Spatial, Phase, And Temporal Distributions of Perfluorooctane Sulfonate (PFOS) and Perfluorooctanoate (PFOA) in Tokyo Bay, Japan

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The spatial distribution, partitioning, and time trends of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) were investigated in the water column and bottom sediment of Tokyo Bay, Japan, during 2004–2006. A total of 480 water and 60 sediment samples obtained by regular 20-station samplings ascertained the three-dimensional distributions of these compounds and changes in the seawater structure in the whole bay. The median of volume-based average water-borne concentrations of PFOS and PFOA was 3.7 and 12 ng/L, respectively. The median concentrations in sediment were 0.61 (PFOS) and 0.20 (PFOA) ng/g-dry. Vertical mixing of the water column probably affected the vertical distribution of these compounds. The negative correlations between PFOS and PFOA concentrations and water salinity and the horizontal distributions of their concentrations suggested that freshwater inputs into the bay were the source of these compounds. A mixing model estimated the average PFOS concentration in the freshwater inputs to be 29 ng/L. The common logarithm of the partition coefficients between the dissolved and suspended-particle-sorbed phases varied among samples, with the average of 4.2 (PFOS) and 3.5 (PFOA). Our analyses indicated no apparent time trends in the concentrations of these compounds during 2004–2006 in either the freshwater input or the bay.

Introduction

Perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) have been detected worldwide in humans (*1, 2*), wildlife (*2, 3*), ambient water (*4–10*), and aquatic sediment

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(*11*). These compounds have been a focus of concern because of their persistence in the environment (*12*), retention in human body (*13*), and toxicities (*12, 14, 15*). PFOS was recently added to the Stockholm Convention on Persistent Organic Pollutants list (*16*). These compounds are members of perfluorinated alkylated substances which have been produced for more than 50 years (*12*). Product applications developed using perfluorooctanesulfonyl fluoride (POSF) through formation of *N*-alkyl perfluorooctane sulfonamides have been used in surfactants and surface coatings and protections. These POSF-based products may have ultimately degraded or metabolized to PFOS (*13*). Salts of PFOA, particularly ammonium perfluorooctanoate, have been used as surfactants and processing aids in the production of fluoropolymers and fluoroelastomers (*13*).

The purpose of our study was to comprehensively elucidate the spatial distribution, partitioning, and time trends of PFOS and PFOA in the water column and bottom sediment of Tokyo Bay, Japan, during 2004–2006, based on quarterly samplings at 20 stations. Ambient water and bottom sediment may be appropriate media for monitoring levels of these compounds in the environment because of their relatively low vapor pressures and high water solubilities (*12, 17*). The Tokyo Bay area is one of the world's most populous areas with many kinds of human activities (*18*). Elevated PFOS and PFOA concentrations have been reported in the bay and its inflowing rivers (*4–9*), but their detailed spatial distribution and partitioning in the bay have not been elucidated. Seasonal samplings are necessary to fully understand their three-dimensional distributions because the seawater structure of the bay changes seasonally (*19, 20*). The extent of mixing of bay water with freshwater inputs may affect the concentrations of these compounds in the bay. Spatial distributions and partitioning of these compounds are an essential basis for predicting their transfer to and potential effects on aquatic organisms, whose habitats are generally localized both horizontally and vertically in the bay (*21*). Their spatial distributions can also provide information on their probable sources. Time trends in the concentrations of these persistent compounds in the environment are of particular interest, but reports of their time trends in ambient water are scarce.

