

Three-dimensional distributions of sewage markers in Tokyo Bay water—fluorescent whitening agents (FWAs)

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Abstract

Three-dimensional distributions of fluorescent whitening agents (FWAs: more specifically, DSBP and DAS1), which are sewage-derived water-soluble markers, were observed in Tokyo Bay water through multi-layer sampling of water at 20 locations. In summer, FWAs predominated in the surface layers, with trace but significant concentration of FWAs in bottom water due to stratification of seawater. In winter, on the other hand, FWAs were extensively mixed into the bottom layers because of the vertical mixing of seawater. In the surface layer, FWA concentrations and the DSBP/DAS1 ratio (the concentration ratio of DSBP to DAS1) were lower in summer than in winter, suggesting more efficient photodegradation of FWAs in euphotic zones during the summer due to stronger solar radiation. Horizontally, FWAs were widely distributed over the surface layer of Tokyo Bay. Surface water with DSBP concentrations above 50 ng/L, corresponding to <200 times dilution of sewage effluent, was found to have spread up to 10 km from the coastline. In addition, an offshore decline in FWA concentrations was observed, showing a half-distance of 10–20 km. The decrease was caused by dilution by seawater of fresh water containing FWAs. The eastern part of the bay was different with respect to surface layers, with higher concentrations seen in northeastern parts. Furthermore, dispersion of combined sewer overflow (CSO)-derived water mass was observed in Tokyo Bay after heavy rain.

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1. Introduction

A broad spectrum of contaminants is discharged into the coastal zone via direct discharge of sewage effluents or rivers receiving sewage. Sewage is known to be a major contributor of pollutants to coastal waters, so gaining an understanding of the spatial distribution and fate of sewage-derived contaminants in coastal zones is essential to manage the coastal environment. To evaluate the impact of sewage on coastal zones, many researchers have employed sewage-derived molecular markers (Eganhouse et al., 1983; Brown and Wade, 1984; Fernández et al.,

1991 and references in Takada and Eganhouse, 1998). Typical markers include coprostanol, which is derived from human feces, and linear alkylbenzenes (LABs), which are unsulfonated residues of the raw material used to manufacture linear alkylbenzenesulfonate (LAS) anionic surfactants. However, most of the markers used so far are hydrophobic, making them unsuitable for tracking the movement of water mass of sewage and tracing water-soluble contaminants derived from sewage. The presence of a wide range of water-soluble contaminants, including natural and synthetic hormones, phenolic endocrine-disrupting chemicals, pharmaceutical chemicals, and antibiotics in sewage, has been extensively demonstrated (Ferguson et al., 2001; Brownawell et al., 2002; Weigel et al., 2002; Atkinson et al., 2003) and their potential hazardousness

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is a major concern. Evaluation of the impact of the sewage-derived water-soluble contaminants on marine environments is now of critical importance. The need for water-soluble markers of sewage has thus been growing in importance. However, only small numbers of water-soluble markers have been proposed (Field et al., 1992; Takada and Eganhouse, 1998; Siegner and Chen, 2002; Buerge et al., 2003; Clara et al., 2004).

In our previous paper (Hayashi et al., 2002), fluorescent whitening agents (FWAs) were proposed as potential water-soluble molecular markers for coastal environments. FWAs, more specifically 4,4'-bis(2-sulfostyryl)biphenyl (DSBP; Fig. 1(a)) and 4,4'-bis[(4-anilino-6-morpholino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulfonate (DAS1; Fig. 1(b)), are contained in laundry detergent and a significant proportion of FWAs are discharged with sewage. FWAs are not efficiently removed during the sewage treatment processes due to their non-biodegradable and water-soluble nature and, consequently, high levels of FWAs are found in sewage effluents (Poiger et al., 1996). FWAs have for this reason been proposed as molecular markers of sewage effluents in aquatic environments (Stoll et al., 1997; Hayashi et al., 2002). However, no studies have been conducted to test their utility as molecular markers in coastal environments. Thus, in the present study, intensive observation of FWAs was conducted in coastal waters (Tokyo Bay).

Tokyo Bay is a semi-enclosed coastal sea, surrounded by one of the world's most urbanized areas (the Tokyo Metropolitan area) with a population of approximately 26 million people. Annually, approximately 2 km³ of sewage effluents drain into the inner part of the bay directly or via rivers. Contamination associated with these huge amounts of wastewater inputs is an increasingly urgent

concern in Tokyo Bay. It has been demonstrated that hydrophobic sewage-derived markers (e.g., coprostanol, LABs, trialkylamines) are widely distributed in Tokyo Bay's coastal sediments (Ogura, 1983; Ogura and Ichikawa, 1983; Takada et al., 1992; Chalaux et al., 1995). However, there is virtually no information on the distribution of hydrophilic molecular markers in the water column in Tokyo Bay. The distribution of LAS, which are surfactants contained in household and industrial detergents and which can be utilized as hydrophilic markers of sewage, has been reported by Kikuchi et al. (1986) in the surface waters of Tokyo Bay. However, they did not take samples from deeper water layers, and their sampling locations and times were too limited to reveal any details of the distribution of sewage-derived contaminants in the water column of Tokyo Bay. This is partly because LAS are relatively biodegradable and their concentrations in Tokyo Bay water are low, thus requiring large samples of water (2 L) to enable their analysis. Compared with LAS, FWAs are persistent and can be detected with high sensitivity using fluorescent detectors coupled with high-performance liquid chromatography. Therefore, much smaller volumes of water (i.e., 0.1 L) allow their reliable determination in coastal waters. In the present study, three-dimensional and close monitoring of FWAs was conducted to trace the details of the behavior and movement of sewage-derived water mass in Tokyo Bay.

In the present study, monthly samplings throughout the year of 5 depth-layers at 20 locations was conducted to record and map the vertical and spatial distributions of FWAs in the Tokyo Bay water column. The objectives of this work were to demonstrate the utility of FWAs by close tracking of sewage-derived water-soluble contaminants in marine environments and to gain an understanding of the oceanic processes influencing the distribution of sewage-derived contaminants in the coastal zone.

2. Samples

2.1. Site description

Tokyo Bay covers 1200 km², has an average depth of 15 m and a water residence time of 1–3 months (Hattori, 1983). Annually, 10 km³ of fresh water from rivers drains into the bay. The Edogawa River (3.4 km³ of annual fresh water discharge), the Arakawa River (2.4 km³), the Sumidagawa River (1.6 km³) and the Tamagawa River (1.2 km³) contribute about 90% of the fresh water that arrives in the bay (The Japan Scientists' Association, 1979). The approximate breakdown of the human population in these rivers' drainage basins is 3.8 million for the Edogawa River, 1.3 million for the Arakawa River, 5.6 million for the Sumidagawa River and 2.8 million for the Tamagawa River, respectively. Eighty-eight percent of domestic waste and industrial wastewater generated in the area is channeled to municipal sewage treatment plants (STPs) and subjected to primary and secondary treatment

