Marine Pollution Bulletin 99 (2015) 28–34

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Persistent organic pollutants carried on plastic resin pellets from two beaches in China

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ARTICLE INFO

Article history:
Received 5 January 2015
Revised 31 July 2015
Accepted 2 August 2015
Available online 19 August 2015

Keywords:
Microplastics
PCBs
PAHs
OCPs

ABSTRACT

Microplastics provide a mechanism for the long-range transport of hydrophobic chemical contaminants to remote coastal and marine locations. In this study, plastic resin pellets were collected from Zhengmingsi Beach and Dongshan Beach in China. The collected pellets were analyzed for PAHs, PCBs, HCHs, DDTs, chlordane, heptachlor, endosulfan, aldrin, dieldrin and endrin. The total concentration of PCBs ranged from 34.7–213.7 ng g^{-1} and from 21.5–323.2 ng g^{-1} in plastic resin pellets for Zhengmingsi Beach and Dongshan Beach respectively. The highest concentrations of PCBs were observed for congeners 44, 110, 138, 155 and 200. The total concentration of PAHs ranged from 136.3–1586.9 ng g^{-1} and from 397.6–2384.2 ng g^{-1} in the plastic pellets, whereas DDTs concentration ranged from 1.2–101.5 ng g^{-1} and from 1.5–127.0 ng g^{-1} for the two beaches. The elevated concentrations of pollutants appear to be related to extensive industrial development, agricultural activity and the use of coal in the area.

1. Introduction

Although concern about small plastic debris in the oceans was reported in the early 1970s (Carpenter et al., 1972; Carpenter and Smith, 1972; Colton et al., 1974), its potential ecological effects have grained significant attention in recent years. Part of the concern with plastic debris originates from its widespread, nearly ubiquitous, distribution both in open waters and coastal areas. In fact, it is estimated that plastics represent between 60% and 80% of the total quantity of debris in marine environments (Gregory and Ryan, 1997; Derraik, 2002). Once released to the environment, the particles may be broken into smaller pieces, and because they decompose at an extremely slow rate and float, may be transported 100s to potentially 1000s of km from their origin. During transport, small pieces of the plastic debris may be ingestion by biota, a process that has been shown to directly harm a wide range of marine organisms (Thompson et al., 2004; Teuten and Rowland, 2007; Browne et al., 2008; Boerger et al., 2010; Murray and Cowie, 2011; van Franeker et al., 2011; Cole et al., 2013; Rochman et al., 2013; Tanaka et al., 2013). In addition, plastic debris tends to exhibit a relatively large ratio of surface area to volume and, combined with their chemically reactive nature, have a significant ability to accumulate (sorb) hydrophobic persistent organic pollutants (POPs) such as PCBs, PAHs, DDT and Hexachlorocyclohexane (HCHs) from water and the atmosphere onto the particle surface (Mato et al., 2001; Ogata et al., 2009). The sorption of contaminants on particles that are <5 mm in size (referred to as microplastics) is particularly high. Within a few weeks microplastic particles can accumulate pollutants on the particle surface at concentrations that are orders of magnitude greater than in the surrounding water (Mato et al., 2001; Teuten et al., 2009; Rios et al., 2010; Hirai et al., 2011). Following sorption onto the particles, the contaminants are carried along with the plastics from their original source (Endo et al., 2005; Ogata et al., 2009; Galgani et al., 2010; Van et al., 2012). Thus, microplastics have a large capacity to facilitate the transport of contaminants through the marine environment. If the microplastics are ingested by biota, the accumulated contaminants may be leached (desorbed) and accumulated in organisms, after which they may even be transferred through the food chain (Engler, 2012; Wright et al., 2013).

Two types of microplastics have been extensively examined in the literature: (1) pieces of plastic that have been broken off of larger, manufactured plastic products, and (2) pellets composed of plastic resin that represent the raw materials from which plastic products are manufactured. Both may be composed of a wide range of mass-produced compounds including polyethylene terephthalate (PET), high-density polyethylene (HDPE), polyvinyl chloride

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http://dx.doi.org/10.1016/j.marpolbul.2015.08.002
0025-326X/

(PVC), low-density polyethylene (LDPE), polypropylene (PP) and polystyrene (PS). In this study we focus on plastic resin pellets because they normally do not contain dyes, initially exhibit very low levels of POPs and, therefore, with regards to chemical monitoring, are easier to study than fragments of plastic associated with manufactured products (Fotopoulou et al., 2012). These plastic pellets are cylinder or disk shaped, and are general small (<a few mm in diameter). Studies have found that they are often unintentionally released into the environment during production and transport, after which they are discharged to the marine environment via streams and rivers (Galgani et al., 2010).

Earlier studies of plastic pellets have argued that based on their ability to accumulate POPs, their relative abundance on coastal beaches, and the ability to easily collected large numbers of pellets from most sites, they can serve as passive sampling media to identify pollution hot spots on a global scale (Ogata et al., 2009). This led in 2006 to the launch of the "International Pellet Watch" programme, a programme that analyzes pellets obtained from concerned citizens from around the world to identify and map POPs concentrations. However, while the "International Pellet Watch" programme has obtained samples from Hong Kong, additional data from coastal areas in China are lacking. Furthermore, the existence and concentration of many POPs such as organochlorine pesticides (OCPs) in plastic marine debris has rarely been reported in the previous literature. Though some kinds of pesticide are not used worldwide, others have been widely used both locally and regionally for a long period. These pesticides often can be detected in the soil or water in high concentrations.

