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Spatial variability in persistent organic pollutants and polycyclic aromatic hydrocarbons found in beach-stranded pellets along the coast of the state of São Paulo, southeastern Brazil

Satie Taniguchi [a,*], Fernanda I. Colabuono [a], Patrick S. Dias [a], Renato Oliveira [a], Mara Fisner [a], Alexander Turra [a], Gabriel M. Izar [c], Denis M.S. Abessa [c], Mahua Saha [b], Junki Hosoda [b], Rei Yamashita [b], Hideshige Takada [b], Rafael A. Lourenço [a], Caio A. Magalhães [a], Márcia C. Bícego [a], Rosalinda C. Montone [a]

[a] Universidade de São Paulo, Instituto Oceanográfico, Praça do Oceanográfico, 191, 05508-120 São Paulo, SP, Brazil
[b] Laboratory of Organic Geochemistry, Tokyo University of Agriculture and Technology, Tokyo, Japan
[c] Universidade Estadual Paulista (UNESP), Praça Infante D. Henrique s/n°, 11330-900 São Vicente, SP, Brazil

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ABSTRACT

High spatial variability in polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organochlorine pesticides, such as DDTs, and polybrominated diphenylethers was observed in plastic pellets collected randomly from 41 beaches (15 cities) in 2010 from the coast of state of São Paulo, southeastern Brazil. The highest concentrations ranged, in ng g^{-1}, from 192 to 13,708, 3.41 to 7554 and <0.11 to 840 for PAHs, PCBs and DDTs, respectively. Similar distribution pattern was presented, with lower concentrations on the relatively less urbanized and industrialized southern coast, and the highest values in the central portion of the coastline, which is affected by both waste disposal and large port and industrial complex. Additional samples were collected in this central area and PCB concentrations, in ng g^{-1}, were much higher in 2012 (1569 to 10,504) than in 2009/2010 (173 to 309) and 2014 (411), which is likely related to leakages of the PCB commercial mixture.

1. Introduction

The shoreline of the state of São Paulo is located on the southeastern coast of Brazil, extends for 860 km and includes one of the most economically important metropolitan areas in South America. Sixteen cities make up the São Paulo shoreline, with a total of 2.166 million habitants (Brasil, 2015) and the same problems as all large coastal metropolises, such as atmospheric pollution (Lamparelli et al., 2001), overpopulation during holidays and the summer season, and large quantities of inadequately managed waste (Gutberlet, 1997), such as the Santos sewage outfall, which is a significant source of contamination in Santos Bay (Abessa et al., 2005). Moreover, the existence of a major industrial center (Cubatão Industrial Complex), the largest port (Port of Santos) and the largest oil terminal (Almirante Barroso Maritime Terminal) in Latin America also contribute significantly to the input of organic contaminants in the marine environment. As a result of anthropogenic activities in this area, many pollutants, such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs), have been found in the environment (e.g., Lamparelli et al., 2001; Bícego et al., 2006).

Pollution by PAHs has been the focus of attention due to the widespread occurrence and high degrees of toxicity. The main source of PAHs is anthropogenic, including the burning of fossil fuels or biomass and the release of hydrocarbons related to the petroleum industry (Baumard et al., 1999). PCBs, OCPs and polybrominated diphenylethers (PBDEs) are ubiquitous environmental contaminants that are recognized as persistent organic pollutants (POPs) (Jones and de Voogt, 1999). Once in seawater, these contaminants are adsorbed at concentrations of up to 10^6 to the surface of small plastic pellets that are released unintentionally into the environment during manufacturing and transport, reaching a large number of beaches around the world (Mato et al., 2001). Plastic pellets are easily collectable and have been used as a low-cost monitoring medium to assess organic pollutants in the marine environment (Ogata et al., 2009; Karapanagioti et al., 2011; Hirai et al., 2011; Heskett et al., 2012; Fisner et al., 2013a,b).

Organic pollutants associated with plastic pellets exhibit a high degree of variability among countries, with higher concentrations in areas subjected to considerable industrial (PCBs and DDTs) or agricultural (HCHs) activities (International Pellet Watch, http://www.pelletwatch.org/maps/). The open sea and remote beaches have lower

* Corresponding author.
E-mail address: satie@usp.br (S. Taniguchi).

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concentrations of organic pollutants (Hirai et al., 2011). Although the global and local components of spatial variability in the occurrence of organic pollutants in plastic pellets have been addressed, regional patterns still require clarification.

In the present study, PAHs, PCBs, OCPs and PBDEs were evaluated in plastic pellets sampled from 41 beaches (15 cities) along the coastline of the state of São Paulo (southeastern Brazil) and spatial variability was investigated. Moreover, samples from the central portion of the coastline, which is the most affected area, were collected during 2009/2010, 2012 and 2014 for the determination of temporal trends in PCB levels.

2. Material and methods

Plastic pellets were collected from the sand surface with tweezers and placed in aluminum envelopes identified with a label. Sampling was conducted in two different ways. Firstly, plastic pellets of different colors were collected in 2010 from 41 beaches located in 15 cities along the coast of the state of São Paulo (Fig. 1), which has an extension of 860 km, 427 km of which are formed by beaches (http://www.cidadespaulistas.com.br). The pellets were chosen randomly to obtain results that represent the overall pollution of each area. Secondly, time-series samples were collected from the central coast of the state near the Port of Santos and Cubatão Industrial Complex in 2009/2010, 2012 and 2014. During these sampling events, only yellowing pellets were collected to reduce individual differences in POP concentrations and allow a better comparison with other areas of the world. Yellowing pellets tend to have higher concentrations of POPs, since they have been in seawater for a longer time and consequently have accumulated more contaminants (Endo et al., 2005; Ogata et al., 2009). The central area is known as Baixada Santista and includes the cities of Peruíbe, Itanhém, Mongaguá, Praia Grande, São Vicente, Cubatão, Santos, Guarujá and Bertioga, which together have a population of approximately 1.8 million people, out of the 2.04 million (Brasil, 2015) who live along the entire shoreline of the state of São Paulo.

