Marine Pollution Bulletin xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Marine Pollution Bulletin

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

Spatial variability in the concentrations of metals in beached microplastics

M.C. Vedolin[a,*], C.Y.S. Teophilo[a], A. Turra[b], R.C.L. Figueira[a]

[a] *Laboratório de Química Inorgânica Marinha, Departamento de Oceanografia Química, Instituto Oceanográfico, USP, São Paulo, SP, Brazil*
[b] *Laboratório de Manejo, Ecologia e Conservação Marinha, Departamento de Oceanografia Biológica, Instituto Oceanográfico, USP, São Paulo, SP, Brazil*

ARTICLE INFO

Keywords:
Pellets
Microplastics
Metals
Inorganic pollutants
Pollution
São Paulo coast

ABSTRACT

Heavy metals and microplastics have been considered as threats to the marine environment and the interactions between these two pollutants are poorly understood. This study investigates the interactions between metals adsorbed in pellets collected randomly from 19 beaches along the coast of São Paulo State in southeastern Brazil, comparing these levels with those in virgin pellets. The samples were analyzed for Al, Cr, Cu, Fe, Mn, Sn, Ti and Zn by inductively coupled plasma optical emission spectroscopy (ICP-OES). The polymers were solubilized via acid digestion. The highest levels occurred with Fe (227.78 mg kg^{-1} - Itaguaré) and Al (45.27 mg kg^{-1} - Guaraú) in the same areas, which are closer to the Port of Santos. The metal adsorption on pellets collected is greater than that on virgin pellets. In this context, pellets can be considered to be a carrier for the transport of metals in the environment, even in small quantities.

1. Introduction

Since the development of the first synthetic polymer, “Bakelite”, in 1909, a number of low cost techniques have been developed to produce a plastic product that is durable, inert and resistant (Plastics Europe, 2011). However, the properties that make plastics so useful (e.g., low density, durability) have created a problem related to the management of waste due to improper discarding (Barnes et al., 2009; Hopewell et al., 2009), especially in the oceans.

Microplastics are commonly defined as any plastic particles measuring < 5 mm in diameter, but they can also be classified as “primary microplastics”, which include production pellets and microbeads, or “secondary microplastics”, which come from larger plastic items that have degraded and consequently fragmented (Andrady, 2011; GESAMP, 2016). Plastic pellets are composed of polymers, usually polyethylene, polystyrene or polypropylene; these pellets are from 2 to 5 mm in diameter and are used as raw materials in the production of plastic items (Ogata et al., 2009). They can be found in a range of aquatic environments, which suggests that they can be lost during loading and transportation, both on land and at sea, and during their handling at plastic transformation factories and harbors (Carpenter et al., 1972; Gregory, 1977, 1978; Ryan, 1988; EPA, 1992; Mato et al., 2001; Moore et al., 2001a; Reddy et al., 2006; Costa et al., 2009; Ogata et al., 2009).

In addition to their visual impacts, microplastics in the marine environment are a threat to animals by accumulation, entrapment, entanglement, suffocation and fouling (Thompson et al., 2004; Colabuono et al., 2009; Gregory, 2009; Majer et al., 2012; GESAMP, 2016). In the marine environment, these particles are able to sequester contaminants from sea water, contaminants such as polychlorinated biphenyl (PCB), dichlorodiphenyltrichloroethane (DDT), polycyclic aromatic hydrocarbons (PAHs) and metals (Mato et al., 2001; Endo et al., 2005; Ogata et al., 2009; Ashton et al., 2010; Holmes et al., 2012, 2014; Brennecke et al., 2016). Thus, they can act as a source of these contaminants to organisms via ingestion, since they may be mistaken for food items (Teuten et al., 2009) or accidentally ingested by filter-feeders (Santana et al., 2016a). Most of these pollutants are toxic and bioaccumulative, and if leached from pellets and assimilated by an organism, can be introduced into the food chain (Browne et al., 2013).

