TRANSFER OF PERSISTENT ORGANIC POLLUTANTS FROM SEDIMENT TO BENTHIC FISH IN LABORATORY TANKS

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Abstract
We investigated the transfer of persistent organic pollutants (POPs) to a benthic fish species, marbled sole (*Pleuronectes yokohamae*), from either bottom sediment (BS) or suspended sediment (SS) in the laboratory. One-year-old marbled sole were held for 28 days in 2 exposure tanks (BS and SS) and 1 control tank, and sampled on days 14 and 28. Transfer of *op′*-DDE from sediment to fish was demonstrated in the BS tank. The relative compositions of the compounds in the fish samples from the SS and control tanks were similar to that in the food. The apparent transfer of POPs may be affected by the ratio of concentrations of these compounds in sediment to those in food, and therefore in fish.

Introduction
Aquatic sediment potentially acts as a secondary source of persistent organic pollutants (POPs), because these compounds in aquatic environment tend to accumulate in sediments owing to their hydrophobicity. Transfer of these compounds from sediment to aquatic organisms is of concern, because this may lead to the exposure of humans or other organisms at higher trophic levels through the food web. However, a limited number of studies of transfer to fish, in particular, have been conducted [1, 2]. Recently, we reported a time-dependent increase in polychlorinated biphenyl (PCB) concentrations in a benthic fish species, marbled sole (*Pleuronectes yokohamae*), in the presence of bottom sediment [3, 4]. Marbled sole is commonly caught and eaten in Japan. It is an appropriate test species because it lives on and in sediments and is therefore potentially susceptible to the transfer of POPs from these sediments. In this study, we investigated the transfer of selected POPs, other than PCBs, to marbled sole in the presence of bottom and suspended sediment in the laboratory. Preliminary results and a discussion of factors affecting the extent of apparent transfer are presented.

Materials and Methods
Setup of the experiment
The experiment was conducted for 28 days using a total of 15 one-year-old marbled sole placed in 2 exposure (BS and SS) and 1 control tanks. The tanks were made of glass (60 cm × 30 cm × 45 cm H) and held 60 L of seawater during the experiment. One exposure tank had a layer of BS about 1 cm thick, which was let suspended by the activity of the fish. Both BS and SS were therefore present in the BS tank. The other exposure tank contained a nominal 100 mg/L of SS, which was kept suspended by circulating water flow. Only a small amount of SS accumulated in the bottom of the SS tank, and the accumulated SS was neglected in the study. The control tank had no sediment. The water temperature was kept at 20 °C. The marbled sole (5.4–32.7 g-wet, mean 14.7 g-wet at day 0; n = 15) were obtained from a hatchery and reared at our institute. Clay–silt (mean particle diameter 4 μm) sediment containing 1.7% organic carbon was taken from Tokyo Bay (depth about 10–15 m) and used without spiking. Seawater (salinity 36, pH 8.0 during the exposure period), collected from Sagami Bay and stored at our institute, was used as test water and rearing water. Commercial fish food was fed during the experiment at 1% of fish mass per day.

Two marbled sole were sampled on day 0, and four or five sole were placed in each tank. Two or three sole were sampled from each tank on days 14 and 28. Ten liters of the seawater in each tank was withdrawn every 2 days, and 10 L of fresh seawater was added. The sampled water was pooled for the two periods of 1–14 days and 15–28 days. The SS concentration in the BS and SS tanks were measured at each water exchange, and sediment particles were added to compensate for the loss in the sediment tanks. Sediment samples were taken from the BS tank just before and just after the experiment (days 0 and 28).

Chemical analysis
The sampled marbled soles were sacrificed by freezing after deactivated in ice-cold water. They were washed to remove sediment particles from the body surface. The gastrointestinal tract was opened and washed to

remove any remaining sediment or food inside. Whole body samples were homogenized, pooled to make one sample for each sampling of each tank, and stored below −20 °C until analysis. Before extraction, the homogenized samples were thawed and then dehydrated by anhydrous sodium sulfate or diatomite (Hydromatrix, Varian Inc.). The water samples were separated into particulate and dissolved phases by passage through a pre-combusted glass fiber filter (GF) of 0.3 μm (nominal) pore size (GF-75, ADVANTEC) [4].

