



## Desorption kinetics of hydrophobic organic contaminants from marine plastic pellets

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### ABSTRACT

This study investigated the desorption behavior of polychlorinated biphenyls (PCBs) from marine plastic pellets. Long-term desorption experiments were conducted using field-collected polyethylene (PE) pellets. The results indicate that the desorption kinetics highly depends on the PE-water partition coefficients of PCB congeners. After 128 d of the experiment, the smallest congener considered (CB 8) had desorbed nearly completely (98%), whereas major fractions (90–99%) of highly chlorinated congeners remained in the pellets. An intraparticle diffusion model mostly failed to reproduce the desorption kinetics, whereas an aqueous boundary layer (ABL) diffusion model well approximated the data. The desorption half-lives are estimated to 14 d to 210 years for CB 8 to CB 209 in an actively stirred solution (ABL thickness: 30 μm). Addition of methanol to water enhanced the desorption to a large extent. A need for further work to explore roles of organic matter in facilitating solute transfer is suggested.

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### 1. Introduction

Plastic debris is found in marine environments throughout the world, including remote sites such as in the middle of the Pacific Ocean (Moore et al., 2001; Goldstein et al., 2012). Among the most frequent forms of marine plastic debris are plastic pellets (or resin pellets) (Derraik, 2002), which are industrial feedstock for plastic production and are typically 3–5 mm in size. Predominant polymer types of plastic pellets found in marine environments are polyethylene (PE) and polypropylene (PP) (Endo et al., 2005; Ogata et al., 2009; Andrady, 2011). These organic polymers can accumulate hydrophobic contaminants from water. The occurrence of hydrophobic contaminants in marine plastic pellets has widely been reported (Mato et al., 2000; Endo et al., 2005; Rios et al., 2007, 2010; Ogata et al., 2009; Hirai et al., 2011; Karapanagioti et al., 2011; Heskett et al., 2012). Moreover, marine plastic pellets can also contain chemicals that have been added to pellets as plastic additives (Teuten et al., 2009). Because of the buoyancy and durability, these pellets can be transported in a long range, carrying the sorbed contaminants and chemical ingredients with them (Heskett et al., 2012). In addition, some marine organisms are known to ingest plastic pellets, and it has been of concern whether ingestion of environmental plastic pellets could be a significant route of organic contaminants to organisms (Teuten et al., 2009).

The potential of marine plastics to contribute to the contaminant dynamics has been discussed in two recent papers (Zarfl and Matthies, 2010; Gouin et al., 2011), both on the basis of thermodynamically-based model calculations (i.e., assuming sorption equilibrium). Zarfl and Matthies (2010) investigated a potential role of plastics as a vector for contaminants to the Arctic. Gouin et al. (2011) simulated equilibrium distributions of organic chemicals among marine compartments including water, sediment, plastic debris, and biota. Estimations based on the equilibrium assumption may provide useful implications for multi-phase environmental distributions of contaminants, provided that the time needed to reach sorption/desorption equilibrium is relatively short compared to the time scale of model simulations. Mato et al. (2000) however have indicated a fairly slow sorption of polychlorinated biphenyls (PCBs) and DDE from seawater to PP pellets. They performed a six-day sorption experiment in the field and estimated the equilibrium time to be as much as several years (Mato et al., 2000). Recently, Rochman et al. (2013) conducted a longer term experiment (i.e., 12 months), observing a similar trend. Thus, it is sensible to further our understanding of sorption/desorption kinetics to/from plastic pellets to evaluate them as a potential contaminant-carrier. Particularly, desorption of chemicals from marine plastics has been far less studied before than sorption. Understanding of chemical leaching from plastic pellets is needed also for evaluating the transport of chemicals from ingested pellets to organisms, because chemicals have to desorb from ingested pellets in the gastrointestinal tract before being taken up by the organism.

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In this study, we investigated desorption mechanisms of PCBs from PE pellets. PCBs were chosen as test chemicals because of their frequent occurrence in marine plastics and of the presence of many congeners having differing physico-chemical properties. A bench-scale experimental system was set up to measure long-term desorption kinetics of PCBs from PE pellets. Plastic pellets used for the desorption experiments were collected from a beach and were used without spiking of standard chemicals in the lab. Thus, we used real marine plastic samples and monitored desorption of “native” PCBs that had been sorbed in the environment. Desorption kinetic models were evaluated as to how well the models describe the observed desorption behavior of PCB congeners. Comparison between experimental and modeling results is important, as it could provide insights into desorption mechanisms. Moreover, an experimentally validated model can offer the possibility to estimate the desorption behavior of contaminants that are not tested here. Finally, desorption half-lives and equilibrium times were estimated from a model to provide implications for field-occurrence of contaminants in plastic pellets.

## 2. Materials and methods

### 2.1. Plastic pellets

Environmental plastic pellets were collected from a beach in Le Harve, the Normandy region of France. PE pellets were sorted out using a PlaScan-SH near-infrared spectrometer (OPT Research Inc. Tokyo, Japan). Following previous work (Endo et al., 2005), PE pellets without pigments but with a visible yellow color due to discoloration were selected and used for desorption experiments since they were thought to have relatively high PCB concentrations. PCB concentrations in discolored PE pellets from this site were 365–908 ng/g (five replicate analysis; see Ogata et al. (2009) for the method). These levels of PCB concentrations fall in the upper end of the results of global monitoring of PCBs in marine PE pellets (Ogata et al., 2009).