Until recently, interactions between metals and plastic pellets had not been considered, because polymers are considered to be relatively inert toward aqueous metal ions (Plastics Europe, 2011). However, recent studies recorded the presence of adsorbed metals in plastics due to surface alterations in the marine environment (Ashton et al., 2010; Holmes et al., 2012, 2014). Fotopoulou and Karapanagioti (2012) described the surface of beached pellets as rough and with pronounced cavities compared to virgin pellets. These alterations increase the surface area and generate anionic active sites such as carbonyls for the adsorption of metals from seawater (Holmes et al., 2012, 2014), which might explain why there are lower concentrations of trace metals in newly released (virgin) pellets than in beached pellets.

The sources of metals to the oceans are diverse, though many arise

---

[*] Corresponding author at: Departamento de Oceanografia Química, Instituto Oceanográfico, Universidade de São Paulo, Praça do Oceanográfico, 191, Cidade Universitária, São Paulo, SP 05508-120, Brazil.

E-mail address: ma.vedolin@usp.br (M.C. Vedolin).

http://dx.doi.org/10.1016/j.marpolbul.2017.10.019
Received 11 April 2017; Received in revised form 5 October 2017; Accepted 7 October 2017

Please cite this article as: Vedolin, M.C., Marine Pollution Bulletin (2017), http://dx.doi.org/10.1016/j.marpolbul.2017.10.019

from the irresponsible dumping of sewage, of industrial and household waste and many other sources, such as release from surfaces covered by antifouling coatings, or urban drainage, atmospheric deposition, disposal of mining residues, among others. Some metals found on plastic debris derive from the manufacturing process (additives), but several metals have been found to occur on plastic debris as a result of environmental sorption (Holmes et al., 2012, 2014; Rochman et al., 2014). Nobre et al. (2015) showed that beached pellets have lower toxicity than virgin pellets, although their toxicity may vary as a function of the different additives, like organic compounds, used in their production.

The environmental risks posed by microplastics are defined as a combination of their presence (number; e.g., Turra et al., 2014) and potential effects on the environment (e.g., concentration of contaminants such as PCBs and PAHs) (GESAMP, 2016). Recent studies have shown the spatial variability of the contamination in beached pellets by organic pollutants on various spatial scales ranging from meters to global (Ogata et al., 2009; Karapanagioti and Klontza, 2008; Karapanagioti et al., 2010; Frias et al., 2010; Hirai et al., 2011; Heskett et al., 2012; Fisner et al., 2013a, 2013b; Taniguchi et al., 2016), but no information is available about the concentrations of metals specific to the Brazil area. The main objective was to determine the concentrations of metals in pellets from 19 beaches along the coast of the São Paulo state, assess their variability and also compare them to those levels found in virgin pellets.

2. Materials and methods

2.1. Sampling

This investigation was developed on the coast of São Paulo State in southeastern Brazil (23°21′54.20″S/44°44′21.94″O and 25°18′30.81″S/48° 5′37.25″O). São Paulo has a coastline of approximately 620 km, which is highly urbanized, especially in the central coast region known as “Baixada Santista”. This region is heavily impacted by the Port of Santos (the largest port in Latin American) and the Industrial Complex of Cubatão (Harari and Gordon, 2001; Silva et al., 2011). As a result of the anthropogenic activities in this area, many pollutants, such as PCBs and PAHs, have been found in sediment samples (Bícego et al., 2006). The transport of plastic pellets through Santos Harbor is responsible for 50,000 tons of granules/month (Fisner et al., 2013a, 2013b), and a large quantity of pellets has been reported on nearby beaches (Turra et al., 2014; Moreira et al., 2016).

Pellets were collected randomly from nineteen coastal beaches along the São Paulo coast during 2012 (Fig. 1). Approximately 300 pellets were collected by hand from each site and stored in polyethylene bags. Each sample was washed with sea-water and dried under ambient conditions. In the laboratory, pellets from each site were pooled in 3 replicates with 100 pellets for subsequent analyses.

2.2. Sample digestion

The samples of beached pellets were subjected to partial acid digestion following the method US EPA 3050B (USEPA, 1996). The three 100 pools of pellets (~2 g each) were taken in a 50 mL beaker and then 10 mL of HNO_3 (1:1), 5 mL of pure HNO_3, 3.0 mL of H_2O_2 (30% V/V), and 10 mL of HCl were added at 90 °C. Subsequently, these digests were filtered and diluted to 40 mL with Millipore Milli-Q water. The samples were analyzed for Al, Cr, Cu, Fe, Mn, Sn, Ti and Zn by inductively coupled plasma optical emission spectroscopy (ICP-OES; Varian, model 710ES).