The analytes were aldrin, dieldrin, endrin, DDTs (*op′*-DDT, *op′*-DDE, *op′*-DDD, *pp′*-DDT, *pp′*-DDE, *pp′*-DDD), *cis*- and *trans*-chlordane, heptachlor, and hexachlorobenzene (HCB). Water samples were GF-filtered and the dissolved phase was extracted by solid-phase extraction (SPE). Sediment, fish, food and water (GF and SPE disk) samples were solvent-extracted and then purified by silica-gel column chromatography and by sulfuric acid treatment (not the drins). All the analytes in the purified concentrated extracts were identified and quantitated by an isotope-dilution or internal-standard method on an HRGC/HRMS system equipped with an HT8-PCB column (30 m × 0.25 mm [i.d.], SGE) for chlordane, heptachlor, and HCB, or an RH-17 column (30 m × 0.25 mm [i.d.], Inventex) for the drins and DDTs.

Results and Discussion

The internal-standard recovery was satisfactory, ranging mostly within 50% to 120%. Blank values were sufficiently low, if detected, not to affect the discussion presented here. Aldrin was not detected (< 0.4 pg/g-wet) in 4 out of the 7 fish samples, and was therefore omitted from the following discussion.

The concentrations in water and sediment samples are shown in Figure 1. The dissolved-phase concentrations of some compounds were higher in the BS and SS tanks than in the control, but those of others were not. The particulate-phase concentrations of all compounds (except those below the detection limits) in the BS and SS tanks were much higher than in the control tank and differed little between the first and last 2 weeks. The concentrations in BS did not change during the 4-week test period. The concentrations in the particulate phase per SS mass were comparable between the SS of the BS tank and the BS, but some differences were found between the SS of the SS tank and the BS (e.g., higher in SS tank: *op′*- and *pp′*-DDT; lower in SS tank: *op′*- and *pp′*-DDE). The mean SS concentrations during days 1–14 and 15–28 were 53.4 and 76.0 mg/L, respectively, in the SS tank and 671 and 419 mg/L in the BS tank.

Ratios of concentrations in the fish in the BS tank to those in the control tank (lipid basis) are plotted in Figure 2 against the ratios of concentrations in the BS to those in food (S:F ratio, g-wet/g-dry). This plot shows the transfer of *op′*-DDE from sediment to fish. At day 14, the concentration of *op′*-DDE had increased to about 38 times the control value, whereas those of chlordanes, dieldrin, endrin, heptachlor, and HCB had fallen to below half of the control values. At day 28, the *op′*-DDE concentration stayed high at 27 times the control value, whereas no other compound increased or decreased by a factor of more than 2. The above discussion was based on g-lipid basis concentrations, and also applies to g-wet basis concentrations. The observed difference in the apparent transfer between *op′*-DDE and other compounds are not likely explained by the difference in octanol-water partition coefficient (Kow), because these compounds lie in a range of similar Kow values (log Kow: 5.2–6.2; 5.8 for *op′*-DDE [5]).

The relative compositions, or profiles, of the 12 compounds in the fish samples from the BS tank showed considerable variation from the control, whereas those from the control and SS tanks were similar to those in the food (Figure 3, SS-tank fish not shown). The compounds whose concentrations decreased relative to those in the control in the first 2 weeks showed increased concentrations in the following 2 weeks, resulting in a composition at day 28 intermediate between those of the food and the sediment. This time trend of decrease and increase cannot be accounted for by the dissolved or particulate concentrations, because these concentrations stayed relatively constant in each tank (Figure 1).

The ratios of concentrations in the BS-exposed fish to those of the control suggest that the S:F ratio affected the apparent transfer of the compounds from sediment to fish. The S:F ratio is relatively high (about 40) for *op′*-DDE, the fish concentration of which increased markedly, and relatively low (< 0.43 on a g-lipid basis, and <1.1 on a g-wet basis) for the compounds whose concentrations in fish decreased below half of the control after

14 days (Figure 2). In the SS tank, no compounds increased or decreased in concentration by a factor of more than 2 compared to the control values, except *op′*-DDE which increased to 2.6 (day 14) and 2.2 (day 28) times the control values. However, reducing the concentrations of these compounds in food may allow clearer observation of their transfer to fish under both exposure conditions.

In conclusion, transfer of *op′*-DDE from sediment to fish was demonstrated. Apparent transfer of POPs may be affected by the ratio of concentrations of these compounds in sediment to those in food, and therefore in fish. The quantitative contributions from various potential routes of exposure, namely water, food, and sediment ingestion, will be examined statistically in a future study.