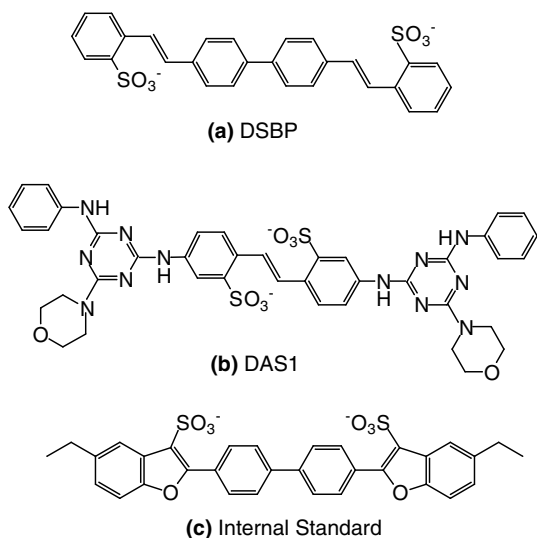


Fig. 1. Structures of FWAs investigated in this study. Full names: (a) DSBP, 4,4'-bis(2-sulfostyryl)biphenyl; (b) DAS1, 4,4'-bis[(4-anilino-6-morpholino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulfonate; (c) internal standard, 4,4'-bis(5-ethyl-3-sulfobenzofur-2-yl)biphenyl.

prior to their discharge into the rivers and Tokyo Bay. The remaining 12% of domestic waste is directly discharged into streams and rivers without treatment and is ultimately carried into the bay.

2.2. Sample collection

Two types of survey, a vertical distribution survey and a horizontal distribution survey, were conducted.

2.2.1. Vertical distribution survey

The sampling locations are shown in Fig. 2(a). Water samples were collected at F3, F6 and St. 06 from January 2003 to December 2003 from the RV *Seiyo Maru* (Tokyo University of Marine Science and Technology). Sample collection was conducted monthly except in March, April and May. Water samples were taken using an 8 L Teflon-coated Niskin Rosette sampler, previously rinsed with methanol (MeOH), equipped with a conductivity, temperature and depth profiler (CTD; Falmouth Scientific Inc., ICTD). Samples were collected at 5-m depth intervals through the water column at stations F3 (0, 5, 10, 15 and 20 m) and F6 (0, 5, 10, 15, 20 and 25 m). At St. 06, samples were collected from 8 depth layers (0, 5, 25, 50, 100, 150, 200 m and bottom water). Immediately after the collection, samples were transferred to 1-L amber glass bottles, and stored in a cooler with ice in the dark. The vertical profiles of basic physical and chemical parameters in the water

column for each location were also measured by CTD at 1-m intervals. The data from CTD was kindly supplied from Dr. Ishimaru and Dr. Horimoto at Tokyo University of Marine Science and Technology.

2.2.2. Spatial distribution survey

The sampling locations are shown in Fig. 2(b). Water samples were collected at 19 locations (except for Stn. 20) in December 2002 and 20 locations in May 2003, August 2003 and October 2003, respectively. To collect samples synoptically (i.e., at same time and under the same oceanographic conditions), all samples were collected within 4 h during each sampling trip, using three hired fishing boats. The neap tide or transition period from spring tide to neap tide was selected and, therefore, the tidal levels varied within 40 cm for individual sampling events. Water samples were taken from the surface and bottom layers using a Go-Flo sampler which had been rinsed with methanol (MeOH). To prevent contamination from ship and from bottom sediment, the depths of the surface layer and bottom layer were set at 10% and 90% of water depth for each sampling location, respectively. Immediately after collection, samples were transferred to 1-L amber glass bottles and stored in a cooler with ice in the dark. The vertical profiles of the basic physical and chemical parameters in the water column at each location were measured by the CTD data logger for conductivity, temperature and depth profile.

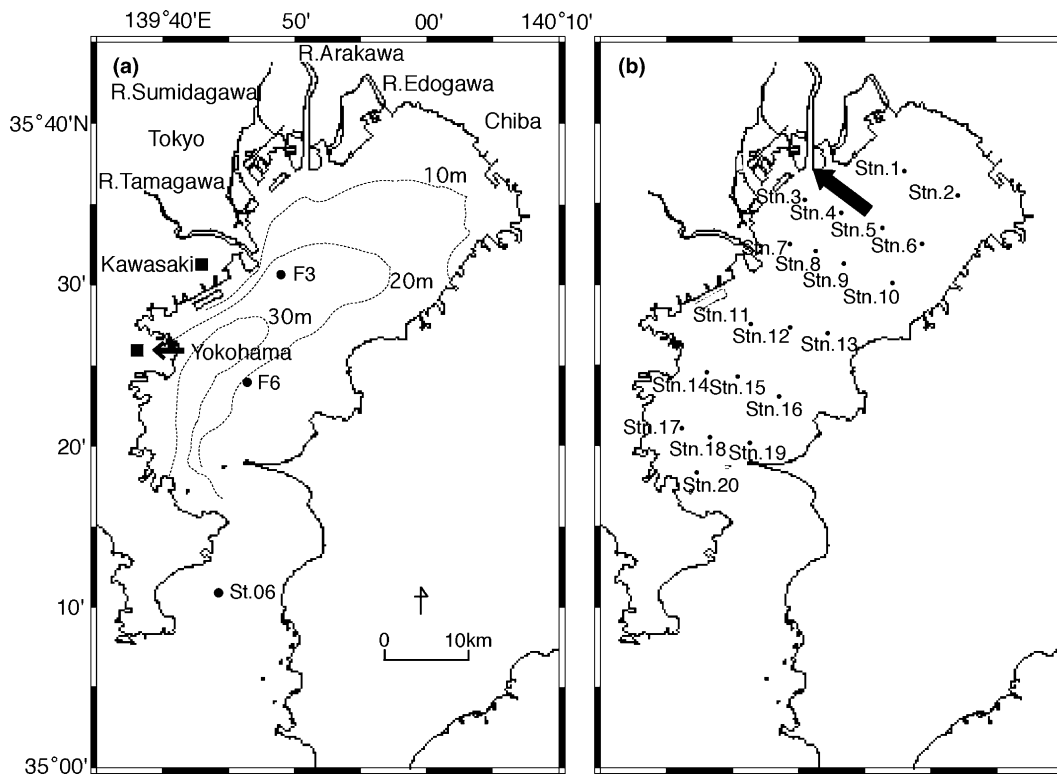


Fig. 2. Study area and sampling locations: (a) vertical distribution survey, (b) spatial distribution survey. An arrow in (b) indicates the position of river mouth.

3. Analytical methods

Soon after transporting the seawater samples to the laboratory, 0.5–1 L of each sample was filtered through a pre-baked glass fiber filter (47 mm \varnothing , GF/F, Whatman). Only dissolved FWAs contained in the filtrates were analyzed in this study. The filtrates were stored at 4 °C until analysis with no preservatives added. All samples were analyzed within 7 days of collection. Our preliminary experiments (Hayashi et al., 2002) confirmed that less than 10% of FWA had degraded after 1 week of storage. All analyses were performed in a dark room under yellow light illumination to minimize photodegradation.

