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Polychlorinated biphenyls and organochlorine pesticides in plastics ingested by seabirds

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ABSTRACT

The occurrence of plastic objects in the digestive tract was assessed in eight species of Procellariiformes collected in southern Brazil and the occurrence of polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in the ingested plastics pellets and plastic fragments was evaluated. PCBs were detected in plastic pellets (491 ng g^{-1}) and plastic fragments (243–418 ng g^{-1}). Among the OCPs, *p,p′*-DDE had the highest concentrations, ranging from 68.0 to 99.0 ng g^{-1}. The occurrence of organic pollutants in post-consumer plastics supports the fact that plastics are an important source carrying persistent organic pollutants in the marine environment. Although transfer through the food chain may be the main source of exposure to POPs to seabirds, plastics could be an additional source for the organisms which ingest them, like Procellariiformes which are the seabirds most affected by plastic pollution.

Plastics are synthetic organic polymers that can be found in coastal and oceanic waters worldwide. These products are among the most persistent macroscopic pollutants in the marine environment (Rios et al., 2007) and can be harmful to biota. A number of studies have reported the ingestion of plastics by fish, sea turtles and seabirds (Furness, 1985; Colabuono et al., 2009; Tourinho et al., 2010) as well as their harmful effects on organisms (Ryan and Jackson, 1987; Ryan, 1988; Pierce et al., 2004).

Plastic debris has been found to accumulate contaminants due to its hydrophobic nature (Mato et al., 2001; Rios et al., 2007). There have been several reports of polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs), such as DDTs, in plastic pellets collected from beaches around the world (Mato et al., 2001; Endo et al., 2005; Ogata et al., 2009). Rios et al. (2007) have reported the occurrence of organic contaminants in post-consumer plastic debris and state that these plastics are important sources of persistent organic pollutants (POPs).

PCBs and OCPs are organic contaminants of great concern, recognized as POPs, due to their hydrophobic nature and persistence in the environment, which allows these compounds to be bioconcentrated and biomagnified throughout the food chain (Ritter et al., 1995; Lallas, 2001). There is concern regarding the possible transfer of these contaminants from plastics to marine organisms that ingest them. This may be a significant pathway for the chemicals in plastics to enter marine organisms (Ryan et al., 1988; Derraik, 2002; Tanabe et al., 2004).

Seabirds, especially Procellariiformes (albatrosses and petrels), are a group of marine animals most affected by plastic pollution. These birds often confuse plastics with prey and these objects can remain in their digestive tract for several months before being eliminated (Ryan and Jackson, 1987). Therefore, the Procellariiformes have the highest incidence of plastic ingestion among seabirds (Furness, 1985; Azzarello and Van Vleet, 1987; Ryan, 1988; Tourinho et al., 2010). Thus, in addition to transfer through the food chain, plastic ingestion may be another source of organic contaminants for these top predators.

In the present study, the occurrence of plastic objects in the digestive tract was assessed in eight species of Procellariiformes collected in southern Brazil and the occurrence of PCBs and OCPs in the ingested plastics was evaluated.

Thirty-four White-chinned petrels (*Procellaria aequinoctialis*), three Spectacled petrels (*Procellaria conspicillata*), six Great shearwaters (*Puffinus gravis*), six Manx shearwaters (*Puffinus puffinus*), 31 Black-browed albatrosses (*Thalassarche melanophris*), 13 Atlantic Yellow-nosed albatrosses (*Thalassarche chlororhynchos*), three Wandering albatrosses (*Diomedea exulans*) and one Tristan albatross (*Diomedea dabbenena*) were collected on the beaches in the state of Rio Grande do Sul (Brazil) as well as from longline fisheries off southern Brazil (29°S–34°S; 45°W–52°W) between 1991 and 2008 (Fig. 1).

