ESTIMATED MASS BALANCES OF PERFLUORINATED CHEMICALS IN TOKYO BAY

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Introduction

Perfluorinated chemicals (PFCs) have been used widely as surfactants, lubricants, paper and textile coatings, polishes, food packaging, and fire-retarding foams over the past fifty years. Some of these chemicals, such as perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), are persistent in the environment and have been found in wild animal samples around the world [1, 2]. Due to the fact that PFCs have quite different chemical properties compared with conventional POPs, their environmental behavior and exposure pathway to human and wildlife need to be clarified. In this study, PFOS and PFOA were monitored in the seawater and sediment from Tokyo Bay and in water of six major rivers that run into the bay. Then, their mass balances and behaviors in the bay were investigated.

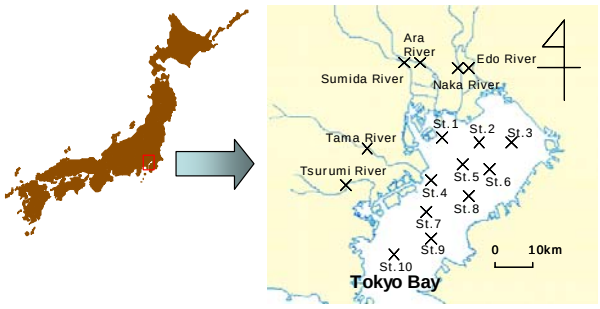

Figure 1 Sampling stations in Tokyo Bay and in six rivers that flow into the bay

Materials and Methods

Study area: Tokyo Bay was selected as a study area because it is one of the most heavily impacted costal areas by the human activities in Japan. In its basin, the bay has the largest metropolis in Japan, Tokyo, with population of over ten million and lot of industries.

Sampling in Tokyo Bay: Seawater and sediment samples were collected on February 9 and 10, 2004 by boats. Seawater samples for dissolved PFC analysis were collected from three layers (surface [0.5 m water depth], middle layer [half of water depth] and bottom [2 m above sea bottom]) at 8 stations (St. 1, 3, 4, 5, 7, 8, 9, and 10) in the bay (**Figure 1**). Large volumes of seawater (40 – 100 L) from the three layers for particulate phase PFC analysis were collected at two stations (St. 1 and 4). Surface sediments were collected by a Smith-Macintyre sediment sampler at all the 10 stations.

Sampling in Rivers: River water samples for both dissolved and particulate phase PFC analysis were collected on December 2 and 3, 2004 from the six major rivers that flow into the bay (**Figure 1**). The river flows on the sampling day were around the annual average flow of that year.

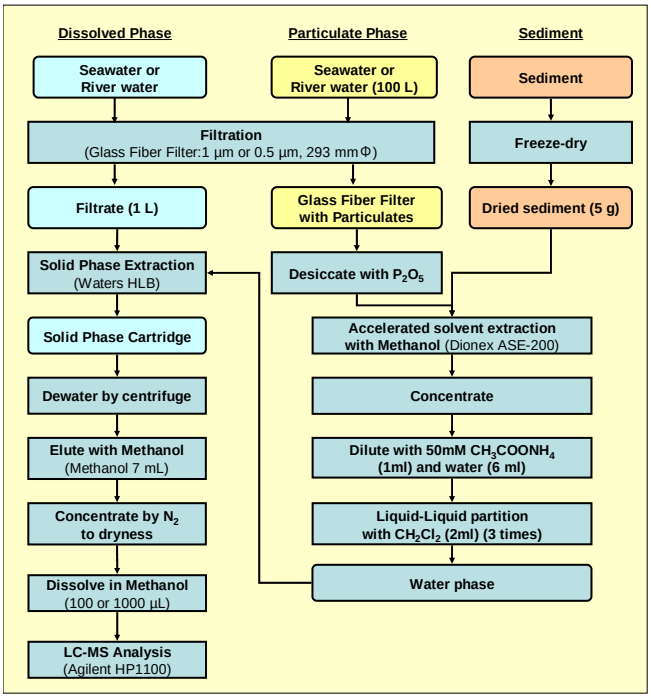

Figure 2 Analytical procedures

Analysis: Dissolved and particulate phase PFCs in sea and river water and those in surface sediment were analyzed as shown in **Figure 2**.

