Cod: 4.1022

POPS MONITORING IN BRAZIL AND ITALY USING PLASTIC RESIN PELLETS: COMPARATIVE STUDY BETWEEN OPEN OCEAN AND ENCLOSED SEA

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Introduction:

The presence of plastic in the marine environment is a common phenomenon especially highlighted in the last decades due to the excessive consumption and disposal of single-use plastic products used in everyday life (Andrady, 2011). Derived from crude oil, resin pellets are the raw material from which, through specific melting and molding processes at high temperatures, plastic is molded for multiple applications. Resin pellets are small cylindrical granules with size generally <5mm in diameter (Ogata et al., 2009). Polyethylene (PE) and polypropylene (PP) pellets can be carried by surface runoff, streams, rivers and eventually end up in the ocean due to their buoyancy and lightness. They may be introduced in the ocean through accidental spills during transport (Heskett et al., 2012). Plastic resin pellets sorb hydrophobic organic compounds, including persistent organic pollutants (POPs). POPs such as polychlorinated biphenyls (PCBs) and organochlorine pesticides are present in aquatic systems worldwide as a consequence of their widespread usage, long-range transport, and persistence. Individual POPs have characteristic patterns of distribution depending on regional pat- terns of usage and their physico-chemical properties. When considering the global distribution of POPs it is important to understand their transport mechanism and to identify any hot spots where regulatory and remediation efforts are required. To evaluate the effectiveness of the regulations and remediation, monitoring of POPs is essential and the importance of global monitoring of POPs was emphasized at the Stockholm Convention (Secretariat of the Stockholm Convention). Pellets have ability to accumulate POPs with a concentration factor of up to ~106relative to surrounding seawater (Mato et al., 2001). Because of their ubiquitous occurrence on world beaches and their ease of collection and shipment, plastic resin pellets are used as passive samplers by International Pellet Watch (IPW; Takada, 2006). IPW is a volunteer-based global monitoring program designed to monitor the pollution status of the oceans and to understand the risks associated with chemicals in marine plastics. IPW has drawn global pollution maps of POPs and identified hot spots (Ogata et al., 2009 and Karapanagioti et al., 2011).

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 (IPW). The open sea and remote beaches have lower 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 pattern is still require clarification.

In the present study, POPs like PCBs and OCPs were evaluated in plastic pellets sampled from 8 beaches along the coastline of Atlantic Ocean (southeastern Brazil) and spatial variability was investigated. In the same way, pellets were sampled and studied from the 5 beaches along the coast of Mediterranean sea (Italian peninsula) to compare the distribution and concentration of POPs between Open Ocean and closed sea. The objective of this paper is to provide an overview of POPs pollution status and a comparative study in Brazil and Italian coast.

2. Material and methods

Plastic pellets were collected from the sand surface with tweezers and placed in aluminum envelopes identified with a label. The pellets were chosen randomly to obtain results that represent the overall pollution of each area. Pellets were collected in from 8 beaches along the coast of the state of São Paulo (Fig. 1a) from 2009-2014 and from 5 beaches of Italy from 2006 to 2012 (Fig. 1b). During these sampling events, only yellowing pellets were collected since they have been in seawater for a longer time and consequently have accumulated more contaminants (Endo et al., 2005; 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. POPs were extracted from pellets by

soaking 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 p,p'-DDE), and Fraction III (p,p'-DDT, p,p'-DDD, 4 HCH isomers [a, b, c, d], and polycyclic aromatic hydrocarbons [PAHs]). PCBs and DDE in Fraction II were determined by gas chromatography/ion-trap mass spectrometry (GC-MS). DDT, DDD, and the four HCH isomers in Fraction III were determined by gas chromatography/electron capture detector (GC-ECD). The sum of all congeners quantified (i.e., PCB#66, 101, 110, 149, 118, 105, 153, 138, 128, 187, 180, 170, 206) is expressed as Σ13 PCBs. 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 rom Buenos Aires, Argentina. The relative standard deviations of the concentrations of the target compounds were 1–14%. Recovery was tested by spiking the aliquots of the extracts with authentic standards; recoveries were >95%. A procedural blank was run with every set analyzed (five pools). Analytical values <3x the corresponding blank were considered to be below the limit of quantification.

