

# Plastic Resin Pellets as a Transport Medium for Toxic Chemicals in the Marine Environment

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Plastic resin pellets (small granules 0.1–0.5 centimeters in diameter) are widely distributed in the ocean all over the world. They are an industrial raw material for the plastic industry and are unintentionally released to the environment both during manufacturing and transport. They are sometimes ingested by seabirds and other marine organisms, and their adverse effects on organisms are a concern. In the present study, PCBs, DDE, and nonylphenols (NP) were detected in polypropylene (PP) resin pellets collected from four Japanese coasts. Concentrations of PCBs (4–117 ng/g), DDE (0.16–3.1 ng/g), and NP (0.13–16 µg/g) varied among the sampling sites. These concentrations were comparable to those for suspended particles and bottom sediments collected from the same area as the pellets. Field adsorption experiments using PP virgin pellets demonstrated significant and steady increase in PCBs and DDE concentrations throughout the six-day experiment, indicating that the source of PCBs and DDE is ambient seawater and that adsorption to pellet surfaces is the mechanism of enrichment. The major source of NP in the marine PP resin pellets was thought to be plastic additives and/or their degradation products. Comparison of PCBs and DDE concentrations in marine PP resin pellets with those in seawater suggests their high degree of accumulation (apparent adsorption coefficient:  $10^5$ – $10^6$ ). The high accumulation potential suggests that plastic resin pellets serve as both a transport medium and a potential source of toxic chemicals in the marine environment.

## Introduction

Plastic resin pellets are small granules generally with the shape of a cylinder or a disk with a diameter of a few millimeters. These plastic particles are industrial raw material transported to manufacturing sites where “user plastics” are made by remelting and molding into the final products. Resin pellets can be unintentionally released to the environment,

both during manufacturing and transport. The released resin pellets are carried by surface runoff, stream, and river waters eventually to the ocean. Resin pellets can also be directly introduced to the ocean through accidental spills during shipping. Because of their environmental persistence, they are distributed widely in the ocean and found on beaches and on water surfaces all over the world (1–6). A growing production of plastic leads to a measurable increase in plastic pollution in the ocean. A significant increase in concentrations of plastic particles, including resin pellets, in the sea-surface has been observed in the North Pacific from the 1970s to the late 1980s (4, 7).

Some studies in 1970s reported that marine plastic resin pellets contain polychlorinated biphenyls (PCBs) (2, 8). They were either adsorbed from ambient seawater or came from plasticizers used until the 1970s in most countries, although neither hypothesis has been proven conclusively. Many species of marine organisms (e.g., seabirds) accumulate large numbers of plastic particles in their stomachs (8–16). It is thought that they ingest plastic particles not only accidentally but also selectively by mistaking them for food (12, 14). An increase in the frequency and quantity of plastic ingested by seabirds has been reported, which reflects the increase in plastic pollution in the ocean (15). In this context, there is concern about the possible transfer of PCBs and other pollutants from ingested plastics to organisms and subsequent adverse effects (8–10, 17). A positive correlation between the mass of ingested plastics and PCB concentrations in fat tissue of Great Shearwaters *Puffinus gravis* has been documented (18). Plastic resin pellets may serve as a carrier of toxic chemicals in the marine environment.

Limited information about the nature and sources of chemicals contained in the marine plastic pellets has been reported. There are two plausible mechanisms by which chemicals are incorporated in the marine plastic pellets. One is adsorption of hydrophobic chemicals (e.g., PCBs) onto plastic resin pellet surfaces from seawater because of the low polarity (i.e., hydrophobic nature) of the plastic surfaces (19). Plastic resin pellets may act like hydrophobic adsorbents in the sea. Another plausible mechanism may be plastic additives and related chemicals contained with resins. Various synthetic chemicals are contained in plastic resin pellets as additives, and some are potentially harmful to wildlife. PCBs are one class of chemicals that had been identified in marine plastic pellets (2, 8), and their source(s) have not yet been confirmed by experimental data. The lack of the information is partly due to the fact that their basic composition is highly variable, and analytical procedures are under development. Marine plastic pellets consist of various types of polymers (e.g., polypropylene, polyethylene, polystyrene) having different surface structures and, therefore, different affinities to pollutants. Each polymer type contains different additives.

The present study has focused on polypropylene (PP) pellets, one common type of pellet found in the ocean (2, 6), using near-infrared spectroscopy for selecting the polymer. First, we have examined the conditions for extraction of PCBs, DDE, and nonylphenol (NP) through repeated Soxhlet extraction using different organic solvents. These contaminants have been selected as target compounds because PCBs and DDE are hydrophobic and widely distributed in the ocean, whereas nonylphenol and/or its derivatives are used as additives for plastics (20). PCBs and DDE are well-known toxic chemicals. Toxicity of NP is currently a concern, because their endocrine disrupting activities have been recently revealed (21–24). We have determined the concentrations and distribution patterns of these toxic chemicals in PP resin