Results and Discussions

Observed PFOS and PFOA concentrations:

The concentrations of PFOS and PFOA are shown in **Table 1**. PFOS and PFOA existed almost exclusively in dissolved phase both in sea and river water. The concentrations of dissolved PFOS in river water were higher than those in seawater by one order of magnitude except for Edo River. The concentrations were a little higher near the head than the entrance of the bay and a little higher in surface than in bottom of the sea. As opposed to PFOS, there was little difference in dissolved concentrations of PFOA between sea and river water. In the bay, dissolved PFOA concentrations were quite uniform (between 7.0 – 18.2 ng/L) and there was no decreasing tendency in concentration toward the entrance of the bay.

Concentrations of PFOS and PFOA in surface sediment of the bay were between 0.3 – 0.9 and below 0.1 ng/g-dry sediment, respectively.

Input of PFOS and PFOA from the six major rivers into the Bay: Amounts of annual PFOS and PFOA transport from the six rivers to the bay were estimated based on the following three assumptions in order to consider the uncertainty involved, because only one sample was measured for each river in this study.

(1) Both dissolved and particulate phase PFC concentrations, expressed in ng/L and ng/g dry suspended solid, respectively, were constant for each river whole year round. Thus, amount transported in dissolved phase was directly proportional to the river water flow. And that in particulate phase was proportional to the amount of suspended solid (SS) transported, which was estimated from the relationship between SS concentration and river water flow.

(2) The amount of daily transport was constant for whole year. Thus, the amount of transport on the day of sampling was used to estimate the annual amount of transportation for each river.

Table 1 Levels of PFOS and PFOA in river water, seawater and sediment

Sampling Points		PFOS Dissolved phase ($ng \cdot l^{-1}$)	PFOS Particulate phase or Sediment ($ng \cdot g^{-1}$)*	PFOA Dissolved phase ($ng \cdot l^{-1}$)	PFOA Particulate phase or Sediment ($ng \cdot g^{-1}$)*
River Water					
Edo River		3.0	18.8	5.7	Intf.
Naka River		14.2	9.9	16.7	0.70
Ara River		24.9	14.6	10.5	Intf.
Sumida River		65.7	33.4	14.0	2.1
Tama River		74.4	33.1	16.4	0.88
Tsurumi River		114	21.9	20.5	Intf.
Sea water or sediment in Tokyo Bay					
St. 1	Surface	7.3	3.7	12.6	Intf.
	Middle	5.7	2.2	13.4	Intf.
	Bottom	5.7	4.2	13.7	Intf.
	Sediment	NA	0.4	NA	＜0.1
St. 2	Sediment	-	0.9	-	＜0.1
St. 3	Surface	3.0	-	12.4	-
	Middle	4.8	-	14.1	-
	Bottom	3.4	-	13.7	-
	Sediment	NA	0.7	NA	＜0.1
St. 4	Surface	3.4	2.0	12.4	3.4
	Middle	3.6	1.1	11.8	2.4
	Bottom	2.0	1.9	8.2	1.1
	Sediment	NA	0.4	NA	＜0.1
St. 5	Surface	3.8	-	14.4	-
	Middle	3.4	-	13.2	-
	Bottom	2.9	-	13.1	-
	Sediment	NA	0.6	NA	＜0.1
St. 6	Sediment	NA	0.6	NA	＜0.1
St. 7	Surface	2.0	-	13.3	-
	Middle	2.6	-	13.1	-
	Bottom	1.5	-	7.0	-
	Sediment	NA	0.4	NA	＜0.1
St. 8	Surface	5.0	-	16.9	-
	Middle	3.3	-	17.8	-
	Bottom	2.8	-	17.6	-
	Sediment	NA	0.4	NA	＜0.1
St. 9	Surface	3.4	-	18.2	-
	Middle	3.5	-	17.9	-
	Bottom	1.8	-	7.8	-
	Sediment	NA	0.5	NA	＜0.1
St. 10	Surface	2.6	-	17.7	-
	Middle	2.2	-	11.8	-
	Bottom	1.8	-	10.7	-
	Sediment	NA	0.3	NA	＜0.1
LOQ (Limit of quantification)		0.05	0.1	0.05	0.1

