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Toxic Metals Derived from Plastic Litter on a Beach

Etsuko NAKASHIMA, Atsuhiko ISOBE, Shin'ichiro KAKO,
Takaaki ITAI and Shin TAKAHASHI

*Center for Marine Environmental Studies (CMES), Ehime University,
Bunkyo-cho 2-5, Matsuyama, Ehime 790-8577, Japan*

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Abstract—Toxic metals are widely used in plastic products as plasticizers, these toxic metals may leach out into marine environment when plastic are degraded. In order to evaluate this risk, we attempted to quantify the toxic metals derived from marine plastic litter. We had preliminary estimated the quantity of macro plastic litter (530 ± 201 kg) using combination of aerial photography, *in situ* mass measurements and identification of plastic litter. In this study, we further developed the previous study into the quantification of toxic metals derived from plastic litter over a beach using a handheld X-ray fluorescence (XRF) analyzer. As a result, the mass of lead (Pb) over the Ookushi beach was the greatest (315 ± 227 g) than other metals. Especially, PVC fishing floats contribute the abundance of Pb. These toxic metals within polymers are often used in pigments and are potentially released into the beach environment after degradation of plastics.

Keywords: marine/beach litter, balloon aerial photography, types of polymers, toxic metals

INTRODUCTION

The marine pollution by beach litter has been recognized as a serious trans-border environmental issue due to their flotation and transportation over a long distance (Coe and Rogers, 1997). Hence, the protection of the marine environment from such pollution must involve international cooperation with neighboring countries. On the other hand, marine litter poses a great threat to marine wildlife because of the ingestion of plastics by animals and entanglement in drift nets (Derraik, 2002). In polymers, toxic metals are widely used as plasticizers, catalysts, stabilizing additives, and pigments (Takahashi *et al.*, 1999, 2008; Teuten *et al.*, 2009; Sakai *et al.*, 2009). These metals may leach out and transfer from the plastic to animals in the environment when plastic are degraded or digested. However, only few reports on toxic metals derived from marine litter are available (Teuten *et al.*, 2009). Hence, the objectives of this study are (i) to develop a reliable new method to measure the total litter mass over a beach and (ii) to quantify the mass of toxic metals in marine plastic litter over a beach. To this end, we attempt to use a balloon attached with a digital camera and a handheld XRF analyzer.

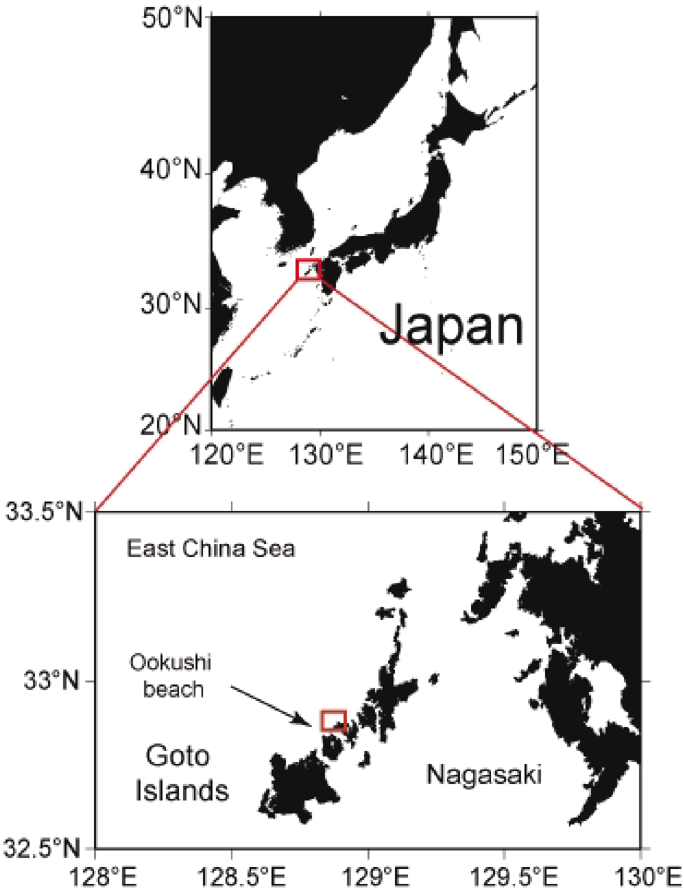

Fig. 1. Study area. The location of Ookushi beach, Goto Islands with their enlarged map.

