

## Toxic Metals in Polyethylene Plastic Litter

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**Abstract**—In this study we established a novel and reliable method to estimate the total weight of beach litter and metal content of such litter material in Ookushi beach, Goto Island, Japan. Using a digital camera attached to a balloon, we calculated the area of beach covered by litter, and then conducted *in-situ* measurements of the litter weight. By multiplying this area (123.5 m<sup>2</sup>) by the average litter-weight per unit area, the weight of beach litter was estimated as 716 ± 259 kg using a *t*-test with 95% confidence limit. Among the randomly collected beach litter, plastics comprised 74% of the total weight, of which light plastics such as polyethylene (PE; 234 ± 96 kg) were prevalent. Concentrations of toxic metals were estimated using handheld X-ray fluorescence analyzer. Among various toxic metals, lead (Pb) and total chromium (Cr) were detected in PE plastic litter. The concentration of Pb and total Cr of PE litter was estimated as 45 ± 14 mg/kg and 14 ± 6 mg/kg respectively. Thereafter, total Pb and total Cr were calculated as 10 ± 5 g and 3 ± 2 g, respectively. These heavy metals within polymers are often used in pigments and are potentially released into the beach environment.

**Keywords:** marine/beach litter, balloon aerial photography, polymer types, 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 (Morrison, 1999).

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). However, only few reports on chemical pollution derived from marine litter are available (Teuten *et al.*, 2009). In a study to quantify the chemical substances carried by litter, in the present study, first, we established a reliable

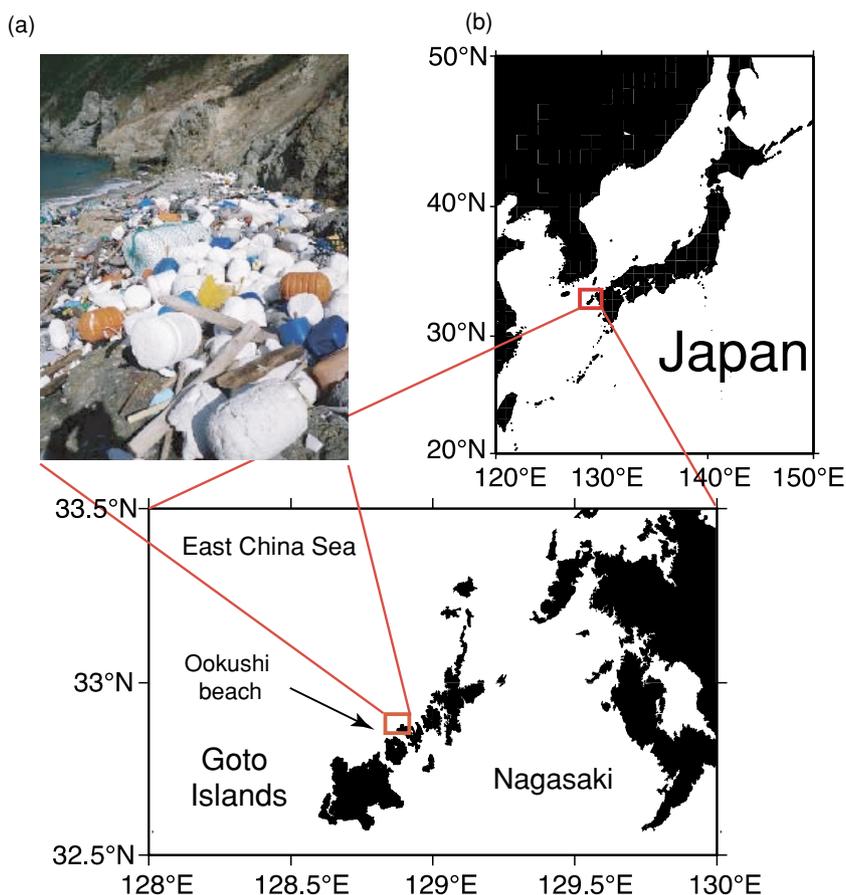


Fig. 1. Study area. (a) Beach litter photograph taken in Goto Islands, Nagasaki, Japan (b) the location of Goto Islands with their enlarged map.