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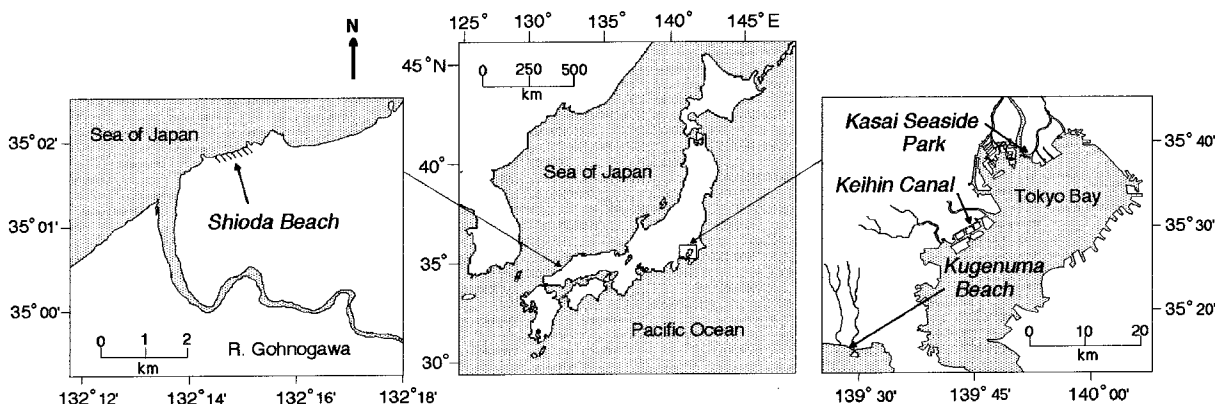


FIGURE 1. Sampling locations.

pellets collected from four locations along the Japanese coast. Finally, the sources and chemical forms of the pollutants in the PP plastic pellets have been studied in a field adsorption experiment and the repeated extraction.

## Materials and Methods

**Collection of Resin Pellets.** Resin pellets were collected from four coastal sites in Japan (Figure 1); Kasai Seaside Park and Keihin Canal in Tokyo Bay, Kugenuma Beach facing the Pacific Ocean, and Shioda Beach facing the Sea of Japan in 1997 and 1998. At Kasai Seaside Park, Kugenuma Beach, and Shioda Beach, resin pellets were collected on the beaches just above the high tide line. The resin pellets were picked up one by one from the sand surface using solvent-rinsed stainless tweezers or by hand using polyethylene gloves, prior testing confirmed that no residues of PCBs, DDE, and NP were leached from the gloves. At Shioda Beach the resin pellets were sampled using bare hands. Differentiation of the plastic resin pellets from sands and other materials were made by eye in the field and confirmed by infrared spectroscopy in the laboratory. At Keihin Canal the pellets floating on the water surface were collected using a solvent-rinsed stainless steel net. The samples were stored in pre-baked glass bottles at  $-30^{\circ}\text{C}$  until analysis.

Before chemical analysis, collected samples were classified according to their polymer types (e.g. polypropylene, polyethylene, polystyrene) using near-infrared spectroscopy for plastics (PlaScan-SH, OPT Research Inc. Tokyo, Japan), and PP resin pellets were retained for chemical analysis. During the classification, the resin pellets were handled using solvent-rinsed stainless steel tweezers.

**Chemical Analysis.** All solvents were distilled in glass. All glassware was rinsed with methanol, dichloromethane (DCM), and distilled hexane several times and/or baked at  $380\text{--}400^{\circ}\text{C}$  to remove organic contamination.

PP resin pellets taken from sea-surface were dried for 3 days in a clean room before extraction. One gram (dry weight) of PP resin pellets was extracted by Soxhlet extraction with hexane for more than 8 h at 5–10 cycles/h. Fine plastic particles in the extract were removed by passage through quartz wool. PCBs, DDE, and NP in the extracts were purified and fractionated by methods described elsewhere (25, 26). Briefly, the organic extracts were fractionated using 5%  $\text{H}_2\text{O}$  deactivated silica gel column chromatography. PCBs+DDE and NP were eluted with hexane/DCM (75:25) and hexane/DCM (35:65), respectively. Hexane/DCM (75:25) eluent was further fractionated using fully activated silica gel column chromatography to obtain a PCBs+DDE fraction. PCBs+DDE and NP were determined by capillary gas chromatograph equipped with electron capture detector and mass detector, respectively (26, 27). The PCBs concentration was calculated from the sum of 23 major congeners ( $\Sigma\text{PCB}$ ; IUPAC no. 8/5,

28, 52, 44, 66/95, 90/101, 110/77, 118, 132/153, 105, 138/160, 187, 128, 180, 170/190, 206) based on 16 chromatographic peaks. NP concentration is expressed as the sum of 11 chromatographic peaks ( $\Sigma\text{NP}$ ).

Reproducibility and recovery for the analytical procedure were examined using plastic resin pellet extracts collected from Kugenuma Beach. Reproducibility was determined by four replicate analyses of the aliquots. Coefficient of variation of NP, PCBs, and DDE concentrations were 3.8%, 4.9%, and 6.8%, respectively. Recovery was determined by analyzing another set of four aliquot extracts to which the chemical standards were spiked. The recoveries of NP, PCBs, and DDE were 86.1%, 105%, and 90.8%, respectively.