MATERIALS AND METHODS

Measurement of total litter weight over Ookushi beach

A beach survey was carried out on October 22, 2009 on the Ookushi beach in Goto Islands, Nagasaki, Japan (Fig. 1). Ookushi beach is located neither within a narrow channel nor behind a headland (see Fig. 1), and thus it can be assumed that the beach is directly influenced by litter floating across the East China Sea with north-eastward ocean currents (Isobe, 2008). Moreover, because of its inaccessibility, this beach is unlikely to be cleaned and thus it is an appropriate beach on which to base a case study on the mass and composition of beach litter in the absence of direct anthropogenic disturbance. Our previous paper (Nakashima *et al.*, 2011a) presented preliminary data on the mass of plastic litter (kg) over the

Table 1. Estimation of mass of toxic metals over the Ookushi beach. Mass of type of polymer were cited from Nakashima *et al.* (2011b).

		PE (n = 549)	PP (n = 294)	PET (n = 75)	PVC (n = 17)	PS (n = 39)	Total
Cr	Litter mass (kg)	292 ± 120	102 ± 52	—	—	—	
	Concentration (mg/kg)	25 ± 10	33 ± 20	<LOQ	<LOQ	<LOQ	
	Standard Deviation	119	177				
	Mass of metal (g)	7 ± 4	3 ± 3	—	—	—	11 ± 5
Cd	Litter mass	292 ± 120	—	—	19 ± 13	—	
	Concentration	34 ± 16	<LOQ	<LOQ	150 ± 57	<LOQ	
	Standard Deviation	187			106		
	Mass of metal	10 ± 6	—	—	3 ± 2	—	13 ± 7
Sn	Litter mass	—	—	—	19 ± 13	—	
	Concentration	<LOQ	<LOQ	<LOQ	570 ± 360	<LOQ	
	Standard Deviation				682		
	Mass of metal	—	—	—	11 ± 10	—	11 ± 10
Sb	Litter mass	—	102 ± 52	69 ± 46	—	—	
	Concentration	<LOQ	100 ± 127	180 ± 16	<LOQ	<LOQ	
	Standard Deviation		1108	68			
	Mass of metal	—	10 ± 14	12 ± 9	—	—	22 ± 16
Pb	Litter mass	292 ± 120	102 ± 52	—	19 ± 13	—	
	Concentration	90 ± 40	86 ± 60	<LOQ	15,000 ± 6,200	<LOQ	
	Standard Deviation	477	523		11,688		
	Mass of metal	26 ± 16	9 ± 8	—	280 ± 226	—	315 ± 227

Ookushi beach based on their type of polymer. The data were shown in Table 1. So here Subsection "Measurement of total litter weight over Ookushi beach" briefly describes the quantitative methods we implemented in previous study. Refer to Nakashima *et al.* (2011a) for a thorough description.

Measurements of the beach litter density were carried out on 23, October, 2009, a day after the taking aerial photography, on the Ookushi beach. We randomly placed ten square boxes each with an area of 4 m^2 (2 m $\times$ 2 m) over where the litter covered completely. The densities of litter vary largely among the boxes as shown later, so the estimating the density of litter per unit area (kg/m^2) requires the estimate of the margin of error, on the basis of a *t*-test with the confidence limit of 95%.

In order to estimate the total litter mass (kg) over the beach by multiplying the total litter-covered area (m^2) obtained by aerial photography with measurements of the beach litter mass per unit area (kg/m^2).

Sampling and classification of beach litter material

Besides the *in-situ* beach survey mentioned above, we collected litter samples randomly from each square box on the Ookushi beach to investigate the materials in it, especially the types of plastics and polymers. To measure the weight of each material, all litter samples carried to our laboratory were classified into specific categories: plastic, multiple material products (e.g., beach sandals), polystyrene foam, wood products, metal, glass, rubber, fabric, paper, vinyl and others. Plastic samples were further investigated using a near-infrared spectrometer for plastics (Plascan-SH, OPT Research Inc., Tokyo, Japan) to identify their polymer types such as polyethylene (PE), polypropylene (PP), poly ethylene terephthalate (PET), poly vinyl chloride (PVC), polystyrene (PS), acrylonitile-butadiene-stylene (ABS), acrylonitrile-stylene (AS), polyamide (PA) and polyurethane (PUR). In our preliminary study (Nakashima *et al.*, 2011a), it had been already found that PE, PP, PET, PVC, PS accounted for 98% among plastic litter collected from the Ookushi beach. Therefore, our quantification of the total masse of plastic litter (kg) was focused on these 5 types of polymer over the Ookushi beach. The mass were quantified by multiplying the mass (kg) of plastic litter with the mass ratio of type of polymer by considering the propagation of error. The result is shown in Table 1. 974 samples had been selected randomly from all collected samples preceded to the next step; the analysis of toxic metals using XRF analyzer.