FWAs in the aqueous samples were analyzed based on the method by Poiger et al. (1996). The details of the analytical procedure have been described previously (Hayashi et al., 2002). Briefly, the FWAs from 100 mL of filtrate were extracted, except for samples from St. 06 with 500 mL, using an octadecylsilica (ODS) cartridge (Sep-Pak tC18 plus), Waters; resin weight 900 mg. FWAs were eluted with 20 mL of MeOH. The eluent was roto-evaporated to dryness and re-dissolved in an appropriate volume (0.5–2 mL) of *N,N*-dimethylformamide/water/MeOH (1:1:2). The FWAs were analyzed on an HPLC (Hewlett–Packard G1310) equipped with a fluorescence detector (Hitachi F1000) with a postcolumn UV irradiator (Photochemical Reactor; Aur Industry). Separation was performed using a reverse-phase column (HP ODS Hypersil, 5 μ m, 4.6 mm i.d., 200 mm) operated at 25 °C with an eluent flow rate of 1 mL/min. A 25 min linear gradient from 30% acetonitrile/methanol (1:1) (eluent A)/70% 0.1 M ammonium acetate buffer at pH 6.5 (eluent B) to 70% A/30% B was used. The precision of the method, expressed as the relative standard deviation for DSBP and DAS1, was 3.8% and 1.8%, respectively. Recoveries of spiked DSBP and DAS1 were $92.0 \pm 2.8\%$ and $93.5 \pm 1.6\%$, respectively. To monitor the performance of the method during analysis, a recovery surrogate (Fig. 1(c); 4,4'-bis(5-ethyl-3-sulfobenzofuryl)biphenyl) was spiked into every sample before solid phase extraction. The recovery of the surrogate was greater than 90% for all the samples. No recovery correction was made. For each set of analyses, field blanks for seawater sampling consisting of distilled water were performed for every sampling and extraction procedure. Normally, 0.03 ng of DSBP and 0.01 ng of DAS1 were detected in 500 mL distilled water. The method detection limit was set to 10 times the field blank value and was 0.5 ng/L for DSBP and 0.3 ng/L for DAS1, respectively. These values were below the FWA concentrations detected in Tokyo Bay (0.5–314.1 ng/L for DSBP and 0.6–103.1 ng/L for DAS1).

4. Data processing

Composite color figures (Figs. 3–5, 7, 10–12) of the measured data were created using GMT (Generic Mapping Tool; Hawaii University), which is a software package that

can be used to manipulate columns of tabular data, time-series, and gridded data sets, then display these data in a variety of forms ranging from simple x – y plots to maps and color, perspective, and shaded-relief illustrations (Wessel and Smith, 1991). Figs. 7, 10 and 11 show FWA contour maps of Tokyo Bay, which are based on the x (longitude) and y (latitude) plots of sampling locations (Stn. 1–Stn. 20; Fig. 2(b)). Fig. 12 show salinity contour maps. The range of (x , y) coordinates in this map was from 139°35' E to 140°05' E and from 35°17' N to 35°40' N, respectively. The color patterns show FWA concentrations (Figs. 7 and 11), the DSBP/DAS1 ratio (Fig. 10) and salinity (Fig. 12), respectively. Figs. 3–5(a), (b) and (c) is a color image of salinity, temperature and density using 1-m water depth contour intervals. FWA concentrations (Figs. 3–5(d) and (e)) are produced using 5-m contour intervals at F3 and F6. For St. 06, the contour figure is produced based on FWA concentrations in the sampling depth of water (i.e., 0, 5, 25, 50, 100, 150, 200 m and bottom water). On the Figure for FWA concentrations (Figs. 3–5(d) and (e)), we have plotted outlines in white from March to May to mask out FWAs data, which were not collected during this period.

5. Results and discussion

5.1. Seawater structure in Tokyo Bay

Fig. 3 (station F3), Fig. 4 (station F6) and Fig. 5 (station 06) show profiles of water temperature (a), salinity (b) and density (c) from January to December 2003, respectively. The seasonal variation in the seawater structure in Tokyo Bay observed in the present study is explained as follows. In the winter (January and February), cooling causes surface water to sink due to its increased density, which results in a well-mixed and isothermal water column. From April or May, the surface water is gradually warmed by increasing solar radiation and a thermocline begins to develop in the summer (July and August). In late autumn (November), however, surface water cools and the vertical mixing of the water column again takes place.

Lower salinity was observed in the surface water than in deeper layers at all the investigated stations. This is caused by input of fresh water from the rivers to the surface water. Salinity in surface layers (0–5 m) showed seasonal variation, with higher salinity in winter and lower salinity in summer. The lowest salinity at the sea surface was observed in July and August at all the stations. This seasonality was especially marked at station F3, due to its close proximity to mouths of rivers delivering large volumes of fresh water. These seasonal variations in salinity were caused by rainfall in catchments with high precipitation in summer but which were dry in winter.

The density profiles derived from both the water temperature and salinity indicate that in winter (January and February), the seawater was extensively mixed and homogenized. Due to vertical mixing, a homogeneous chemical