**Repeated Solvent Extraction.** To optimize the extraction condition and to study the interaction of pollutants with PP pellet surface and/or matrix, repeated extraction was conducted using hexane and methanol, respectively. PP resin pellets collected from the harbor of Tokyo University of Fisheries in the Tokyo Bay were used for the experiment. One gram of pellets was Soxhlet extracted twice (8 h each) with *n*-hexane, while another 1 g sample was extracted three times (8 h each) with methanol. The Soxhlet turnover rate was set at 5–10 cycles/h for hexane extraction and 3–4 cycles/h for methanol extraction. The extracts from all these tests were analyzed and compared.

**Field Adsorption Experiment.** A field adsorption experiment, where virgin plastic pellets were deployed on the sea surface, was conducted to examine whether plastic pellets can adsorb hydrophobic pollutants from seawater. The experiment was carried out in Keihin Canal (Figure 1), which is located in the Keihin industrial complex in Tokyo Bay, on December 16–22, 1998. During this period, there were no rainy or windy days, and the sea was calm. The water temperature and salinity during the experiment were  $\sim 12^{\circ}\text{C}$  and  $\sim 28\text{‰}$ .

Virgin PP resin pellets (products number: J104W) were obtained from Grand Polymer Co. Ltd. Japan. Our prior analysis showed no significant PCBs ( $<0.01\text{ ng/g}$ ), DDE ( $<0.002\text{ ng/g}$ ), and NP ( $<6\text{ ng/g}$ ) in the virgin pellets. Approximately 12 g of the pellets was placed in stainless steel mesh baskets (30 cm diameter and 13 cm height; Figure 2), and the baskets were left drifting on the sea surface. Under these conditions, the pellets were in a single layer and could float freely in the basket in full contact with surface seawater. Eight baskets were placed out at the beginning of the experiment, and one basket was recovered for analysis each day. To determine intervariation, three baskets were recovered on the last day (day 6) and analyzed. The recovered pellets were stored in glass bottles at  $-30^{\circ}\text{C}$  in the laboratory. Just before analysis, the pellets were air-dried in the clean room for 3 days. Eight grams of the dried pellets was analyzed as described above. Nondeployed virgin pellets were also

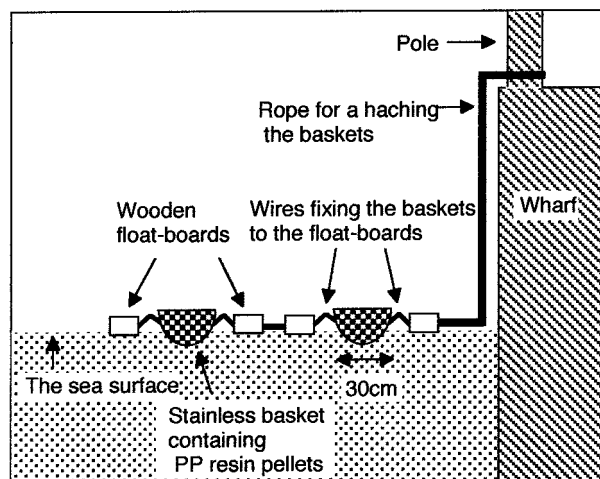


FIGURE 2. Schematic illustration of adsorption experiment.

analyzed along with the sample pellets and considered as day 0 sample.

To evaluate the contribution of adsorption of atmospheric chemicals to the pellets, the virgin PP resin pellets were exposed to ambient air during the same period (i.e., 6 days) as their deployment on the sea. The pellets were put in an open stainless container and placed on the roof of a building ca. 2 m above the ground near the place of the seawater deployment. Before analysis, dust on the pellets was washed out with a small amount of water, and the pellets were air-dried and analyzed in the same way as the pellets exposed to the seawater.

When the experiment started, 20 L of seawater were collected at the deployment site with a stainless steel bucket. The seawater was filtered with prebaked glass fiber filter (293 mm Ø; Whatman GF/F) using a Teflon diaphragm pump and stainless steel filter holder. The filters containing particulate matter were freeze-dried and extracted with Soxhlet apparatus with DCM for 8 h at 3–4 cycles/h. Eight liters of the filtrates were liquid–liquid extracted with DCM 3 times using a 10-L volume glass separatory funnel. Both extracts were analyzed for PCBs, DDE, and NP by the same method as the extracts from pellets previously mentioned.

## Result and Discussion

**Analytical Method for Resin Pellets.** The results of repeated extraction indicate that hexane is an appropriate solvent for the Soxhlet extraction of polypropylene resin pellets. No significant amount (<1%) of the target compounds (i.e. PCBs, DDE, and NPs) was detected in the second hexane extracts compared with the first extraction (Table 1). On the other hand, substantial amounts (12–80%) of the target compounds were detected in second methanol extracts (Table 1). Even in the third methanol extraction, 7–43% of the analytes were found, indicating that methanol is insufficient as extraction solvent. The difference in extraction efficiency between hexane and methanol is related to the form in which the compounds are present on/in the plastic resin pellets and will be discussed below.