Acknowledgements
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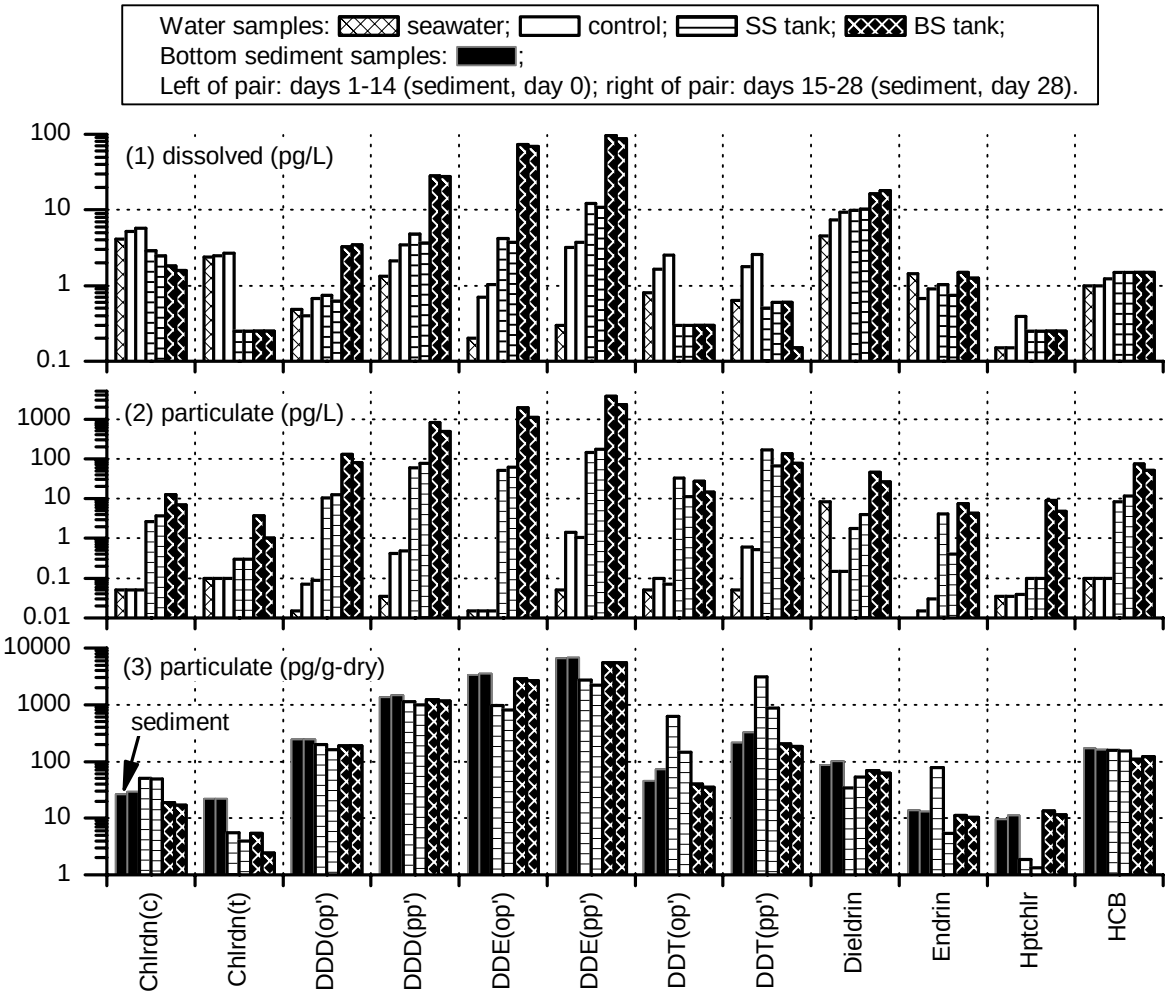

Figure 1. Concentrations of POPs in water and sediment samples. Water samples from suspended sediment (SS) tank, bottom sediment (BS) tank, and control tank, as well as seawater (panels 1 and 2) and bottom sediment (panel 3) are shown. Paired bars: left, days 1–14; right, days 15–28. Values below the detection limit were treated as half the detection limit of each compound.