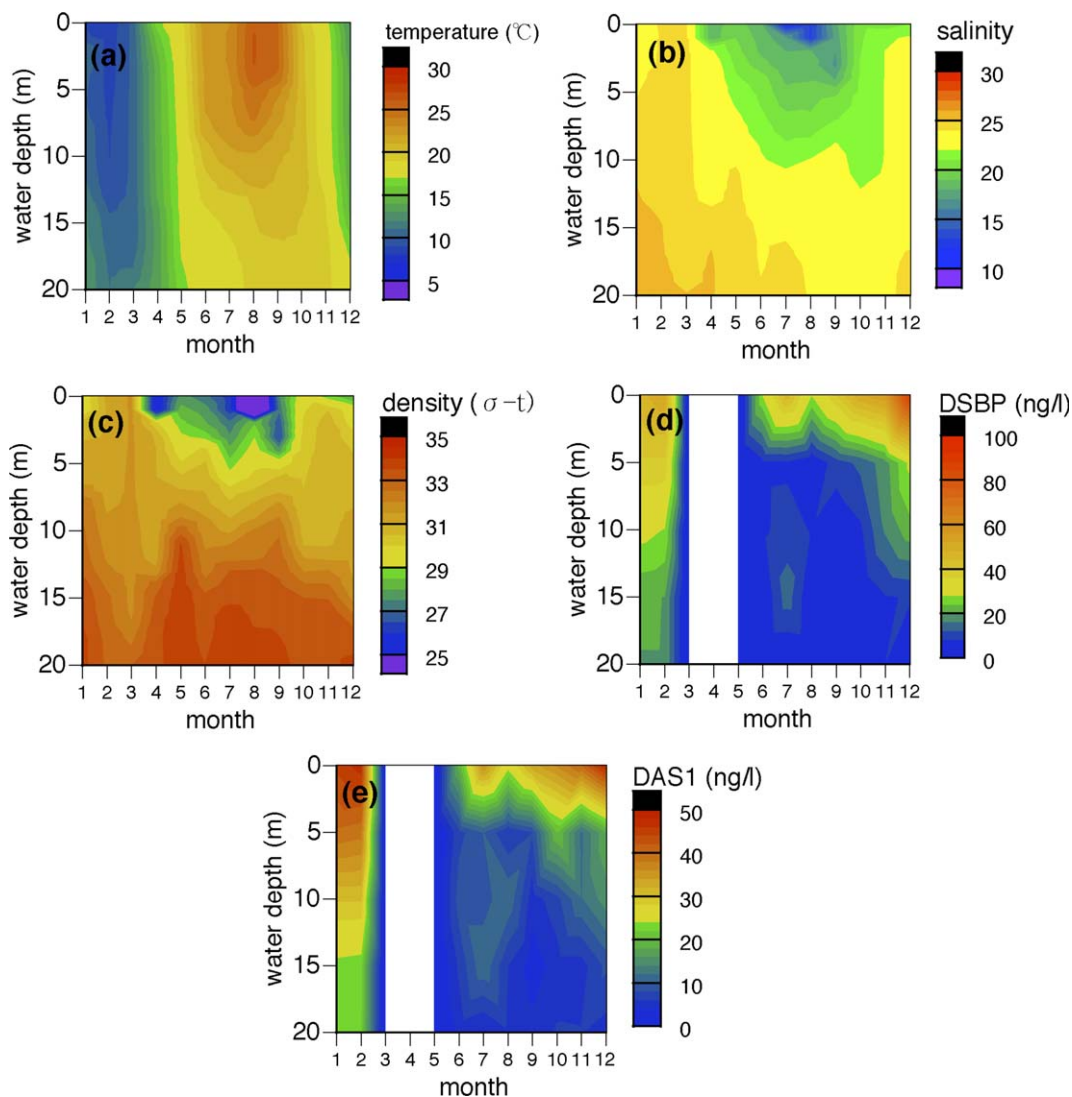


Fig. 3. Vertical profiles at F3: (a) temperature, (b) salinity, (c) density, (d) DSBP and (e) DAS1.

composition was expected throughout the water column in winter. In the summer (July and August), on the other hand, the seawater was stratified by warming and a greater input of fresh water. These seawater structures were consistent with those normally observed in Tokyo Bay (Kaizuka, 1993).

5.2. Vertical distribution of FWAs in water column

Figs. 3–5 also show the vertical profiles of DSBP (d) and DAS1 (e) concentrations at F3, F6 and St. 06, respectively, obtained through a vertical distribution survey. DSBP and DAS1 concentrations in the water column ranged from 2.4–86.7 ng/L and 2.9–47.8 ng/L at F3; 1.9–26.5 ng/L and 2.2–18.3 ng/L at F6; and 0.5–10.4 ng/L and 0.6–8.2 ng/L at St. 06. In summer, FWAs were predominantly found in the surface layers, but trace concentrations of FWAs were observed in the deeper layers below the thermoclines at F3 and F6. For example, at F3 in August, only 5% of DSBP was detected at a depth of 20 m compared with

the level in the surface water. This is consistent with the seawater structure, i.e., stratification of water mass in summer. FWAs supplied from the rivers and the outfalls were, due to stratification, prevented from being transported across the thermoclines. As a result, FWAs were present mainly in the surface layer and showed a steep concentration gradient in the summer. In winter, on the other hand, FWAs were mixed into deeper layers of the water column and FWA concentrations exhibited a weak vertical gradient in the water column. For example, DSBP concentration in bottom water (20 m depth) at F3 in January (19.8 ng/L) was approximately 40% of that in the surface water (46.8 ng/L). Similar deeper penetration of FWAs was observed in the other sampling trips in winter at F3 and F6. This is again explained by the seawater structure: the FWAs supplied from the rivers and sewage outfalls were more efficiently transported down into the deeper layers due to vertical mixing of seawater in the winter.

An interesting seasonal variation of FWA concentrations in surface layer was also observed: they were higher

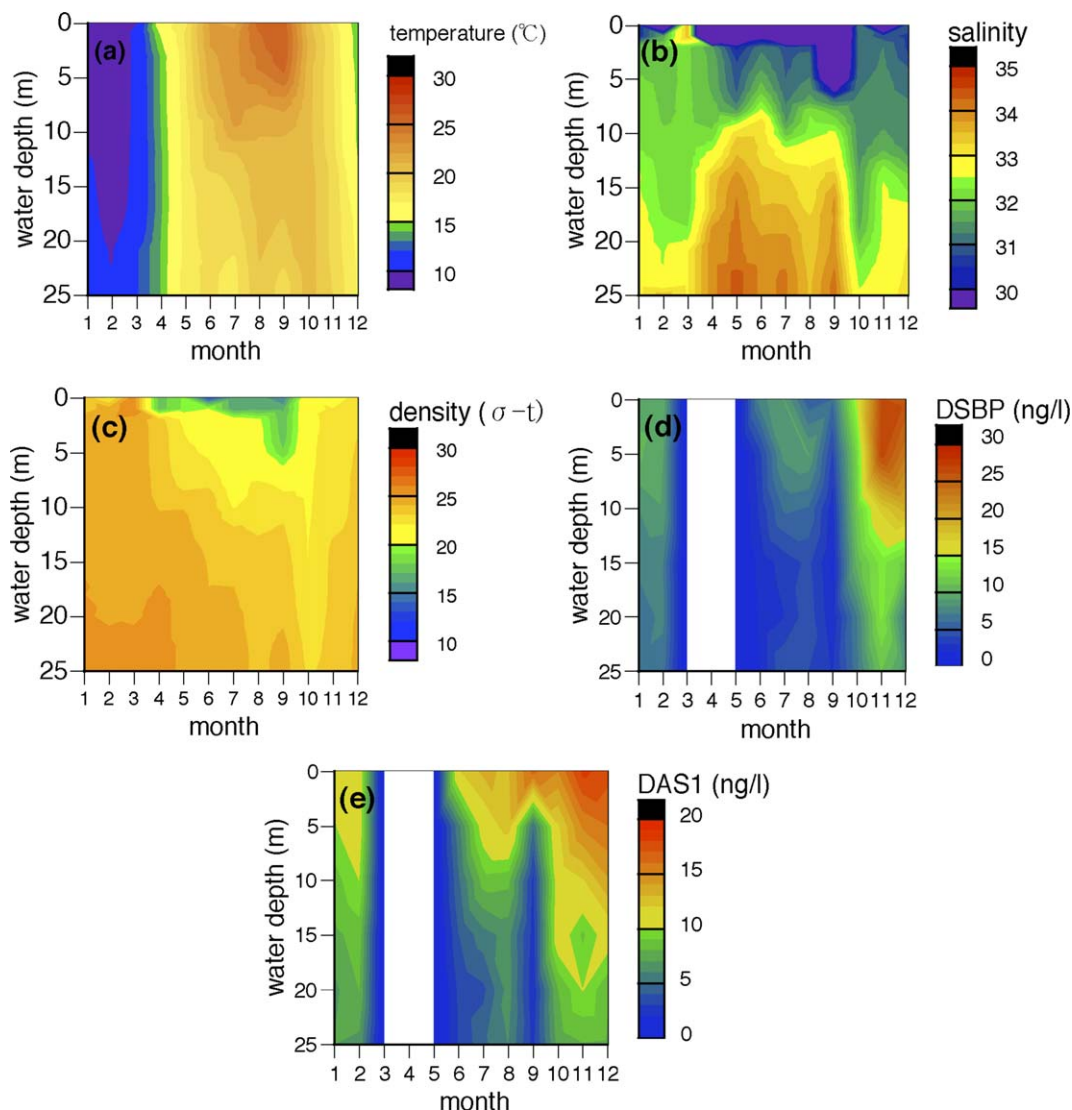


Fig. 4. Vertical profiles at F6: (a) temperature, (b) salinity, (c) density, (d) DSBP and (e) DAS1.

in winter and lower in summer. The seasonal variation (i.e., lower FWA concentrations in the surface water in summer) can be explained by more efficient photodegradation of FWAs in summer due to stronger solar radiation. This explanation is supported by a lower DSBP/DAS1 ratio in summer than in winter (Fig. 6). As demonstrated in our previous papers (Hayashi et al., 2002; Managaki and Takada, 2005), the DSBP/DAS1 ratio is an index for estimating the degree of photodegradation of the FWAs, and a lower DSBP/DAS1 ratio indicates more photodegradation, since DSBP is more susceptible to photodegradation. Similar seasonal variations in FWA concentrations have been reported for rivers and estuaries flowing into Tokyo Bay (Hayashi et al., 2002). This vertical distribution of FWAs was explained by photodegradation of FWAs in euphotic zones.