Because the solvent extracts of plastics contain numerous kinds of organic chemicals, extensive cleanup is necessary prior to GC determinations. Our two-step-column chromatography procedure provided sufficient purification, and no interference was found on chromatograms of PCBs/DDE and NP fractions.

### Pollutants Contents of Resin Pellets in the Environment.

All the examined marine PP resin pellets contained significant amounts of PCBs, DDE, and NP. The PCBs content (sum of 23 congeners) ranged from 3.97 ng/g to 117 ng/g (Table 2).

TABLE 1. Extraction Efficiency<sup>a</sup> of the Pollutants from Marine PP Pellets<sup>b</sup> by Repeated Soxhlet Extraction

| extraction<br>period (h) |   | %                 |      |     |
|--------------------------|---|-------------------|------|-----|
|                          |   | ΣPCB <sup>c</sup> | DDE  | NP  |
| Hexane                   |   |                   |      |     |
| first                    | 8 | 100               | 100  | 100 |
| second                   | 8 | 0.03              | 0.01 | 1   |
| MeOH                     |   |                   |      |     |
| first                    | 8 | 100               | 100  | 100 |
| second                   | 8 | 16                | 12   | 80  |
| third                    | 8 | 13                | 7    | 43  |

<sup>a</sup> Percentage of extracted amount relative to the first extraction. <sup>b</sup> PP pellets were collected from the harbor of Tokyo University of Fisheries on February 28, 2000. One gram of PP pellets was subjected to the repeated Soxhlet extraction. <sup>c</sup> Sum of 16 chromatographic peaks consisting of 23 congeners selected according to NOAA's NS&T Program: IUPAC no. 8/5, 28, 52, 44, 66/95, 90/101, 110/77, 118, 132/153, 105, 138/160, 187, 128, 180, 170/190, 206.

TABLE 2. PCBs, DDE, and Nonylphenol Contents in Marine Polypropylene Resin Pellets

|                    | ΣPCB <sup>a</sup><br>(ng/g) | DDE<br>(ng/g) | nonylphenol<br>(μg/g) |
|--------------------|-----------------------------|---------------|-----------------------|
| Kasai Seaside Park | 97.3                        | 2.0           | 16                    |
| Keihin Canal       | 117                         | 3.1           | 8.9                   |
| Kugenuma Beach     | 43.5                        | 1.6           | 12                    |
| Shioda Beach       | 3.97                        | 0.16          | 0.13                  |

<sup>a</sup> PCBs contents: sum of 16 chromatographic peaks consisting of 23 congeners selected according to NOAA's NS&T Program: IUPAC no. 8/5, 28, 52, 44, 66/95, 90/101, 110/77, 118, 132/153, 105, 138/160, 187, 128, 180, 170/190, 206.

There have been only a few reports on PCBs content in marine plastic pellets. PCBs have been detected in polystyrene pellets from northeastern Long Island Sound (8) and polyethylene pellets from Auckland foreshore (2). The presence of DDE and NP in marine plastic pellets has not yet been reported. PCBs and DDE concentrations in the PP resin pellets collected around Tokyo are in the same range as environmental concentrations found in Tokyo Bay sediments (hundreds ng/g for PCBs and several ng/g for DDE (28)). NP contents in the PP resin pellets were 2 orders of magnitude higher than those found in Tokyo Bay sediment (0.1–0.6 μg/g (26)).

**Sources of the Pollutants in Plastic Resin Pellets.** The field adsorption experiment results demonstrate that PCBs and DDE adsorb to PP resin pellets from seawater (Figure 3). During the experiment, PCBs and DDE in the deployed pellets showed steady concentration increase with time. These increasing trends clearly indicate that ambient seawater is the source of PCBs and DDE found in the marine PP resin pellets and that adsorption to pellet surfaces is the mechanism of enrichment. As PP resin pellets are made of saturated hydrocarbon units, their surfaces are nonpolar and adsorb hydrophobic pollutants such as PCBs and DDE through hydrophobic sorption. It was previously suggested that PP granules are similar in polarity to that found in the hydrocarbon solvent and PP is expected to have a very nonpolar surface (19). The results of repeated solvent extraction (Table 1) are consistent with hydrophobic sorption of PCBs and DDE on PP pellets. The pollutants were extracted with *n*-hexane entirely, whereas they were not extracted completely with methanol (Table 1). We conclude that the nonpolar surface of PP pellets attracts the hydrophobic pollutants and a polar solvent (i.e. MeOH) is too weak to break the hydrophobic interaction. On the other hand, hydrophobic pollutants could be readily partitioned between the nonpolar surface of the pellets and hydrophobic solvent (i.e. hexane).