Virgin low-density PE pellets (Santec LD M652) were provided courtesy of Asahi Kasei Corporation (Tokyo, Japan) and used as received. Background PCB concentrations in these virgin PE pellets were analyzed and no detectable PCBs were found.

### 2.2. Desorption experiments

A 2-L amber glass bottle was filled with 1.5 L of HPLC-grade distilled water (Wako Chemicals, Osaka, Japan). Salt water could also be used for the experiments, but the difference from fresh water is expected to be small (Endo et al., 2012). PE pellets from the field (40 pieces) were packed in a meshed metal tea infuser ball with a diameter of 50 mm and was fixed in the glass bottle using a metal wire. Desorption of PCBs to water occurred from these PE pellets and, thus, we refer to these pellets as “source pellets”. Immediately after the source pellets were introduced into water, 10 times the amount of virgin pellets compared to the source pellets were put into the glass bottle. These virgin pellets sorb PCBs from water and serve as an infinite sink, thus referred to as “sink pellets”. A similar approach was used by Pignatello (1990) and Cornelissen et al. (1997) for investigation of chemical desorption from soil particles. A larger amount of sink pellets relative to source pellets was added so that sink pellets have a much larger surface area than source pellets. This guarantees that the overall mass transfer kinetics from source to sink pellets is controlled by the desorption kinetics from the source pellets and not largely influenced by the sorption kinetics to the sink pellets. The system was continuously stirred with a glass-covered stir-bar using an IUCHI TMS-6 magnetic stirrer. As an indication of the stirring speed, the number of

circulations of a sink pellet in the water was counted by eyes, which was 25 rounds per minute. The sink pellets were replaced with clean virgin pellets of the same amount 1, 2, 4, 8, 16, 32, 64, and 128 d after the beginning of the experiment. The sampled sink pellets were dried with silica gel in a desiccator and stored at  $-30\text{ }^{\circ}\text{C}$  until PCB analysis. After the sampling of the sink pellets on day 128, the source pellets were collected, dried, and stored as for sink pellets. Photographs and a schematic illustration of the experimental setup are provided in the [Supplementary material](#).

Desorption experiments were also conducted with 25 vol% methanol/water and 50 vol% methanol/water for comparison purposes. While using methanol–water mixtures is not directly relevant to environmental situations, desorption data with methanol mixtures are useful to validate desorption models, as addition of methanol causes systematic changes in model parameters (as explained below). Using a methanol mixture has the additional advantage that more PCB congeners can be detected in sink pellets than with pure water (see the results). The experimental setup was the same as for pure water. All desorption experiments were carried out in a temperature controlled room ( $25\text{ }^{\circ}\text{C}$ ).

Throughout the desorption experiments, PCB concentrations in the sink pellets should stay much lower than those of the source pellets so that the sink pellets can work as an infinite sink. This condition was evaluated later with the experimentally determined concentrations.

### 2.3. PCB analysis

Plastic pellets were extracted with three times 100 mL *n*-hexane in an Erlenmeyer flask. The plastic pellets and *n*-hexane solution were stirred at 120 rpm. An extraction time of 12 h was given for each step. In a preliminary experiment, the fourth extraction step was applied and only <1% of the total mass extracted was detected for any PCB congener, indicating that the three times extraction is enough for extracting PCBs from PE pellets. The method for analyzing the *n*-hexane extract followed that of Ogata et al. (2009). Briefly, extracts were spiked with surrogate standards, concentrated using a rotary evaporator, cleaned up with an activated silica gel column (SIL-A-200, 60–200 mesh, Sigma–Aldrich, St. Louis, MO), and analyzed for PCB concentrations. A gas chromatograph equipped with an ion trap mass spectrometer (Trace GC Ultra and Polaris; Thermo Fisher Scientific, Waltham, MA) was used for quantitative analysis of PCBs. Instrumental conditions have been described by Hirai et al. (2011). Chromatographic peaks that correspond to 38 PCB congeners were quantified. Congeners that often occurred below the quantification limits or with interfering peaks were eliminated from the consideration. This was the case with many highly chlorinated PCB congeners in the pure water system. Some missing data points were interpolated from the other measured data, assuming a linear increase of the desorbed fraction, as shown in the [Supplementary material](#) (Tables S1–S3).

### 2.4. Desorption models

Desorption kinetics from a PE pellet to clean water are determined by two processes: diffusion within the PE pellet and diffusion through the aqueous boundary layer (ABL). Here, three models were evaluated to describe the experimental data. In all cases, a perfectly spherical, homogeneous PE pellet and an ABL thickness that is independent of the compounds were assumed.

#### 2.4.1. Intra-particle diffusion (IPD) model

In case diffusion in the PE pellet (i.e., IPD) is much slower than diffusion through the ABL, the desorption kinetics of a compound can be described as (Crank, 1979; Grathwohl, 1998),

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