References

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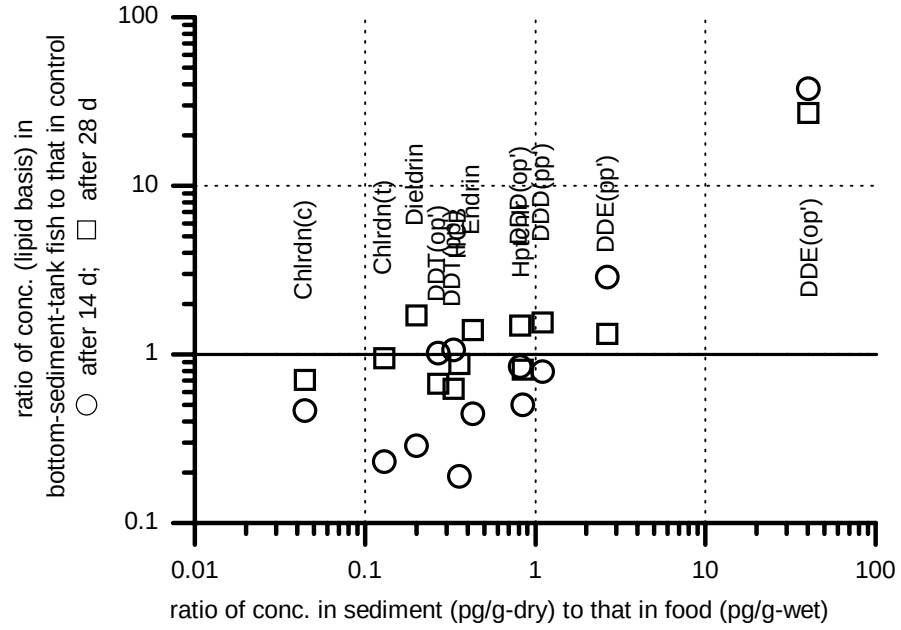

Figure 2. Ratios of concentrations in fish in bottom sediment (BS) tank to the concentrations in the control tank (lipid basis), plotted against ratios of concentrations in BS to those in food (S:F ratio).

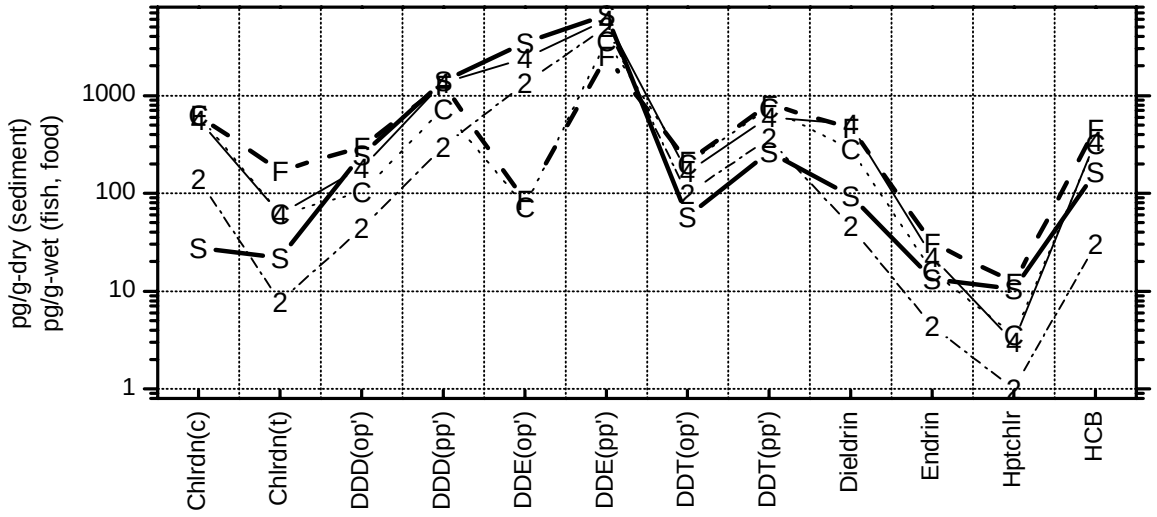

Figure 3. Comparison of the composition of POPs in sediment-exposed fish to that in other samples. S, bottom sediment; F, food; C, fish in control tank; 2, fish in bottom sediment (BS) tank after 14 days; 4: fish in BS tank after 28 days. Note that the units differ between sediment and fish or food.