All plastics found in the proventriculus and ventriculus of the birds were collected, dried at room temperature and separated into three categories: plastic pellets, which have either polyethylene or polypropylene as the raw material in the form of small spheres or cylinders and that are melted and molded to create plastic products (US EPA, 1992); plastic fragments, which are rigid pieces of

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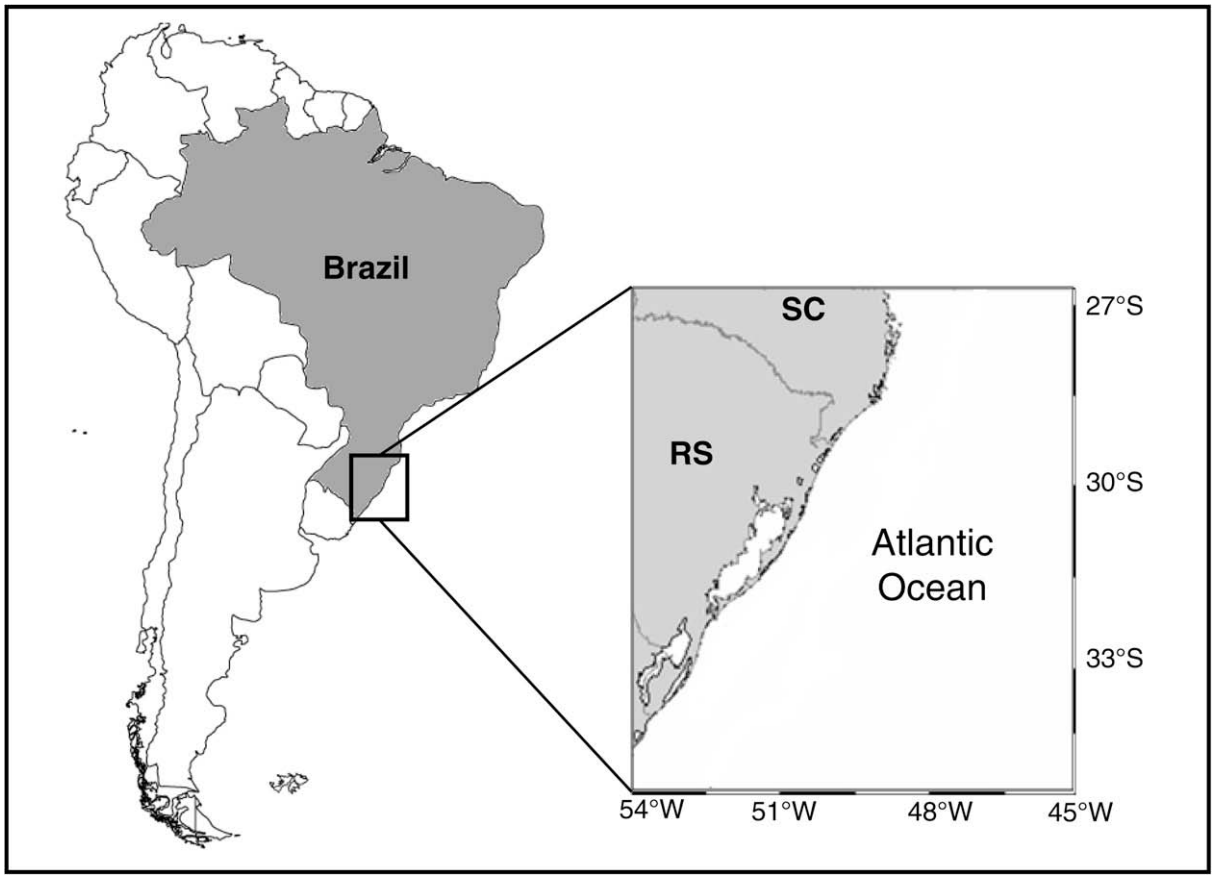

Fig. 1. Location of the study area; birds were collected along the coast of the state of Rio Grande do Sul (RS) and from longline fisheries off southern Brazil.

larger objects or pieces of plastic bags and packaging either discarded or lost at sea; and nylon line. The samples were wrapped in aluminum foil and frozen at −20 °C until analysis.