Materials and Methods

Sampling. Twenty sampling stations were established that covered Tokyo Bay horizontally and vertically (Figure 1, Table 1). Tokyo Bay and its catchment area are described in the Supporting Information (SI). One-day sampling campaigns were conducted quarterly during 2004–2006, using two or three boats, on 19 February, 26 May, 22 August, and 28 October 2004; 24 February, 12 May, 17 August, and 26 October 2005; and 22 February, 17 May, 16 August, and 16 November 2006. Water samples were collected with GO-FLO Water Samplers (model 1080, General Oceanics, Inc., Miami, FL) at 10% and 90% of water depths, representing the upper and lower water layers at each sampling station, immediately transferred to a solvent-rinsed glass bottle, cooled during transport, and stored in a cool and dark place. They were normally extracted within four days. Surface sediment samples (about 5 cm depth) were collected by using Smith-MacIntyre grab samplers once each year (August) at the same stations, transferred to a stainless-steel container, cooled during transport, and stored at −20 °C. The sediment samples can be viewed as representing sedimentation of roughly 10 years before sampling, considering the sedimentation rates (*22*) and surface mixing in the bay. To demonstrate water
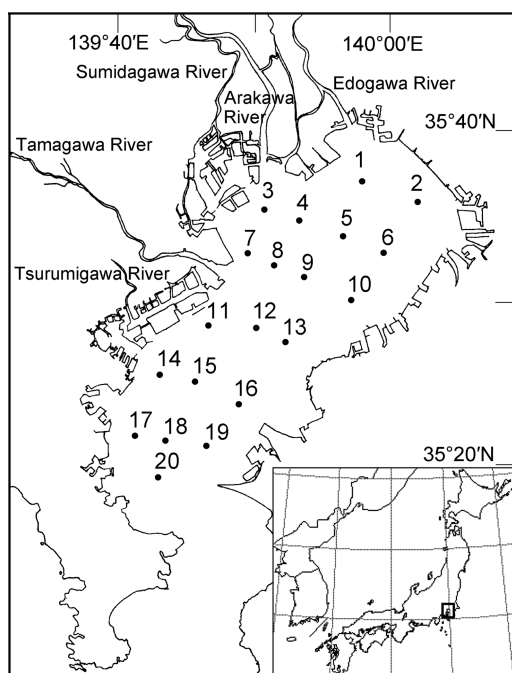
FIGURE 1. Tokyo Bay and the sampling stations.

sample variability, triplicate samples were obtained by repeated deployment of a sampler at each depth at st. 8 on 17 May 2006 and analyzed separately. Salinity and water temperature, which are important measures of water-column structure and freshwater mixing, were recorded at the sampling depths at each station with a conductivity, temperature and depth profiler (XR 420-CTD, RBR Ltd., ON, Canada; or Sonde 4a, HYDROLAB, Loveland, CO). Additionally, during the May, August, and November 2006 samplings, continuous vertical profiles of salinity and water temperature were recorded at st. 1−10. Suspicious salinity measurements were removed before data analysis. Seawater density was calculated (23) from the measured temperature and salinity.

Chemical Analysis. See SI for details (4, 5, 24). For determination of total (dissolved + particulate) concentra-

tions of PFOS and PFOA in water, about 100 mL aliquots of the samples were filtered through a precombusted glass-fiber filter. The methanol extract of the freeze-dried filter was obtained by sonication and centrifuged, and the supernatant was concentrated. The filtrate and the concentrated supernatant were combined, spiked with labeled surrogate compound(s) in methanol (depending on the sampling date; 5 ng of sodium dodecyl-d_{25} sulfate, 1 ng of $^{13}C_2$-labeled PFOA, or 1 ng each of $^{13}C_4$-labeled PFOS and $^{13}C_2$-labeled PFOA), and then purified by using a C18 solid-phase extraction (SPE). The SPE eluate was concentrated and finally dissolved in 500 μL of 1:1 (v/v) methanol in Milli-Q water. For the separate determination of dissolved and particulate concentrations, about 500 mL aliquots of the water samples were filtered through a precombusted glass-fiber filter. The filtrate and filter were spiked with the surrogate compound(s), and then separately purified similarly as described above. Freeze-dried sediment samples of about 1.0 g-dry were extracted and purified by the same procedure used for the filter samples. All samples were acidified just prior to SPE. Identification and quantification were conducted by injecting an aliquot of the final concentrated extract into a liquid chromatograph (LC) connected to a triple-quadrupole-type tandem mass spectrometer equipped with a C18 LC column. Quantification was based on the internal standard method. Concentrations were reported when the signal-to-noise ratio (S/N) of the peak was >8. Phase-separated concentrations were measured in 62 samples (31 upper layer samples) collected at the May ($n = 2$), August (40), and November (20) 2006 samplings. Total concentrations are reported unless otherwise specified. Suspended solids (SS) were determined by passing the water sample through a precombusted glass-fiber filter and weighing the dried residue on the filter. The particulate organic carbon (POC) content in water and the organic carbon (OC) content in the sediment were measured with an elemental analyzer after removing inorganic carbonate with hydrochloric acid.