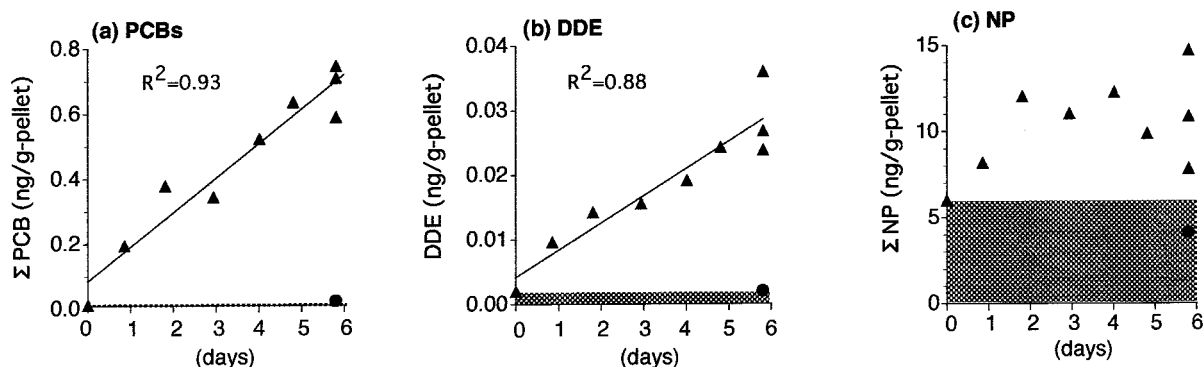


FIGURE 3. Concentration of  $\Sigma$ PCBs, DDE, and nonylphenol in deployed PP pellets during the field adsorption experiment. Solid triangle: exposed to seawater; solid circle: exposed to atmosphere. Shading indicates analytical blank (0 day deployed PP pellets). Solid lines are linear regression lines.

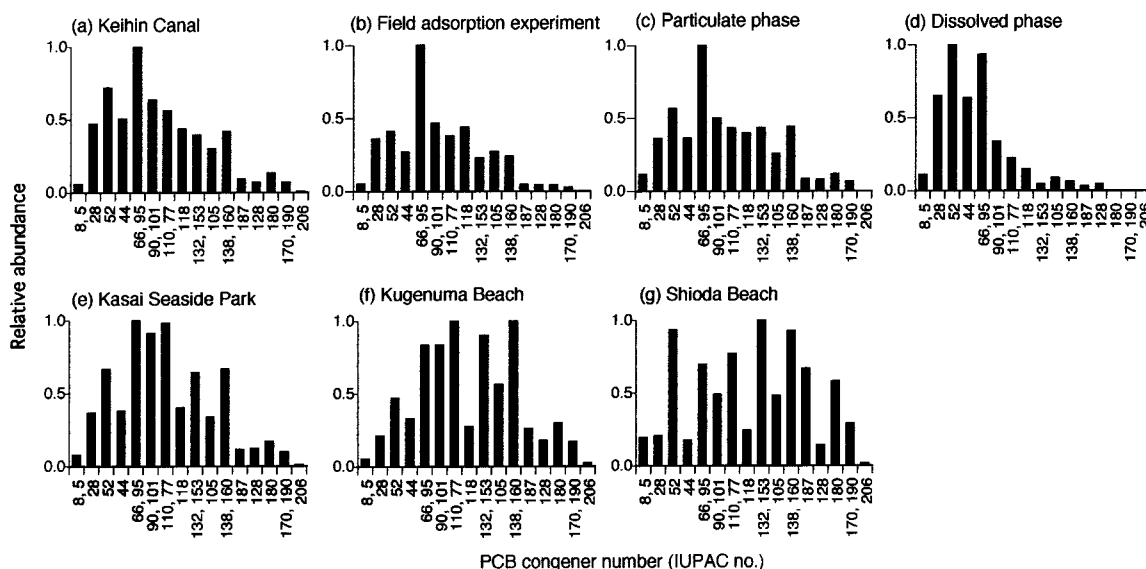


FIGURE 4. PCB congener profiles of (a) marine PP pellets collected from Keihin Canal, (b) deployed PP pellets in the Field Adsorption Experiment carried out at Keihin Canal, (c) seawater particulate phase from Keihin Canal, (d) seawater dissolved phase from Keihin Canal, (e) marine PP pellets collected from Kasai Seaside Park, (f) marine PP pellets from Kugenuma Beach, and (g) marine PP pellets from Shioda Beach. Y-axis is the relative abundance of individual congeners to the highest congeners.