5.3. Spatial distributions of FWAs in Tokyo Bay

Spatial distributions of DSBP in surface seawater (10% of water depth) are illustrated in Fig. 7. The FWA concen-

trations of surface layers ranged from 6.8–314.1 ng/L for DSBP (Fig. 7) and 6.9–103.1 ng/L for DAS1 (figures not shown), respectively. Higher FWA concentrations were observed in the northwestern parts of the bay. This can be explained by a larger input of sewage in this area. Densely populated cities (Tokyo, Kawasaki and Yokohama; Fig. 2(a)) are situated along the northwestern coast. Several rivers (the Edogawa, Arakawa, Sumidagawa, Tamagawa, and Tsurumigawa Rivers) pass through these areas and carry sewage effluent along with them into the northwestern part of the bay, delivering large amounts of sewage to those locations. Also, several sewage treatment plants that directly discharge secondary effluent to the bay are situated on the northwestern coast. Along the coast, the maximum concentrations of both DSBP and DAS1 were observed in the northwestern head of the bay, closest to the mouths of the Sumidagawa River and the Arakawa River. These rivers account for approximately 40% of the freshwater inflow to the bay. Furthermore, higher FWA concentrations were observed in river water samples

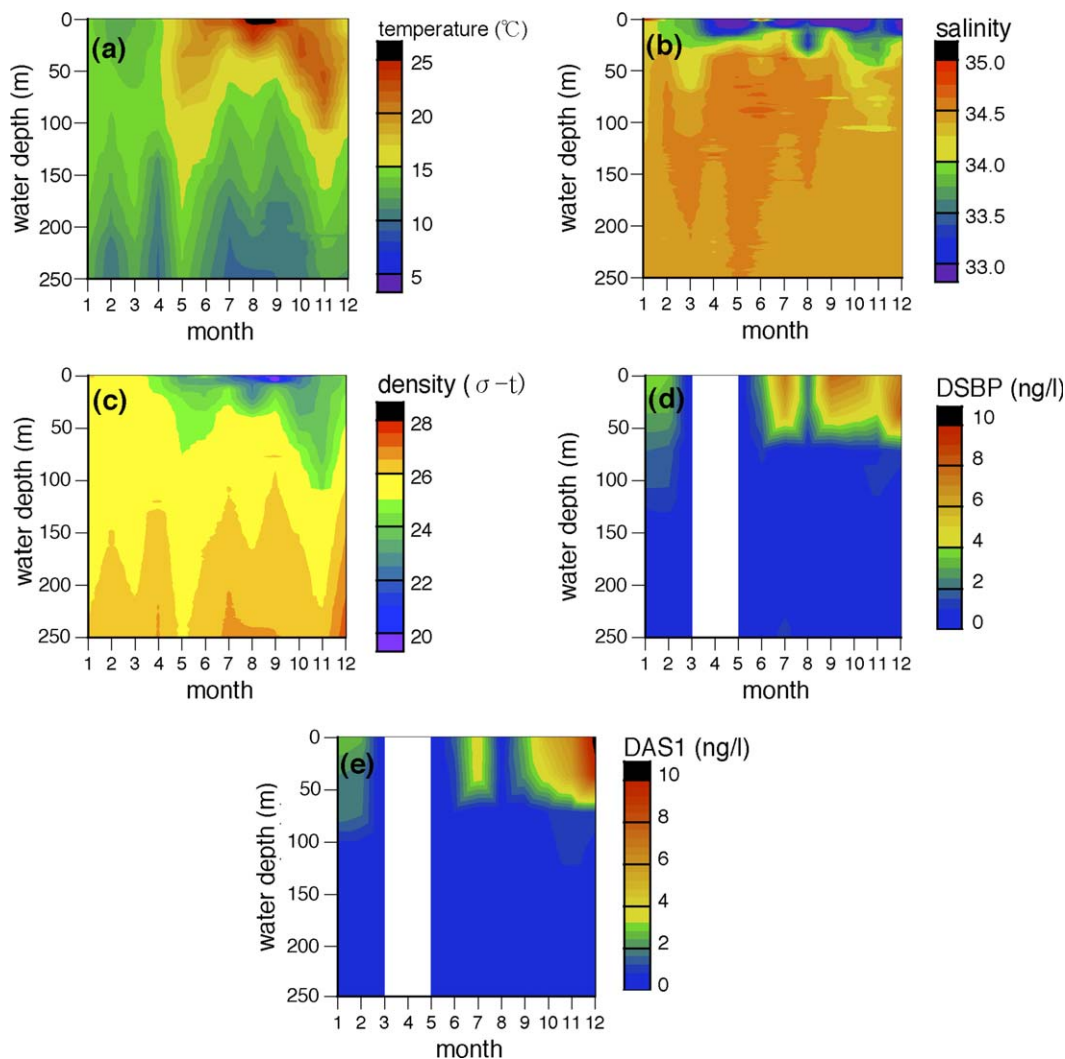


Fig. 5. Vertical profiles at St. 06: (a) temperature, (b) salinity, (c) density, (d) DSBP and (e) DAS1.

collected from the Sumidagawa River and the Arakawa River than in the other rivers flowing into the bay (Managaki and Takada, 2005). These larger inputs of FWAs from the rivers could explain the maximum FWA concentrations in the northwestern head of the bay.

The Spatial Distribution Survey demonstrated that FWAs were widely distributed in the bay. Surface water with DSBP concentrations of greater than 50 ng/L spread over half of the bay up to 10 km off the coast. Because DSBP concentrations in secondary effluents in Tokyo have been reported to be approximately 10,000 ng/L (Hayashi et al., 2002), the dilution factor of the sewage effluent in the surface water of Tokyo Bay within 10 km of the coast is calculated to be approximately 200 or less. This dilution factor could be useful in predicting the concentrations of any water-soluble contaminants contained in sewage effluents in Tokyo Bay. Diffuse sources of sewage other than these secondary effluents may interfere with this calculation. However, the majority (88%) of sewage generated in the catchment is subjected to secondary treatment and only 12% of sewage (gray water) is discharged into streams and

rivers without treatment. Also, overflow of untreated sewage from combined sewage systems during heavy rain (CSO) supplies significant amounts of untreated sewage directly to Tokyo Bay via several pumping stations and STP outfalls along the coast. Both these additional inputs of untreated sewage may affect the above calculation. However, DSBP concentrations in untreated sewage were approximately 20,000 ng/L, only double that in secondary effluents. Thus, these diffuse sources, rather than secondary effluents could not significantly affect the calculation of the dilution factor (i.e., 50% at most).

