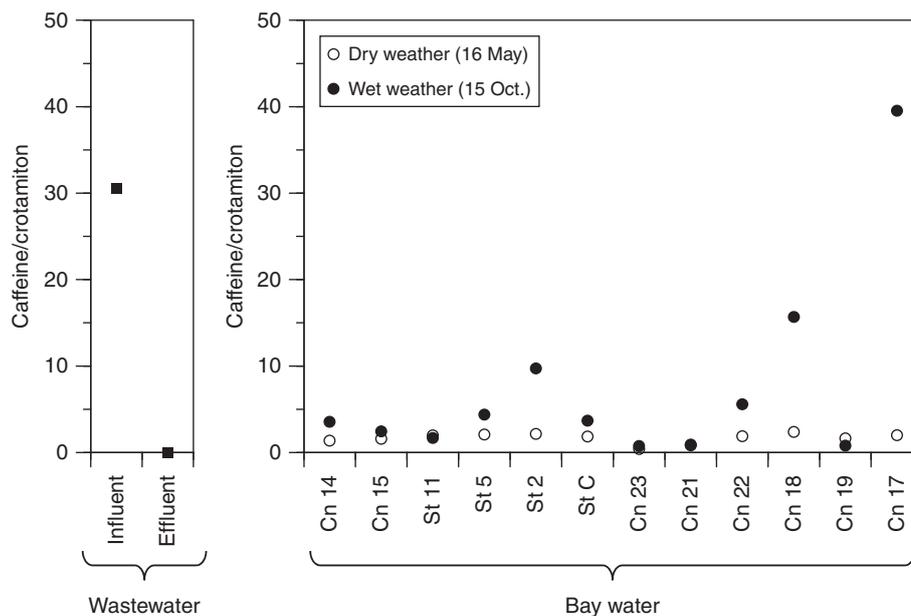


Fig. 4. Comparison of caffeine/crotamiton between dry weather (16 May) and wet weather (15 October). Wastewater data come from Narumiya et al.<sup>[35]</sup>

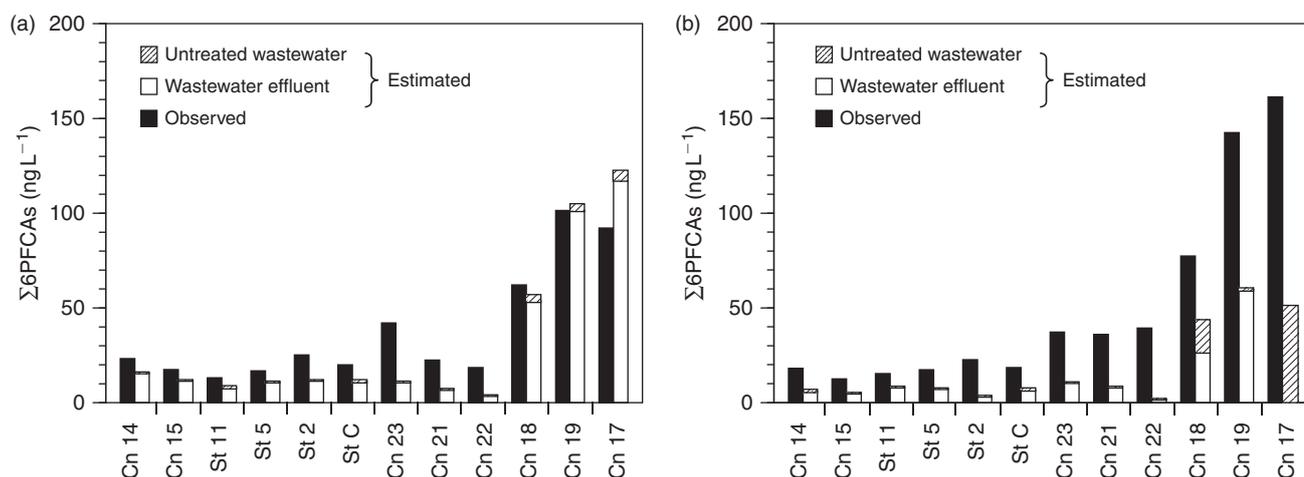


Fig. 5. Comparison between observed and wastewater-derived PFCA concentrations during (a) dry weather (16 May) and (b) wet weather (15 October).

