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.

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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 $13,500 \pm 8400$ 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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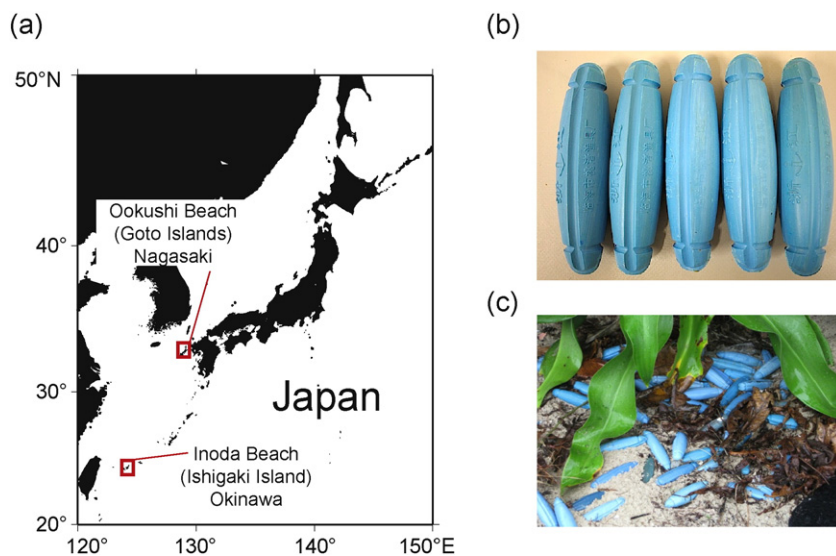
Fig. 1. (a) Location of Ookushi and Inoda beaches (red squares). Polyvinyl chloride fishing floats (PVC float) were collected from Inoda Beach. (b) Photograph of PVC floats used in leaching experiments. (c) PVC floats littering Inoda Beach (Ishigaki Island, Okinawa, Japan).

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., $13,000 \pm 8400$ 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

converted to those obtained from the corresponding ICP-MS values on this regression curve. It is well known that, in quantifying using XRF analysis, arsenic interferes with Pb due to the similarity of each main characteristic X-ray, and thus, we used the second X-ray (i.e., Lβ_1, 12.612 keV) to avoid the interference. We also confirmed that no arsenic is in the PVC floats used for ICP-MS analyses.

2.2. Leaching Experiments Using New PVC Floats

In the leaching experiments, a single PVC float was placed in a glass vial filled with 820 ml Elix pure water (Elix, EMD Millipore, Merck KGaA, Darmstadt, Germany). Ten purchased PVC floats were used for the following leaching experiments, and ten vials were prepared in addition to a control vial without a float. A single-type vial was used to standardize the volume ratio of water to a PVC float in all experiments. Each experimental vial was shaken continuously at 120 rpm using a shaking water bath (SWB-17/25, AS ONE Corp., Osaka, Japan) for 120 h, during which water temperature was maintained at 25.5 ± 1.0 °C. During each 120-h experiment, 10 ml of water was sampled from the glass vials every 24 h, and the same volume of pure water was added thereafter to each vial. A volume of 0.5 ml nitric acid (for ultratrace analysis; Wako Pure Chemical Industries Ltd., Osaka, Japan) was added to the 10-ml samples. The above set of experiments is hereafter referred to as the 120-h leaching experiment.

For ease of experiment, pure water instead of seawater was used in the experiment; otherwise seawater contain an abundant variety of metallic salts (such as sodium salts, magnesium salts, and potassium salts), which are known to interfere with measuring Pb using ICP-MS. For this reason, we preliminarily analyzed Pb in seawater with a type of disk car-

tridge (Empore, 3M Science, St. Paul, MN, USA) whose surface adsorbs and accumulates selectively aqueous Pb without metallic salts. To evaluate the effectiveness of the disk cartridge, three recovery tests had been tried that standard Pb (100 µg l^{-1}) was added into artificial seawater (Daigo's Artificial Seawater SP, Nihon Pharmaceutical Co., Ltd., Tokyo, Japan), and Pb was measured by ICP-MS after removal of the metallic salts using disk cartridges. The recovery rates resulted in low values ranging from 3 to 15% with considerable variation, which implied that Pb passed through disk cartridges due to its low adsorption. This technical problem prevented us to measure Pb in seawater.

