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The potential of oceanic transport and onshore leaching of additive-derived lead by marine macro-plastic debris

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ABSTRACT

The long-distance transport potential of toxic lead (Pb) by plastic marine debris was examined by pure water leaching experiments using plastic fishery floats containing high level of additive-Pb such as 5100 ± 74.3 mg kg^{-1}. The leaching of Pb ended after sequential 480-h leaching experiments, and the total leaching amount is equivalent to approximately 0.1% of total Pb in a float. But it recovered when the float was scratched using sandpaper. We propose that a "low-Pb layer," in which Pb concentration is negligibly small, be generated on the float surface by the initial leaching process. Thickness of the layer is estimated at 2.5 ± 1.2 μm, much shallower than flaws on floats scratched by sandpaper and floats littering beaches. The result suggests that the low-Pb layer is broken by physical abrasion when floats are washed ashore, and that Pb inside the floats can thereafter leach into beaches.

1. Introduction

Plastic products that reach the ocean as marine plastic debris can travel great distances over long periods because of their light weight and durability. In East Asia, plastics are currently the most common type of marine/beach debris (Zhou et al., 2011; Kusui and Noda, 2003; Hong et al., 2014; Kuo and Huang, 2014). Thus, a large amount of plastic marine debris originating from East Asian countries is even found on beaches of remote islands such as the Goto Islands of Japan (Fig. 1a; Kako et al., 2010; Nakashima et al., 2011, 2012). Plastic marine debris washed ashore on beaches is not only an eyesore but can be a transport vector of (i) chemicals absorbed on plastic debris surfaces from the surrounding seawater and (ii) additives originally incorporated in plastics (Teuten et al., 2009). Contaminants (i) are well known as hydrophobic persistent organic pollutants (POPs) and polycyclic aromatic hydrocarbons that absorb on plastic particles from ambient seawater because of the hydrophobic nature of plastic surfaces (Teuten et al., 2009). Not only POPs but also metals are detected in relatively high concentrations on surfaces of beached pellets, suggesting the accumulation of metals in marine plastic debris from seawater (Aston et al., 2010; Holmes et al., 2010). In addition, additive-derived metals are widely used in manufacturing plastics. Some of these are known toxic substances, functioning as catalysts. Examples are antimony trioxide commonly incorporated into polyethylene terephthalate (Takahashi et al., 2008), and stabilizers like lead stearate that enhance smoothness and stability of polyvinyl chloride (PVC) polymer (Minagawa, 1966). Despite their benefits, these metals are known to be toxic to plants, animals and microorganisms (Fairbrother et al., 2007). The European Union (EU) has therefore implemented a directive for "Restriction of Hazardous Substances" (RoHS) in electrical and electronic equipment for six toxic substances (including Pb) to reduce the risk to human health (European Union, 2003a); Pb should not be contained with a concentration higher than 0.1 wt.% (i.e., 1000 mg kg^{-1}) in products. This regulation is applied to mixed recycled plastic (European Union, 2003b), and there have been a number of reported violations of these regulatory standards for plastic products, such as paints or stabilizers used in children's toys (Becker et al., 2010; Wäger et al., 2012).

In our earlier research, we detected high-concentration metals contained in marine plastic debris washed ashore on Ookushi Beach in Japan (Fig. 1a; Nakashima et al., 2012). In particular, PVC fishing floats contain the greatest quantity of Pb such as 13,500 ± 8400 mg kg^{-1} (Fig. 1b and c). Of particular interest is that additive-derived toxic metals leach into the beach environment after plastic marine debris washes ashore. Therefore, we estimated the potential risk of toxic metal that could leach into that environment from such debris. In Nakashima et al. (2012), balloon aerial photography in conjunction with a beach survey gave an estimated Pb mass derived from marine plastic litter at 313 ± 247 g. Total Pb mass that could leach from PVC

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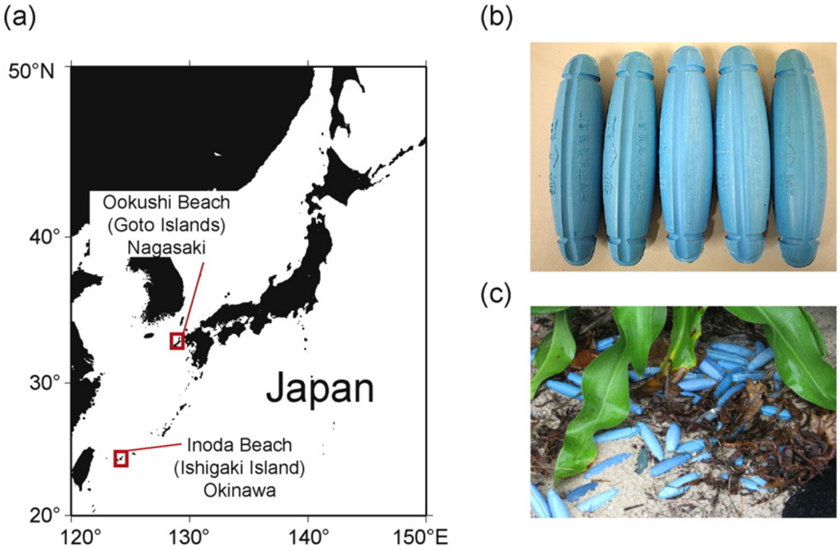