Pellets were analyzed as sediment samples, i.e., we assumed that they have some capacity to adsorb and desorb (leach) metals and other chemical compounds on/from their surfaces; thus, they were considered as a potential source of contamination for the marine environment. In this way, one certified reference material for sediment (SS-1) from EnvironMAT™ SPC Science were subjected to the same analytical procedure in order to evaluate the precision and accuracy of the method. Additionally, four types (polypropylene, high density polyethylene and two grades/colors of polyethylene, black and blue) of virgin resin pellets were obtained from a local plastic processing facility (Braskem SA, São Paulo) and analyzed accordingly for comparison with the data collected from the beached pellets.

2.3. Data analysis

Differences in the levels of metals between each site were evaluated using a non- parametric Kruskal-Wallis test followed by the post hoc Dunn's test. The elements Cr and Sn, which usually exhibited values below the detection limit of the method were excluded from analyses. Differences between virgin pellets samples were also evaluated using ANOVA (one-way) followed by the post hoc Tukey test.

To visualize the similarities among and between samples (beached and virgins), a non-Metric Multidimensional Scaling (nMDS) was applied to the similarity matrix (Bray Curtis similarity) and permutational multivariate analyses of variance (PERMANOVA). The trace statistic for the null hypothesis of no group differences was calculated with 999 permutations.

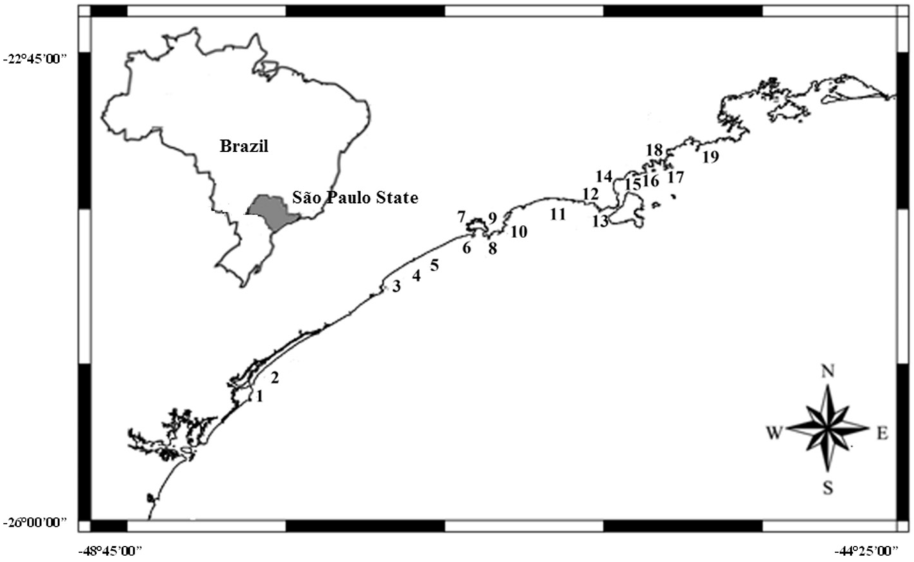

Fig. 1. Beaches (municipalities) where pellets were sampled along the São Paulo state coast in 2012. Note: 1- Cardoso Island (Cananeia); 2- Boqueirão do Sul (Ilha Comprida); 3- Arpoador (Peruíbe); 4- Guaraú (Peruíbe); 5- Ruínas (Peruíbe); 6- Sonho (Itanhaém); 7- Vila São Paulo (SP) (Mongaguá); 8- Guilhermina (Praia Grande); 9- Gonzaga (Santos); 10- Enseada (Guarujá); 11- Itaguaré (Bertioga); 12- Boraceia (São Sebastião); 13- Santiago (São Sebastião); 14- Massaguaçu (Caraguatatuba); 15- Tabatinga (Caraguatatuba); 16- Sete Fontes (Ubatuba); 17- Anchieta Island (Ubatuba); 18- Grande (Ubatuba); and 19- Fazenda (Ubatuba).