Sorption of pollutants to pellet surfaces is also supported by PCBs congener profiles. During the field adsorption experiment, seawater (dissolved and particulate phases) and marine PP resin pellets were also collected and analyzed for PCBs (Figure 4, and Table 3). Due to differential partitioning among the congeners based on different hydrophobicities, PCBs in the dissolved phase are enriched in lower chlorinated congeners, while PCBs adsorbed to the particulate phase are enriched in higher chlorinated congeners (e.g., CB#132, 153, 138). The congener profile of PCBs measured in the deployed pellets during the adsorption experiment was rich in high chlorinated congeners and was more correlated to congener profiles found in the particulate phase ( $r^2 = 0.96$ ) than to congener profiles in the dissolved phase ( $r^2 = 0.74$ ). This is consistent with the hypothesis that hydrophobic pollutants are adsorbed onto plastic pellets through sorption processes where more hydrophobic components (i.e. higher chlorinated congeners) preferentially partition to nonpolar plastic surfaces. Furthermore, the PCB profile found in the deployed pellet was similar to profile found in the marine PP resin pellets ( $r^2 = 0.94$ ), indicating that the field adsorption experiment accurately represented the contaminant distribution of PP resin pellets in the seawater.

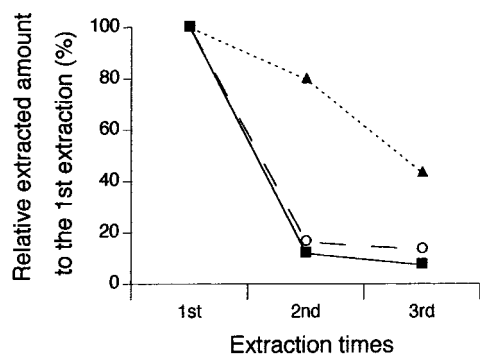
Exposure of PP resin pellets to the atmosphere during their floating on the sea-surface and stranding on beaches may facilitate adsorption of atmospheric pollutants onto the

pellets. However, no significant PCBs or DDE concentrations were observed in the PP resin pellets exposed to air during the same period as the field adsorption experiment (Figure 3). This indicates that adsorption from the atmosphere does not directly contribute to enrich the PP resin pellets with PCBs or DDE.

NP contents in the deployed PP resin pellets were not significant throughout the experiment compared to the blank, and no significant enrichment in NP concentrations was observed with time (Figure 3c), although substantial concentration of NP was observed in the seawater in the canal (Table 3). This suggests other sources of NP than adsorption from seawater. A plausible source is plastic additives applied in the manufacturing of PP resin pellets. NP were used as antioxidants in the plastic industry (29). Also, trisnonylphenol phosphite (TNP), polymer antioxidants, could generate NP by oxidation and subsequent hydrolysis (30). In addition, NP is contained in the TNP antioxidants (31), because TNP are synthesized from NP, and unreacted raw material stays in the product. Furthermore, nonylphenol polyethoxylates (NPnEO) are also used as an antistatic agent, and NP is generated by degradation of NPnEO (32, 33). TNP and NPnEO are currently in use as additives in the Japanese plastic industries (30, 34).

The repeated methanol extraction supports the additive-derived NP hypothesis (Figure 5 and Table 1). PCBs and DDE





**FIGURE 5.** Extracted amounts of PCBs, DDE, and nonylphenol relative to first extraction on repeated methanol extraction of PP pellets. Pellets were collected from the harbor of Tokyo University of Fisheries, Tokyo Bay. Eight-hour-Soxhlet extraction with methanol was sequentially repeated 3 times. Solid triangle: nonylphenol, open circle: PCBs, and solid square: DDE.

**TABLE 3.** Concentration of PCBs, DDE, and NP of Seawater and Marine PP Pellets and Their Apparent Distribution Coefficients in Keihin Canal

| PCB congener | concentration                       |                                       |                                             | log K'd <sup>d</sup> for |                  |
|--------------|-------------------------------------|---------------------------------------|---------------------------------------------|--------------------------|------------------|
|              | dissolved phase <sup>a</sup> (pg/L) | particulate phase <sup>b</sup> (pg/L) | marine PP pellet <sup>c</sup> (ng/g-pellet) | particulate phase        | marine PP pellet |
| 8, 5         | 13                                  | 17                                    | 1.2                                         | 5.48                     | 4.98             |
| 28           | 76                                  | 55                                    | 9.4                                         | 5.21                     | 5.09             |
| 52           | 116                                 | 86                                    | 14.3                                        | 5.22                     | 5.09             |
| 44           | 74                                  | 55                                    | 10.1                                        | 5.22                     | 5.14             |
| 66, 95       | 108                                 | 152                                   | 19.9                                        | 5.49                     | 5.26             |
| 90, 101      | 39                                  | 76                                    | 12.6                                        | 5.64                     | 5.51             |
| 110, 77      | 26                                  | 66                                    | 11.2                                        | 5.75                     | 5.63             |
| 118          | 17                                  | 61                                    | 8.7                                         | 5.90                     | 5.71             |
| 132, 153     | 5                                   | 66                                    | 7.9                                         | 6.47                     | 6.19             |
| 105          | 10                                  | 39                                    | 6.0                                         | 5.93                     | 5.77             |
| 138, 160     | 7                                   | 67                                    | 8.3                                         | 6.31                     | 6.06             |
| 187          | 3                                   | 13                                    | 1.8                                         | 5.92                     | 5.73             |
| 128          | 5                                   | 12                                    | 1.4                                         | 5.73                     | 5.45             |
| 180          | nd <sup>e</sup>                     | 17                                    | 2.7                                         | na <sup>f</sup>          | na <sup>f</sup>  |
| 170, 190     | nd <sup>e</sup>                     | 10                                    | 1.4                                         | na <sup>f</sup>          | na <sup>f</sup>  |
| 206          | nd <sup>e</sup>                     | nd <sup>e</sup>                       | 0.2                                         | na <sup>f</sup>          | na <sup>f</sup>  |
| ΣPCB         | 499                                 | 792                                   | 117                                         | 5.55                     | 5.37             |
| DDE          | (pg/L)                              | (pg/L)                                | (ng/g-pellet)                               |                          |                  |
|              | 11                                  | 37                                    | 3.1                                         | 5.87                     | 5.44             |
| NP           | (ng/L)                              | (ng/L)                                | (μg/g-pellet)                               |                          |                  |
|              | 106                                 | 35.0                                  | 8.90                                        | 4.86                     | 4.92             |