3. Results and discussion

The analytical results of POPs (PCBs, DDTs and HCHs) were done for all pellet samples. The median concentrations of Polychlorinated biphenyls (PCBs) in 5 pools from eight locations on the Brazil coast and Italian coast were shown in Fig 2. PCBs concentrations ranged from 1.51 µg/g to 3.59 µg/g–pellets in the coast of Brazil, whereas it ranged from 46ng/g to 212 ng/g pellets in the coast of Italy. Significantly high dichloro-diphenyl-trichloroethaneand its metabolites DDT (0.89-23.3 µg/g pellets) and DDE (2.27-8.89 µg/g pellets) were found in most of the beaches in Brazilcompare to 8.5 ng/g to 51 ng/g pellets in Italy. On the other hand, HCH concentrations in the pellets were lower than PCBs and DDTs at most of the locations in Brazil (1.9 ng/g – 21.36 ng/g pellets) and Italy (0.3 to 0.5 ng/ g pellets).Hexachlorocyclohexane (HCH) did not exhibit considerable differencesamong the samples collected from Brazil and Italy. However extremely high concentration of PCBs and DDTs in brazil coast could be due to the high influence of industrial and urban inputs as well as products used in agriculture and against vectors that cause diseases, such as malaria in Brazil compare to Italian peninsula. Currents also seem to play an important role in the transportation of contaminants in the open Atlantic Ocean than closed area of Mediterranean sea (Taniguchi et al., 2016).The plastic pellets demonstrated the contribution of local sources of contaminants as well as compounds accumulated during the transport of pellets through different types of environments before reaching the beaches.

Acknowledgements

Authors are thankful to International Pellet Watch, Japan for supporting with data and various people from brazil and Italy for collecting the samples.

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Fig. 1. Plastic pellets were collected from a) Coast of Atlantic ocean (Brazil) and b) coast of Mediterranean sea (Italy)

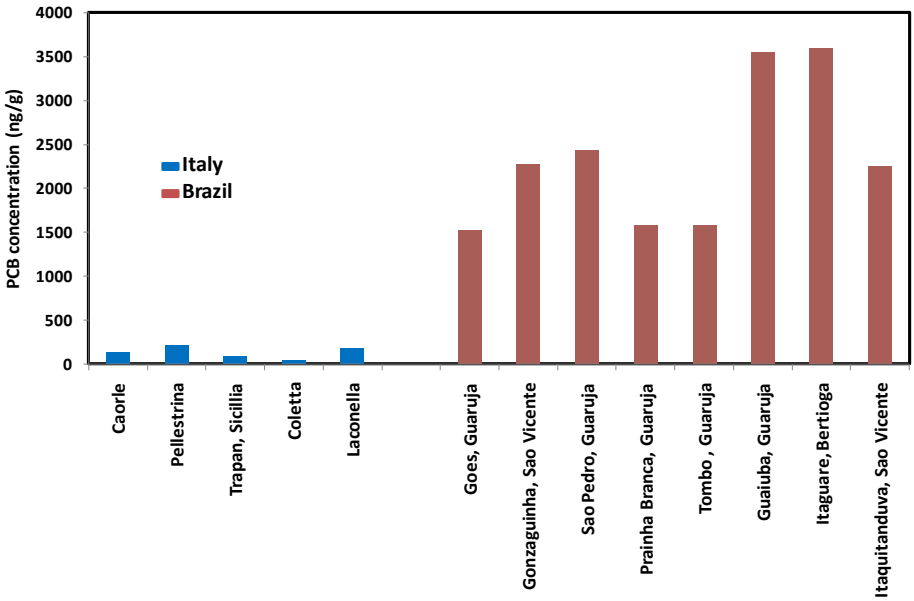

Fig. 2. Polychlorinated biphenyls (PCBs) in each sample of plastic pellets collected along coast of Italy and Brazil (total PCB = sum of 13 congeners: PCB 66, 101, 105, 110, 118, 128, 138, 149, 153, 170, 180, 187 and 206).