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Regional distribution of styrene analogues generated from polystyrene degradation along the coastlines of the North-East Pacific Ocean and Hawaii

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ABSTRACT

Beach sand and seawater taken from the coastlines of the North-East Pacific Ocean and Hawaii State were investigated to determine the causes of global chemical contamination from polystyrene (PS). All samples were found to contain styrene monomer (SM), styrene dimers (SD), and styrene trimers (ST) with a concentration distribution of styrene analogues in the order of ST > SD > SM. The contamination by styrene analogues along the West Coast proved more severe than in Alaska and other regions. The Western Coastlines of the USA seem be affected by both land- and ocean-based pollution sources, which might result from it being a heavily populated area as the data suggest a possible proportional relationship between PS pollution and population. Our results suggest the presence of new global chemical contaminants derived from PS in the ocean, and along coasts.

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1. Introduction

Plastics have become indispensable for modern life and, over the past six decades the rapid expansion of human activities has increased plastic production significantly, making the disposal of plastic materials a huge waste management problem (Rochman et al., 2013). The ocean now serves as the ultimate sink for plastic waste as well as a host of other synthetic chemicals. In the ocean discarded plastic breaks into smaller plastic debris, which fragments into microplastics (- μm particles: <1 mm) that directly affect animal life and increase human health risks (Browne et al., 2008; Thompson et al., 2004). Plastic fragments pose a significant hazard to many marine animals, through entanglement, smothering, and ingestion (Avery-Gomm et al., 2012; Derraik, 2002; Laist,

1987; Stephanis et al., 2013). Plastic debris can also act as a vector for transporting persistent, bio-accumulating and toxic substances (Frias et al., 2010; Colabuono et al., 2010; Koelmans et al., 2013; Teuten et al., 2007; UNEP, 2011). Unfortunately, plastic debris is found everywhere in the oceans and coastal seawaters. The ubiquitous presence of anthropogenic plastic wastes must be recognized as an urgent global environmental issue (UNEP, 2011).

Despite the growing concern of plastic marine contamination as a major environmental problem no quantitative description exists for the extent of plastic pollution in the ocean (Rochman et al., 2013; UNEP, 2011). The only indicator for quantitatively explaining plastic marine pollution is the concentration (or density) of plastic debris, established by counting the number of plastic debris per unit area (Browne et al., 2010; Law et al., 2010; Rees and Pond, 1995; Ryan, 2013; Thompson et al., 2004). This counting technique assumes the detection of all floating debris within a fixed distance of a ship, however, the detection is easily influenced by differences in the sampling techniques and detection of plastic debris due to

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size, type and density (Rees and Pond, 1995). The extent of violations of this assumption varies among the studies, producing many biases (Law et al., 2010; Ryan, 2013). In particular, the method suggests a greater abundance of small debris compared to large debris (Ryan, 2013). Using counting this technique on the surface seawaters of the western North Atlantic Ocean and the Caribbean Sea, during 22-year period from 1986 to 2008 showed no significant increase or strong temporal trend in the concentration of plastic debris (Law et al., 2010). As a result, there are no data available to confirm oceanic sinks caused by visible plastic debris; explaining the presence of unknown sinks of plastic debris in the marine environment requires a new indicator or data.

Due to their resistance to physical, chemical and biological degradation, plastics (as polymers) are considered to be stable materials (Lithner et al., 2011; Lucas et al., 2008) and are widely considered to not decompose at low temperature, through light or wave action. However, there remains a significant absence of quantitative information on the sinks of plastic debris in the ocean, i.e., the degradation of plastic debris. Recently the authors of this study have discovered that even in daily life polystyrene (PS) as a plastic polymer can decompose even at low temperatures (Saido et al., 2003, 2012). Therefore, it is likely the huge quantities of PS plastic waste scattered throughout oceans generate copious quantities of degraded and eluted products, which may dissolve in any body of water or adsorb on the surface of sandy soil (Saido et al., 2014). Furthermore, although plastic polymers do not interfere with biochemical activity, such as a biodegradation (Guillet et al., 1974; Jones et al., 1974; Lucas et al., 2008; Premraj and Doble, 2005), when they degrade into low molecular weight chemicals, such as styrene monomer (SM) and styrene analogues or oligomers (styrene dimer: SD; styrene trimer: ST), plastic polymers may pose a significant threat to living organisms (Kitamura et al., 2003; Ohyama et al., 2001). This study examines this aspect in detail, to determine the mechanism or the process by which the decomposition of PS generates chemicals. This represents a first step in establishing the relationship between plastic pollution from PS in the ocean and styrene analogues as low molecular weight chemicals.

This study reports on the regional distribution of styrene analogues originating from PS decomposition as a sink in the coastline of the North-East Pacific Ocean and Hawaiian Islands. This study relied on a practical sampling technique applicable to seawater and sand sample, to measure the extent of PS pollution in those regions.