<sup>a</sup> Seawater components, which was collected from Keihin Canal, through glass fiber filter (GF/F). <sup>b</sup> Seawater components, which was collected from Keihin Canal, on glass fiber filter (GF/F); solid: 4.5 mg/L; organic carbon: 0.44 mg/L. <sup>c</sup> Collected pellets which were floating on Keihin Canal. <sup>d</sup> K'd: apparent distribution coefficient K'd for particulate phase =  $S(\mu\text{g/Kg})/D(\mu\text{g/L})$ ; K'd for pellet =  $P(\mu\text{g/Kg})/D(\mu\text{g/L})$ ; where S, D, and P are the concentrations of target compounds in the particulate phase, dissolved phase, and pellets, respectively. <sup>e</sup> nd: not detected. <sup>f</sup> na: not available.

extracted in the second methanol extraction were 16% and 12% of the first methanol extractions, respectively. In contrast, the NP released in the second extractions were 80% of the amounts released during the first extractions. Larger amounts of NP in the second extraction imply that additive-derived NP is incorporated within the matrix of plastic resin pellets, and they are difficult to leach out with the weak solvent (i.e., methanol).

However, there still remains a possibility that PP pellets could adsorb NP which contributes some parts of NP in the marine PP pellets, because NP are widely distributed in urban

environments due to the extensive usage of NPEO surfactants and NP has hydrophobic moiety in the molecule. To evaluate this possibility, a longer-term experiment is required.

Marine plastic pellets may act as significant source of NP to marine organisms. It is thought that biomagnification of NP through the food chain could not be occurring due to their hydrophilic group and metabolizable nature, although these conclusions have not been well proved. Ahel et al. (35) measured NP in macrophytic algae, fish, and wild duck and suggested that biomagnification of NP did not take place, although its bioaccumulation was observed. This suggests that biomagnification may not play an important role to transfer NP, unlike PCBs and DDE, to animals and birds in higher trophic levels. In these contexts, direct ingestion of plastic pellets could be a direct and important route of NP to higher animals. Our results indicate that NP is trapped deep in the pellets, and this may suggest that NP is not easily transferred to biological tissue when ingested. However, because the contents of NP are 2 orders of magnitude higher than PCBs and DDE, even slow or partial transfer of NP to biological tissue by this route could have serious consequences for marine organisms. Furthermore, because seabirds retain pellets in their ventriculus for several months or more, and the pellets are worn down in these muscular structures (16, 36, 37), the trap of NP in plastic matrix would not reduce their bioavailability to seabirds.

**Adsorption Characteristics of Resin Pellets.** For the marine PP resin pellets collected from the sea surface of Keihin canal, apparent adsorption coefficients (K'd) of PCBs and DDE were calculated using their concentrations in the pellets and surrounding water (Table 3). The apparent adsorption coefficients for the pellets were  $10^5$ – $10^6$ . This range is similar to that for suspended particles collected from the same location at the same time as the PP resin pellets were collected. Specific surface area of the PP resin pellets was determined at  $\sim 25 \text{ cm}^2/\text{g}$  based on the measured diameter and height of cylindrical pellets. It is 2 orders of magnitude lower than those for suspended particles,  $\sim 10^4 \text{ cm}^2/\text{g}$ , which is calculated on the assumption that the suspended particles are spheres of  $1 \mu\text{m}$  diameter. Large adsorption coefficients for the PP resin pellets with small surface areas indicate that the PP resin pellets have a higher affinity for hydrophobic pollutants than marine micro particles. This can be attributed to the hydrophobic surfaces. The high pollutant concentrations in the PP resin particles may also be due to the marine microlayer. Some hydrophobic contaminants such as organochlorine pesticides and PCBs are known to be hyperconcentrated in the air-sea interface microlayer (38, 39). Because the plastic pellets float on sea surface, they could easily adsorb the contaminants from the contaminant-enriched microlayer.