method to measure the litter-covered area over a beach by aerial photography using a digital camera attached to a balloon. Next, special attention was given to differentiate plastic litter into their polymer types (e.g., polypropylene, polyethylene, and so forth) using a near-infrared spectrometer. Different chemicals are present in different quantities in plastic polymer types (Takahashi *et al.*, 1999, 2008; Teuten *et al.*, 2009). Then, to estimate litter-borne chemical substances, we measured toxic metals in marine plastic litter collected from Ookushi beach, using handheld X-ray fluorescence analyzer. Thus, we were able to estimate the total weight of toxic metals (mg) carried by plastic litter by multiplying the estimated plastic litter's weight (kg) by the amount of toxic metals measured by fluorescence analyzer (mg/kg). This is the first study to attempt to estimate the total weight of toxic metals derived from marine plastic litter over a beach.

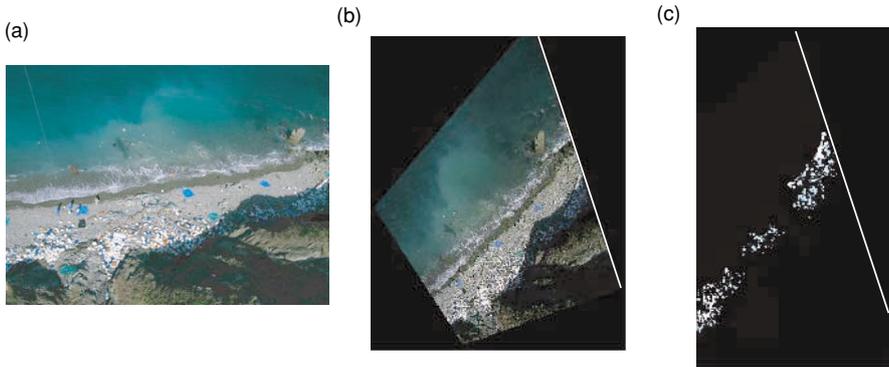


Fig. 2. Photos taken by balloon aerial photography. (a) One of the original photographs of entire coast taken by the aerial camera. (c) A converted image after applying the projective transformation to (b). (d) Lightness map on which pixels with lightness higher (smaller) than the threshold value were changed to white (black) ones.

## 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). This beach has never been cleaned up because of its inaccessibility, and so we could investigate the amount and composition of litter here to understand the litter scenario in the absence of external disturbance. The details of the method of measurement of total litter weight over Ookushi beach has been described by Nakashima *et al.* (2010).

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  $4 \text{ m}^2$  ( $2 \text{ m} \times 2 \text{ m}$ ) over where the litter covered completely. The densities of litter very largely among the boxes as shown later, so the estimating the density of litter per unit area requires the estimate of the margin of error, on the basis of a *t*-test with the confidence limit of 95%.

### *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

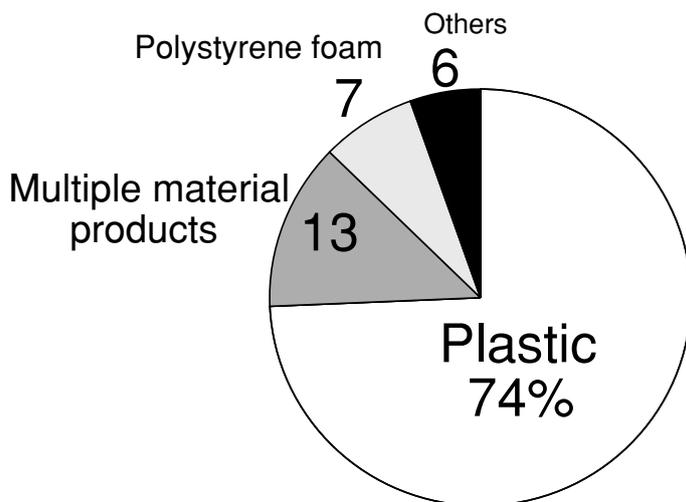


Fig. 3. Composition (%) of marine litter collected from Ookushi beach.