The usage of pure water is indeed a limitation of the present experimental design. For instance, we have to note that Pb leaching rate (leaching speed) in the actual ocean is likely to differ from that estimated from the experimental results. In fact, the Pb leaching from PVC floats must be accelerated because abundant aqueous ions (e.g., carbonate (CO_3^{2-}) and sulfate (SO_4^{2-})) in seawater may immediately form lead salts (lead sulfate ($PbSO_4$) and lead stearate ($Pb(C_{18}H_{35}O_2)_2$)) from lead carbonate ($PbCO_3$) in PVC floats via a surface ion exchange mechanism. In the present study, it is assumed that the total amount of Pb leaching into seawater becomes similar to that into pure water over the course of the infinitely long drift in the actual ocean, even if the leaching rate in pure water is different from that in seawater.

The 120-h leaching experiments were repeated four times (480 h total). Immediately after each experiment, all pure water in the glass vials was exchanged with new water to avoid equilibration of Pb concentration in the water. This water exchange allowed simulation of the situation in which seawater surrounding the PVC float continuously varies during long-distance transport in the ocean. After the fourth exchange, the floats used in the 120-h leaching experiments were scarified

Table 1
Experimental data used for estimating each leaching rate (R_i).

0-120 hours						240-360 hours		
Sample No.	R_{0-120} [µg hour^{-1}]	C_∞	[µg L^{-1}]	c_f [mg cm^{-3}]	a [cm^2]	Sample No.	$R_{240-360}$ [µg hour^{-1}]	C_∞ [µg L^{-1}]
1	1.0		146	6.3	129	1	0.16	24
2	0.7		96	6.4	132	2	0.10	15
3	1.0		146	6.4	132	3	0.10	14
4	1.1		157	6.3	132	4	0.15	22
5	0.5		68	5.8	136	5	0.16	23
6	1.0		142	6.5	132	6	0.15	23
7	1.0		147	6.5	132	7	0.15	21
8	1.1		163	6.4	139	8	0.17	26
9	1.1		164	6.3	136	9	0.14	20
10	0.7		95	6.4	136	10	0.13	19
Average	**0.9**		**132**	**6.3**	**134**	**Average**	**0.14**	**21**
Standard Deviation	0.23		33	2.0	2.9	Standard Deviation	0.025	3.5
Error	0.17		25	1.5	2.2	Error	0.018	2.7
120-240 hours						**360-480 hours**		
	$R_{120-240}$						$R_{360-480}$	
1	0.32		47			1	0.02	3.4
2	0.31		46			2	0.01	1.4
3	0.51		74			3	0.01	1.8
4	0.51		75			4	0.01	2.1
5	0.52		77			4	0.02	2.5
6	0.42		61			6	0.07	9.6
7	0.40		58			7	0.02	3.1
8	0.44		65			8	0.11	17
9	0.41		60			9	0.08	11
10	0.29		43			10	0.02	3.3
Average	**0.41**		**61**			**Average**	**0.04**	**5.5**
Standard Deviation	0.086		12			Standard Deviation	0.035	5.1
Error	0.065		9.5			Error	0.026	3.8

Refer to text for meaning of each variable.

with sandpaper (#120) and used again in the subsequent experiment with pure water. The latter experiment was conducted to reproduce the situation in which PVC floats washing ashore onto beaches are scarified by the abrasive action of coastal sand. It was confirmed that the sandpaper contained no Pb by analysis of 10 replicate measurements using XRF. As in the previous 120-h leaching experiments, 10 ml of water sampled every 24 h was injected into the ICP-MS to measure Pb concentration. To ensure accurate estimation of Pb leaching in pure water, Pb loss to the glass vial surfaces was evaluated by a recovery test (Nakashima et al., 2012). Analysis of data from this test indicated that an average 1.8% of Pb was lost on the glass surfaces, so this figure was added to the Pb mass that could leach for each glass vial. Although there were three concentration values that exceeded thrice the standard deviation from average in the first 120-h leaching experiment (samples 2, 5 and 10; Table 1), there was little variation during the next 120 to 480-h leaching experiments. Therefore, all data from every PVC float ($n = 10$) are reported here.