Clearly declining trends in FWA concentrations were observed from the northwestern coast of the bay toward the open ocean. DSBP concentrations in the northwestern parts ranged from ~100 ng/L to ~300 ng/L, whereas those in southeastern parts ranged from ~10 ng/L to ~50 ng/L. Half-distance values, where FWA concentrations decrease by half, were calculated by plotting FWA concentrations against distances from the northwestern coast for individual surveys. Fig. 8 illustrates the DSBP vs. distance diagram for the May survey, clearly indicating an offshore

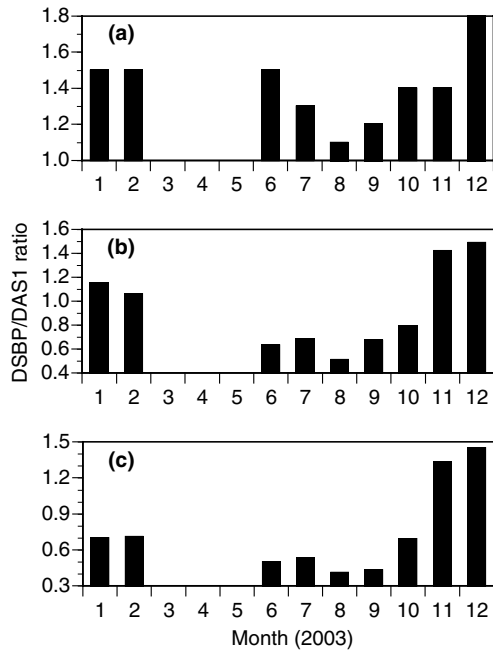


Fig. 6. DSBP/DAS1 ratio in surface layer (0 m) in vertical survey: (a) station F3, (b) station F6 and (c) station St. 06.

declining trend in DSBP concentration. Based on the regression line (Fig. 8), the half-distance value was calculated to be approximately 15 km. In other surveys, the FWA concentration vs. distance diagrams has shown a clear declining trend in FWA concentrations with distance from the coast, showing similar half-distance values of 10–20 km.

The offshore declining trend in FWA concentrations can be ascribed to dilution of sewage-containing water mass by seawater and photodegradation of FWAs. Fig. 9 shows the relationship between salinity and DSBP concentrations. As salinity increases, FWA concentrations decrease, indicating that dilution by seawater is one of the causes of the declining trend in FWA concentrations with distance offshore. However, significant negative curvatures were observed from a two end-member DSBP-salinity dilution line (theoretical dilution line), indicating active removal of FWAs from surface waters during offshore transport. FWAs are susceptible to photodegradation, whereas they are non-biodegradable and have less affinity to particles. FWAs removal from the surface water can therefore be ascribed to their photodegradation. To investigate the degree of photodegradation during transport, we examined the DSBP/DAS1 ratio. Fig. 10 shows the spatial distribution of the DSBP/DAS1 ratio in surface seawater. Higher DSBP/DAS1 ratios (~2 to ~4) were observed in the north-western part of the bay and the ratio showed the offshore declining trend to approach ~1 toward the southeastern part of the bay. These ratios indicate that the water mass in the northwestern part is freshly supplied from river and/or sewage outfalls and that photodegradation proceeded during offshore transport.

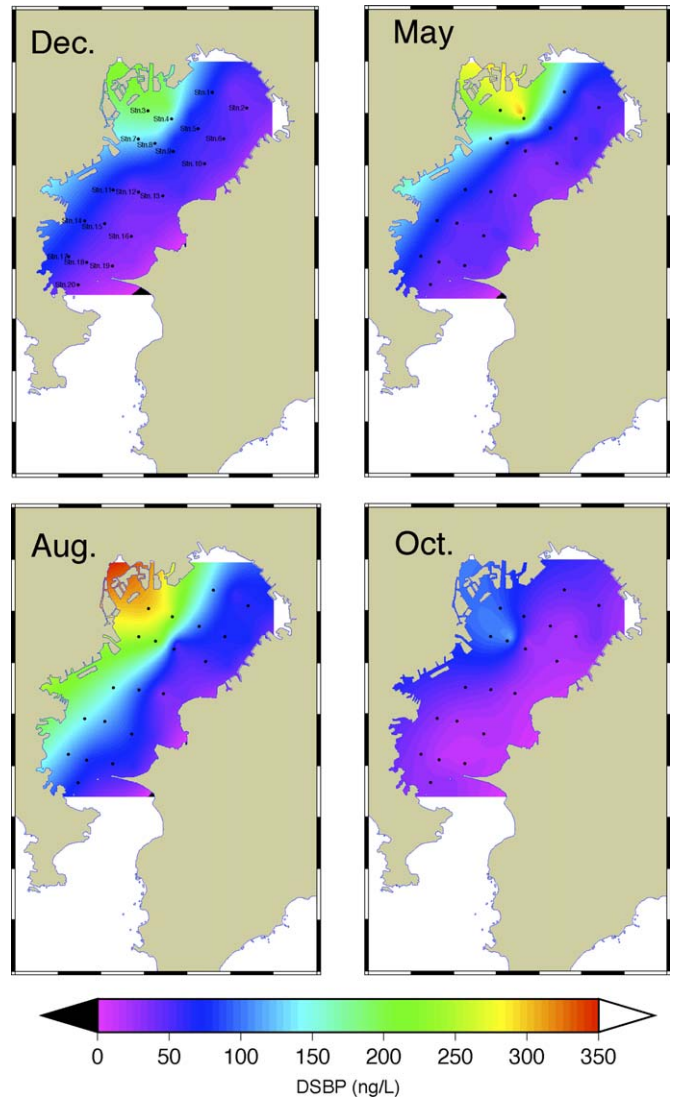


Fig. 7. Spatial distributions of DSBP in surface water.

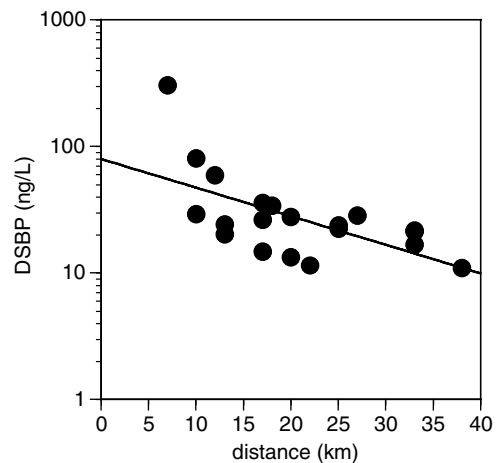


Fig. 8. DSBP concentration in surface water vs. distance from the river mouth on May 2003. The location of the river mouth is indicated in Fig. 2(b) with an arrow.