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), acrylonitrile-butadiene-styrene (ABS), acrylonitrile-styrene (AS), polyamide (PA) and polyurethane (PUR).

#### *Chemical analysis*

The handheld XRF analyzers (Innov-X, a-6500) used in this study was manufactured by Innov-X Systems, Inc., Woburn, MA. The traditional analysis requires the use of large non-portable systems and sample pre-treatments. The advantage of this handheld XRF analyzer is the nondestructive inspection; this unit enabled us a prompt measurement analysis of toxic metals in litter samples.

The present study focused on lead (Pb) and total chromium (Cr) because these toxic elements are regulated by EU regulation on packaging and packaging waste. Accuracy of these analyses was examined using standard reference materials, EC680k and EC681k (European Reference Materials). Uncertainty in measurement of Pb and total Cr range from 3.5% to 7.6% as determined by 10 measurements using the reference materials.

Quantitation limit ( $10\sigma$ ) of Pb and total Cr were determined, 11 mg/kg and 12 mg/kg found by 10 times duplicate measurements of virgin PE pellets (Grand Polymer Co. Ltd. Japan).

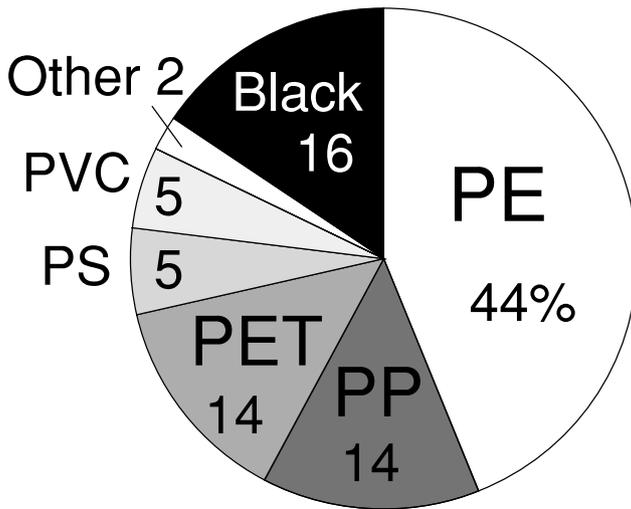


Fig. 4. Composition (%) of marine plastic litter identified using near-infrared spectrometer for plastics.

## RESULTS

### *Total weight of beach litter on the Ookushi beach*

We computed the total weight of litter washed ashore on the Ookushi beach using the area computed by balloon aerial photography (Fig. 2) in conjunction with *in-situ* litter-density measurements inside the ten square boxes. The total area covered by beach litter was found as  $123.5 \text{ m}^2$  by counting pixels on the entire beach. The average of litter density within the ten boxes placed on Ookushi beach was  $5.8 \text{ kg/m}^2$ . Multiplying the total litter-covered area ( $123.5 \text{ m}^2$ ) by the averaged litter density yields the best estimate of the total litter weights to be  $716 \pm 259 \text{ kg}$  by a *t*-test with a 95% confidence limit.

### *Composition and total weight of each polymer type*

Plastics prevail among various materials inside the ten boxes on the Ookushi beach as also observed globally by Derraik (2002). The weight of plastics accounts for 74% (Fig. 3, i.e.,  $532 \pm 202 \text{ kg}$ ) of all materials on the Ookushi beach. Furthermore smaller density plastics such as PE (polyethylene) was predominant than heavier materials (Fig. 4). Therefore, in the present study, we focused on the estimation of toxic heavy metals derived from PE plastic litter on the Ookushi beach.