2.3. Computation of Pb Leaching Amount From a Single PVC Float

As shown later (Section 3.1), the amount of Pb leaching from the PVC floats decreased exponentially as the four 120-h leaching experiments were repeated. This suggests that Pb leaching from the floats also decreases during drift in the ocean although the leaching rate was underestimated in the experiments using pure water. Thus, we were able to estimate the total amount of Pb leaching from the floats during long-term transport as follows. First, the amount of Pb leaching from a float per unit time during each 120-h leaching experiment (hereafter referred to as "leaching rate (R)") was estimated by

$$R_i = C_\infty V / 120\,\text{h}, \tag{1}$$

where C_∞ denotes the Pb concentration at the end of each 120-h experiment, V is the volume of Elix pure water (0.82 l), and subscript i (0–120, 120–240, 240–360 and 360–480 h) refers to periods of each experiment. Leaching rates in every experiment were calculated over the entire experimental duration of 480 h.

Each leaching rate R_i computed in the four 120-h leaching experiments was regarded as the value at the midpoint of each experimental period (i.e., 60, 180, 300 and 420 h from the beginning of the first 120-h experiment), and was approximated by the following exponential equation using a least squares method.

$$R(t) = R_0 e^{-\alpha t}, \tag{2}$$

where $R(t)$ symbolizes the leaching rate as a function of time (t), R_0 is the initial leaching rate, and α is the leaching coefficient. Temporally integrating Eq. (2) from 0 to infinity yields the total amount of Pb that can leach from a single PVC float (M; g, hereafter referred to as total leaching amount of Pb), as follows:

$$M = \int_0^\infty R_0 e^{-\alpha t}\,\mathrm{d}t. \tag{3}$$

As shown later (Section 3.1), we assumed that the PVC float after the leaching experiments might be covered by a "low-Pb layer," in which Pb concentration became negligibly small because of diffusion from the float surface to the surrounding water as shown later in Section 3.1. Thus, finally, the thickness (d; m) of that low-Pb layer, defined as that from which Pb leaches from a PVC float, was simply estimated as

$$d = M/(\overline{a c_f}), \tag{4}$$

where $\overline{a}$ is the average surface area of the float and $\overline{c_f}$ is the average Pb mass per unit volume of the float (measured by XRF). The units of $\overline{c_f}$ are weight per unit volume (i.e., 6.3×10^{-3} g cm^{-3} (i.e., 6.3 mg cm^{-3}) as shown in Table 1). Eq. (4) assumes that all Pb within the layer thickness ($= d a c_f$) leaches completely to the surrounding water, and the Pb concentration within the layer becomes negligibly small insufficient for a Fickian diffusion process (leaching) to be continued afterward.

2.4. Observation of Surface Scratches on PVC Float Surface Using a Metallograph

Of particular interest is whether scratches observed on PVC floats washed ashore on beaches are deeper than the thickness of the low-Pb layer mentioned above. If this is the case, it is likely that Pb beneath the low-Pb layer formed during oceanic transport would leach onto the beaches through any physical damage, such as scratching by coastal sand. We could simulate this "re-leaching" in the leaching experiments using the PVC float scratched by sandpaper.

We compared depths of surface scratches on three PVC floats that were purchased (new) and artificially scarified, collected on Inoda Beach (Fig. 1a) on 11 March 2011. Cross-sections of each PVC float were observed by a metallograph (VANOX-T, AHMT-513, Olympus Corp., Tokyo, Japan) appropriate for measuring the layer thickness computed in the study (Section 3.2). A new, unused PVC float was also observed for reference. Before measurement, each float was cut into 2-cm squares, and each segment was fixed in a cup filled with epoxy resin liquid composed of epoxy hardener and EpoxyCure® epoxy resin (Buehler, Lake Bluff, Illinois, USA). The mixed epoxy resin liquid was solidified at room temperature under atmospheric pressure overnight. To observe cross-sections, each fixed segment was ground under 3 lb pressure by a grinder (Beta & Vector, Buehler) with a coarse file (#280), second-cut file (#320), and smooth file (#600) for 3 min each. The cross-sections of PVC floats were photographed using 100
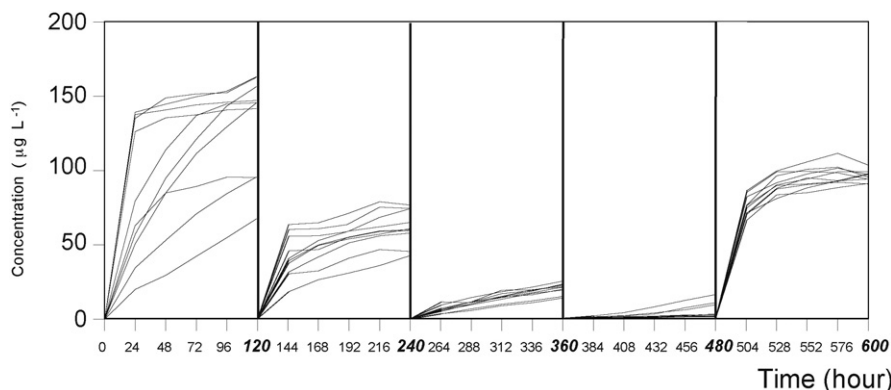

Fig. 2. Results of leaching experiments using purchased PVC floats. Curves indicate Pb concentration (ordinate) in water versus time (abscissa).