Data Quality Assurance and Quality Control. See SI for details. Analytical reproducibility and method recovery of PFOS and PFOA in the water and sediment samples were confirmed to be satisfactory. Method and sampling blanks were confirmed to be negligible. The agreement between

TABLE 1. Sampling Stations, Water Depth, Suspended Solid (SS) Concentration in Water, Total Organic Carbon (TOC) Content in Sediment, and PFOS and PFOA Concentrations in the Upper (10% depth) and Lower (90% Depth) Water Layers and in Sediment[a]

sampling station	longitude (°N)	latitude (°E)	depth (m)	SS upper (mg/L)	SS lower (mg/L)	TOC (mg/g-dry)	PFOS upper (ng/L)	PFOS lower (ng/L)	PFOS sediment (ng/g-dry)	PFOA upper (ng/L)	PFOA lower (ng/L)	PFOA sediment (ng/g-dry)
1	35.6172	139.9667	11	15	7.4	22	6.3	3.5	0.74	22	15	0.35
2	35.5975	140.0344	12	8.3	8.2	12	5.5	3.3	0.63	25	11	0.31
3	35.5900	139.8467	12	11	8.2	23	9.0	3.9	0.46	16	11	0.22
4	35.5794	139.8897	14	8.5	7.4	31	6.5	3.1	1.4	14	9.2	0.29
5	35.5644	139.9431	16	6.6	6.5	33	6.4	2.9	1.1	16	9.1	0.27
6	35.5481	139.9931	17	7.2	8.0	34	5.7	3.2	0.71	16	9.7	0.26
7	35.5478	139.8264	19	11	8.6	22	8.5	2.9	0.35	16	7.7	0.17
8	35.5358	139.8581	21	10	7.8	31	6.4	2.6	0.77	15	7.9	0.23
9	35.5250	139.8953	22	9.1	7.3	31	4.9	2.5	0.60	17	3.5	0.21
10	35.5033	139.9531	20	8.1	9.1	33	5.2	2.6	0.66	17	7.7	0.27
11	35.4658	139.7775	32	8.0	7.5	29	6.0	2.0	0.65	16	4.8	0.11
12[b]	35.4639	139.8367	31	8.1	8.4	29	5.1	1.8	0.57	17	4.3	0.16
13	35.4500	139.8725	23	8.4	7.9	27	4.4	2.0	0.55	17	5.3	0.20
14	35.4158	139.7183	37	8.2	10	17	6.1	1.4	0.21	16	2.9	0.11
15	35.4083	139.7614	19	8.1	6.9	9.6	4.5	2.6	0.43	17	5.0	0.39
16	35.3856	139.8150	14	6.9	7.0	3.5	4.0	3.2	0.25	13	8.6	0.11
17	35.3528	139.6881	44	6.8	11	18	5.2	1.0	0.31	13	2.1	0.15
18	35.3486	139.7253	26	7.1	6.5	3.3	3.3	2.2	0.13	11	6.3	0.19
19	35.3433[c]	139.7753	14	7.6	8.6	2.7	3.1	2.4	0.20	12	6.6	0.19
20	35.3103	139.7167[d]	52	8.0	6.2	7.3	4.7	0.88	0.13	14	1.7	0.16

[a] Medians of measured values among samplings during 2004−2006 are shown for depth, SS, TOC, PFOS, and PFOA. [b] 35.4603°N, 139.8267°E in 2004 and February 2005. [c] 35.3389°N in 2004 and February 2005. [d] 139.7081°E in 2004 and February 2005.

the total concentration and the sum of the separately determined dissolved and particulate concentrations was good.

Data Analysis. Median values are adopted as representative of the central tendency of the observed concentrations, considering the data distribution (see Results). The difference in concentrations between the two layers was examined by the Wilcoxon signed rank test (i.e., sampling stations matched) against the null hypothesis that the central tendencies of the distributions were equal, and the associated Hodges−Lehmann estimator (25). To focus on relative horizontal spatial trends in each layer at each sampling, the 20 sampling stations were ranked in descending order according to the observed concentrations of each compound, and the ranks of each sampling station were averaged over the 12 water or three sediment samplings. These average ranks were used to assess the spatial distributions, in addition to the median concentrations at each sampling station. To assess the central tendency of ratios, the geometric mean and the 95% confidence interval (95% CI) based on the t-statistic of the log-transformed ratios were used. The 95% CI of population correlation coefficients was estimated by Fisher's z transformation. These 95% CIs are indicated in square brackets. Statistical analyses were carried out with Microsoft Excel (ver. 2003, Microsoft, Redmond, WA), SPSS for Windows (ver. 15.0J, SPSS Inc., Chicago, IL), Statistica (ver. 7.1, StatSoft, Inc., Tulsa, OK), and StatXact (ver. 8, Cytel Inc., Cambridge, MA).