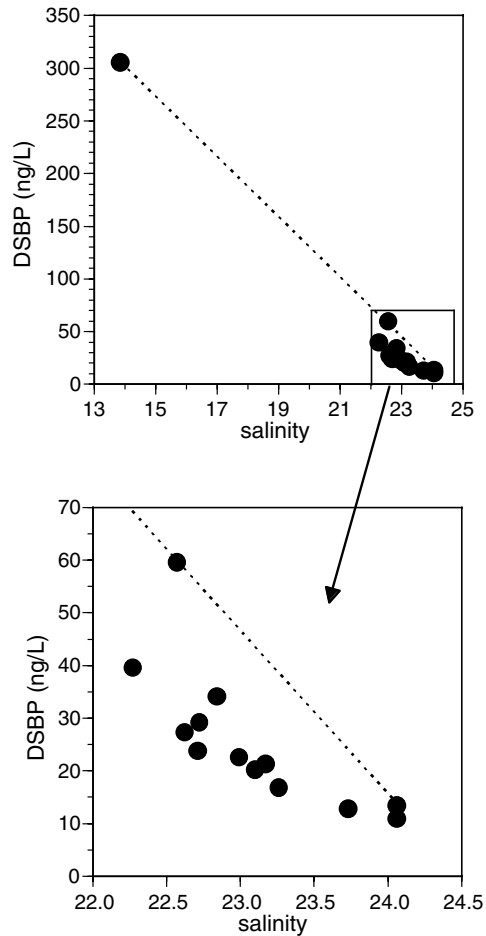


Fig. 9. DSBP vs. salinity in surface water from Tokyo Bay in May 2003. Dotted line indicates the theoretical mixing line.

Of the four sampling trips, the August sampling trip measured the highest concentrations of FWAs in the surface water (DSBP: 94.2 ± 71.6 ng/L, DAS1: 33.8 ± 13.9 ng/L). Also, higher DSBP/DAS1 ratios (4–5 in the northwestern head) were observed during the August sampling trip. These results indicate a greater input of river water and/or sewage effluents during this period. It was noted that in the 2 days preceding the sampling trip, heavy precipitation in the form of rain was observed in the catchment, which must have induced an overflow of untreated sewage from the combined sewer system in the catchment and supplied large volumes of untreated sewage to the coastal zone through outfalls. This combined sewer overflow (CSO) explains the higher FWA concentrations and higher DSBP/DAS1 ratios observed during the August sampling trip. Results from this August sampling trip appeared to be inconsistent with the results from the vertical distribution survey, which showed lower FWA concentrations and lower DSBP/DAS1 ratios during the summer due to stronger solar radiation, but the most likely explanation of this discontinuity in FWA concentrations and compositions was due to lack of rain for several days preceding the monthly observations (the vertical distribution survey).

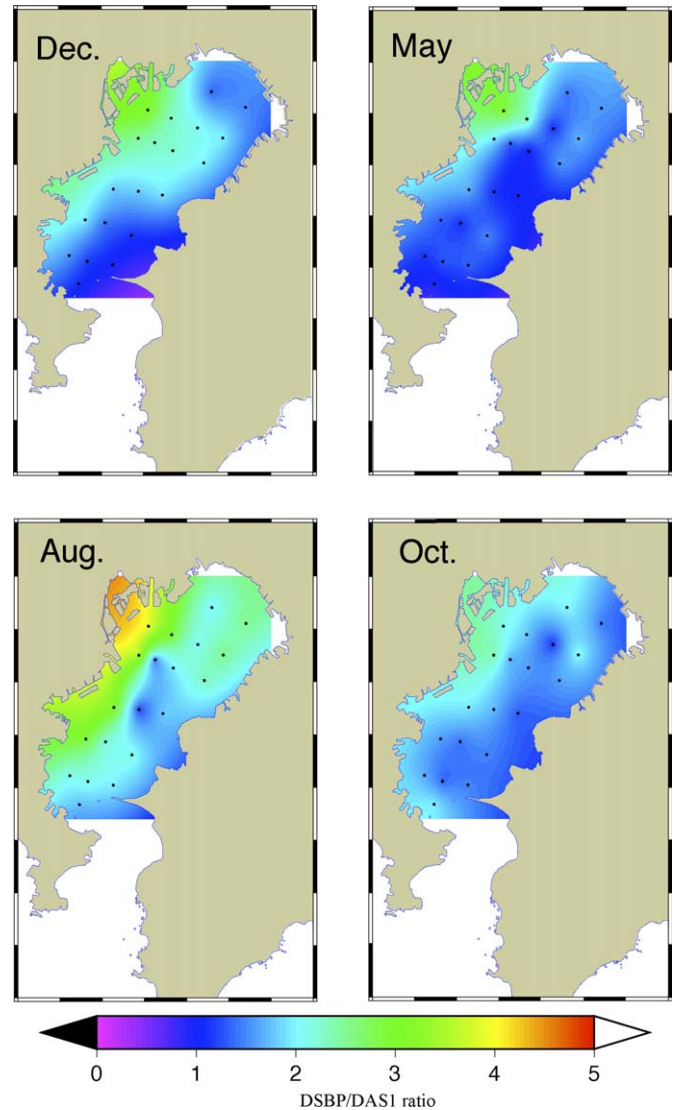


Fig. 10. Spatial distributions of DSBP/DAS1 ratio in surface water.

Further observations of FWAs in summer are needed to confirm whether the discrepancy between two observations (i.e., the vertical distribution survey vs. the horizontal distribution survey) was due to the effect of heavy rain.

Fig. 11 shows the spatial distribution of DSBP in bottom water (90% of water depth) in Tokyo Bay. The range of concentrations of DSBP and DAS1 detected in the bottom water were 1.0–23.2 ng/L and 1.9–14.7 ng/L, respectively. The FWA concentrations in bottom water were several times lower than those in the surface water, although analysis revealed FWAs in the bottom waters to be present at significant concentrations. FWA concentrations in the bottom waters showed the maximum in northeastern or southeastern parts of the bay with a declining trend toward the open ocean. These concentration profiles with maximum in the eastern parts were markedly different from those of surface water, which showed the maximum in the northwestern parts. Concentrations of FWA in seawater are dictated by various processes such as physical

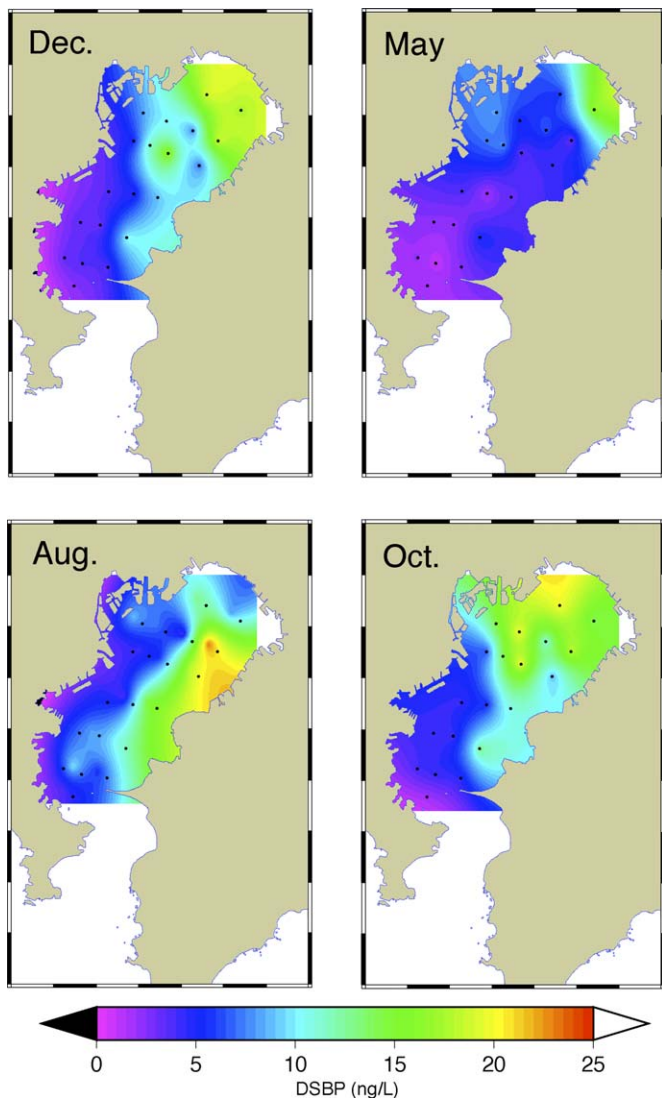


Fig. 11. Spatial distributions of DSBP in bottom water.