Fig. 1. (a) Location of Ookushi and Inoda beaches (red squares). Polyvinyl chloride fishing floats (PVC float) were collected from Inoda Beach. (b) Photograph of PVC floats used in leaching experiments. (c) PVC floats littering Inoda Beach (Ishigaki Island, Okinawa, Japan).

plastic debris over a year onto Ookushi Beach was estimated at 0.6 ± 0.6 g year^{-1}, from a leaching experiment together with a Fickian diffusion model analysis. This leaching experiment examined the solubility of Pb into pure water because our attention was paid for how much Pb in plastic debris littered on beaches may leach into the surrounding water (such as rain water). The high variability of leaching Pb mass was possibly due to different manufacturers of plastic debris in the marine environment.

Based on the aforementioned leaching experiment, it is suggested that durable plastic marine debris acts as a transport vector of toxic metals such as Pb. However, one may question why additive-derived metals in plastic marine debris do not leach completely into seawater, particularly if they have traveled long distances and possibly long periods in the ocean, and why Pb are still extensively detected in plastic debris washed ashore on beaches. The objective of this study is to answer these questions by focusing on additive-derived Pb leaching from fishery floats made from PVC, based on 5-day leaching experiments using newly-purchased floats in pure water (not seawater for ease of the experiments; shown later in Section 2.2). To investigate the potential of long-distance oceanic transport and leaching of additive-derived Pb from the PVC fishing floats on beaches, we computed the amount of Pb leaching from a single new PVC fishing float to compare this amount with the total Pb amount in the float. Although we start with these simple questions, we forward a scenario in which the additive-derived metals are transported onto beaches along with plastic marine debris.

2. Materials and Methods

2.1. Materials and Analytical Methods for Leaching Experiments

Fishery floats made from PVC (hereafter referred to as PVC floats; Fig. 1b) were chosen for the experiments because of their high Pb concentration (e.g., 13,000 ± 8400 mg kg^{-1}), as reported by Nakashima et al. (2012). Such high concentrations are probably caused by lead stearate, and greatly exceed the EU regulatory standard of Pb (1000 mg kg^{-1}). Although the PVC float is a specific marine plastic debris, it is also common debris that we can collect straightforwardly on various beaches around Japan (Fig. 1c). The transport of additive-derived Pb in the PVC floats was examined by the following leaching experiment. Fundamental procedures of this experiment using PVC floats are in Nakashima et al. (2012), so the description below focuses on adaptations of those procedures.

In the present study, the PVC floats (13.5 cm × 3.3 cm × ϕ3.0 cm, average 39.5 g; Fig. 1b) used for the leaching experiments were not those littered on the actual beaches, but newly purchased directly from a single Chinese manufactory to minimize variation of Pb leaching because of both flaws on float surface and different Pb concentrations in PVC floats provided by various manufactories. Although several dozen float manufacturers in China could be identified from textual information on the float surface, the purchased floats were similar to those littering beaches (Fig. 1b and c; samples corrected on Inoda Beach of Ishigaki Island, Okinawa, Japan).

Properties of the purchased floats were examined as described below before the leaching experiments. Surface areas of purchased PVC floats were measured using a 3D laser scanner (DAVID 3D Solutions GbR, Braunschweig, Germany). Pb concentrations in the floats were measured using a handheld Energy Dispersive X-ray fluorescence analyzer (Innov-X XRF Analyzer, Alpha-6500, Innov-X Systems, Inc., Woburn, Massachusetts, USA; hereafter referred to as XRF) equipped with X-ray tube of tungsten anode, where the energy range is 10–40 kV. The XRF is an appropriate analyzer to subsequent leaching experiments because it allows us to measure the concentrations of Pb in the PVC floats with non-destructive analysis. Based on ten-time measurements of virgin pellets (Grand Polymer Co. Ltd., Tokyo, Japan), the lower limit of quantitation of Pb using the XRF was found to be 8.0 mg kg^{-1}, which was calculated as ten times the standard deviation of 0.8 mg kg^{-1} obtained from these ten experiments. To improve the accuracy of analysis, the XRF was calibrated beforehand against an inductively coupled plasma mass spectrometry system (ICP-MS, Agilent 7500cx, Agilent Technologies, Santa Clara, California, USA) (Nakashima et al., 2012). Microwave digestion using acids has been employed to decompose plastics before ICP-MS analysis. Prepared PVC plastics ($n = 11$) were cut into small fragments for the analyses. Every 0.2 g of samples was digested with polytetrafluoroethylene vessels using 3 ml nitric acid and 5 ml sulfuric acid (for ultratrace analysis, Wako Pure Chemical Industries, Ltd., Osaka, Japan). After microwave digestion, samples were diluted to a volume of 50 ml with pure water (Milli-Q water, Millipore, Merck KGaA, Darmstadt, Germany) and were injected into ICP-MS. The accuracy of ICP-MS was calibrated by using EC680k and EC681k (European Reference Materials) as reference materials (low density polyethylene). A regression curve was obtained as $y = 2724e^{10.2x}$, where the concentration of Pb measured using XRF (ICP-MS) is assigned to x (y); the correlation coefficient was 0.98. The concentrations of Pb measured using the XRF were therefore