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Baseline

Monitoring of a wide range of organic micropollutants on the Portuguese coast using plastic resin pellets

Kaoruko Mizukawa^a, Hideshige Takada^{a,*}, Maki Ito^a, Yeo Bee Geok^a, Junki Hosoda^a, Rei Yamashita^a, Mahua Saha^a, Satoru Suzuki^b, Carlos Miguez^c, João Frias^d, Joana Cepeda Antunes^d, Paula Sobral^e, Isabelina Santos^e, Cristina Micaelo^e, Ana Maria Ferreira^e

^a Laboratory of Organic Geochemistry (LOG), Tokyo University of Agriculture and Technology, Fuchu, Tokyo 183-8509, Japan

^b Center for Marine Environmental Studies (CMES), Ehime University, Matsuyama 790-8577, Japan

^c Dep. de Biologia, Universidade de Aveiro, 3810-193 Aveiro, Portugal

^d IMAR, Instituto do Mar, Departamento de Ciências e Engenharia do Ambiente, Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa, 2829-516 Monte de Caparica, Portugal

^e IPMA, Instituto Português do Mar e da Atmosfera, Avenida de Brasília, 1449-006 Lisboa, Portugal

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ABSTRACT

We analyzed polychlorinated biphenyls (PCBs), dichlorodiphenyl dichloroethane and its metabolites, hexachlorocyclohexanes (HCHs), polycyclic aromatic hydrocarbons (PAHs), and hopanes, in plastic resin pellets collected from nine locations along the Portuguese coast. Concentrations of a sum of 13 PCBs were one order of magnitude higher in two major cities (Porto: 307 ng/g-pellet; Lisboa: 273 ng/g-pellet) than in the seven rural sites. Lower chlorinated congeners were more abundant in the rural sites than in the cities, suggesting atmospheric dispersion. At most of the locations, PAH concentrations (sum of 33 PAH species) were ~100 to ~300 ng/g-pellet; however, three orders of magnitude higher concentrations of PAHs, with a petrogenic signature, were detected at a small city (Sines). Hopanes were detected in the pellets at all locations. This study demonstrated that multiple sample locations, including locations in both urban and remote areas, are necessary for country-scale pellet watch.

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1. Introduction

International Pellet Watch (IPW) is globally monitoring persistent organic pollutants (POPs) by using plastic resin pellets. Plastic resin pellets are small granules, generally in the shape of a cylinder or disk with a diameter of a few millimeters. These plastic particles are the industrial feedstock of plastic products. A small portion of them are spilled into the environment during land handling and transport. Because polyethylene (PE) pellets, a major type of plastics, are lighter than water, such spilled PE pellets are carried by surface runoff, streams and rivers, and finally reach the ocean. Because of their persistent nature, such pellets are distributed all over the world. Hydrophobic organic pollutants are sorbed into and concentrated in the pellets from surrounding sea water (Mato et al., 2001). Meanwhile, the importance of global monitoring of POPs has been emphasized in the Stockholm Convention (UNEP, 2001). Thus, we initiated the IPW in 2005 (Takada, 2006). The advantage of the IPW method is its extremely low sampling and shipment cost, in comparison to conventional monitoring using

water, sediment and biological samples. In our previous study (Ogata et al., 2009), we examined the utility of the IPW method as a means of global monitoring, by comparing it with mussel monitoring. Polychlorinated biphenyl (PCB) concentrations in pellets correlated well with those in mussel from the same area, indicating the reliability of the IPW method as a global monitoring technique.

Our previous paper (Ogata et al., 2009) elucidated the spatial pattern of POPs in 17 countries. However, for most of the countries, only a few locations were investigated and thus the calculated pollution levels for the countries may have been inaccurate. For example, only one location (Kato Achaia), a remote area, was available in Greece in the first report (Ogata et al., 2009), and showed the lowest PCB concentration (5 ng/g-pellet) in the world. However, our follow-up study (Karapanagioti et al., 2011), based on four locations in Greece, revealed two orders of magnitude higher concentrations of PCBs (230 and 260 ng/g-pellet) in two locations near the capital, Athens, a highly industrialized area. Similarly, the first report of the IPW (Ogata et al., 2009) sampled only one, remote location in Portugal (Aveiro), suggesting a possible underestimation of POP contamination levels in Portugal. Thus, here we added pellet samples from eight locations on the Portuguese coast to obtain a more detailed assessment of the pollution levels in Portugal,

^{*} Corresponding author. Tel.: +81 423 67 5825; fax: +81 423 60 8264. *E-mail address*: shige@cc.tuat.ac.jp (H. Takada).

based on the 9-pellet sample. Furthermore, in the previous, country-wide study in Greece, urban and remote locations were hydrologically distinguished due to the complex geographical setting (thousands of islands and peninsulas). In contrast, in the present study, all the sample locations were on the same coastline, facing the Atlantic Ocean, within 50–100 km of each other. This provided an opportunity to enhance both our understanding of pellet-sample location selection, and discussion of the behavior of POPs.