2. Materials and methods

2.1. Chemicals and materials

Previous studies provide detailed description of the standard preparation of SM, 2,4-diphenyl-1-butene (SD1), 1,3-diphenyl propane (SD2), and 2,4,6-triphenyl-1-hexene (ST) used in this study (Saido et al., 2003, 2014). Briefly, commercial PS virgin pellets (average number of molecular weight: 500,000, Teijin Chem., Japan) were dissolved in 500 mL benzene, precipitated in 1500 mL methanol, and allowed to dry in vacuo (3 mm Torr). Precipitated PS and a heating medium, polyethylene glycol (PEG, reagent grade, Wako Chem., Tokyo, Japan), were added in a submerged round-bottomed flask and thermally decomposed at 280 °C for 120 min. Thermally decomposed products were dissolved and recovered in 10 mL benzene, which was transferred into a separatory funnel, and washed three times with 10 mL pure water to remove PEG. After freezing for 3 h at −80 °C to facilitate the precipitation, the mixture was thawed and centrifuged at 5000 rpm for 10 min. Mixing the supernatant with approximately 10 g of anhydrous sodium sulfate removed the water content overnight. The standard working materials, including SM, SD1, SD2, and ST, were prepared after filtering. The standard materials were determined quantitatively by a gas chromatograph/mass spectrophotometer (GC/MS) adopted internal standard method. Hereafter, the sum of the concentrations of SD1 and SD2 will be referred to as SD.

The dichloromethane (DCM) extraction solvent, biphenyl (BP) surrogate and phenanthrene (PH) used as an internal standard were of reagent grade and purchased from Wako Chem. (Tokyo, Japan). The study also used ACS grade reagents obtained from Sigma−Aldrich. All solutions were made with high-purity water from a Millipore ultrapurification system (>18 MΩ cm).

2.2. Field sampling and preparation

Seawater and sand samples were collected from each coast of the region selected in this study (see Fig. 1 and Supplementary Material Table S1 and Fig. S1–S4); sampling method used at each coast sampling point is described in detail in previous studies (Saido et al., 2003, 2014), with sand samples taken from the surface at low and high tides and from a 30 cm depth along the seashore. Approximately 100 g sand was collected, and stored in a glass container.

Seawater samples were taken from a water depth of 40 cm, and subjected to cotton plug filtration using a stainless steel beaker. The volume of seawater sampled was 2.5 L; in the field the seawater sample spiked with surrogate BP was immediately extracted with a portable shaker (Sanada Co., Tokyo, Japan) with an extraction condition of 40 stroke min^{-1}; each sample was extracted four times, with a total 100 mL DCM. Equipment containing plastic material was excluded from all experimental procedures to eliminate any errors in the sampling and extraction.

2.3. Sample preparation in the laboratory

Subsequent to dehydration by freeze-drying overnight, the sand samples were measured to within 5.0 g using a balance and spiked with surrogate BP prior to extraction (Saido et al., 2003, 2014). Each sand sample was extracted with 5 mL benzene by ultrasonication for 1 min. This extraction step was repeated four times and the extracts combined to 20 mL and evaporated to dryness by a rotary evaporator at 30 °C. After adding 0.5 mg L^{-1} PH as an internal standard, the eluate was completely dissolved into 1 mL of benzene.

For seawater samples, in the field about 100 mL of the DCM extract was mixed with approximately 10 g anhydrous sodium sulfate overnight. The extract was evaporated to dryness by a rotary evaporator at 30 °C. After adding 0.5 mg L^{-1} PH as an internal standard, the eluate was completely dissolved into 1 mL of benzene.

2.4. Analytical method

Previous studies describe the analytical method used in this study in detail (Saido et al., 2003, 2014) using an HP 6890 GC with a JEOL Auto MS-II equipped with a 30 m × 0.32 mm i.d. (0.25 μm film thickness) DB-1 capillary column (J&W Scientific, Folsom, CA). The MS was operated at 70 eV in the electron ionization mode. The mass scanning range for styrene analogues was from m/z 78 to 312. The ion source temperature was maintained at 200 °C with an interface temperature of 250 °C. The injector was held at 250 °C with 1 μL of extract injected in splitless mode. Helium was used as a carrier gas with a constant flow of 1.4 mL min^{-1}. The oven temperatures were: standby at 40 °C for 5 min, ramped to 290 °C at 15 °C min^{-1}, and held for 5 min. The total run time was 30 min. BP and PH were used as surrogate and internal standard, respectively.

2.5. Calibration and recovery test

Serial dilutions of the stock standard solution produced a standard mixed solution containing SM, SD, and ST. The MS of each standard substance was obtained in the total ion monitor of GC/MS scanning mode. The monitoring channel for target chemicals in the selected ion detection was set by determining the m/z of the main fragmented ions. The calibration curve of each target chemical was obtained using
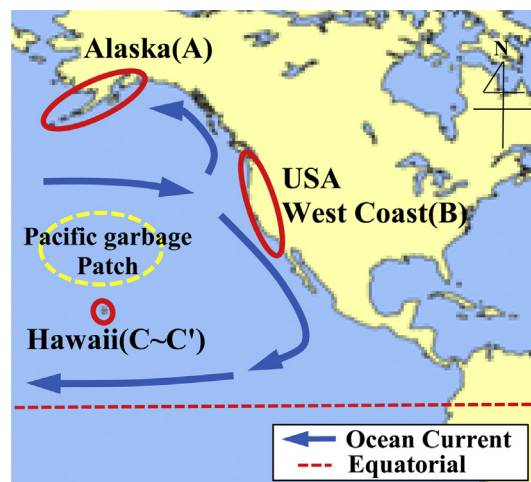

Fig. 1. Regions for monitoring the concentrations of styrene analogues (Detailed sampling locations are shown in the Supporting Information: Table 1S and Figs. 1S–5S).