Analytical procedure and data processing

In this study, a XRF analyzers (Innov-X Systems, Inc., MA, U.S.A.), had been employed because it was expected that there was large margins of error of concentrations of toxic metals due to variations of litter. The conventional methods such as technique using inductivity coupled plasma mass spectrometry system (ICP-MS) require a considerable amount of time for preparation and analysis of samples. Therefore we can say a handheld XRF analyzer is an

Table 2. Quantative limitation of variation of XRF analyzer (Innov-X, alpha-6500) for analysis of plastic. Quantative limitation were determined by 30 measurements of polyethylene virgin pellets (Grand Polymer Co. Ltd., Japan). Variation of analysis were examined by 30 measurements of standard reference materials (EC680k, EC681k: European Reference Materials).

	Cr	Cd	Sn	Sb	Pb
Quantative limitation [mg/kg]	15	60	37	17	12
Variation [%]	7.7	9.3	13	16	3.5

appropriate analyzer for quantification of toxic metals in plastic litter. This handheld XRF allows us to estimate of margin of error with large amount of samples such as 974 pieces of samples.

We had focus our effort on the 5 elements; chromium (Cr), cadmium (Cd), tin (Sn), antimony (Sb) and lead (Pb) which were detected in marine plastic samples (Nakashima *et al.*, 2011b) and they are designated as toxic substances in the Agency for Toxic Substances & Disease Registry (ATSDR), U.S.A. Quantitation limit (10σ) of these elements were determined (Table 2), they are examined by 10 times duplicate measurements of virgin PE pellets (Grand Polymer Co. Ltd., Japan).

In the quantification process, the concentration less than quantative limit is assumed to be zero (0 mg/kg). The measurements of sample were performed by repeating 10 times per sample due to their uncertainty (Table 2). The values are averaged as one sample value. The concentrations of metals are averaged and estimated the margin of error based on types of polymers. Error is calculated using a *t*-test with confidence interval and are converted into error estimate of mass by considering the propagation of error. Only averaged concentrations of toxic metals more than quantative limit of XRF analyzer are shown. Multiplying the concentration (mg/kg) with the mass (g) of each polymer litter gives us the total mass (g) of toxic metals carried by plastic litter. The calculated masses (g) of metals based on types of polymers are summed as total mass by considering the propagation of error. All quantative values in Table 1 are rounded to be practical based on integral number.

RESULTS AND DISCUSSION

Total mass of plastic litter and each polymer on the Ookushi beach

Nakashima *et al.*, (2011a) already reported the total area covered by beach litter was found to be 123.5 m^2 on Ookushi beach, Nagasaki, Japan. The mass of marine litter within the 10 boxes placed on beach ranged was 5.8 ± 2.1 kg/m^2. The standard deviation (2.8 kg/m^2) was used to calculate the margin of error for the density. The margined of error was calculated as $\pm 2.262 \times 2.8/\sqrt{9} \approx \pm 2.1$ kg/m^2 by a *t*-test with a 95% confidence interval, where the value 2.262 is the area of *t*-distribution at 95% confidence limit with 9 as the degree of freedom. This density

Table 3. Frequency of toxic metals in plastic litter over the Ookushi beach.