In addition, the present study analyzed 33 polycyclic aromatic hydrocarbons (PAHs), including methyl PAHs and hopanes, in pellets, as new target compounds for the IPW. PAHs are introduced to the marine environment via petroleum pollution, in addition to inputs of combustion products of organic matter (e.g., fossil fuel, biomass). Because of their toxicity, PAHs have been monitored in seawater, sediments, and biota. However, there has been only two reports on PAHs in pellets (Karapanagioti et al., 2011 and Van et al., 2012). In these study the number of PAH species was rather limited (18 species). The present study increased the number of target compounds up to 33. Hopanes, pentacyclic triterpanes, are contained in crude oil and some refined petroleum products such as lubricating oil and asphalt. Hopanes are sourcespecific and persistent to a variety of environmental alterations (microbial and photolytic degradation), and therefore have been used as petroleum biomarkers. PAHs and hopanes in pellets can thus be used as markers of petroleum pollution in the IPW. However, no detailed investigation has been conducted on the utility of these compounds.

The present study conducted detailed-scale monitoring of POPs (i.e., PCBs, DDTs, and HCHs), PAHs, and hopanes, in pellets collected from nine locations on the Atlantic coast of Portugal. In terms of IPW protocol, the present study provided (1) further information on the selection of sampling locations in respective countries, and (2) preliminary evaluation of hopanes as markers of petroleum pollution.

2. Materials and methods

Plastic resin pellets from eight Portuguese beaches were collected in 2008 and 2012 (Fig. 1). In addition, the analytical results



Fig. 1. Sampling locations of resin pellets.

on pellets from Aveiro, where POP concentrations had been reported in our previous study (Ogata et al., 2009), were included in the present study. Among the total of nine locations, Lisboa and Porto are large cities in Portugal, with Lisboa the capital and Porto the second-largest city. The other seven locations are in rural areas. More detailed information, including the coordinates of the sampling locations, is listed in Table 1, where the nine locations are listed in latitudinal order from north to south (illustrated in Fig. 1). Pellets were sorted and POPs analyzed as in Ogata et al. (2009). Pellets were sorted with a near-infrared spectrometer (Plascan-WTM OPT Research Inc., Tokyo, Japan) into polyethylene (PE), polypropylene (PP), and other polymers. Yellowing PE pellets (with a yellowness of ≥ 40) were selected for chemical analysis. Median POP values were obtained by analyzing 5 pools of pellets (each pool consisting of five randomly selected pellets) from each location.

POPs were extracted from pellets by soaking the pellets in hexane. The extracts were separated through fully activated silica gel columns into three fractions: Fraction I (n-alkanes and hopanes), Fraction II (PCBs and DDE), and Fraction III (DDT, DDD, 4 HCH isomers $[\alpha, \beta, \gamma, \delta]$, and polycyclic aromatic hydrocarbons [PAHs]). The hopanes in Fraction I were determined by gas chromatography/ mass spectrometry (GC-MS). The PCBs and p,p'-DDE in Fraction II were determined by gas chromatography/ion-trap mass spectrometry. The sum of all the quantified congeners (i.e., CB#66, 101, 110, 149, 118, 105, 153, 138, 128, 187, 180, 170, 206) is expressed as \sum 13 PCBs. The p,p'-DDT, o,p'-DDT, p,p'-DDD, o,p'-DDD and the four HCH isomers in Fraction III were determined by gas chromatography/electron capture detection. The PAHs in Fraction III were quantified by GC-MS. The sum of all 33 quantified PAH species is expressed as \sum 33 PAHs. The instrumental conditions for the organochlorine compounds are described in Ogata et al. (2009), and those for the hopanes and PAHs in Saha et al. (2009). No recovery correction was applied to any components, except for the PAHs, because good recoveries had been confirmed prior to the sample analysis. PAH concentrations in the samples were recovery-corrected using recoveries of surrogates (i.e., deuterated PAHs) spiked before analysis, as described in Saha et al. (2009). The reproducibility of this analytical procedure (i.e., column chromatography and instrumental determination) was confirmed by analysis of four aliquots from a single extract of pellets from Buenos Aires, Argentina, for PCBs, DDTs and HCHs; and an extract from Tokyo Bay for PAHs and hopanes. The relative standard deviations of the concentrations were less than 14% for PCBs, DDTs, and HCHs, and less than 10% for PAHs and hopanes. Recovery was tested by spiking the aliquots of the extracts with authentic standards; recoveries were >95% for PCBs, DDTs, and HCHs, and >74% for PAHs and hopanes. A procedural blank using only solvent was run with every set analyzed (5 pools). Analytical values <3× the corresponding blanks were considered below the limit of quantification (LOQ). The LOQs were normally 0.07 ng/g-pellet for $\sum 13$ PCBs, 0.1 ng/gpellet for DDT, 0.04 ng/g-pellet for DDE, 0.07 ng/g-pellet for DDD, 0.4 ng/g-pellet for HCHs, 4 ng/g-pellet for total hopanes and 50 ng/g-pellet for \sum 33 PAHs.

3. Results and discussion

The analytical results of POPs in all the pellets are listed in Table 2 and Table S1. Table 2 shows the median concentrations of POPs from 5 pools from nine locations on the Portuguese coast. PCB concentrations ranged from 10.5 to 307 ng/g-pellet. PCB concentrations in the two major cities, Porto (307 ng/g-pellet) and Lisboa (273 ng/g-pellet), were one order of magnitude higher than in the rural areas (10.5–41.7 ng/g; Fig. 2). This is consistent with the monitoring of PCBs using sediments (Castro and Vale, 1995), where concentrations of PCBs in sediments from the Tagus estuary in Download English Version:

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