Table 2
Leaching rate (R_i) estimated at four 120-h leaching experiments.

Sample No.	R_{0-120} [µg hour^{-1}]	$R_{120-240}$	$R_{240-360}$	$R_{360-480}$	R_0 [µg hour^{-1}]	α [hour^{-1}]
1	1.0	0.32	0.16	0.02	2.1	0.010
2	0.7	0.31	0.10	0.01	1.9	0.012
3	1.0	0.51	0.10	0.01	3.3	0.013
4	1.1	0.51	0.15	0.01	3.7	0.013
5	0.5	0.52	0.16	0.02	1.5	0.0090
6	1.0	0.42	0.15	0.07	1.6	0.0080
7	1.0	0.40	0.15	0.02	2.4	0.011
8	1.1	0.44	0.17	0.11	1.5	0.0070
9	1.1	0.41	0.14	0.08	1.6	0.0070
10	0.7	0.29	0.13	0.02	1.5	0.010
Average					**2.1**	**0.010**
Standard Deviation					0.8	0.0023
Error					0.6	0.0023
					R_0	α
					2.1 ± 0.6	**0.010 ± 0.0023**

These values are used for compute initial leaching rate (R_0) and leaching coefficient (α) by least squares fit of Eq. (2).

magnifications with a camera attached to the metallograph, allowing the depth of flaws on the float surface to be observed directly.

3. Results and Discussion

3.1. Transport Potential of Additive-derived Pb in a PVC Float

The results obtained in leaching experiments are shown in Table 1 and Fig. 2. New PVC floats before the leaching experiment contained high level of additive-Pb such as 6.3 ± 1.5 mg cm^{-3} shown as c_f in Table 1 (which is equivalent to 5100 ± 74.3 mg kg^{-1}). This corresponds approximately to 201 ± 2.9 mg per float (39.5 g). Curves in Fig. 2 show that Pb concentrations in the water of the glass vials increased with time in each 120-h leaching experiment, and appeared to reach an equilibrium at the end of those experiments. The maximum concentration (C_∞) of Pb in water reached approximately 70 to 150 µg l^{-1} after the first 120-h experiment, but diminished to <20 µg l^{-1} after 480 h (Fig. 2). This indicates that leaching of additive-derived Pb from the PVC floats ended within a relatively short period (~480 h).

In the fourth experiment, Pb leaching to the surrounding water largely disappeared. According to the Fickian diffusion, the leaching amount is proportional to $\kappa c_f - c$, where κ denotes the non-zero partition coefficient and c the Pb concentration of the surrounding water (Nakashima et al., 2012). Note that κ is obtained as C_∞/c_f and thus, it is

a dimensionless number. c in Elix pure water at the beginning of each 120-h experiment was always zero. Thus, the disappearance of the leaching at the end of the experiment suggests that c_f became negligibly small at least on the float surface, and that the float might be covered by the low-Pb layer described in Section 2.3.

We were able to confirm that the low-Pb layer is very thin by scarifying the surface of PVC floats. That is, C_∞ in the glass vials increased to two-thirds of that found in the first 120-h leaching experiment (Fig. 2). This result indicates that the low-Pb layer is probably sufficiently thin so as to be broken by the sandpaper abrasion. It is reasonable to believe that additive-derived Pb leaches only from the thin layer near the float surface into seawater. This is likely because water penetrability of hydrophobic plastic is low, and because the mass transport in the interior of the floats is much slower than that in the thin surface layer into which seawater penetrates. It is therefore possible that the additive-derived Pb contained inside the floats can be carried a long distance in seawater before leaching onto beaches.