Linear regression analysis was conducted to assess the possible dependence of PFOS and PFOA concentrations on salinity:

$$C = \alpha_{fresh}C_{fresh} + \alpha_{ocean}C_{ocean} \qquad (1)$$

where C, C_{fresh}, and C_{ocean} are the concentration of PFOS or PFOA in each sample, in the freshwater inputs to the bay, and in Pacific Ocean water, respectively. α_{fresh} and α_{ocean} are the respective ratios of freshwater and ocean water in the water samples ($\alpha_{fresh} + \alpha_{ocean} = 1$). Equation 1 transforms to eq 2 by assuming that α_{ocean} equals salinity of each sample (S) divided by salinity of Pacific Ocean seawater (S_{ocean}). The parameters a_0 and a_1 in eq 2 were estimated by weighted least-squares (WLS) regression by using C^{-2} as the weight.

$$C = a_0 + a_1 S \qquad (2)$$

Equation 2 was then used to estimate C_{fresh} by setting $S = 0$ and C_{ocean} by setting $S = S_{ocean}$. In this study, S_{ocean} was set to 35.5 because the maximum observed salinity in the bay was 35.4. Another least-squares regression without weighting (OLS) of log(PFOS concentration) was conducted against log(freshwater ratio $(1 - S/S_{ocean})$) to confirm the WLS regression results.

To evaluate partitioning between the suspended-particle-sorbed (or OC-sorbed) and apparently dissolved phases, observed partition coefficients were calculated for particle−water (K_P^{linear}, eq 3) and OC-water (K_{OC}^{linear}, eq 4), assuming linear relationships.

$$K_P^{linear} = C_{particulate}/C_{dis}(L/kg) \qquad (3)$$

where $C_{particulate}$ (/kg dry matter) is the concentration in the particulate phase and C_{dis} (/L water) is the concentration in the apparently dissolved phase. Similarly,

$$K_{OC}^{linear} = C_{particulate}/([OC]\cdot C_{dis}) \qquad (4)$$

where [OC] (−) is the OC content (dry mass basis) of the suspended particles.

Volume-based average concentrations of PFOS and PFOA in Tokyo Bay water were calculated by taking into account their three-dimensional distributions and the seawater structure of the bay. The total mass of each compound in the bay water was first estimated, and then divided by the volume of water in the bay. The mass of each compound in the bay water was estimated by dividing the bay horizontally into 500×500 m grid squares and coastal subareas, and vertically into two layers corresponding to the upper and lower layer samples, and by summing the masses present in each grid square or subarea. The water column was divided into two layers when stratification was present, by using observed and reported vertical density profiles (19, 26−28). PFOS and PFOA concentrations and pycnocline depth at the closest sampling station were assigned to each grid square or subarea. See SI for details. The total mass of each compound in the water column was divided by the estimated water residence-time in the bay (1.0−1.6 months (19, 29)) to estimate their fluxes through the water column. Their sedimentation fluxes were calculated by multiplying the concentrations in the sediment by the reported sedimentation rates in the bay (22).

Results

Concentration. Table 1 shows the median values at each sampling station of the SS concentration in water, the total organic carbon (TOC) content in sediment, and the PFOS and PFOA concentrations in the upper and lower water layers and sediment. SI Figure S1 shows the data distributions of the PFOS and PFOA concentrations in the upper and lower layers of the water column and in the sediment. The data distributions in normal scale have a long tail to higher values but are roughly symmetrical in log scale. As the median concentrations of both compounds were clearly higher in the upper water layer than in the lower layer (SI Figure S1), data from the two layers were analyzed separately. The median concentrations (range) were PFOS, upper layer, 5.5 ng/L (0.78−17), and lower layer, 2.5 ng/L (not detected [ND]-14); PFOA, upper layer, 16 ng/L (2.7−63), and lower layer, 6.2 ng/L (0.29−35); PFOS, sediment, 0.61 ng/g-dry (0.062−3.6); and PFOA, sediment, 0.20 ng/g-dry (ND-1.4). In the lower layer, log(PFOS concentration) and log(PFOA concentration) were relatively highly correlated ($r = 0.83$ [0.79−0.87], $n = 240$) compared with the other correlations between the log concentrations of each compound in each layer (0.22−0.55).