Our adsorption experiment indicates that amounts of PCBs and DDE adsorbed on the PP resin pellets after a 6-day deployment were 2 orders of magnitude lower than the pollutants concentrations in marine PP resin pellets (Table 2 and Figure 3). Also, a steady increase in PCBs and DDE concentrations throughout the field adsorption experiment was observed. These suggest that the sorption to the PP resin pellets did not reach the equilibrium even after 6 days deployment (Figure 3a,b) and would continue for a longer period. In some experiments with natural sediments, sorption equilibrium with PCBs was achieved within 24 or 48 h (40, 41). The slow sorption to PP resin pellets can perhaps be ascribed to slow diffusion of the pollutants into the polymer matrix. Diffusion of hydrophobic compounds into PP granules has been reported (19). The larger the sorbent particle, the slower the overall sorption equilibrium since diffusion path lengths are longer (42). A larger diameter of PP resin pellets (1–5 mm) could account for a longer sorption period than natural sediments ( $\sim$  several micrometers).

Providing the sorption rate for experimental PP resin pellets is constant and its sorption capacity is as great as that of the marine PP resin pellets, it could take several years for the PCBs and DDE concentrations to reach the level observed for the marine PP resin pellets. Weathering may accelerate the sorption of pollutants on plastic resin pellets and increase the adsorption capacity. Weathering increases the surface area of pellets, and extension of the size of pores in pellets makes the sorbate's effective diffusivity bigger. On the other hand, weathering of polymers introduces a variety of oxygen-containing groups. They increase polarity of the polymer surface. Also, weathering of polymers causes rearrangement of the amorphous part and a slight increase in their crystallinity (43). These factors may decrease the capacity and rate of the hydrophobic sorption of pollutants by plastic pellets. Long-term (weeks to months) adsorption experiments should be conducted in future studies.

**Spatial Differences.** The present study demonstrates the spatial differences in pollutant concentrations and compositions in PP resin pellets (Table 2). PCBs and DDE content of PP resin pellets from Kasai Seaside Park, Keihin Canal, and Kugenuma Beach were 1 order of magnitude higher than that from Shioda Beach. Because the source of PCBs and DDE is thought to be ambient seawater, the differences in pollutant concentrations in marine pellets could reflect the degree of pollution in surrounding environments. The former sites are more urbanized and industrialized than Shioda beach. The Japanese Environmental Protection Agency monitored PCBs and DDE of sea basses, *Lateolabrax japonicus*, in Japanese coastal water (44). Off San-in coast including Shioda Beach (Figure 1), PCBs concentration was 0.04  $\mu\text{g/g-wet}$  ( $n = 5$ ), and DDE concentration was 0.006  $\mu\text{g/g-wet}$  ( $n = 5$ ) in the fish. On the other hand, in Tokyo Bay (Figure 1, close to the three urban sites), PCBs concentration in sea basses was 0.26  $\mu\text{g/g-wet}$  ( $n = 5$ ), and DDE concentration was 0.018  $\mu\text{g/g-wet}$  ( $n = 5$ ) on average, which are much higher than those from San-in coast. The observed correlation between contaminant levels in the PP resin pellets and in biota suggests that plastic resin pellets could be a good indicator of the pollution level in the environments.

PCB congener distributions also varied among sampling sites (Figure 4a,e,f,g) and not so correlated ( $r^2 = 0.41-0.89$ ). PCBs in PP resin pellets from the sites in/near Tokyo Bay were more depleted in higher-chlorinated congeners than the site in the Sea of Japan (i.e., Shioda Beach) (Figure 4). These differences can be attributed to a variety of local contamination sources with different PCB profiles.

The observed spatial differences in pollutant concentrations and their possible correlation with the pollution level in surrounding environments suggest the potential use of plastic pellets as a tool for monitoring of organic micro-pollutants in seawater. However, the pollutant content and congener profile of marine pellets may also reflect their history of exposure to contamination. If pellets are transported over a long distance, the pollutant content in the pellets reflects not only local pollution in the area where they are collected but also pollution along the entire transport path since their discharge. Detection of specific contaminants unique to a certain area may indicate the source or pathway of pellets. The detailed analysis of contaminants in the pellets may provide information about both their source and the oceanographic processes controlling their dispersion and transport in coastal waters.

The present study demonstrates elevated concentrations of pollutants on/in marine PP resin pellets. The resin pellets, therefore, play a role as pollutant transport media in marine environments. Two types of sources of the pollutants are indicated. One is adsorption of hydrophobic pollutants from seawater. PCBs and DDE were found to accumulate in plastic pellets in concentrations up to  $10^5-10^6$  times higher than

surrounding seawater. Another source of pollutants is plastic additives and related chemicals (e.g. degradation products). Although the present study focuses on nonylphenol, some other chemicals used as additives could also be detected in marine pellets. Plastic resin pellets have been also found in the stomachs of marine birds (9-16). The uptake of pellet-sorbed contaminants to their tissues is a concern. The present study indicates plastic resin pellets act as a pollutant accumulator that could transfer hydrophobic pollutants to organisms. Further studies must be done on the transfer of the chemicals from pellets to biological tissue while they transit through the digestive system of birds and other animals.

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