	Cencentration (mg/kg)	Pieces of litter				
		PE	PP	PET	PVC	PS
Cr	<LOQ-10^2	482	257	75	16	39
	10^2–10^3	35	19	0	0	0
	10^3–10^4	29	15	0	1	0
	10^4–10^5	3	3	0	0	0
	Total	549	294	75	17	39
Cd	<LOQ-10^2	505	283	75	13	38
	10^2–10^3	14	5	0	3	1
	10^3–10^4	23	5	0	1	0
	10^4–10^5	7	1	0	0	0
	Total	549	294	75	17	39
Sn	<LOQ-10^2	540	292	75	9	38
	10^2–10^3	6	1	0	2	1
	10^3–10^4	3	1	0	5	0
	10^4–10^5	0	0	0	1	0
	Total	549	294	75	17	39
Sb	<LOQ-10^2	526	281	10	16	37
	10^2–10^3	9	4	0	1	1
	10^3–10^4	13	7	65	0	1
	10^4–10^5	1	2	0	0	0
	Total	549	294	75	17	39
Pb	<LOQ-10^2	429	233	75	3	32
	10^2–10^3	49	27	0	0	4
	10^3–10^4	62	30	0	0	0
	10^4–10^5	9	4	0	3	0
	10^4–10^6	0	0	0	11	0
	Total	549	294	75	17	36

variability is derived mainly from the fact that the material composition inside the boxes varies largely. Multiplying the total litter-covered area (123.5 m^2) by the average density of litter (5.8 kg/m^2) gives an approximate total litter mass for the entire beach of 716 kg. Hence, the margin of error for the total litter mass was calculated to be ±259 kg by multiplying the above margin of error (±2.1 kg/m^2) by calculated total litter-covered area on the beach (123.5 m^2). Therefore, total mass of marine litter was estimated as 716 ± 259 kg.

Since plastics accounted for 74% among materials found in the samples of litter from Ookushi beach. Multiplying the total mass of beach litter (716 ± 259 kg) by the mass ratio of plastic litter (70 ± 10%) gives an approximate total plastic litter mass for the entire beach 530 ± 201 kg. To calculate the total mass of toxic metals incorporated in plastic litter, we multiply the average percent by mass of each type of polymer (Table 1) by the estimated total plastic litter mass of 530 ± 201 kg. This gives us the total mass of each type of polymer (Table 1). The error estimates for each are calculated using the standard deviation derived from the measurements in each box using the same method used to calculate the total mass of litter on the beach (i.e., *t*-test with the 95% confidence interval).

Quantification of concentration and mass of toxic metals

The concentrations of toxic metals range from less than the quantification limits to more than 10,000 mg/kg. Table 3 shows the frequency for concentration of each toxic metal based on each type of polymer, in which almost toxic metals tend to be distributed in lower concentration. However, some samples contained in plastic litter exceed 100 mg/kg which is the EU regulation on packaging and packaging wastes (12% of 974). The concentrations of toxic metals reveal a different tendency in each type of polymer. Especially, PVC plastic litter often content Cd, Sn and Pb with over 100 mg/kg. Sb more than 100 mg/kg was also detected with a high frequency from PET plastic litter (Table 3). Therefore, we estimated the range of toxic metals based on their type of polymer as shown Table 1. Here we take Pb in PE as an example for the estimation of range of concentration of toxic metals. The standard deviation (477 mg/kg) was used to calculate the margin of error for the density. The margined of error was calculated as $\pm 1.96 \times 477/\sqrt{549-1} \approx \pm 40$ mg/kg by a *t*-test with a 95% confidence interval, where the value 1.96 is the area of *t*-distribution at 95% confidence limit with more than 200 as the degree of freedom. 549 is the number of PE sample. The range of concentration of Pb in PE is estimated as 90 ± 40 mg/kg.

Now it is possible to estimate the total mass (g) of toxic metals by plastic litter over Ookushi beach by multiplying the concentration (mg/kg) with the estimated mass of plastic polymer over the beach. Here we demonstrate the quantification of toxic metals taking Pb as example. 292 kg × 90 mg/kg ≈ 26 g, where 292 ± 120 kg is the mass of PE litter. Propagation of error is also considered as follow. $\sqrt{(120/292)^2 + (40/90)^2} \times 26 \approx 16$. The concentration of Pb in PE was calculated as 26 ± 16 g. In the same way, total masses of toxic metals over the beach are calculated as shown Table 1. The greatest toxic metal over a Ookushi beach was Pb such as 315 ± 227 g, especially, PVC fishing floats are strongly contribute to their mass.

We have considered a reliable method to estimate the total weight of toxic metals carried by plastic litter over the beach. This value will be useful for evaluating environmental risks caused by plastic litter. However, more work is required to understand better their risk for marine animals. Therefore, our next step would be to evaluate the risk of toxic metal leaching from marine plastic litter over a beach.

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E. Nakashima (e-mail: nshima@mepl1.cmes.ehime-u.ac.jp)