The variability, including both sampling and analytical variability, was demonstrated to be roughly 10% in the water data, as the three consecutive deployment of the water sampler yielded coefficient of variation (CV) in concentration of 2.1% (average = 7.5 ng/L), 6.2% (3.1 ng/L), 3.2% (36 ng/L), and 12% (17 ng/L) for PFOS in the upper and lower layers and PFOA in the upper and lower layers, respectively. In the case of one PFOS ND value in water and four PFOA ND values in sediment, the detection limits ($S/N = 8$) were estimated to be about 0.4 ng/L and 0.05−0.08 ng/g-dry, respectively. Half the detection limit was assigned to these ND values when necessary in the data analysis.

Spatial Distributions. Observed differences in the density of seawater between the upper and the lower layers indicate the extent of stratification of the water column (SI Figure S2). The lower density of the upper layer was most pronounced in August, followed May, consistent with previous reports of seasonal changes in the seawater structure in the bay, and reflecting greater dilution of the salinity by freshwater from inflowing rivers and heating of the water's surface in warmer seasons (19, 20).

The ranges of PFOS and PFOA concentrations in each layer as well as differences in the concentrations between the two layers were shown in Figure 2. Their concentrations in the upper layer were statistically significantly higher ($p <$
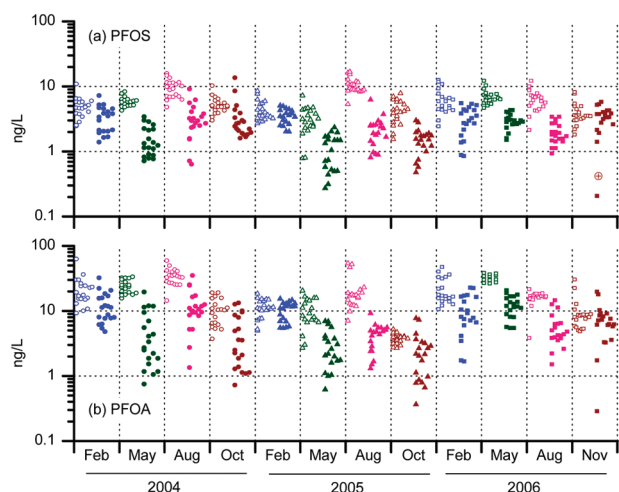
FIGURE 2. Seasonal distributions of PFOS (a) and PFOA (b) concentrations in the upper and lower layers of the water column of Tokyo Bay. Each point represents one sample. Horizontal offsets were chosen arbitrarily to minimize overlap of the points. For each sampling, the upper layer data (open symbols) are plotted on the left and the lower layer data (closed symbols) on the right. ND ($\oplus$) is plotted as the detection limit of the sample.

0.05, $n = 20$) than those in the lower layer at each of the 12 samplings, except for PFOS in November 2006 and PFOA in February 2005 at which the concentrations in the two layers were comparable. In addition, larger differences in PFOS and PFOA concentrations were observed between the two layers along with larger differences in seawater densities between the layers, particularly in August and May (Figure 2 and SI Figure S2), consistent with the greater stratification of the water column in August and May. The range of concentrations in the water column was 3.9, 6.4, 4.8, and 12 for PFOS in the upper layer, PFOS in the lower layer, PFOA in the upper layer, and PFOA in the lower layer, respectively, as represented by the median among the 12 samplings of the maximum-to-minimum concentration ratio at the 20 stations.