### *Amount of toxic heavy metals derived from marine litter polyethylene plastics*

Pb and total Cr were measured by analyzing 432 pieces of plastic samples in

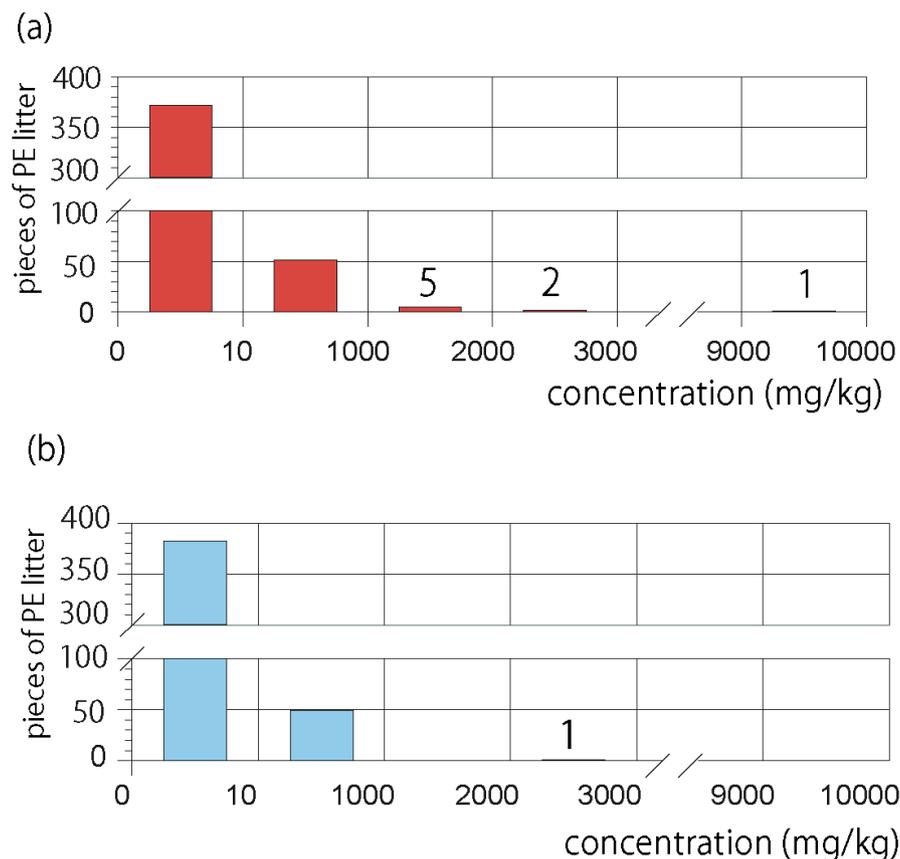


Fig. 5. Frequency plot for concentration ranges of total Cr (a) and Pb (b) in PE plastic litter collected from Ookushi beach.

PE plastic litter collected from Ookushi beach. The levels of Pb and total Cr ranged from less than the quantification limit to 10,000 mg/kg. Figure 5 shows the concentration (mg/kg) of Pb and Cr derived from polystyrene plastic litter. Pb and total Cr contained in PE plastic litter occasionally exceeded 100 mg/kg which is regulated by EU regulation on packaging and packaging waste.

#### DISCUSSION

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. Multiplying the weight percents averaged for each polymer type by the estimated plastic litter weight of  $532 \pm 202$  kg over the beach yielded the weight of PE plastics.

Although concentrations of Pb and total Cr vary largely, we computed the

average and standard deviation of Pb and total Cr, respectively as follows: The concentrations of Pb and total Cr derived from PE plastic litter over Ookushi beach was estimated at  $45 \pm 14$  mg/kg and  $14 \pm 6$  mg/kg, respectively. Therefore, it is possible to estimate the total weight of beach Pb and total Cr carried by PE litter by multiplying the concentration with the estimated PE plastic weight over the beach ( $234 \pm 96$  kg): Pb and total Cr were calculated as  $10 \pm 5$  g and  $3 \pm 2$  g, respectively.

These heavy metals within polymers are often used in pigments such as lead chromate (Sakai *et al.*, 2009) and are potentially released into the beach environment during degradation of plastics. Additionally, highly toxic organic tin compounds were also detected in plastic products made from PVC (Takahashi *et al.*, 1999; Kawamura *et al.*, 2000). These chemical compounds in polymers are widely used for plasticizers, catalysts, stabilizing additives, and pigments. A reliable method to uncover these unknown litter sources and metals is the next target of our litter research.

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