3.2. Estimation of Low-Pb Layer Thickness

To prove that Pb contained in the PVC floats leaches after scratching by beach sand, it was necessary to confirm whether the depth of flaws on the floats littering the beaches was substantially deeper than the
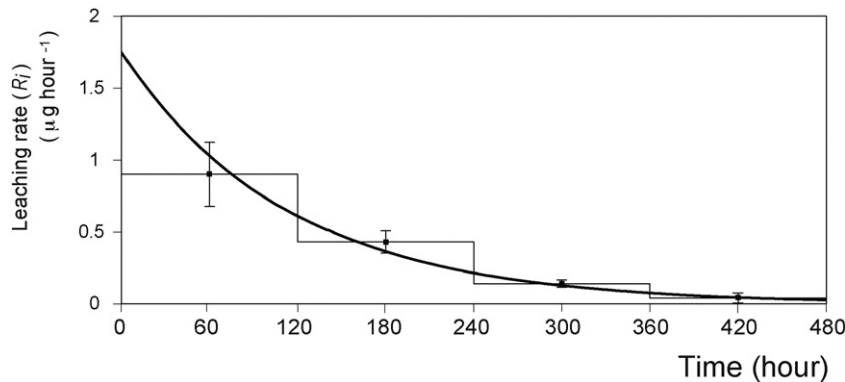
Fig. 3. Leaching rates (R_i in Eq. (1); closed squares with bars show standard deviations) computed on the basis of four 120-h leaching experiments. Also shown is the curve fit by an exponential formula. In fitting by least squares, leaching rate is at midpoint of each experimental period shown by steps.

(a)

(b)

(c)
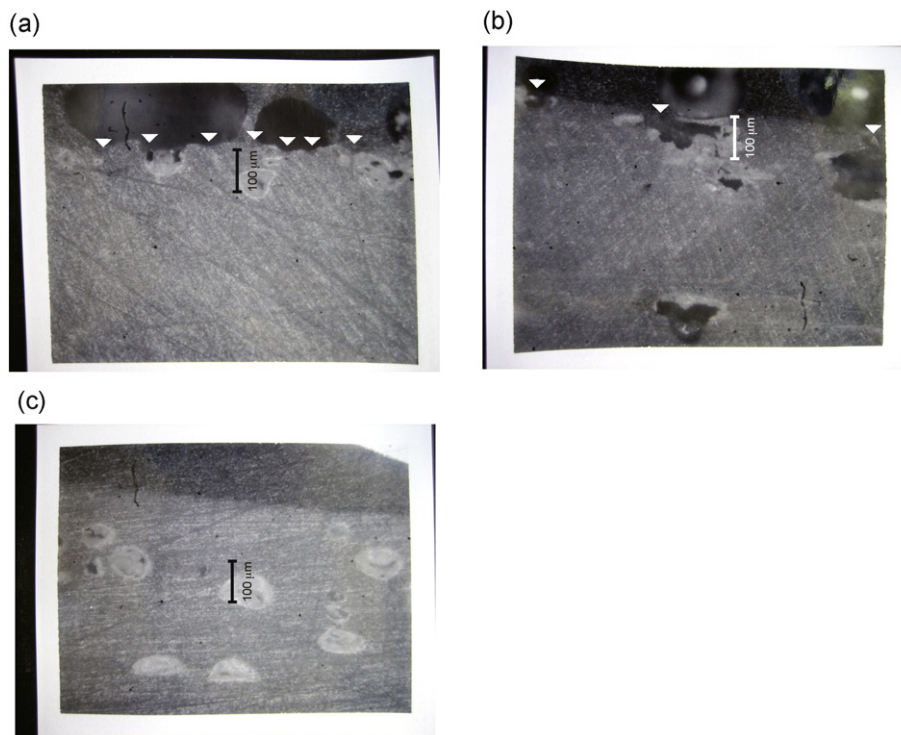
Fig. 4. Photographs of cross-sections of (a) scratched PVC float, (b) littered PVC float, and (c) new PVC float as reference. Visually substantial flaws marked by inverted triangles. Reference scale in the panels represents 100 μm.

thickness of the aforementioned low-Pb layer. We therefore estimated the thickness of that layer.