Concentrations of 6PFCA (PFOA, PFNA, PFDA, PFUA, PFDoDA and PFTrDA) from wastewater were then estimated, for which data in the Kanto region were available<sup>[8,24]</sup>:

$$\sum 6PFCA_{\text{ww}} = \sum 6PFCA_{\text{uww}} + \sum 6PFCA_{\text{wwe}} \quad (5)$$

$$\begin{aligned} \sum 6PFCA_{\text{uww}} &= \text{crotamiton}_{\text{uww}} \times \sum 6PFCA / \text{crotamiton}_{\text{wwi}} \\ &= X \times \text{crotamiton}_{\text{sample}} \\ &\quad \times \sum 6PFCA / \text{crotamiton}_{\text{wwi}} \end{aligned} \quad (6)$$

$$\begin{aligned} \sum 6PFCA_{\text{wwe}} &= \text{crotamiton}_{\text{wwe}} \times \sum 6PFCA / \text{crotamiton}_{\text{wwe}} \\ &= (1 - X) \times \text{crotamiton}_{\text{sample}} \\ &\quad \times \sum 6PFCA / \text{crotamiton}_{\text{wwe}} \end{aligned} \quad (7)$$

where  $\sum 6PFCA_{\text{ww}}$  is the  $\sum 6PFCA$  concentration in the sample from wastewater ( $\text{ng L}^{-1}$ ),  $\sum 6PFCA_{\text{uww}}$  is the

$\sum 6PFCA$  concentration in the sample from untreated wastewater ( $\text{ng L}^{-1}$ ),  $\sum 6PFCA_{\text{wwe}}$  is the  $\sum 6PFCA$  concentration in the sample from wastewater effluent ( $\text{ng L}^{-1}$ ),  $\text{crotamiton}_{\text{uww}}$  is the crotamiton concentration in the sample from untreated wastewater ( $\text{ng L}^{-1}$ ),  $\text{crotamiton}_{\text{wwe}}$  is the crotamiton concentration in the sample from wastewater effluent ( $\text{ng L}^{-1}$ ),  $\sum 6PFCA / \text{crotamiton}_{\text{wwi}}$  is the ratio of  $\sum 6PFCA$  to crotamiton in wastewater influent (0.035–0.24)<sup>[8,24]</sup>,  $\sum 6PFCA / \text{crotamiton}_{\text{wwe}}$  is the ratio of  $\sum 6PFCA$  to crotamiton in wastewater effluent (0.035–0.40)<sup>[8]</sup> and  $\text{crotamiton}_{\text{sample}}$  is the crotamiton concentration in the sample ( $\text{ng L}^{-1}$ ).

The estimated  $\sum 6PFCA$  concentrations derived from wastewater agreed well with the observed values during dry weather (Fig. 5a). This result confirms again that wastewater effluent contributed dominantly to the 6 PFCA in the bay water samples. In contrast, during wet weather, untreated wastewater also contributed to the 6 PFCA at the stations near pumping stations (Cn 17, 18), when the estimated concentrations of  $\sum 6PFCA$  were much lower than observed, owing to the contribution from surface runoff (Fig. 5b). The shortfalls of

$\sum$ 6PFCA concentrations were higher than or comparable to the estimated  $\sum$ 6PFCA concentrations derived from untreated wastewater, suggesting that surface runoff contributed more than half of PFCA contamination via the CSO. During the CSO, surface runoff had a significant effect on the contamination of the bay water.

Our results show that surface runoff was a non-negligible source of PFCAs in the bay. The effects of surface runoff vary widely depending on the weather.<sup>[24]</sup> Comprehensive investigations of PFCAs and sewage markers on several occasions will lead to a greater understanding of the sources.

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