Pellet samples from the 41 beaches were analyzed at the oceanographic institute laboratory of the University of São Paulo. The analysis was carried out in pools containing approximately 1 g of pellets. Each sample was soxhlet-extracted with dichloromethane/n-hexane. The extract was cleaned up through adsorption chromatography using a column of alumina deactivated with 5% water. PAHs, PCBs and PBDEs were identified and quantified using gas chromatography and mass spectrometry (GC/MS). Organochlorine pesticides were analyzed using a gas chromatograph with an electron capture detector (GC–ECD), as described in Colabuono et al. (2010).

The chlorinated pesticides analyzed were DDTs (*o,p′*-DDT, *p,p′*-DDT, *o,p′*-DDD, *p,p′*-DDD, *o,p′*-DDE and *p,p′*-DDE), chlordanes (α- and γ-chlordane, oxychlordane, heptachlor and heptachlor epoxide), HCHs (α-, β-, γ- and δ-HCH), Drins (aldrin, dieldrin, isodrin and endrin), HCB and Mirex. The PCBs investigated were the sum of 51 congeners (IUPAC #8, 18, 28, 31, 33, 44, 49, 52, 56/60, 66, 70, 74, 77, 81, 87, 95, 97, 99, 101, 105, 110, 114, 118, 123, 126, 128, 132, 138, 141, 149, 151, 153, 156, 157, 158, 167, 169, 170, 174, 177, 180, 183, 187, 189, 194, 195, 201, 203, 206, 209). The PBDEs analyzed were IUPAC #28, 47, 99, 100, 153, 154 and 183. The sixteen US EPA priority PAHs (naphthalene, acenaphthylene, acenaphthene, phenanthrene, anthracene, fluorene, fluoranthene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, pyrene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenz[ah]anthracene, benzo[ghi]perylene) and their alkyl substituted compounds were also analyzed.

Quality assurance and quality control were carried out based on Wade and Cantillo (1994) through an analysis of the sample parameters, procedural blanks, matrix spikes, precision tests with matrix replicates and standard reference material (SRM1944 — organic pollutants in sediment from New Jersey) from the US National Institute of Standards and Technology. Both instruments from Agilent Technologies were calibrated with the injection of nine different concentrations of certified standards. The individual identification of OCPs, PCBs, PAHs and PBDEs was based on GC retention times. For PAHs, PCBs and PBDEs, the respective mass to charge ratio (m/z) was also used. The method detection limit (MDL) was based on the standard deviation (Student's t value with 95% confidence) of seven replicates of a spiked sample containing target compounds at a low concentration. The MDL ranged from 1.00 to 3.70 ng g^{-1} for PAHs, 0.51 to 2.12 ng g^{-1} for PCBs, 0.08 to 1.86 ng g^{-1} for OCPs and 0.76 to 1.06 ng g^{-1} for PBDEs. All solvents were organic residue analysis grade (J.T. Baker) and the blanks were checked under the same conditions as those of the analyses. Concentrations of analytes were expressed as ng g^{-1} dry weight.

The time-series samples were analyzed in the laboratory of organic geochemistry of the Tokyo University of Agriculture and Technology (Tokyo, Japan). Yellowing pellets (30 < yellowness < 50) were extracted by soaking with hexane. The extracts were separated using fully activated silica gel column chromatography into three fractions: Fraction I — n-

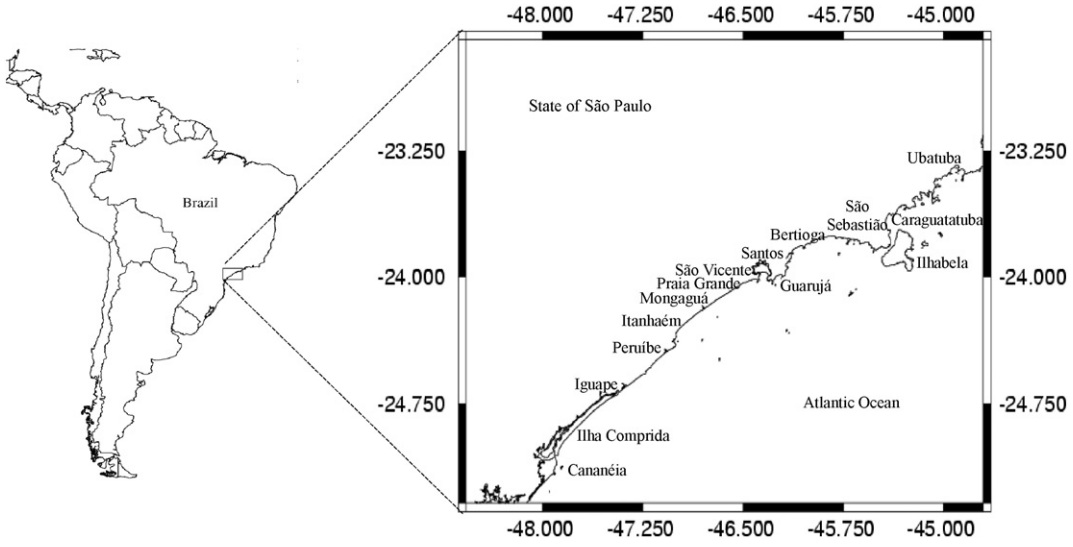

Fig. 1. Coastline of state of São Paulo and location of cities from which plastic pellets were collected.