First, a discrete set of each R_i obtained in the four 120-h leaching experiments was fit by Eq. (2) with a least squares method. R_i of ten samples was used to obtain the exponential function in that equation independently, and R_0 and α were then averaged (Table 2). Average R_0 and α were 2.1 μg h^{-1} and 0.010 h^{-1}, respectively, with the margin of error deduced as $\pm 0.8 \times 2.262/\sqrt{10-1} \approx \pm 0.6$ μg h^{-1}, where 2.262 is area of the t-distribution at 95% confidence level with degree of freedom 9. Error of α was estimated in the same manner as R_0. Thus, an exponential curve (Fig. 3) was approximated using $R(t) = (2.1 \pm 0.6)e^{-(0.010 \pm 0.0023)t}$, where units of $R(t)$ are μg h^{-1}, and hours for t. Temporal integration of the approximate leaching rate $R(t) = R_0 e^{-\alpha t}$ from $t = 0$ to infinity enables estimation of M by $M = R_0/\alpha = 2.1/0.010 = 210$ μg. In addition, error propagation in this estimation was computed by $\pm \sqrt{(0.6/2.1)^2 + (0.0023/0.010)^2} \times 210$ μg $\approx \pm 73$ μg. This total leaching amount is equivalent to approximately 0.1% of total Pb (201 mg) per PVC float.

Next, we estimated d of the low-Pb layer. Substituting M, $\overline{a}$ and $\overline{c_f}$ (Table 1) into the right-hand side of Eq. (4), we obtained $d = 2.5$ μm. In addition, error propagation in this estimation was computed as $\pm \sqrt{(73/210)^2 + (2.9/133)^2 + (2.0/6.3)^2} \times 2.5$ μm $\approx \pm 1.2$ μm.

3.3. Measurement of Scratch Depths on PVC Float Surfaces Littering Beaches

To confirm whether flaws on the surface of PVC floats littering the beaches are sufficiently deep for Pb to leach out, cross-sections of a float artificially scarified by sandpaper, floats littering Inoda Beach, and a new float purchased from a manufacturer were photographed with a metallograph (Fig. 4a, b and c, respectively). Depths were visually measured with each reference scale. Flaw depths on the artificially scarified PVC float were ~20 μm (Fig. 4a). The litter PVC float was damaged, with flaws between 50 μm and 100 μm in depth (Fig. 4b). In contrast,

the new PVC float had no damage on its surface (Fig. 4c). The observations of the artificially scarified float indicate that flaw depths on its surface scratched by sandpaper were an order of magnitude larger than the layer thickness 2.5 ± 1.2 μm. Thus, it is reasonable to conclude that the low-Pb layer was broken by sandpaper scarifying before the 480–600-h experiment shown in Fig. 2, and that Pb contained inside the float re-leached in that experiment. It was also found that the PVC floats scarified on the beaches had flaws significantly deeper than the low-Pb layer. The suggestion here is that Pb preserved in PVC floats during long-distance transport over the sea will again leach Pb upon destruction of the thin low-Pb layer washing ashore. Hence, plastic PVC floats can carry potentially toxic additive Pb over long distances, releasing that Pb as a pollutant into the marine/beach environment by breaking of the low-Pb layer on beaches.

Nevertheless, there remains a question regarding the leaching rate in actual conditions. In the present study, pure water was used for all leaching experiments for ease of experimentation and analysis. In reality, there is leaching of metals from marine plastic debris in seawater. The seawater may accelerate leaching to a rate faster than in our study. Further, the leaching of metals from marine plastic debris into the surrounding seawater may be inhibited by microbial biofilms covering the debris (Lobelle and Cunliffe, 2011), hydrophobic compounds such as POPs adsorbed on the surface (Bakir et al., 2012), and aquatic ion metals repeating an adsorption–desorption cycle on marine plastic litter (Holmes et al., 2010). Thus, the leaching rate, total amount of Pb leaching from PVC floats, and low-Pb layer thickness are quantified more precisely in the actual oceans.

4. Conclusions

The processes uncovered in the present study are as follows. A single plastic fishery float contains additive-Pb with the high concentration of 5100 ± 74.3 mg kg^{-1}. After sequential 480-h leaching experiments using pure water, the total leaching amount is approximately 0.1% of total Pb in a single float. Therefore, additive Pb within the PVC floats

leached only from a thin layer on the float surface during long-distance drift on the sea. PVC floats are covered by a low-Pb layer generated by diffusion control, and Pb within the floats is prevented from leaching into seawater during transport. Pb leaches out when the floats are washed ashore on beaches, because the aforesaid layer is broken by physical damage such as scratching by coastal sand. Thus, additive Pb potentially travels long distances in the ocean because the PVC floats act as an effective transport vector.

Finally, although not a subject in the present work, the speed of Pb leaching from microplastics may be much higher than that computed herein, because of their large surface area to volume ratio. Hopefully, the present study is a step toward evaluating the environmental risk of marine/beach plastic debris to the marine ecosystem.

Acknowledgments

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