Pellets have been used for monitoring purposes to determine spatial variations in the degree of contamination on a global scale, their use to determine the source of organic pollutants has received much less attention though some of research discussed this topic (Van et al., 2012; Mizukawa et al., 2013). In this study, plastic resin pellets were sampled from two beaches in China in July 2012. As teratogenic effect, carcinogenic effect, mutagenic effect, PCBs, DDTs, HCHs, chlordane, heptachlor, endosulfan, aldrin, dieldrin and endrin were listed as Priority Pollutants for elimination on Stockholm Convention on POPs, as well as PAHs also have "three effects" role and are ubiquitous in the environment, these specific organic pollutants carried on pellets are chosen as detected pollutants.

We selected two beaches for study that are characterized by very different pollution regimes, environments that are characterized by different potential sources of contamination. One of the objectives is to study whether the pellets reflect the primary sources of contamination that occur within that particular area, another focus area is on the monitoring of pesticides.

2. Materials and methods

2.1. Sample collection

Plastic resin pellets were collected from two coastal areas in July 2012, Dongshan Beach (39.1318N°, 122.0907E°) and Zhengmingsi Beach (39.9154°, 119.6202E°), the location of the beaches is shown as Fig. 1a. Zhengmingsi Beach is located along the northern coast of the Yellow Sea (Fig. 1b). Dongshan Beach is located along the west coast of the Bohai Sea, adjacent to the Xinkai and Tang estuaries. It is positioned about 2 km from the port of Qinghuangdao, China's largest transportation port of coal (Fig. 1c).

The sampling area on the beaches extended from the edge of the water to the average high tide lines. Plastic resin pellets were identified by the "naked" eye, separated from the sand using forceps, and stored in aluminum foil at 4 °C. A total of 90 plastic resin pellets were collected from Zhengmingsi Beach, whereas a total of 130 were collected from Dongshan Beach for laboratory analysis. In the laboratory, 10 pellets were randomly selected from the total number of pellets collected at a given beach and composited to form a single sample. Thus, 9 samples were analyzed from Zhengmingsi Beach; 13 from Bongshan Beach. In order to make the results of this study comparable to other previous studies, median values are were reported for the analyzed constituents.

2.2. Sample preparation and analysis

Solvents (hexane, dichloromethane, acetone and nonane) used in the analyses were pesticide grade and purchased from Fisher Scientific (J.T. Baker, USA). Sodium sulfate and silica gel (100–200 mesh size) were analytical grade and purchased from Beijing Chemical Reagent Company (Beijing, China). A gas Chromatograph-Mass Spectrometer (GC/MS) was used to analyze for 20 PCB congeners (IUPAC No. 8, 18, 28, 52, 44, 66, 101, 110, 118, 105, 149, 153, 138, 158, 128, 187, 180, 170, 206), 16 PAHs (Naphthalene (Nap), Acenaphthylene (Any), Acenaphthene (Ace), Fluorene (Flu), Phenanthrene (Phe), Anthracene (Ant), Fluoranthene (Fla), Pyrene (Pyr), Benzo(a)anthracene (BaA), Chrysene (Chr), BbF Benzo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(a)pyrene (BaP), Indeno (1,2,3-cd) pyrene (IPY), Dibenzo(a,h)anthracene (DbA), Benzo[ghi]perylene (BghiP)), and DDE. The remaining contaminants, including pp′-DDD, pp′-DDD, HCHs (α-HCH, β-HCH, γ-HCH, δ-HCH), chlordane, heptachlor, endosulfan, aldrin, dieldrin and endrin, were analyzed using a gas chromatograph–election capture detector (GC–ECD).

2.3. Sample analyses

Contaminants associated with the plastic resin pellets were extracted with 10 mL hexane in an ultrasonic bath for 30 min with a 10 μL spiking of the surrogate standard. This procedure was repeated twice, after which the extracts were combined. The extracts were concentrated with a rotary evaporator, and cleaned using multilayer silica columns. The columns were filled from the bottom with 4 g of activated silica gel and 6 g of florisil topped with 1 g of anhydrous Na_2SO_4, and eluted with 40 mL hexane and 80 mL hexane/methylene chloride (1:1, v:v). The first fraction included PCBs, p,p′-DDE and partial Naphthalene. The second fraction contained most PAHs and OCP compounds. Both the eluents were collected and concentrated to 1 mL under a gentle N_2 stream. Known quantities of an internal standard were added to the samples prior to instrumental analysis.

2.4. Quality assurance and quality control

Strict quality controls were implemented to ensure the correct identification and accurate quantification of the target compounds. All equipment was thoroughly rinsed with dichloromethane before and after a set of analysis, and these sample preparations were conducted in a super clean lab to avoid background contamination. Six sample blanks were analyzed and the results demonstrated that all targeted compounds in the blanks were below detection limits. The method's Detection Limits (MDL), calculated as 10 times the standard deviation of the minimum standard solution, were 0.3 ng g^{-1} for PAHs, 0.07 ng g^{-1} for PCBs, 0.027 ng g^{-1} for α-666; 0.052 ng g^{-1} for β-666, 0.026 ng g^{-1} for γ-666, 0.024 ng g^{-1} for δ-666, 0.028 ng g^{-1} for heptachlor, 0.025 ng g^{-1} for aldrin, 0.041 ng g^{-1} for pp′-DDD, 0.028 ng g^{-1} for pp′-DDE, 0.041 ng g^{-1} for pp′-DDT, 0.029 ng g^{-1} for for dieldrin, 0.038 ng g^{-1} for endrin, 0.028 ng g^{-1} for α-endosulfan, 0.036 ng g^{-1} for β-endosulfan, 0.043 ng g^{-1} for Endosulfan sulfate, 0.034 ng g^{-1} for cis-Chlordane 0.033 ng g^{-1} for trans-Chlordane. The final