oceanographic processes (e.g., horizontal and vertical mixing, diffusion, advection by tidal currents and so on), physico-chemical processes of the compounds themselves (e.g., sorption, desorption, photochemical degradation) and biological processes (e.g., microbial degradation, uptake by organisms). This interesting difference in the horizontal distribution of FWAs between surface and bottom waters contributes to understanding of the impact of sewage on the benthic ecosystem. The above differences suggest that sewage-derived contaminants may affect pelagic species and benthic species differently. So far, however, we have not been successful in developing a full explanation of the distribution of FWAs in bottom waters. The following are possible explanations of the distributions of FWAs in bottom waters.

Spatial distributions of FWA in bottom water were similar to those of salinity in bottom water, as illustrated in Fig. 12. This similarity suggests that the mechanism causing the maximum concentrations of bottom FWA concen-

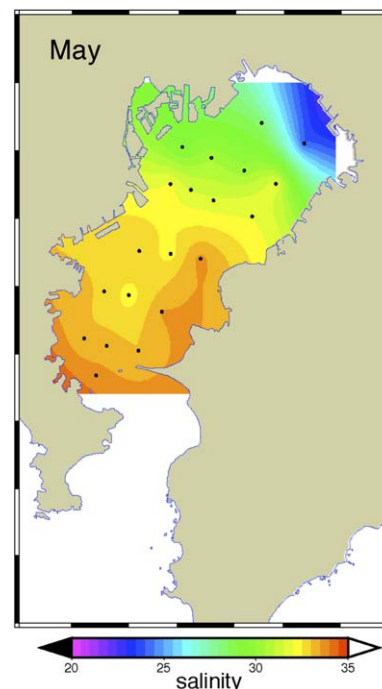


Fig. 12. Spatial distributions of salinity in bottom water in May 2003.

trations in the eastern parts is closely related to the horizontal and vertical mixing of freshwater mass with open ocean water. The northeastern part of Tokyo Bay is relatively shallower than the other parts of the bay (Fig. 2(a)). For example, water depth at Stn. 2, where a relatively high DSBP concentration of 18 ng/L was observed in the December survey, was 12 m; whereas Stn. 17, where a relatively low DSBP concentration of 3 ng/L was observed, had 37 m of water depth (Fig. 2(a)). Due to the shallower water, surface waters with lower salinity and higher FWA concentrations were more mixed vertically with bottom water in the northeastern parts of the bay. Consequently, higher FWA concentrations were observed in the bottom water in the northeastern parts. Bottom currents may also affect the distributions of FWA in bottom water. Numerical models demonstrate that a clockwise circulation of bottom water occurs in winter (Guo and Yanagi, 1996). In this model, open ocean water supplied from the mouth of Tokyo Bay travels northward along the western coast, turns right at the center of the bay, the travels southward along the bay's west coast. In this situation, bottom water in southwestern part is more mixed with seawater from the open ocean. As a result, lower FWA concentrations were observed in southwestern parts. In August, the distribution of FWAs in bottom water was somewhat different to that recorded in the other three sampling trips: maximum FWA concentrations were shifted further to the south than in the other sampling trips. The FWA distributions in bottom water in August might be affected by wind-induced mixing of water. A strong south wind was blowing from 2 weeks to 1 week before the August sampling trip, which might have induced

Ekman transport, which transports surface water south-eastward (Yanagi, 1989). That is, water mass with high FWA concentrations may have been transported to the southeastern part of the bay. The south wind may also have caused penetration of surface water into the bottom in the southeastern parts of the bay and FWAs might have been transported to bottom water there. One week before the sampling trip, the wind direction changed from south to east and Ekman transport stopped. As a result, bottom water mass with high FWA concentrations remained in the southeastern part of the bay. Furthermore, the heavy rain that occurred before the sampling trip may have influenced the distribution of FWAs measured during the August sampling trip.

Physico-chemical and biological processes may also have affected the distribution of FWAs in bottom waters. The contribution of photodegradation of FWAs in bottom water was negligible because the water depth in observed locations was from 10 m to 50 m and little sunlight reached the bottom environment. Also, biodegradation was likely to be insignificant, since no indication of microbial degradation has been reported in laboratory and field observations (Poiger et al., 1996; Hayashi et al., 2002). Desorption of FWAs from particles is likely to affect the distribution of FWAs in bottom water, in consideration of the fact that FWAs were detected in suspended solids (0.1–0.5 µg/g) and bottom sediments (0.01–1.85 µg/g; Managaki and Takada, 2005) in Tokyo Bay, and that their partition coefficients are relatively low. $\log K_d$ of DSBP was reported to be 3.8 ± 0.3 , and 95% of DSBP was present in the dissolved phase in Tokyo Bay water. Thus, desorption of FWAs from bottom sediments in the northeastern part of the bay may contribute to the relatively high DSBP concentrations recorded in bottom water in the region. Based on DSBP concentrations in the bottom sediments (1.74 µg/g) and $\log K_d$ value (3.8 ± 0.3), the equilibrium DSBP concentration is calculated to be 270 ng/L, which is one order of magnitude higher than the dissolved DSBP concentrations in the bottom water. In our previous paper (Managaki and Takada, 2005), higher FWA concentrations were observed in the sediment in northeastern parts of Tokyo Bay. Thus, desorption of FWAs from bottom sediments could account for the higher FWA concentrations in the bottom layer in this region. The partitioning of FWAs would depend on several factors (e.g., pH, ion strength and the content of organic carbon) in the natural environment. Also, FWAs in bottom sediments may form irreversible associations with the sediment matrix which may then inhibit desorption. Desorption experiments using Tokyo Bay sediment need to be conducted as future studies.

6. Conclusion

The intensive monitoring of FWAs in Tokyo Bay water demonstrated the three-dimensional distribution of FWAs as follows:

- (1) *Vertical profiles*: FWAs were localized in surface layers in summer due to stratification, whereas they penetrated into the bottom layers in winter as a result of vertical mixing.
- (2) *Horizontal distribution*: FWAs were widely distributed in the surface layers, although an offshore declining trend in FWA concentrations with a half-distance of approximately 15 km was observed. The patterns of distribution of FWAs in bottom layers were different to those of the surface layers.

These vertical and horizontal distributions of FWAs and their seasonal variations were explained by physical oceanographic processes (stratification, vertical mixing, dilution of freshwater by seawater, horizontal circulation) and photodegradation of FWAs and their seasonality. Our research group is currently constructing a numerical model of FWA behavior using these parameters to explain the three-dimensional distribution of FWAs and their seasonal variation (Kim et al., in preparation). Through revealing the three-dimensional distributions of FWAs in Tokyo Bay it was demonstrated that FWAs are a potentially useful tool for close tracking of sewage-derived water-soluble contaminants in marine environments.

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