*: $ng \cdot g^{-1}$ dry suspended particulate matter or $ng \cdot g^{-1}$ dry sediment.
NA: Not applicable. -: Samples were not collected.
Intf.: Not determined due to interfering peaks.

(3) When daily river water flow was less than the flow of the sampling day, assumption (1) was used to estimate the annual amount of transport. And when river flow was larger that that flow, assumption (2) was used.

Daily river flow data at the sampling sites were obtained from National Land with Water Information Data Management Center [3], except for Naka River and Sumida River. For the two rivers, their daily flows were calculated from those of Ara River by the two correlations and two kinds of estimates were given for each river. Consequently, the total annual flows for 2004 used for the estimation of PFC transport were as follows: Edo River = 3.16×10^9, Naka River = 6.63×10^8 and 3.8×10^9, Ara River = 1.36×10^9, Sumida River = 4.04×10^8 and 1.6×10^9, Tama River = 1.41×10^9 and Tsurumi River = 2.98×10^8 m^3/year. As Naka and Sumida Rivers had two estimated daily flows, total annual input of PFCs to Tokyo Bay was calculated by the six methods (under three assumptions × two kinds of river flow).

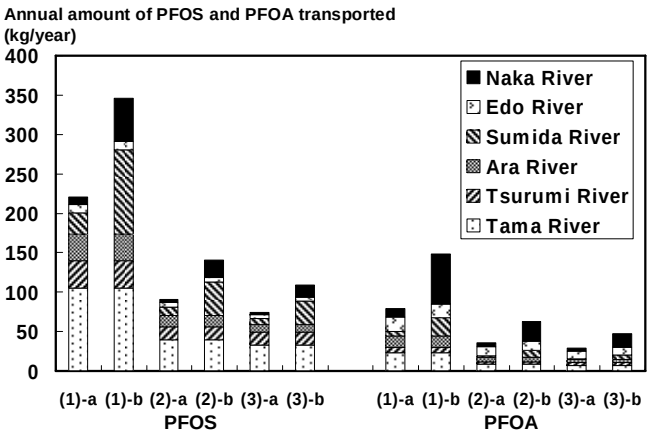

Figure 3 Annual amounts of PFOS and PFOA transported to Tokyo Bay by the six rivers estimate under the three scenarios.
(1): Estimated by proportion to river flow.
(2): Estimated by constant load.
(3): Estimated by proportion to river flow under low daily river flow and by constant load during high river flow.
a: Lower estimates of daily flow for Naka River and Sumida River were used.
b: Higher estimates of daily flow for Naka River and Sumida River.

The results of total annual transport of PFCs estimated by the six methods are shown in **Figure 3**. For both PFOS and PFOA, the amounts estimated under assumption (1) were twice as large as those under assumption (2) and (3). The amounts estimated under assumption (3) were a little smaller than those under assumption under (2). Combining all the estimates, the annual total inputs of PFOS and PFOA ranged over 74 – 346 and 29 – 149 kg/year, respectively. The amounts transported in particulate phase were 0.5 – 4.3 and 0.018– 0.22 kg/year, respectively and contributed only about 1% and 0.1% of total input, respectively.