Plastic pellets and plastic fragments were pooled and analyzed for the presence of PCBs and OCPs. The plastics were not sorted by size, shape or color. Analytical procedures followed those described by the UNEP (1992), with some adaptations. Briefly, the plastics (0.6 g for industrial plastic pellets; 1.0 g for plastic fragments) were extracted in a Soxhlet apparatus for 8 h using 80 ml of *n*-hexane and methylene chloride (1:1, v/v). Prior to extraction, 2,2′,4,5′,6-pentachlorobiphenyl (PCB 103) and 2,2′,3,3′,4,5,5′,6-octachlorobiphenyl (PCB 198) were added to all samples, blanks and reference material as surrogates for chlorinated pesticides and PCBs. Extracts were cleaned using a chromatographic column with 3.2 g of alumina (5% water deactivated), eluted with 20 ml of *n*-hexane and methylene chloride (7:3, v/v). The extract was concentrated to a volume of 1.0 ml in hexane. The internal standard 2,4,5,6-tetrachlorometaxylene (TCMX) was added before gas chromatographic analysis. A procedural blank was run with the set of samples.

The identification and quantification of chlorinated pesticides was performed with a Agilent Technologies 6890N gas chromatograph with an electron capture detector (GC–ECD) using a 30 m × 0.25 mm i.d. capillary column coated with 5% phenyl-substituted dimethylpolysiloxane phase (0.25 μm film thickness). Automatic splitless injections of 2 μl were applied and the total purge rate was adjusted to 50 ml min^{-1}. Hydrogen was used as the carrier gas (constant pressure of 40 kPa at 100 °C), while nitrogen was the make up gas at a rate of 60 ml min^{-1}. Injector and detector temperatures were 280 and 320 °C, respectively. Oven temperature was programmed as follows: 70 °C for 1 min, raised at 40 °C min^{-1} to 170 °C, then raised at 1.5 °C min^{-1} to 230 °C (held for 1 min) and at 30 °C min^{-1} to 300 °C with a final hold of 5 min.

PCBs were quantitatively analyzed using an Agilent Technologies 5973N gas chromatograph coupled to a mass spectrometer (GC–MS) in selected ion mode (SIM 70 eV), using a 30 m × 0.25 mm i.d. capillary column coated with 5% phenyl-substituted dimethylpolysiloxane phase (0.25 μm film thickness). The volume injected was 1 μl in automatic splitless mode. Helium was used as the carrier gas (constant flow of 1.1 ml min^{-1}). The interface, source and quadrupole temperatures were 280, 300 and 200 °C, respectively. Oven temperature was programmed as follows: 75 °C for 3 min, raised at 15 °C min^{-1} to 150 °C, then raised at 2.0 °C min^{-1} to 260 °C and at 20 °C min^{-1} to 300 °C, with a final hold of 1 min.

For quality assurance/quality control (QA/QC), the analytical methodology was validated using a standard reference material (SRM 1941b – organics in marine sediment) purchased from the National Institute of Standards and Technology (USA). SRM 1941b was analyzed in duplicate and average recovery of analytes was 95%. The recovery of analytes in spiked blanks and matrices produced satisfactory results (80–120%). Analytes in procedural blanks were subtracted from the samples. Method quantification limits (QL) ranged from <0.08 to 6.27 ng g^{-1}. Laboratory check solutions were routinely injected into GC–ECD and GC–MS to confirm instrument accuracy and precision. Calibration of the instruments was performed using a nine-level analytical curve. Quantification of analytes followed the internal standard procedure. Surrogate recoveries were acceptable (mean: 93.33; standard deviation: 3.61).

The chlorinated pesticides analyzed in the present study were DDTs (*o*,*p*′-DDT, *p*,*p*′-DDT, *o*,*p*′-DDD, *p*,*p*′-DDD, *o*,*p*′-DDE and *p*,*p*′-