The concentrations of PFOS and PFOA were generally higher at northern sampling stations (st. 1–10) (SI Figure S3). For both compounds in both layers, the three highest-ranking stations were among st. 1–11, and the three lowest-ranking stations were among st. 14–20. For both compound in the lower layer, the three highest-ranking stations were st. 4 or more northern stations, whereas in the upper layer, they were st. 11 or more northern stations. In the upper layer, PFOS concentrations during each sampling were higher at the northwestern stations (3, 7, and 11, in descending order of concentration), whereas PFOA concentrations were higher at the northeastern stations (2, 1, and 10). PFOS and PFOA concentrations in sediment were also generally higher at the northern sampling stations. However, correlations of the log concentrations of the two compounds between the sediment and the lower water layer were weak (PFOS, $r = 0.39$ [0.15–0.59], $n = 60$; PFOA, $r = 0.42$ [0.18–0.62], $n = 56$). The highest-ranking stations for PFOS concentrations in sediment were st. 4 and 5, which were different from those for PFOS concentrations in the lower layer water (st. 3 and 1). These relative horizontal trends based on the average ranks generally accord with the horizontal trends based on median concentrations (Table 1).

PFOS concentrations in both layers of the water column showed a clear increasing trend ($r = 0.78$ [0.73–0.81], log–log scale, $n = 405$) in relation to the freshwater ratio ($1 - S/S_{ocean}$) (Figure 3). The WLS regression of PFOS concentration against salinity ($n = 405$) yielded [PFOS concentration/(ng L^{-1})] = $(29.2 \pm 2.6) - (0.823 \pm 0.077) \times$ salinity (parameters: point
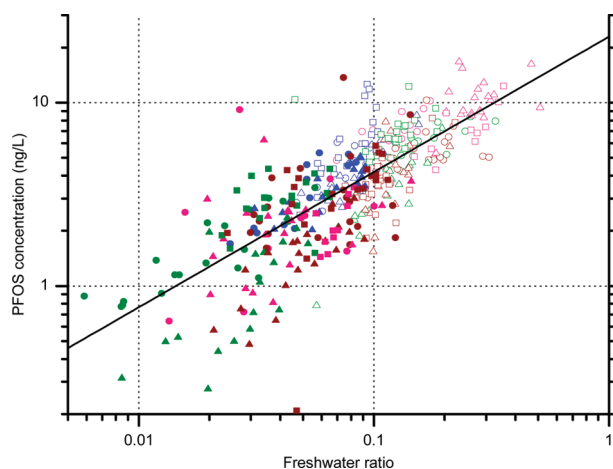

FIGURE 3. Relationship between the PFOS concentration and the freshwater ratio (FWR = $1 - $ ((sample salinity)/(Pacific Ocean seawater salinity))) in the water column. Open and closed symbols indicate upper and lower water layer samples, respectively. Circles, triangles, and squares indicate samples collected in 2004, 2005, and 2006, respectively. Blue, green, pink, and brown indicate samples collected in winter (February), spring (May), summer (August), and autumn (October or November), respectively. The equation of the regression line is log[PFOS concentration/(ng L^{-1})] = $(1.36 \pm 0.07) - (0.738 \pm 0.059) \times$ log FWR (parameters: point estimates $\pm$ half of 95% CI).

estimates $\pm$ half of 95% CI). PFOS C_{fresh} was determined to be 29 ng/L [27–32], and C_{ocean} to be close to zero (-0.011 ng/L [-0.14 to 0.12]), by extrapolation. Similar regressions for the seasonal data suggested that PFOS C_{fresh} was higher in winter (February) (48 ng/L versus about 29–32 ng/L in other seasons). The regression result for log(PFOS concentration) against log(freshwater ratio) supported these results by yielding an extrapolated PFOS C_{fresh} of 23 ng/L [20–27] (Figure 3), with similar differences among seasons. Yearly regression estimates of C_{fresh} were inconsistent between the two regression methods (WLS and OLS of log concentrations); the former suggested slightly higher C_{fresh} in 2006, whereas the latter suggested that C_{fresh} was highest in 2005. Although PFOA concentrations also tended to increase as the freshwater ratio increased, the correlation was lower ($r = 0.57$ [0.50–0.63], log–log scale) and the data were more scattered.

Partitioning. Partition coefficients were calculated for the 58 and 49 samples with detected concentrations in both phases, for PFOS and PFOA, respectively. These partition coefficients varied by more than 1 order of magnitude among samples. For PFOS and PFOA, $\log K_P^{linear}$ ranged 3.4–5.0 (log of the geometric mean, 4.2) and 2.7–4.2 (3.5), respectively, and $\log K_{OC}^{linear}$ from 4.5–5.9 (5.2) and from 3.4–5.5 (4.5), respectively (SI Figure S4). K_{OC} values were calculated under the assumption that these compounds were predominantly sorbed to the OC fraction of the particles. In November 2006, the water column was more vertically mixed, compared with the more stratified water column in May and August 2006. Therefore, the partition coefficients of samples from November 2006 may reflect more homogeneous conditions. The partition coefficients for this data subset (PFOS, $n = 16$; PFOA, $n = 8$; water temperature, 17.2–18.9 °C) did fall within a narrower range, but the median values were similar to those of the whole data set (see SI Figure S4).