Outflow of PFOS and PFOA from the bay to the ocean: Conservative estimates of amount of PFOS and PFOA outflow from the bay to the ocean were 20 and 140 kg/year, respectively. These calculations were based on the total amount of river water inflow and the concentration at the entrance of the bay. These values, however, may be too small as interchange of seawater through the bay entrance was not considered. The actual retention time of seawater in Tokyo Bay was reported to be an average of 1.6 months based on the mass balance model of salt and heat [4]. Based on this retention time, the amounts of PFOS and PFOA outflow were estimated to be 350 and 1900 kg/year, respectively, if their concentrations in the seawater outside the bay were negligible. Thus, the possible amounts of outflow must lie between the two estimates, namely, 20 – 350 kg/year for PFOS and 140 – 1900 kg/year for PFOA.

Amount of PFOS and PFOA deposition to bottom sediment: Amounts of PFOS and PFOS deposition to bottom sediment were estimated based on their concentration in surface sediment and deposition rate reported by Matsumoto (1983) [5]. The result showed that PFOS deposition should be less than 1.3 kg/year and that those for PFOA be negligible (less than 0.2 kg/year).

Mass balance of PFOS and PFOA in Tokyo Bay: Combining the above results, rough mass balances of PFOS and PFOA are shown in **Figure 4**. The figures showed that the sources and/or behaviors of PFOS and POFA were quite different from each other.

In the case of PFOS, amount of annual input from the major rivers was comparable to the sum of deposition to

bottom and outflow to the open sea, indicating the no significant transformation or degradation occurred in the bay.

In contrast, estimated amount of annual PFOA input to the bay from the rivers was much less than the sum of deposition and outflow. This indicated that other large sources were present in the basin. Possible sources may be treated sewage directly discharged to the bay, effluents from industries located around the coast of the bay and atmospheric deposition [6, 7]. Taniyasu et al. (2003) [8] reported higher levels of PFOA near the mouth of the rivers, indicating the existence of input near the coast of the bay. Further study on the PFOA sources besides major river transport is necessary in Tokyo Bay.

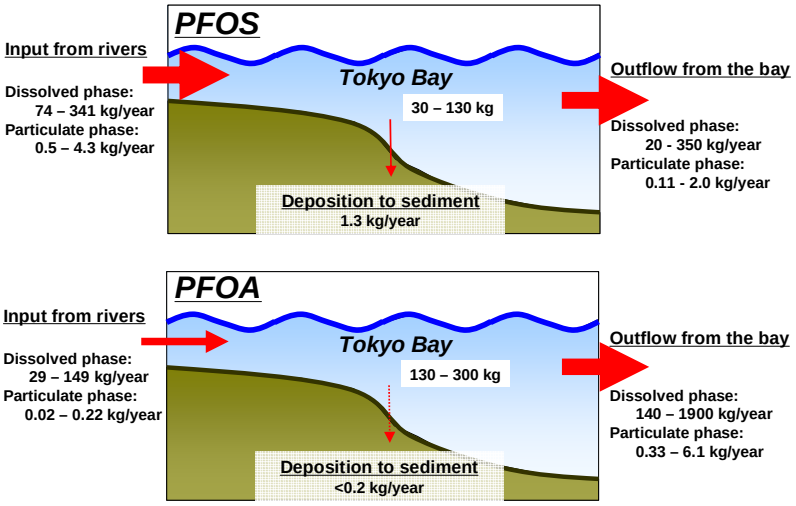

Figure 4 Mass balances of PFOS (upper figure) and PFOA (lower figure) in Tokyo Bay

Conclusions

This study elucidated some of the differences of PFOS and PFOA behaviors in Tokyo Bay. The following conclusions were obtained although the results have uncertainty due to the limited number of samples.

(1) Both PFOS and PFOA existed mainly as dissolved-phase in sea and river water.

(2) In the case of PFOS, estimated annual input from the rivers was comparable to the sum of the amount of outflow to open sea and that of sedimentation to the bottom. This indicated no significant PFOS transformation in the bay.

(3) On the other hand, estimated annual input of PFOA from rivers was smaller than the outflow. This indicated that existence of unknown PFOA sources around the coast of the bay or significant amount of atmospheric deposition.

(4) Bottom sediment was not a major sink of PFOS or PFOA.

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