Volume-Based Average Concentrations in the Water Column, And Fluxes through the Bay. The volume-based average concentrations of PFOS ranged 1.9–5.9 (median of 12 samplings, 3.7) ng/L and that of PFOA ranged 2.7–22 (median, 12) ng/L, whereas the mass of PFOS in the bay ranged 29–87 (median, 54) kg and that of PFOA 40–320 (median, 170) kg (Figure 4). The volume-based average
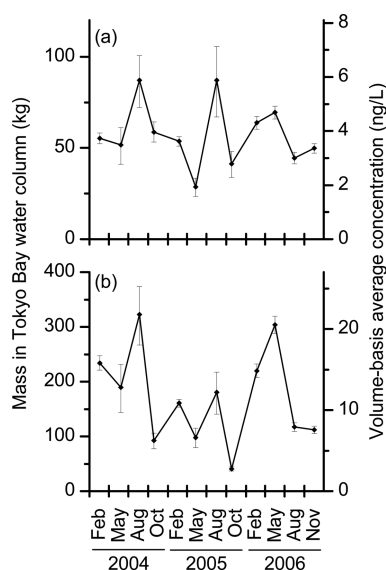
FIGURE 4. Time series of masses and volume-based average concentrations of PFOS (a) and PFOA (b) in the water column of Tokyo Bay. Error bars indicate uncertainty due to assignment of pycnocline depth as well as that due to sampling and analytical variability.

concentrations of the two compounds changed similarly over time ($r = 0.71$ [0.23–0.91], $n = 12$), but neither showed any apparent or statistically significant linear trend in relation to time ($n = 12$; PFOS, $r = -0.14$ [-0.66 to 0.47]; PFOA, $r = -0.24$ [-0.71 to 0.39]). The estimated fluxes of PFOS and PFOA through the water column of Tokyo Bay were 210–1000 and 300–3900 kg/y, respectively, which were about 2–3 orders of magnitude higher than the sedimentation fluxes in the bay (0.84–4.2 and 0.23–0.83 kg/y, respectively).

Discussion

This study elucidated the three-dimensional distributions of PFOS and PFOA in the whole bay taking into account the seasonal change in the seawater structure. 480 measurements were obtained from the water column and 60 from the sediment of Tokyo Bay for each of these compounds, among which only five were ND values. This comprehensive data set thus provides a basis for evaluating potential risks associated with these compounds in the aquatic environment of the bay. Previously reported concentrations of these compounds in Tokyo Bay (4–7) are within or close to the ranges observed in our study. All data analyses in this study assumed no degradation of the two compounds in the bay.

The correlations between [PFOS or PFOA concentration difference between the upper and lower layers] and [the density difference between the two layers] suggest that water column stratification or vertical mixing affects the vertical distributions of these compounds. The concentrations in the upper layer, however, were generally higher than those in the lower layer (although the difference was smaller), even when no vertical density gradient was present (e.g., at most stations at the February samplings), probably reflecting fresh water input into the upper layer and still incomplete vertical mixing.

The higher concentrations in the upper layer and at more northern stations suggest that these compounds enter the bay at its northern part and are input mainly into the upper layer. This inference is supported by the reported considerable input of these compounds via inflowing rivers and effluent of sewage treatment plants (STPs) (7, 8) mainly into the northern part of the bay. The higher PFOA concentrations in the northeastern part of the bay suggest that the

geographical source distribution of PFOA or its behavior may be different from those of PFOS. North to south concentration gradients in the water column and sediment of Tokyo Bay have also been reported for other persistent organic chemicals of anthropogenic origin (dioxins (18), fluorescent whitening agents (20), and polychlorinated biphenyls (30)), so this horizontal distribution may be characteristic for such compounds in Tokyo Bay.

Our simple mixing model (eq 1) provided valuable information regarding the average concentration of PFOS and its seasonal change in the freshwater inputs to Tokyo Bay. The model assumes that the concentrations of PFOS or PFOA in each sample (C) result from mixing of freshwater and ocean water inputs in the bay. The conservative behavior of salinity and the persistence of PFOS and PFOA support the use of this model. The concentration of a compound in freshwater (C_{fresh}) represents the average of its concentration in the various freshwater inputs. Salinity, or the freshwater ratio, represents the extent of mixing of seawater with freshwater. Thus, the negative correlation between the PFOS concentration and salinity indicates that freshwater inputs were the predominant source of PFOS to the bay. The estimated PFOS C_{fresh} falls within its reported concentration ranges in rivers flowing into Tokyo Bay (2.1–140 ng/L) (5, 7–10), and within its concentration range in effluent from the STPs on the shore of the bay (17–1100 ng/L; Serizawa et al., National Institute for Environmental Studies, unpublished data). No data on seasonal differences in the PFOS concentrations of waters flowing into Tokyo Bay are available, however, if the PFOS load from the catchment is relatively constant, the lower water flow in winter due to lower precipitation would account for the higher estimated concentration in the freshwater input in winter. Our regression result for PFOS C_{ocean} is consistent with the reported low concentrations in ocean water not affected by Tokyo Bay (40–75 pg/L in the offshore of Japan (6)). The similar trend of PFOA against salinity to that of PFOS and the similar trend between PFOS and PFOA over time suggest that these compounds in Tokyo Bay share a common major source. The greater variability of the PFOA concentration against the freshwater ratio may reflect a wider spatial distribution of emission sources or a higher variability in the emission rate.

Variability in particulate matter composition and the extent to which equilibrium had been obtained in the sampled waters may account for the variation in partition coefficients between dissolved and suspended-particle-sorbed phases. The partition coefficients of PFOS and PFOA in ambient seawater obtained in this study were several orders of magnitude higher than previously reported limited number of values measured using environmental samples. Odaka and Masunaga (7) reported a field-observed PFOS log K_d of 2.8 ($K_d = 600$ L/kg) in Tokyo Bay (we compared reported K_d values with our K_d^{linear} values). The difference from our results is primarily due to the lower particulate-phase concentrations in their study (dissolved concentrations and SS levels were comparable). Since their samples used for K_d calculations were collected near the mouths of major inflowing rivers, their lower K_d values may reflect particular conditions in these rivers on the sampling day. Even lower partition coefficients (PFOS log K_d, 0.88 (31); PFOS log K_{OC}, 2.4–2.7 (31, 32) PFOA log K_{OC}, 2.11 (32)) have been obtained in experiments using freshwater sediments. However, these experimental values may not be directly comparable to ours because of the much higher ranges of concentrations used in these laboratory experiments (about 10^3–10^6 higher dissolved concentrations than those observed in this study), and the difference in cation concentrations (e.g., [Ca^{2+}]) (32) between freshwater and seawater. It is interesting to note that PFOS and PFOA concentrations at the August 2006 sampling in the lower layer per particulate mass were respectively roughly 68 (geometric mean) (range, 9.5–780)

and 82 (12−340) times those in the bottom sediment collected at the same station at the same time, and respectively 16 (4.4−59) and 20 (4.2−180) times on an OC basis, possibly reflecting differences in source or composition between sediment particles and suspended particulate matter.

Our results showed no apparent trend in the concentration of either compound in the freshwater input or the bay with time. This lack of a linear trend in PFOS during the 12 seasons is consistent with the PFOS C_{fresh} regression results showing no consistent yearly trend. No governmental regulations have been implemented on these compounds in Japan until 2009. Few domestic records of their industrial production, import, or emission are available. Since the fluxes of PFOS and PFOA through the water column were much higher than their sedimentation fluxes, the water column may be the more appropriate medium in which to monitor the levels of these compounds in Tokyo Bay. The potential relationships of the concentrations of these compounds with the stratification of the water column in Tokyo Bay and with the freshwater inputs as indicated by the salinity should be taken into account in the interpretation of such monitoring results. Investigation of degradation rates in the aquatic environment of precursor compounds of PFOS and PFOA may be necessary for a more precise evaluation of their fluxes and partitioning therein.

Supporting Information Available
Additional information about the Materials and Methods. Figures S1−S4. This material is available free of charge via the Internet at http://pubs.acs.org/.

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